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 $A^2\Sigma^+ \rightarrow X^2\Pi$ system
1. Introduction

- OH, a prominent flame emitter, absorber.
  Useful for $T$, $X_{\text{OH}}$ measurements.

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

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

- Separation of terms: Born-Oppenheimer approximation

- \( G(v) = \omega_e(v + 1/2) - \omega_{e\chi_e}(v + 1/2)^2 \)

- Sources of \( T_e, \omega_e, \omega_{e\chi_e} \) \( \Rightarrow \) Herzberg

- Overall system: \( \text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi \)

<table>
<thead>
<tr>
<th>\text{A}^2\Sigma^+</th>
<th>\text{T}_e</th>
<th>\omega_e</th>
<th>\omega_{e\chi_e}</th>
<th>\text{X}^2\Pi</th>
<th>\text{T}_e</th>
<th>\omega_e</th>
<th>\omega_{e\chi_e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{X}^2\Pi</td>
<td>32682.0</td>
<td>3184.28</td>
<td>97.84</td>
<td>0.0</td>
<td>3735.21</td>
<td>82.21</td>
<td></td>
</tr>
</tbody>
</table>

*Let's first look at the upper state \( \Rightarrow \) 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
- $N =$ angular momentum without spin
- $S = 1/2$-integer values
- $J = N+S, N+S-1, \ldots, |N-S|
- $i = 1, 2, \ldots$

$F_i(N) =$ rotational term energy

Now, specifically, for OH?
2. Energy levels

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

For OH:

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

- $F_1(N) = B_v N(N+1) - D_v [N(N+1)]^2 + \gamma_v N$
- $F_2(N) = B_v N(N+1) - D_v [N(N+1)]^2 - \gamma_v (N+1)$

(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 $N$

$\gamma_v(2N+1) \sim 0.1(5) \sim 0.5 \text{cm}^{-1}$ 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
2. Energy levels

The ground state: $X^2Π (Λ=1, S=1/2)$

- Hund’s case $a$
  - $Λ ≠ 0, S ≠ 0, Σ defined$

- Hund’s case $b$
  - $Λ = 0, S ≠ 0, Σ not defined$

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 $X^2Π$ 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

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

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

$$F_1 - F_2 \rightarrow B_v \left( (N+1)^2 - N^2 - (2N + 1) \right) \rightarrow 0$$
2. Energy levels

The ground state: $X^2\Pi$

**Notes:**

4. Some similarity to symmetric top

<table>
<thead>
<tr>
<th>J</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>3</td>
</tr>
<tr>
<td>5/2</td>
<td>2</td>
</tr>
<tr>
<td>3/2</td>
<td>1</td>
</tr>
</tbody>
</table>

Hund’s $a \rightarrow 2|A-B_v|$

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

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

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

Showed earlier that $F_1 < F_2$

$T_e = T_0 + A\Lambda\Sigma$

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

- $5/2$
  - $T_e = T_0 + (-140)(1)(1/2), \Sigma = 1/2$
  - $+ (-140)(1)(-1/2), \Sigma = -1/2$
  - $\Delta T_e = 140 \text{ cm}^{-1}$

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

$1/2$

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

$\Rightarrow \Omega = 3/2$ state lower by 316 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

\[ F_{ic}(J) - F_{id}(J) \approx 0.04 \text{ cm}^{-1} \text{ for typical } J \text{ in OH} \]

\[ c \text{ and } d \text{ have different parity (p)} \]

\[ \text{Splitting decreases with increasing } N \]

\[ F_{ic} = F_i(J) + \delta_c J(J+1) \]
\[ F_{id} = F_i(J) + \delta_d J(J+1) \]

\[ F_{ic} < F_{id} \]

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

where $Y - \Delta N$ (O, P, Q, R, S for $\Delta N = -2$ to $+2$)
$X - \Delta J$ (P, Q, R for $\Delta J = -1$, 0, $+1$)
$\alpha = i$ in $F_{i}$; i.e., 1 for $F_{1}$, 2 for $F_{2}$
$\beta = i$ in $F_{i}$; i.e., 1 for $F_{1}$, 2 for $F_{2}$

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

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

Example: $^{5}S_{R_{21}}$
$\Delta J = +1$, $\Delta N = +2$
$F' = F_{2}(N')$
$F'' = F_{1}(N'')$
3. Allowed radiative transitions

- Allowed transitions

Allowed rotational transitions from N''=13 in the A^2Σ^+ ← X^2Π system

- 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; $\Delta J = \Delta N$)
- $+ \leftrightarrow -$ rule on parity
- $F_{1c} - F_{1d} \approx 0.04N(N+1)$ for OH $\Rightarrow$ for $N \sim 10$, $\Lambda$-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
4. Working example - OH

- Complete steps to calculate absorption coefficient

1. Identify/characterize oscillator strengths using Hönll-London factors
2. Calculate Boltzmann fraction
3. Calculate lineshape function (narrow-band vs broad-band)
4. Calculate absorption coefficient

Absorption coefficient

\[
\frac{P_A}{kT} \quad \text{#/cm}^3 \text{ of species (OH)}
\]

\[
\frac{N_1}{N_a} \quad \text{Fractional pop. in state 1}
\]

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

\[
\phi[s] = \frac{1}{c} \phi[cm]
\]

0.0265 cm$^2$/s

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

Step 1   Step 2
4.1. Oscillator strengths

Absorption oscillator strength

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

or in shorthand notation

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

= \( f_{v''v'} \) = band oscillator strength

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

- \( \sum_{v'} q_{v''v'} = 1 \)
- \( \sum_{J''} S_{J''J'} = (2J''+1)(2S+1)\delta_{g''\epsilon} \)

1 for \( \Lambda = 0 \) (\( \Sigma \) state), 2 otherwise

this sum includes the \( S \) values for all states with \( J'' \)

For OH \( A^2\Sigma^+ \rightarrow X^2\Pi \)

<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

Absorption oscillator strength for $f_{00}$ in OH $A^2Σ^+–X^2Π$

<table>
<thead>
<tr>
<th>Source</th>
<th>$f_{00}$</th>
</tr>
</thead>
<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>
</tr>
<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>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$Q_2(0.5)$</td>
<td>0.667</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{12}(0.5)$</td>
<td>0.333</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_2(0.5)$</td>
<td>0.333</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_1(1.5)$</td>
<td>0.588</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$P_{12}(1.5)$</td>
<td>0.078</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_{21}(1.5)$</td>
<td>0.392</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_2(1.5)$</td>
<td>0.275</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_1(1.5)$</td>
<td>0.562</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{12}(1.5)$</td>
<td>0.372</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{21}(1.5)$</td>
<td>0.246</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_2(1.5)$</td>
<td>0.678</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1(1.5)$</td>
<td>0.165</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{12}(1.5)$</td>
<td>0.235</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_2(1.5)$</td>
<td>0.047</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_2(1.5)$</td>
<td>0.353</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_1(2.5)$</td>
<td>0.530</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$P_{12}(2.5)$</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_{21}(2.5)$</td>
<td>0.242</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_2(2.5)$</td>
<td>0.358</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_1(2.5)$</td>
<td>0.708</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{12}(2.5)$</td>
<td>0.263</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_2(2.5)$</td>
<td>0.214</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_2(2.5)$</td>
<td>0.757</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1(2.5)$</td>
<td>0.256</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{12}(2.5)$</td>
<td>0.173</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{21}(2.5)$</td>
<td>0.050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_2(2.5)$</td>
<td>0.379</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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,

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

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

3. Electronic mode

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

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

\[ \phi = 2, \Lambda \neq 0 \]

\[ g_e = 4 \begin{cases} 2 \Pi \end{cases} \text{OH} \]

\[ g_e = 2 \begin{cases} 2 \Sigma \end{cases} \]

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

A “state”

Elec. level

the sum of this over all levels is 1

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

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

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

Note:

hund’s (a) includes $\Lambda\Omega^2$
4.2. Boltzmann fraction

4. Vibrational mode

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

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

5. Rotational mode (hund’s (b))

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

\[
\theta_r = \frac{hcB_v}{k}
\]

\[
Q_r = \sum_{N=A}^{\infty} (2N + 1) \exp\left(-\frac{hcF(N)}{kT}\right)
\]

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

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

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

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

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

We have 1 loose end to deal with:

narrow-band and broadband absorption measurement.

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.

Proper \( F_i \) now!
4.3. Narrow-band vs broad-band absorption measurement

Narrow-band absorption

Measured quantity

\[ T_\nu = \left( \frac{I}{I_0} \right)_\nu = \exp\left( - S_{12} \phi_\nu L \right) \]

with

\[ S_{12} = \frac{\pi e^2}{m_e c} N_1 f_{12} \left( 1 - \exp \left( \frac{h \nu}{kT} \right) \right) \]

\[ \left( \frac{N_1}{N_l} \right) \]

\[ N_l = \text{tot. no. dens. of } l = \frac{p_l}{kT} \]

\[ \sum_{i \text{ bd. species}} 2\gamma_i X_i \]

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

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

\[ W_{\text{line}} = W_{J''J'} = \int A_\nu d\nu = \int (1 - T_\nu) d\nu = \int_{\text{line}} \{1 - \exp(-K_{J''J'}\phi(\nu)L)\} d\nu \]

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

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

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

(for 1 line from 1 state)
4.3. Narrow-band vs broad-band absorption measurement

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

- Broadband absorption \( \Rightarrow \) Requires use of “curves of growth”

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

- 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,
  \[
  W_{J'',J'} = \int [1 - (1 - K_{J'',J'} \phi(\bar{\nu})L)] d\bar{\nu}
  \]
  \[
  W_{J'',J'} = K_{J'',J'}L = \frac{\pi e^2}{mc^2} N_1 f_{12} L
  \]
  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\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

\[
k_{\nu}[\text{cm}^{-1}] = 2.651 \times 10^{-2} \frac{\text{cm}^2}{\text{s}} \frac{P_{a}}{kT} \frac{N_{a}}{N_{a}} \frac{f_{J''J''}}{\phi(\nu_{0})} \]

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)

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

\[
a = 0.17 \Rightarrow \phi(\nu_{0}) = 3.13\text{cm} \text{ or } 1.04 \times 10^{-10}\text{s}
\]
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.

- \(\lambda\sim309.6\text{nm}, \nu\sim32300\text{cm}^{-1}, T = 2000\text{K}, \Delta\nu_C = 0.05\text{cm}^{-1}\)

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

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

Population fraction in the absorbing state

\[
\frac{N_{f_{(0,5)}}}{N_a} = \frac{\exp[-hcT_e(0)/kT]}{4} \cdot \frac{\exp[-hcG(0)/kT]}{0.287} \cdot \frac{(2J''+1)\exp[-hcF_1(9.5)/kT]}{T/26.66K}
\]

\[
= \frac{1}{4} \cdot 0.264 \cdot 6.29
\]

\[
= 0.25 \cdot 0.920 \cdot 0.0839
\]

\[
= 0.0193
\]
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 \(\text{OH partial pressure}\)

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

\(N_a = P_a / kT\)

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

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

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