Lecture 8: Case Study: UV - OH

UV absorption of OH: \( A^2\Sigma^+ \rightarrow X^2\Pi \) (~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 $T$, $X_{\text{OH}}$ measurements.

Selected region of $A^2\Sigma^+ \leftarrow \chi^2\Pi(0,0)$ 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

\[
E(n, v, J) = T_e(n) + G(v) + F(J)
\]

- Separation of terms: Born-Oppenheimer approximation
- \( G(v) = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 \)
- Sources of \( T_e, \omega_e, \omega_e x_e \) ➔ Herzberg
- Overall system: \( A^2\Sigma^+ \leftarrow X^2\Pi \)

<table>
<thead>
<tr>
<th>( A^2\Sigma^+ )</th>
<th>( T_e )</th>
<th>( \omega_e )</th>
<th>( \omega_e x_e )</th>
<th>( \chi^2\Pi )</th>
<th>( T_e )</th>
<th>( \omega_e )</th>
<th>( \omega_e x_e )</th>
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<tr>
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<td>32682.0</td>
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<td>97.84</td>
<td>0.0</td>
<td>3735.21</td>
<td>82.21</td>
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Let’s first look at the upper state ➔ Hund’s case b!
2. Energy levels

Hund’s case b ($\Lambda=0$, $S\neq 0$) – more standard, especially for hydrides

Recall:

- $\Sigma$, $\Omega$ not rigorously defined
- $N = \text{angular momentum without spin}$
- $S = \text{1/2-integer values}$
- $J = N+S$, $N+S-1$, \ldots, $|N-S|$
- $i = 1, 2, \ldots$

$F_i(N) = \text{rotational term energy}$

Now, specifically, for OH?
2. Energy levels

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

For OH:

- $\Lambda = 0$, $\therefore \Sigma$ 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: $A^2\Sigma^+$

\[
\begin{align*}
F_1(N) &= B_v N(N + 1) - D_v [N(N + 1)]^2 + \gamma_v N \\
F_2(N) &= B_v N(N + 1) - D_v [N(N + 1)]^2 - \gamma_v (N + 1)
\end{align*}
\]

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

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

\[
\gamma_v(2N+1) \sim 0.1(5) \sim 0.5\text{cm}^{-1} \text{ for } N_2
\]

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

- Notes:
  - Progression for $A^2\Sigma^+$
  - “+” denotes positive “parity” for even $N$ [wave function symmetry]
  - Importance? Selection rules require parity change in transition
2. Energy levels

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

![Diagram showing energy levels](image)

- **Hund’s case $a$**
  - $\Lambda \neq 0$, $S \neq 0$, $\Sigma$ defined

- **Hund’s case $b$**
  - $\Lambda = 0$, $S \neq 0$, $\Sigma$ 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 $N$, $\Lambda$ 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”

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

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

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 \( \Lambda \Lambda \)

For large \( N \)

Behaves like Hund’s b, with small (declining) effect from spin

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

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

\[ F_1 - F_2 \rightarrow B_v [(N+1)^2 - N^2 - (2N+1)] \rightarrow 0 \]
2. Energy levels

The ground state: $X^2\Pi$

Notes:

4. Some similarity to symmetric top

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

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

Showed earlier that $F_1 < F_2$

$$T_e = T_0 + A\Lambda\Sigma$$

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

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

$$+ (-140)(1)(-1/2), \quad \Sigma = -1/2$$

$$\Rightarrow \Delta T_e = 140 \text{ cm}^{-1}$$

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

Recall: Hund’s case a has constant difference of 2(A-B$\nu$) 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), $\Omega = 3/2, 1/2$

$$\Rightarrow \Omega = 3/2 \text{ state lower by } 316 \text{ cm}^{-1}$$

Actual spacing is only 188 cm$^{-1}$, reflects that hydrides quickly go to Hund’s case b
2. Energy levels

The ground state: $X^2\Pi$

Notes:
5. Role of $\Lambda$-doubling

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: $A^2Σ^+ (v') \leftarrow X^2Π (v'') \gamma X_{αβ}(N'' \text{ or } J'')$

  where $Y = ΔN$ (O, P, Q, R, S for $ΔN = -2 \text{ to } +2$)
  
  $X = ΔJ$ (P, Q, R for $ΔJ = -1, 0, +1$)

  $α = i \text{ in } F_i'; i.e., 1 \text{ for } F_1, 2 \text{ for } F_2$

  $β = i \text{ in } F_i''; i.e., 1 \text{ for } F_1, 2 \text{ for } F_2$

- **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

- **General selection rules**
  
  - Parity must change $+ \rightarrow -$ or $- \rightarrow +$
  - $ΔJ = 0, ±1$
  - No $Q$ ($J = 0$) transitions, $J = 0 \rightarrow J = 0$ not allowed

Example: $sR_{21}$:

- $ΔJ = +1, ΔN = +2$
- $F' = F_2(N')$
- $F'' = F_1(N'')$
3. Allowed radiative transitions

- Allowed transitions

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

- 12 bands possible (3 originating from each lambda-doubled, spin-split X state)
- Main branches: $\alpha = \beta$; Cross-branches: $\alpha \neq \beta$
- 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; $\Delta J = \Delta N$)
- $+ \leftrightarrow -$ rule on parity
- $F_{1c} - F_{1d} \approx 0.04N(N+1)$ for OH ⇒ for $N\approx10$, $\Lambda$-doubling is $\sim 4\text{cm}^{-1}$, giving clear separation
- If upper state has $\Lambda$-doubling, we get twice as many lines!
3. Allowed radiative transitions

- Allowed transitions

Allowed rotational transitions from \( N'' = 13 \) in the \( A^2\Sigma^+ \leftrightarrow X^2\Sigma^+ \) 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 \( \Lambda \)-doubling
Complete steps to calculate absorption coefficient

1. Identify/characterize oscillator strengths using Hönl-London factors
2. Calculate Boltzmann fraction
3. Calculate lineshape function \(_{(narrow\text{-}band\text{ vs broad\text{-}band)}\)
4. Calculate absorption coefficient

Absorption coefficient

\[
\frac{0.0265\ cm^2/s}{N_1/N_a} \times \frac{P_A}{kT} \times \frac{1}{c} \phi(s) = \phi(cm)
\]

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

Step 4  Step 5
4.1. Oscillator strengths

Absorption oscillator strength

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

or in shorthand notation

\[ f_{J''J'} = f_{n''n'} q_{v''v'} \frac{S_{J''J'}}{2J''+1} = f_{v''v'} \]

= band oscillator strength

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Notes: \( q_{v''v'} \) and \( S_{J''J'} \) are normalized

- \( \sum_{v'} q_{v''v'} = 1 \)
- \( \sum_{J'} S_{J''J'} = (2J''+1)(2S+1) \delta_{g''_i=4} \) for \( \Sigma''=4 \) for \( \Lambda=0 \) (\( \Sigma \) state), 2 otherwise

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For OH \( \Lambda^2\Sigma^+-X^2\Pi \)

<table>
<thead>
<tr>
<th>((v', v''))</th>
<th>( f_{v''v'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0)</td>
<td>0.00096</td>
</tr>
<tr>
<td>(1,0)</td>
<td>0.00028</td>
</tr>
</tbody>
</table>
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

\[
\frac{(2J'+1)}{2J''+1} \cdot \frac{f_{1e}}{q_{v'n'}} \cdot \frac{S_{J'J''}}{2J''+1} = \left( \frac{2J''+1}{2J'+1} \right) \cdot \frac{f_{2e}'}{q_{v'n''}} \cdot \frac{S_{J''J'}}{2J'+1}
\]

In this way, there are no remaining electronic degeneracy and we require, for detailed balance, that \( f_{1e} = f_{1e}' \), \( q_{v'n'} = q_{v'n''} \) and \( S_{J''J'} = S_{J',J''} \).

- Do we always enforce \( \sum_{J''} S_{J''J'} = (2J''+1) \) for a state? No!

- But note we do enforce

\[
\sum_{J''} S_{J''J'} = (2J''+1) (2S+1) \delta \quad (14.17)
\]

and

\[
\sum_{J''} S_{J''J'} = (2J'+1) (2S+1) \delta \quad (14.19)
\]

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 \( \Sigma-\Sigma \) and \( \Pi-\Pi \), where there are equal “elec. degeneracies”, i.e., \( g''_{el} = g'_{el} \). But for \( \Sigma-\Pi \) (as in OH), we have an issue. In the \( X^2 \Pi \) state, \( g_{el} = 4 \) (2 for spin and 2 for \( \Lambda \)-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 \( \sum_{J'} S_{J',J''} = (2J'+1)4 \) as required by (14.19).
4.1. Oscillator strengths

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

<table>
<thead>
<tr>
<th>Source</th>
<th>$f_{00}$</th>
</tr>
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<tbody>
<tr>
<td>Oldenberg, et al. (1938)</td>
<td>0.00095 ± 0.00014</td>
</tr>
<tr>
<td>Dyne (1958)</td>
<td>0.00054 ± 0.0001</td>
</tr>
<tr>
<td>Carrington (1959)</td>
<td>0.00107 ± 0.00043</td>
</tr>
<tr>
<td>Lapp (1961)</td>
<td>0.00100 ± 0.0006</td>
</tr>
<tr>
<td>Bennett, et al. (1963)</td>
<td>0.00078 ± 0.00008</td>
</tr>
<tr>
<td>Golden, et al. (1963)</td>
<td>0.00071 ± 0.00011</td>
</tr>
<tr>
<td>Engleman, et al. (1973)</td>
<td>0.00096</td>
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<tr>
<td>Bennett, et al. (1964)</td>
<td>0.0008 ± 0.00008</td>
</tr>
<tr>
<td>Anketell, et al. (1967)</td>
<td>0.00148 ± 0.00013</td>
</tr>
</tbody>
</table>
### 4.1. Oscillator strengths

**Absorption oscillator strength**

<table>
<thead>
<tr>
<th>Transition</th>
<th>$S_{J'J}/(2J'^{+}+1)$</th>
<th>$\Sigma F_1(J)$</th>
<th>$\Sigma F_2(J)$</th>
<th>$\Sigma [F_1(J)+F_2(J)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{12}(0.5)$</td>
<td>0.667</td>
<td>0</td>
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<td>2</td>
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<tr>
<td>$Q_2(0.5)$</td>
<td>0.667</td>
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<td>$R_{12}(0.5)$</td>
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<td>$R_2(0.5)$</td>
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<td>$Q_1(1.5)$</td>
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<td>$Q_{12}(1.5)$</td>
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<td>$R_3(2.5)$</td>
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**Hönl-London factors for selected OH transitions**

<table>
<thead>
<tr>
<th>Transition</th>
<th>$S_{J'J}/(2J'^{+}+1)$</th>
<th>$\Sigma F_1(J)$</th>
<th>$\Sigma F_2(J)$</th>
<th>$\Sigma [F_1(J)+F_2(J)]$</th>
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</tr>
<tr>
<td>$R_2(9.5)$</td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_3(9.5)$</td>
<td>0.462</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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,

\[ \frac{N_i}{N} = g_i e^{-\varepsilon_i / kT} / Q \]

\[ Q = Q_e \cdot Q_v \cdot Q_r \]

3. Electronic mode

\[ g_e = (2S + 1) \phi \]

\[ \phi = 1, \Lambda = 0 \]

\[ g_e = 4 \]

\[ 2 \Pi \]

\[ \text{OH} \]

\[ g_e = 2 \]

\[ 2 \Sigma \]

\# of rot. levels produced by spin splitting & \Lambda-doubling = 4 for \( 2 \Pi \)

\[ \sum S_{J''J'} = 2J'' + 1 \text{ for each state} \]

Elec. level

the sum of this over all levels is 1

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

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

\[ \text{Note:} \]

hund's (a) includes \( A\Omega^2 \)
4.2. Boltzmann fraction

4. Vibrational mode

\[
\frac{N(n, v)}{N(n)} = \exp\left(-\frac{\hbar c G(v)}{kT}\right) / Q_v
\]

\[
Q_v = \sum_v \exp\left(-\frac{\hbar c G(v)}{kT}\right)
\]

5. Rotational mode (hund’s (b))

\[
\frac{N(n, v, N)}{N(n, v)} = (2N+1) \exp\left(-\frac{\hbar c F(N)}{kT}\right) / Q_r
\]

\[
Q_r = \sum_{N=\Lambda}^{\infty} (2N+1) \exp\left(-\frac{\hbar c F(N)}{kT}\right)
\]

\[
Q_r = \frac{T}{\theta_r} \text{ for } T \gg \theta_r
\]

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 \( J \)?

\[
\frac{N(n, v, N, J)}{N(n, v, N)} = \frac{(2J+1)}{(2N+1)(2S+1)}
\]

Since # of states in \( N \) is \((2N+1)(2S+1)\phi, \)

while # of states in \( J \) is \((2J+1) \phi \)

\[
\approx \frac{1}{2} \text{ for OH as expected}
\]

\[
\frac{N(n, v, N, J, p)}{N(n, v, N, J)} = \frac{1}{\phi}
\]

(fraction with spectral parity)
4.2. Boltzmann fraction

6. Combining

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

\[
= \frac{N(n)N(n,v)N(n,v,N)N(n,v,N,J)N(n,v,N,J,p)}{N N(n) N(n,v) N(n,v,N) N(n,v,N,J)}
\]

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

\[
= \frac{Q_e Q_v Q_r}{Q_e Q_v Q_r}
\]

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:* narrow-band and broadband absorption measurement.
4.3. Narrow-band vs broad-band absorption measurement

Narrow-band absorption
Measured quantity

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

- Oscillator strength for transition
- Boltzmann fraction of species \( l = F_{\nu*,j*,...}(T) \)

thus, if \( T_\nu \) (e.g. \( T_{\nu_0} \)) is measured, and
if \( L, p, 2\gamma, T, f_{12} \) are known

\[ = \sum_{i} 2\gamma_i X_i \]

bd. species

then can solve for \( N_l \) → Quantity usually sought
4.3. Narrow-band vs broad-band absorption measurement

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

- Broadband absorption

   ![Diagram of broadband absorption](image)

   Integrated area is called: integrated absorbance, or eq. width

   **Eq. width** $W_{J''J'}$ (cm$^{-1}$)

   (for 1 line from 1 state)

   $$W_{\text{line}} = W_{J''J'} = \int A(\nu) d\nu = \int (1 - T(\nu)) d\nu$$

   $$= \int_{\text{line}} \{1 - \exp(-K_{J''J'}(\nu)L)\} d\nu$$

   **Transform variables**

   $$\bar{\nu} = \frac{\Delta \nu_D}{\sqrt{2 \ln 2}} x$$

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

   **Integrated area**
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”

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

- Procedure: measure \( W_{J''J'} \), calculate \( \Delta \nu_D \) and \( a \), infer \( K_{J''J'} \), convert \( K_{J''J'} \) to \( N_{\text{species}} \)

- Note:
  1. Simple interpretation only in optically thin limit,
  \[
  W_{J''J'} = \int [1 - (1 - K_{J''J'} \phi(\bar{v})L)] d\bar{v}
  \]
  \[
  W_{J''J'} = K_{J''J'}L = \frac{\pi e^2}{mc^2} N_{1,f_{12}}L
  \]
  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!
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.
  - \(\lambda\approx309.6\text{nm},\ \nu\approx32300\text{cm}^{-1},\ T=2000\text{K},\ \Delta\nu_C = 0.05\text{cm}^{-1}\)

Express \(k_\nu\) as a function of OH partial pressure

\[
k_\nu[\text{cm}^{-1}] = 2.651 \times 10^{-2} \frac{\text{cm}^2}{\text{s}} \frac{P_a}{kT} \frac{N_{(n,x,x,\nu,J,A)}}{N_a} \phi(\nu_0)
\]

\(N_a = P_a / kT\)

1. Oscillator strength (using tables)

\[
f_{Q(9)} = f_{\nu''\nu'} \frac{S_{J''J'}}{2J''+1} = 0.00096 \times 0.947 = 9.09 \times 10^{-4}
\]

2. Lineshape factor (narrow-band)

\[
\Delta \bar{\nu}_D(2000\text{K}) = 0.25\text{cm}^{-1}
\Delta \bar{\nu}_C(2000\text{K}) = 0.05\text{cm}^{-1}
\]

\[
\left\{ \begin{array}{l}
a = 0.17 \Rightarrow \phi(\nu_0) = 3.13\text{cm} \quad \text{or} \quad 1.04 \times 10^{-10}\text{s}
\end{array} \right.
\]
4.4. Example calculation (narrow-band)

Consider spectral absorption coefficient of the (0,0)Q_1(9) line in the OH A^2Σ^+–X^2Π system, at line center.

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

*Express $k_\nu$ as a function of OH partial pressure*  

$$k_\nu \left[ \text{cm}^{-1} \right] = 2.651 \times 10^{-2} \frac{\text{cm}^2}{\text{s}} \frac{P_a}{kT} \frac{N_{(n,\nu,x,J,\Lambda)}}{N_a} f_{J^0,J^1} \phi(\nu_0)$$

$N_a = P_a / kT$

### Population fraction in the absorbing state

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

<table>
<thead>
<tr>
<th>$N_{f_{ic}(0.5)}/N_a$</th>
<th>$Q_e$</th>
<th>$Q_v$</th>
<th>$Q_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\exp(0)}{4}$</td>
<td>$\exp[-2660K/T]$</td>
<td>$0.287$</td>
<td>$\frac{20\exp[-2313K/T]}{T/26.66K}$</td>
</tr>
<tr>
<td>$= 0.25$</td>
<td>$0.264$</td>
<td>$6.29$</td>
<td></td>
</tr>
<tr>
<td>$1/4$</td>
<td>$0.287$</td>
<td>$75.0$</td>
<td></td>
</tr>
<tr>
<td>$= 0.0193$</td>
<td>$0.920$</td>
<td>$0.0839$</td>
<td></td>
</tr>
</tbody>
</table>
4.4. Example calculation (narrow-band)

- Consider spectral absorption coefficient of the \((0,0)Q_1(9)\) line in the \(\text{OH} \ A^2\Sigma^+ - X^2\Pi\) system, at line center.
  - \(\lambda \sim 309.6\text{nm}, \nu \sim 32300\text{cm}^{-1}, T = 2000\text{K}, \Delta \nu_C = 0.05\text{cm}^{-1}\)

Express \(k_\nu\) as a function of OH partial pressure

\[
k_\nu \left[ \text{cm}^{-1} \right] = 2.651 \times 10^{-2} \text{ cm}^2 \text{s}^{-1} \frac{\text{P}_a}{kT} \left( \frac{N_{n,v,x,j,J,A}}{N_a} \right) f_{J'\nu,J} \phi(\nu_0) \]

\[
N_a = \frac{P_a}{kT}
\]

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

\[
= 177 \text{ cm}^{-1} \text{ atm}^{-1} \left( \text{P}_a \text{[atm]} \right)
\]

Beer’s Law \(I_\nu = I_\nu^0 \exp(-k_\nu L)\)

- 59% absorption
  - for \(L = 5\text{cm}, X_{\text{OH}} = 1000\text{ppm}, T = 2000\text{K}, P = 1\text{atm}\)
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