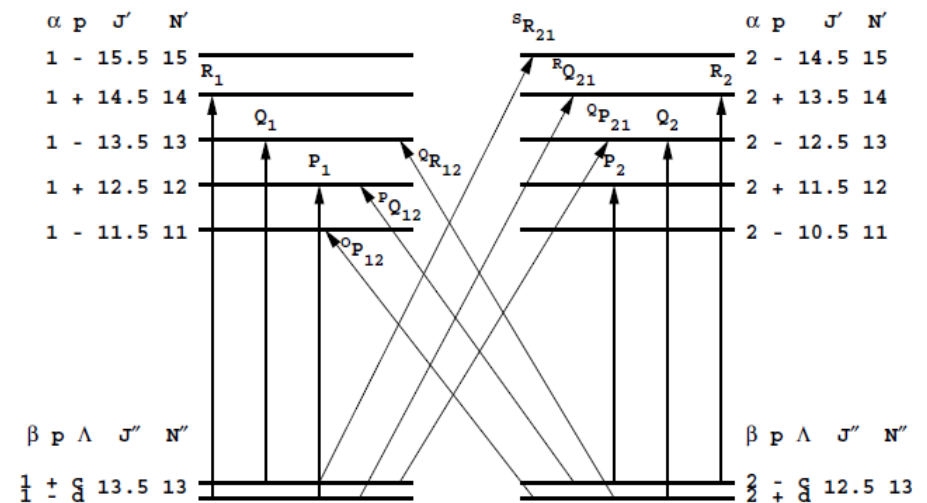# Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 8: Case Study: UV - OH

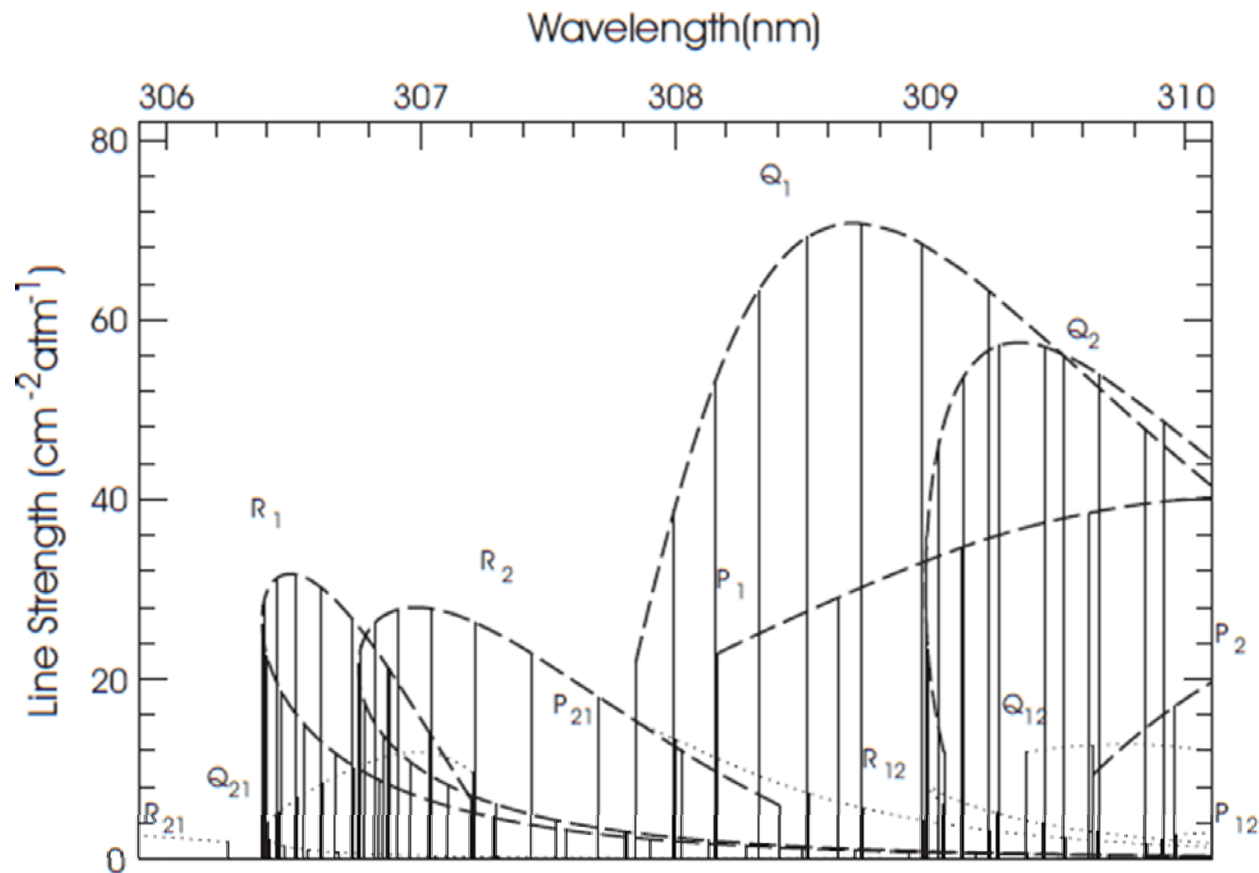*UV absorption of OH: $A^2\Sigma^+ - X^2\Pi$ (~300nm)*

1. Introduction
2. OH energy levels
   - Upper level
   - Lower level
3. Allowed radiative transitions
   - Transition notations
   - Allowed transitions
4. Working example - OH

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

1. Introduction

- OH, a prominent flame emitter, absorber.

  Useful for T, X_{OH} measurements.

Wavelength(nm)

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

1. Introduction

- Steps in analysis to obtain spectral absorption coefficient

    1. Identify/calculate energy levels of upper + lower states

    2. Establish allowed transitions

    3. Introduce "transition notation"

    4. Identify/characterize oscillator strengths using Hönl-London factors

    5. Calculate Boltzmann fraction

    6. Calculate lineshape function

    7. Calculate absorption coefficient

2. Energy levels

- Term energies

Angular momentum energy (nuclei + electrons)

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

elec. q. no. →
vib. q. no. →
ang. mom. q. no. →

Electronic energy

Vibrational energy

- 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}]

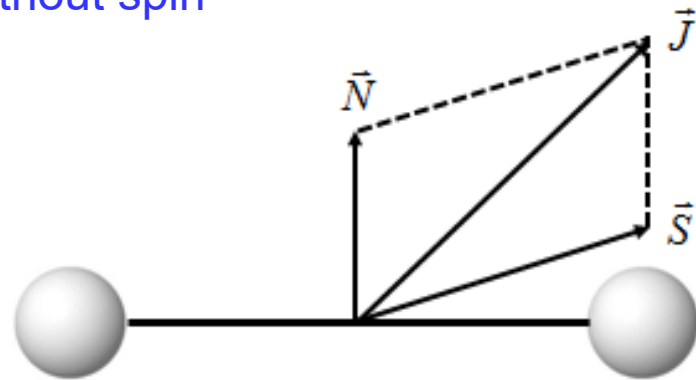| $A^2\Sigma^+$	T_e	ω_e	$\omega_e x_e$	$X^2\Pi$	T_e	ω_e	$\omega_e x_e$
	32682.0	3184.28	97.84		0.0	3735.21	82.21

Let's first look at the upper state ➡ Hund's case b!

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2. Energy levels

- Hund's case b (Λ=0, S≠0) – 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|
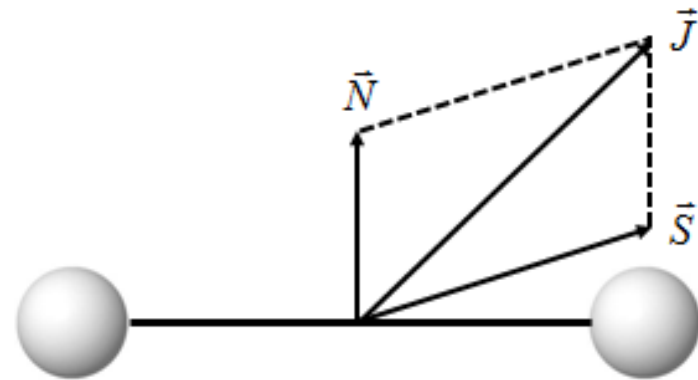
- i = 1, 2, …

  $F_i(N)$ = 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 ➡ 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 $J = N - 1/2$

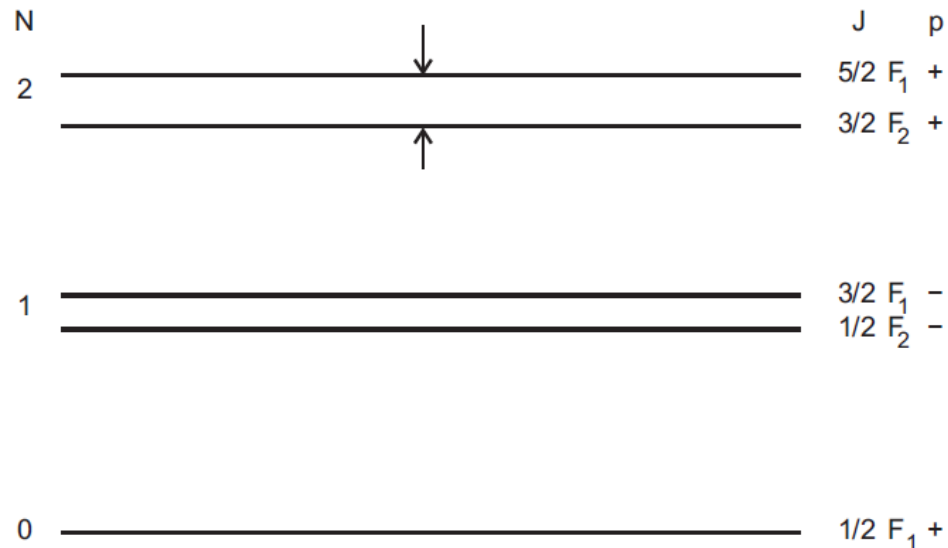Common to write either $F_1(N)$ or $F_1(J)$

2. Energy levels

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

$$F_1(N) = B_v N(N+1) - D_v[N(N+1)]^2 + \gamma_v N$$
$$F_2(N) = B_v N(N+1) - D_v[N(N+1)]^2 - \gamma_v(N+1)$$
$$\left(\text{splitting constant } \gamma_v \approx 0.1\text{cm}^{-1} \text{ for OH } A^2\Sigma^+\right)$$

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
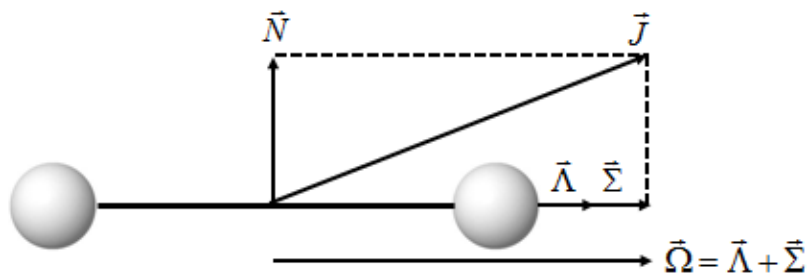Compare with $\Delta\nu_D(1800K) = 0.23\text{cm}^{-1}$

✎ 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: $X^2\Pi$ ($\Lambda=1$, $S=1/2$)

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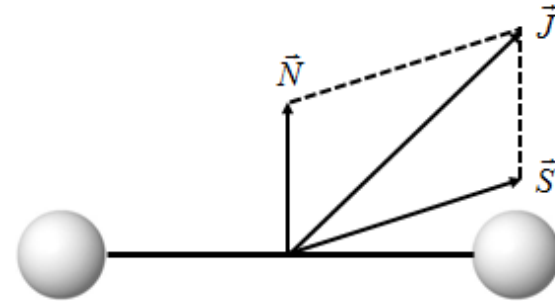
Hund's case *b*
$\Lambda = 0$, $S \neq 0$, Σ not defined

✎ Note:

1. Rules less strong for hydrides

2. OH behaves like Hund's a @ <u>low</u> N
   like Hund's b @ <u>large</u> 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 "<u>intermediate case</u>"

2. Energy levels

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

  ✎ Notes:

  3. For "intermediate/transition cases"

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

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

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

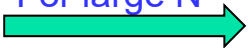Note: $F_1(N) < F_2(N)$

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

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

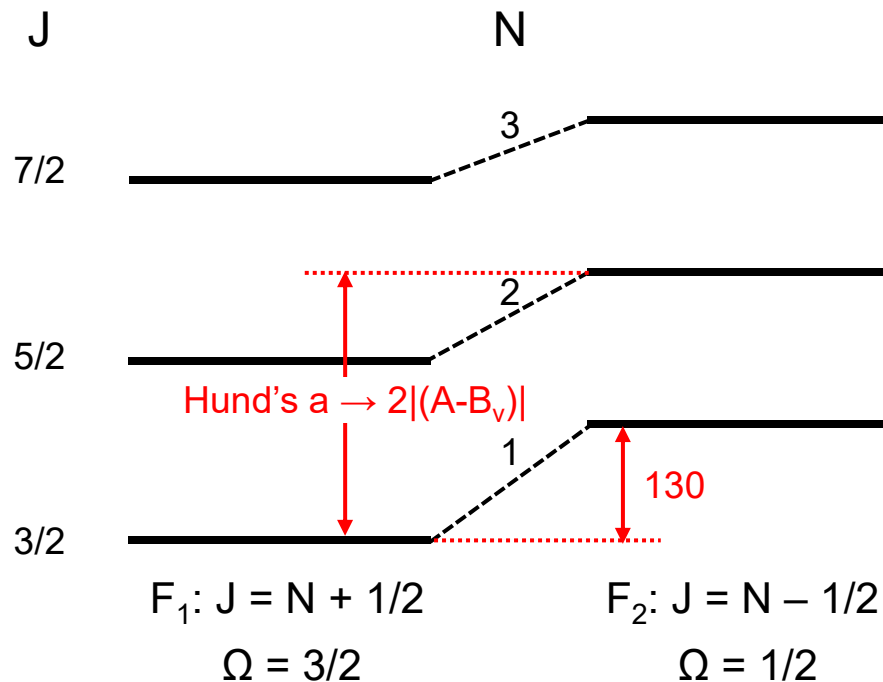$$F_2 \rightarrow B_v\left[N^2 - \Lambda^2 + N\right]$$

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

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2. Energy levels

- The ground state: $X^2\Pi$
  - Notes:
    4. Some similarity to symmetric top

J   N   J

7/2   3   5/2

5/2   2   3/2

Hund's a → $2|(A-B_v)|$

1   1/2

130

3/2

F_1: J = N + 1/2 F_2: J = N − 1/2

Ω = 3/2   Ω = 1/2

Showed earlier that $F_1 < F_2$

$T_e = T_0 + A\Lambda\Sigma$

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

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

           + (-140)(1)(-1/2), Σ = -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}
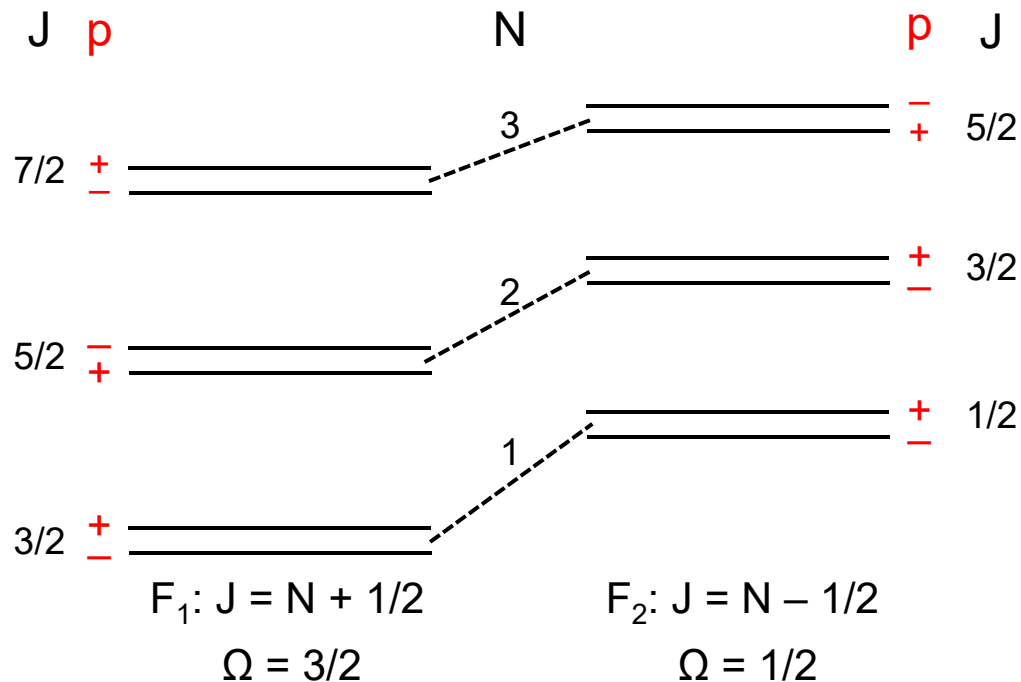
Actual spacing is only 188 cm^{-1}, reflects that <u>hydrides quickly go to Hund's case **b**</u>

2. Energy levels

- The ground state: X²Π

  - Notes:

    5. Role of Λ-doubling

J p   N   p J

$$F_{ic} = F_i(J) + \delta_c J(J+1)$$
$$F_{id} = F_i(J) + \delta_d J(J+1)$$
$$F_{id} < F_{ic}$$

3   − 5/2
7/2 +   +
     −

2   + 3/2
5/2 −   −
     +

1   + 1/2
3/2 +   −
     −

F_1: J = N + 1/2 F_2: J = N − 1/2

Ω = 3/2   Ω = 1/2

- $F_{ic}(J) - F_{id}(J) \approx 0.04$ cm⁻¹ for typical J in OH

- c and d have different parity (p)

- Splitting decreases with increasing N

Showed earlier that $F_1 < F_2$

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

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3. Allowed radiative transitions

- Transition notations

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

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

where $Y - \Delta N$ (O, P, Q, R, S for ΔN = -2 to +2)

$X - \Delta J$ (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 $R_1 7$

1. Y suppressed when $\Delta N = \Delta J$
2. β suppressed when $\alpha = \beta$
3. Both N'' and J'' are used

Example: $^S R_{21}$:

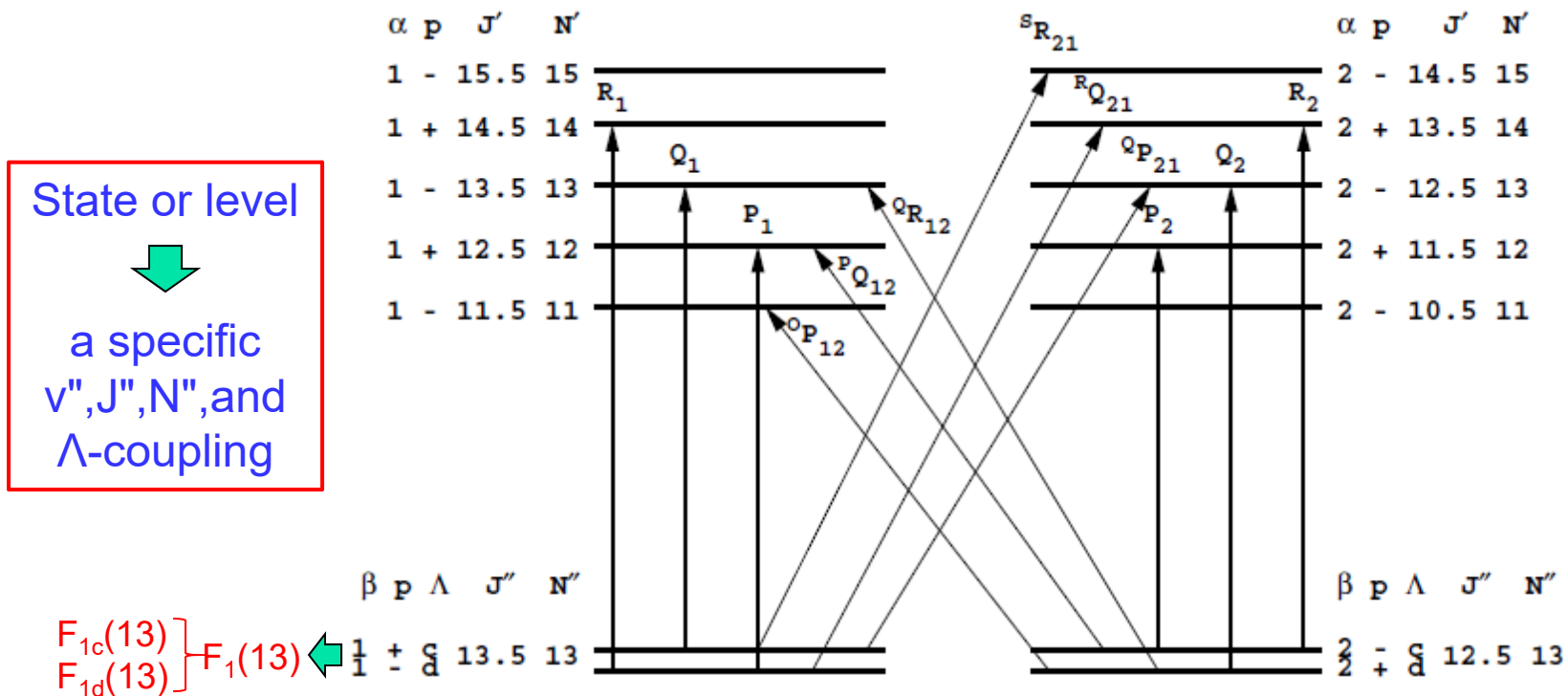ΔJ = +1, ΔN = +2

F' = F_2(N')

F'' = F_1(N'')

- General selection rules
  - Parity must change + → – or – → +
  - ΔJ = 0, ± 1
  - No Q (J = 0) transitions, J = 0 → J = 0 not allowed

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

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; ΔJ = ΔN)

■ + ↔ − rule on parity

■ $F_{1c}-F_{1d} \approx 0.04N(N+1)$ for OH ➡ for N~10, Λ-doubling is ~ 4cm^{-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
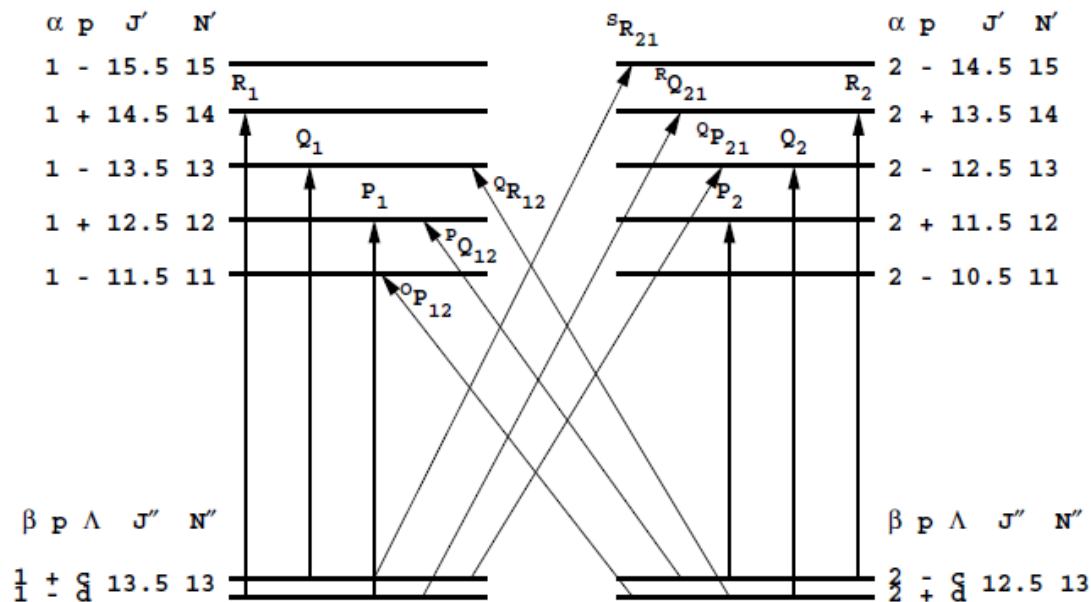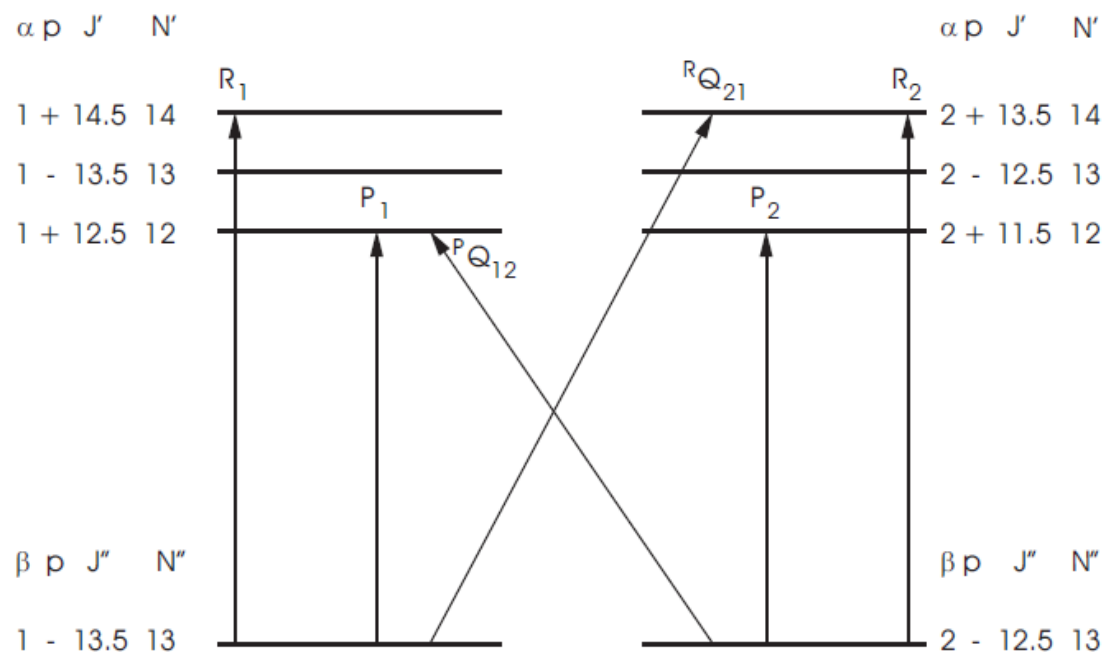

- Note:

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. Working example - OH

■ Complete steps to calculate absorption coefficient

1. Identify/characterize <u>oscillator strengths</u> using Hönl-London factors

2. Calculate <u>Boltzmann fraction</u>

3. Calculate <u>lineshape function</u>
   (narrow-band vs broad-band)

4. Calculate absorption coefficient

Absorption coefficient

#/cm³ of species (OH), $= \dfrac{p_A}{kT}$

#/cm³ in state 1, $= N_a \dfrac{N_1}{N_a}$ ← Fractional pop. in state 1

$$k_\nu, \mathrm{cm}^{-1} = \left[\frac{\pi e^2}{m_e c}\right] N_1 f_{12}\left(1 - \exp^{-\frac{h\nu}{kT}}\right)\phi(\nu - \nu_0)$$

0.0265 cm²/s

$\phi[s] = (1/c)\ \phi[cm]$

To do: evaluate f_{12}, N_1/N_a

↑ Step 1   ↑ Step 2

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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 $\;f_{J''J'} = f_{n''n'} q_{v''v'} \dfrac{S_{J''J'}}{2J''+1}$

$= f_{v''v'}$ = 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

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

- $\displaystyle\sum_{J'} S_{J''J'} = (2J''+1)\underbrace{(2S+1)\delta}_{g''_{el}=4 \text{ for } X^2\Pi}$

1 for Λ = 0 (Σ state), 2 otherwise

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

4.1. Oscillator strengths

- 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

4.2. Boltzmann fraction

1. We seek the fraction of molecules in a single state for which

$$\sum_{J'} S_{J''J'} = 2J''+1$$

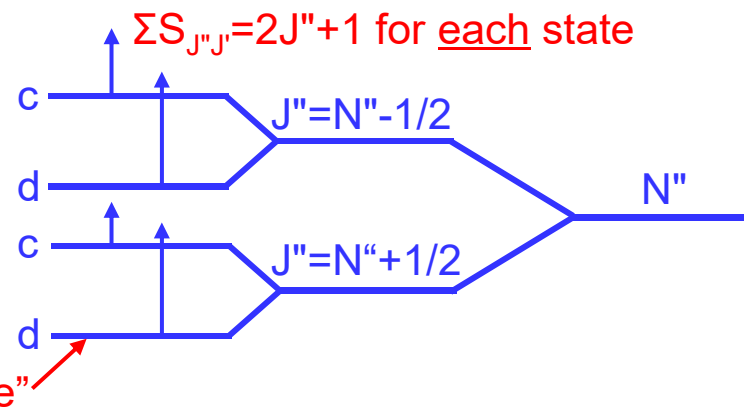2. In general,

$$N_i / N = g_i e^{-\varepsilon_i / kT} / Q$$

$$Q = Q_e \cdot Q_v \cdot Q_r$$

3. Electronic mode

$$g_e = (2S+1)\phi \leftarrow \begin{array}{l} \phi = 1, \Lambda = 0 \\ \phi = 2, \Lambda \neq 0 \end{array}$$

$$\Rightarrow \left. \begin{array}{ll} g_e = 4 & {}^2\Pi \\ g_e = 2 & {}^2\Sigma \end{array} \right\} OH$$

# of rot. levels produced by spin splitting & Λ-doubling = 4 for ${}^2\Pi$

ΣS$_{J''J'}$=2J''+1 for each state

c ——
d ——
J"=N"-1/2
c ——
J"=N"+1/2
d —
N"

A "state"

Elec. level

the sum of this over all levels is 1 →

$$\frac{N(n)}{N} = (2S+1)\phi \exp(-hcT_e(n)/kT)/Q_e$$

$$Q_e = \sum_n (2S+1)\phi \exp(-hcT_e(n)/kT)$$

✎ Note:

hund's (a) includes AΩ²

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4.2. Boltzmann fraction

4. Vibrational mode

$$\frac{N(n,\mathrm{v})}{N(n)} = \exp(-hcG(\mathrm{v})/kT)/Q_\mathrm{v}$$

$$Q_\mathrm{v} = \sum_\mathrm{v} \exp(-hcG(\mathrm{v})/kT) \quad \Leftarrow \quad$$

Again, each of these →1 when summed

5. Rotational mode (hund's (b))

- $$\frac{N(n,\mathrm{v},N)}{N(n,\mathrm{v})} = (2N+1)\exp(-hcF(N)/kT)/Q_r$$

$$\theta_r = hcB_v/k$$

$$Q_r = \sum_{N=\Lambda}^{\infty}(2N+1)\exp(-hcF(N)/kT) \quad \Longrightarrow \quad Q_r = \frac{T}{\theta_r} \text{ for } T \gg \theta_r$$

✎ Note: don't use F$_1$+F$_2$(N) here; until we add spin splitting

Now what about fraction of those with N in a given J?

- $$\frac{N(n,\mathrm{v},N,J)}{N(n,\mathrm{v},N)} = \frac{(2J+1)}{(2N+1)(2S+1)}$$

Since # of states in N is (2N+1)(2S+1)ϕ, while # of states in J is (2J+1) ϕ

≈ ½ for OH as expected

- $$\frac{N(n,\mathrm{v},N,J,p)}{N(n,\mathrm{v},N,J)} = \frac{1}{\phi}$$

(fraction with spectral parity)

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4.2. Boltzmann fraction

6. Combining

$$\frac{N(n, \mathrm{v}, N, J, p)}{N} = \frac{N_1}{N} \quad \text{(i.e., the Boltzmann fraction in \underline{state} 1)}$$

$$= \frac{N(n)}{N} \frac{N(n, \mathrm{v})}{N(n)} \frac{N(n, \mathrm{v}, N)}{N(n, \mathrm{v})} \frac{N(n, \mathrm{v}, N, J)}{N(n, \mathrm{v}, N)} \frac{N(n, \mathrm{v}, N, J, p)}{N(n, \mathrm{v}, N, J)}$$

$$= \frac{(2J+1)\exp\left(-\frac{hc}{kT}\left[T_e(n) + G(\mathrm{v}) + F_i(N)\right]\right)}{Q_e Q_\mathrm{v} Q_r}$$

Proper F$_i$ now!

✎ Note:

1. The fraction in a given state is 1/4 of that given by rigid rotor!

2. Always know $\Sigma(N_i/N) = 1$, both in total and for each mode separately.

We have 1 loose end to deal with:

\underline{narrow-band} and \underline{broadband} absorption measurement.

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4.3. Narrow-band vs broad-band absorption measurement

- Narrow-band absorption

Measured quantity

$$T_\nu = (I/I_0)_\nu = \exp(-S_{12}\phi_\nu L) \text{ with } S_{12} = \left[\frac{\pi e^2}{m_e c}\right] N_1 f_{12}\left(1 - \exp^{-\frac{h\nu}{kT}}\right)$$

Oscillator strength for transition

$$\left(\frac{N_1}{N_l}\right)\left(N_l = \text{tot. no. dens. of } l = \frac{p_l}{kT}\right)$$

Boltzmann fraction of species l = $F_{v'',J'',...}(T)$

thus, if T_ν (e.g. $T_{\nu 0}$) is <u>measured</u>, and

if L, p, 2γ, T, f_{12} are <u>known</u>

$$= \sum_i 2\gamma_i X_i$$

bd. species

then can solve for N_l ← Quantity usually sought

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4.3. Narrow-band vs broad-band absorption measurement

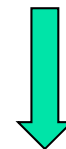*Let's look at the classical (old-time) approach, pre 1975*

- Broadband absorption

1 line →

Instrument broadening (no change in eq. width)

Eq. width $W_{J"J'}$ (cm^{-1})
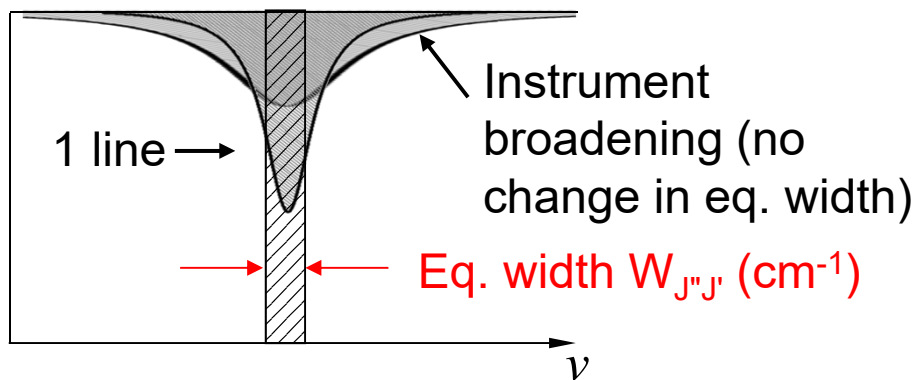
Integrated area is called: integrated absorbance, or eq. width

v

(for 1 line from 1 state) $\quad W_{line} = W_{J"J'} = \int A_{\bar{v}} d\bar{v} = \int (1 - T_{\bar{v}}) d\bar{v}$

$$= \int_{line} \{1 - \exp(-K_{J"J'}\phi(\bar{v})L)\} d\bar{v}$$

$$K_{J"J'} = S_{J"J'} P_i$$

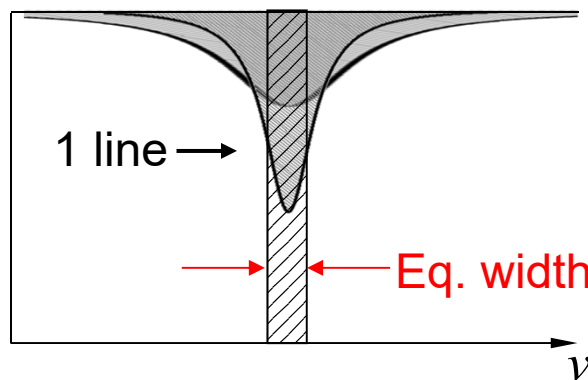Transform variables $\quad \bar{v} = \dfrac{\Delta \bar{v}_D}{2\sqrt{\ln 2}} x$

$$W_{J"J'} = \frac{\Delta \bar{v}_D}{\sqrt{\ln 2}} \int_0^\infty \left\{ 1 - \exp\left[-K_{J"J'} L \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta \bar{v}_D} V(x,a) \right] \right\} dx$$

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4.3. Narrow-band vs broad-band absorption measurement

Let's look at the classical (old-time) approach, pre 1975

- Broadband absorption ➡ Requires use of "curves of growth"

1 line →

← Eq. width $W_{J''J'}$ (cm^{-1}) →

$$W_{J''J'} = \frac{\Delta\bar{v}_D}{\sqrt{\ln 2}} \int_0^\infty \left\{ 1 - \exp\left[-K_{J''J'}L\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\bar{v}_D}V(x,a) \right] \right\} dx$$

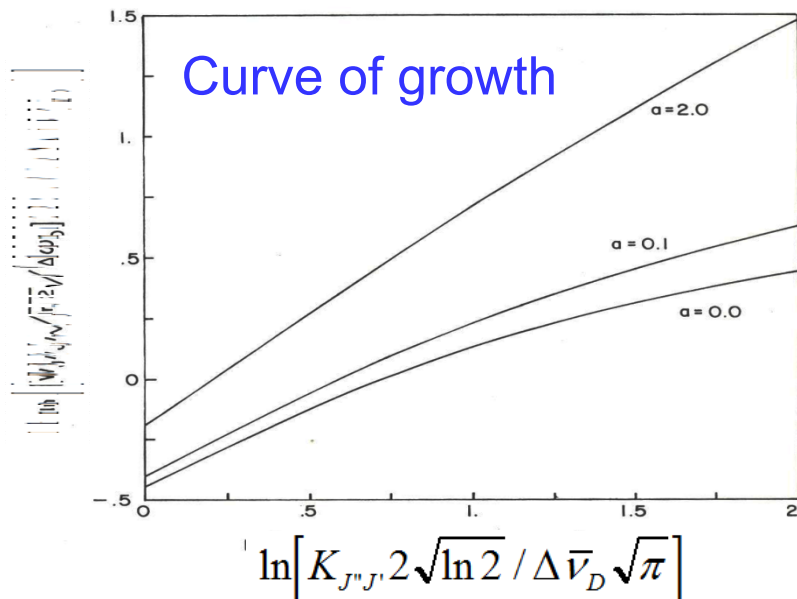- Procedure: measure $W_{J''J'}$, calculate Δv_D and a, infer $K_{J''J'}$, convert $K_{J''J'}$ to $N_{species}$
- Note:

1. Simple interpretation only in optically thin limit,

$$W_{J''J'} = \int \left[1 - \left(1 - K_{J''J'}\phi(\bar{v})L \right) \right] d\bar{v}$$

$$W_{J''J'} = K_{J''J'}L = \frac{\pi e^2}{mc^2} N_1 f_{12} L$$

2. Measured eq. width is indep. of instrument broadening!

3. **Before lasers, use of absorption spectroscopy for species measurements require use of Curves of Growth!**

Curve of growth

a = 2.0

a = 0.1

a = 0.0

$\ln\left[K_{J''J'} 2\sqrt{\ln 2} / \Delta\bar{v}_D \sqrt{\pi} \right]$

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4.4. Example calculation (narrow-band)

- Consider spectral absorption coefficient of the (0,0)Q$_1$(9) line in the OH A$^2\Sigma^+$–X$^2\Pi$ system, at line center.

  - λ~309.6nm, ν~32300cm^{-1}, T = 2000K, $\Delta\nu_C$ = 0.05cm^{-1}

    Express k_ν as a function of OH partial pressure

$$k_\nu\left[\text{cm}^{-1}\right] = 2.651 \times 10^{-2} \frac{\text{cm}^2}{\text{s}} \frac{P_a}{kT} \frac{N_{(n,v,\Sigma,J,\Lambda)''}}{N_a} \; f_{J''J'} \; \phi(\nu_0) \qquad N_a = P_a / kT$$

❸   ❶   ❷

❶ Oscillator strength (using tables)

$$f_{Q_1(9)} = f_{v''v'} \frac{S_{J''J'}}{2J''+1} = 0.00096 \times 0.947 = 9.09 \times 10^{-4}$$

❷ Lineshape factor (narrow-band)

$$\left. \begin{array}{l} \Delta\bar{\nu}_D(2000\text{K}) = 0.25\text{cm}^{-1} \\ \Delta\bar{\nu}_C(2000\text{K}) = 0.05\text{cm}^{-1} \end{array} \right\} a = 0.17 \Rightarrow \phi(\nu_0) = 3.13\text{cm} \ \text{ or } \ 1.04 \times 10^{-10}\text{s}$$

4.4. Example calculation (narrow-band)

- Consider spectral absorption coefficient of the (0,0)Q_1(9) line in the OH A$^2\Sigma^+$–X$^2\Pi$ system, at line center.

  - $\lambda \sim 309.6$nm, $\nu \sim 32300$cm^{-1}, T = 2000K, $\Delta\nu_C = 0.05$cm^{-1}

  Express k_ν as a function of OH partial pressure

$$k_\nu \left[\text{cm}^{-1}\right] = 2.651 \times 10^{-2} \frac{\text{cm}^2}{\text{s}} \frac{P_a}{kT} \frac{N_{(n,\text{v},\Sigma,J,\Lambda)''}}{N_a} \; f_{J''J'} \; \phi(\nu_0) \qquad N_a = P_a / kT$$

❸ **➌** **①** **②**

❸ Population fraction in the absorbing state

$$\frac{N_{f_{1c}(0.5)}}{N_a} = \frac{\exp\left[-hcT_e(0)/kT\right]}{Q_e} \cdot \frac{\exp\left[-hcG(0)/kT\right]}{Q_v} \cdot \frac{(2J''+1)\exp\left[-hcF_1(9.5)/kT\right]}{Q_r}$$

$$= \frac{\exp(0)}{4} \qquad \cdot \qquad \frac{\exp\left[-2660\text{K}/T\right]}{0.287} \cdot \frac{20\exp\left[-2313\text{K}/T\right]}{T/26.66\text{K}}$$

$$= \frac{1}{4} \qquad \cdot \qquad \frac{0.264}{0.287} \qquad \cdot \qquad \frac{6.29}{75.0}$$

$$= 0.25 \qquad \cdot \qquad 0.920 \qquad \cdot \qquad 0.0839$$

$$= 0.0193$$

4.4. Example calculation (narrow-band)

- Consider spectral absorption coefficient of the (0,0)Q₁(9) line in the OH A²Σ⁺–X²Π system, at line center.

  - $\lambda \sim 309.6nm$, $\nu \sim 32300cm^{-1}$, T = 2000K, $\Delta\nu_C = 0.05cm^{-1}$

    Express k_ν as a function of OH partial pressure

$$k_\nu\left[cm^{-1}\right] = 2.651 \times 10^{-2} \frac{cm^2}{s} \frac{P_a}{kT} \frac{N_{(n,\nu,\Sigma,J,\Lambda)''}}{N_a} \; f_{J''J'} \; \phi(\nu_0) \qquad N_a = P_a/kT$$

$$k_\nu\left[cm^{-1}\right] = \left(2.651 \times 10^{-2} \frac{cm^2}{s}\right)\left(P_a[atm]\right)\left(3.66 \times 10^{18} \frac{cm^{-3}}{atm}\right)\left(1.93\%\right)\left(9.09 \times 10^{-4}\right)\left(1.04 \times 10^{-10} s\right)$$

$$= 177 \frac{cm^{-1}}{atm}\left(P_a[atm]\right)$$

Beer's Law $I_\nu = I_\nu^0 \exp\left(-k_\nu L\right)$

⟹ 59% absorption

for L = 5cm, X_{OH} = 1000ppm, T = 2000K, P = 1atm

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4.4. Example calculation (narrow-band)

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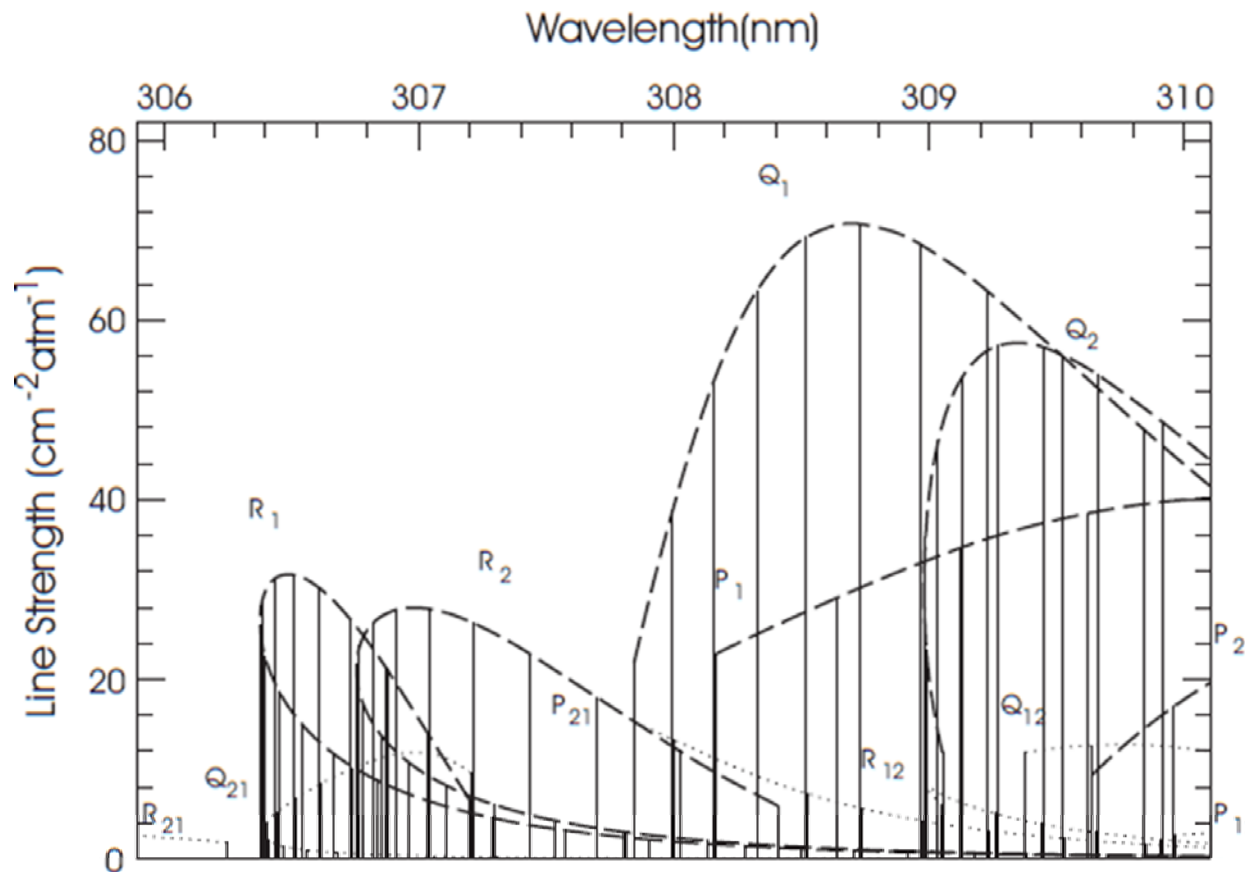
✎ Notes:

- Lines belonging to a specific branch are connected with dashed or dotted curve

- Thicker dashed lines – main branches; thin dotted lines – cross branches

- Bandhead in R branches if $B_{v'} < B_{v''}$; Bandhead in P branches if $B_{v'} > B_{v''}$

- Note bandhead in $^RQ_{21}$ branch

Next:
TDLAS, Lasers and Fibers

- Fundamentals
- Applications to Aeropropulsion