Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 7: Electronic Spectra of Diatomics

1. Term symbols for diatomic molecules
2. Common molecular models for diatomics
3. Improved treatments
4. Quantitative absorption
1. Term symbols for diatomic molecules

Term symbols characterize key features of electron spin and orbital angular momentum.

**Important terms**

- **projection of orbital angular momentum onto the internuclear axis.**
  - **Magnitude:** \( |\vec{\Lambda}| = \Lambda \hbar \)
  - **Symbols:** 
    - \( \Lambda \)
    - \( \Sigma \)
    - \( \Pi \)
    - \( \Delta \)

- **total electronic spin angular momentum (the sum of electron spin in unfilled shells)**
  - **Magnitude:** \( |\vec{S}| = S \hbar \), \( S \) will have 1/2-integer values

- **projection of \( \vec{S} \) onto the internuclear axis (only defined when \( \Lambda \neq 0 \).**
  - **Magnitude:** \( |\vec{\Sigma}| = \Sigma \hbar \)
  - **Allowed values:** \( \Sigma = S, S - 1, \ldots, -S \) \( (2S + 1 \text{ values}) \)

- **sum of projections along the internuclear axis of electron spin and orbital angular momentum**
  - \( \vec{\Omega} = \vec{\Sigma} + \vec{\Lambda} \)
  - \( \Omega = \Lambda + S, \Lambda + S - 1, \ldots, |\Lambda - S| \) \( (2S + 1 \text{ values for } \Lambda \geq S) \)

For an atom: \( ^{2S+1}L_J \)

For a diatomic: \( ^{2S+1}\Lambda_\Omega \)
1. Term symbols for diatomic molecules

Examples

NO
The ground state for NO is $X^2\Pi$
$S = 1/2, \Lambda = 1, \Omega = 3/2, 1/2$
There are two spin-split sub-states: $^2\Pi_{1/2}, ^2\Pi_{3/2}$
Separation: 121cm$^{-1}$

CO
The ground state for CO is $X^1\Sigma^+$
$S = 0$ and $\Lambda = 0$, therefore $\Omega$ is unnecessary. This is a rigid rotor molecule. Easiest case!

O$_2$
The ground state for O$_2$ is $X^3\Sigma_g^-$
$S = 1, \Lambda = 0$
The $^-$ and $g$ are notations about symmetry properties of wave functions. This is an example of a molecule that is modeled by Hund’s case $b$
2. Common molecular models for diatomics

Four common molecular models

<table>
<thead>
<tr>
<th>Model</th>
<th>$\Lambda$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid Rotor</td>
<td>$\Lambda = 0$, $S = 0$</td>
<td></td>
</tr>
<tr>
<td>Symmetric Top</td>
<td>$\Lambda \neq 0$, $S = 0$</td>
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<td>Hund’s $a$</td>
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<td></td>
</tr>
<tr>
<td>Hund’s $b$</td>
<td>$\Lambda = 0$, $S \neq 0$</td>
<td></td>
</tr>
</tbody>
</table>

- This lecture: Rigid Rotor, Symmetric Top
- Followed by: Hund’s $a$, Hund’s $b$

$2S + 1 = 1 \Rightarrow$ “singlets”
no influence of electron spin on spectra
Spin important through interaction of $\Lambda$ and $\Sigma$
2. Common molecular models for diatomics

- Rigid rotor (\(^1\Sigma\))

- \(\Lambda = 0, S = 0 \implies ^1\Sigma\) type, \(\Omega\) is not defined

- \(\Lambda = 0\) means the projection of the orbital angular momentum onto the A-axis is zero, and rotation must thus be around the B-axis

\[ I_A \approx 0 \]
\[ I_B = I_C \]
2. Common molecular models for diatomics

Rigid rotor \( (^1\Sigma) \)

Rotational Energy

\[
F(J) = B_v J(J+1) - D_v J^2(J+1)^2
\]

Total Energy

\[
\Delta E = \Delta T_e + \Delta G + \Delta F
\]

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

Selection Rules

Rotational spectra:

\[
\Delta J = J' - J'' = +1
\]

Rovibrational spectra:

\[
\Delta v = v' - v'' = +1
\]

\[
\Delta J = \pm 1
\]

Rovibronic spectra:

\[
\Delta v \text{ determined by Frank-Condon factors}
\]

\[
\Delta J = \pm 1
\]

*Note: an alternate form is sometimes used*

\[
\Delta \alpha = \alpha_{\text{final}} - \alpha_{\text{initial}}
\]

\[
\alpha = J \text{ or } v
\]
2. Common molecular models for diatomics

- Rigid rotor ($^1\Sigma$)

**Intensity Distribution**

Within each band ($v'$, $v''$), the intensity distribution follows the Boltzmann distribution for J modified by a J-dependent branching ratio (i.e., for the P and R branch), known as the Hönl-London factor.

The relative intensities among all the vibrational bands originating from a single initial level $v_{initial}$ to all possible final levels $v_{final}$ are given by Franck-Condon factors.

The relative total emission or absorption from $v_{initial}$ depends directly on the Boltzmann fraction in that level, i.e., $n_{v_{initial}}/n$.

**Examples**

Most stable diatomics: CO, Cl₂, Br₂, N₂, H₂ are rigid rotors

Exceptions: NO ($X^2\Pi$), O₂($X^3\Sigma$)

Note: no $X\Delta$ states for diatomics – all $X$ states are $\Sigma$ or $\Pi$!

Some linear polyatomics: CO₂($\tilde{X}^1\Sigma^+_g$), HCN and N₂O ($\tilde{X}^1\Sigma^+$) are rigid rotors with $^1\Sigma$ ground states.

Nuclear spin will have an impact on the statistics of homonuclear diatomic molecules.
2. Common molecular models for diatomics

- Symmetric top

- $\Lambda \neq 0$, $S = 0$ (non-zero projection of orbital angular momentum on the internuclear axis and zero spin) $\Rightarrow$ ground states $^1\Pi$, $^1\Delta$

- Important components

  - $\vec{N}$ angular momentum of nuclei
  - $\vec{\Lambda}$ A-axis projection of electron orbital angular momentum
  - $\vec{J}$ total angular momentum; $\vec{J} = \vec{N} + \vec{\Lambda}$

Only the axial component of orbital angular momentum is used, because only $\vec{\Lambda}$ is a “good” quantum number, i.e., a constant of the motion
2. Common molecular models for diatomics

- Symmetric top ($\Lambda \neq 0$, $S = 0$)

Rotational Energy: $F(J) = BJ(J + 1) + (A - B)\Lambda^2$, $J = \Lambda, \Lambda + 1, ...$

$A, B = \frac{h}{8\pi^2 c I_{A,B}}$

Same spacing as the rigid rotor, but with a constant offset

Since $I_A < I_B$, $A > B$, lines with $J < \Lambda$ are missing, as $J = \Lambda, \Lambda + 1, ...$

Selection Rules:

$\Delta \Lambda = 0, \Delta J = \pm 1, 0$  ($\Delta J = 0$ is weak)

$\Delta \Lambda = \pm 1, \Delta J = \pm 1, 0$

As a result of having a Q branch (i.e., $\Delta J = 0$), the bands for a symmetric top will be double-headed, in contrast to the single-headed character of rigid rotor bands.
2. Common molecular models for diatomics

Symmetric top ($\Lambda \neq 0$, $S = 0$)

Spectra for $\Delta \Lambda = 0$ ($^1\Pi \leftrightarrow ^1\Pi$ or $^1\Delta \leftrightarrow ^1\Delta$)

\[
T' = B' J' (J' + 1) + (A' - B') \Lambda^2 + G(v') + T_e',
\]

\[
T'' = B'' J'' (J'' + 1) + (A'' - B'') \Lambda^2 + G(v'') + T_e''.
\]

$\bar{\nu}_\infty = \text{upper (for } J' = 0 \text{)} - \text{lower (for } J'' = 0 \text{)} = \text{constant}$

\[
P(J'') = \bar{\nu}_\infty - (B' + B'') J + (B' - B'') J^2
\]

\[
Q(J'') = \bar{\nu}_\infty + (B' - B'') J + (B' - B'') J^2
\]

\[
R(J'') = \bar{\nu}_\infty + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2
\]

$\begin{align*}
m_p &= -J \\
m_Q &= +J \\
m_R &= J + 1
\end{align*}$

P and R branches: $\bar{\nu} = \bar{\nu}_\infty + am + bm^2$

Q branch: $\bar{\nu} = \bar{\nu}_\infty + bm + bm^2$

where $a = B' + B''$, $b = B' - B''$
2. Common molecular models for diatomics

- Symmetric top ($\Lambda \neq 0, S = 0$)

Spectra for $\Delta \Lambda = 0$

- P and R branches: $\nu = \nu_\infty + am + bm^2$
- Q branch: $\nu = \nu_\infty + bm + bm^2$

where $a = B' + B''$, $b = B' - B''$

Notes:
- Band heads in the Q and R branches for the typical case of $B'<B''$.
- $m_P = -J$, $m_Q = +J$, $m_R = J+1$
- $J_{\text{min}} = 2$ for $^1\Delta \leftarrow ^1\Delta$
  - $m_{\text{min}} = 3$ for R branch
  - $m_{\text{min}} = 2$ for Q branch
  - $|m_{\text{min}}| = 3$ for P branch
- Missing lines near the origin

Intensity Distribution

Relative intensities depend on $n_J/n$, and Hönl-London factors ($S_{J}^{P,Q,R}$) - “relative intensity factors / line strengths” → breakdown of the principle of equal probability.
2. Common molecular models for diatomics

Example – 1: Hönl-London Factors for Symmetric Top (see Herzberg)

For $\Delta \Lambda = 0$

\[
S^R_J = \frac{(J + 1 + \Lambda)(J + 1 - \Lambda)}{J + 1} \approx J + 1 \ (J \gg \Lambda)
\]

\[
S^Q_J = \frac{(2J + 1)\Lambda^2}{J(J + 1)} \approx \frac{2\Lambda^2}{J} \approx 0
\]

\[
S^P_J = \frac{(J + \Lambda)(J - \Lambda)}{J} \approx J
\]

Notes:

1. $\Sigma S_J = 2J + 1$, the total degeneracy!
2. The R-branch line for a specific J, is $\sim J + 1/J$ times as strong as the P-branch line
3. For $\Delta \Lambda = \pm 1$, $J \gg \Lambda$

\[
S^R_J = \frac{(2J + 1)}{4}
\]

\[
S^Q_J = \frac{(2J + 1)}{2} \sum S_J = 2J + 1
\]

\[
S^P_J = \frac{(2J + 1)}{4}
\]

Q branch lines are twice as strong as P and R lines!

$\Delta \Lambda$ value is important in determining the relative line and branch strengths of rovibronic spectra.
2. Common molecular models for diatomics

Example – 2: Symmetric Top Ground State

If $X = {}^1\Pi$, possible transitions (Recall $\Delta \Lambda = 0, \pm 1$)

<table>
<thead>
<tr>
<th>$^1\Pi \leftarrow {}^1\Pi$</th>
<th>$^1\Delta \leftarrow {}^1\Pi$</th>
<th>$^1\Sigma \leftarrow {}^1\Pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \Lambda = 0$</td>
<td>$\Delta \Lambda = 1$</td>
<td>$\Delta \Lambda = -1$</td>
</tr>
</tbody>
</table>

1. Three separate “systems” of bands possible from $X^1\Pi$
2. Hönl-London factors for $\Delta \Lambda = \pm 1$ differ from for $\Delta \Lambda = 0$ (see previous page)
3. Electronic Spectra of Diatomic Molecules: Improved Treatments (add Spin)

1. Review of angular momentum
2. Interaction of $\Lambda$ and $\Sigma$
3. Hund’s case a ($\Lambda \neq 0$, $S \neq 0$)
4. Hund’s case b ($\Lambda = 0$, $S \neq 0$)
5. $\Lambda$-doubling
3.1. Review of angular momentum

Review – then add spin

- Term symbol

- 4 models
  - Rigid Rotor \( \Lambda = S = 0 \) e.g., \( \text{N}_2, \text{H}_2: X^1\Sigma \)
  - Symmetric Top \( \Lambda \neq 0; S = 0 \) e.g., \( ^1\Pi \)
  - Hund’s a \( \Lambda \neq 0; S \neq 0 \) e.g., OH, NO (both \( X^2\Pi \))
  - Hund’s b \( \Lambda = 0; S \neq 0 \) e.g., \( \text{O}_2: X^3\Sigma \)
Electronic angular momentum for molecules

- Orbital angular momentum of electrons
  1. Separate from spin and nuclear rotation
  2. Strong electrostatic field exists between nuclei.
     
     So \( \vec{L} \) precesses about field direction (internuclear axis) with “allowed” components along axis
     
     \[ m_l = L, L-1, ..., -L \equiv \Lambda \]

  3. If we reverse direction of electron orbit in \( \vec{E} \) field, we get the same energy but \( \Lambda \rightarrow -\Lambda \) (\( \Lambda \) doubling)
3.1. Review of angular momentum

Electronic angular momentum for molecules

- Spin of electrons

1. To determine \( L \) and \( S \) for molecule, we usually sum \( l \) & \( s \) for all electrons. e.g., \( S = \sum_i s_i \)

So even number of electrons \( \Rightarrow \) integral spin

odd number of electrons \( \Rightarrow \) half-integral spin

2. For \( \Lambda \neq 0 \), precession of \( L \) about internuclear axis \( \Rightarrow \) magnetic field along axis. So \( m_s \) is defined. \( m_s \equiv \Sigma = S, S-1, \ldots -S. \)

Note for change of orbital direction, energy of electron spinning in magnetic field changes \( \Rightarrow \) no degeneracy \( \Rightarrow 2S+1 \) possibilities (multiplets)

3. For \( \Lambda = 0 \), no magnetic field exists and the projection of \( S \) on the nuclear axis is not conserved (\( \Sigma \) not defined)
3.1. Review of angular momentum

Electronic angular momentum for molecules

Total electronic angular momentum

1. Total electronic angular momentum along internuclear axis is $\vec{\Omega} = \vec{\Lambda} + \vec{\Sigma}$
   
   But since all in same direction, use simple addition
   
   $\Omega = |\Lambda + \Sigma|$

2. For $\Lambda \neq 0$, magnetic field $H \propto \Lambda$.

   Magnetic moment of “spinning” electron $\mu_H \propto \Sigma$.

   So interaction energy is proportional to $E \sim \mu H \sim \Lambda \Sigma$, or
   
   $T_e = T_0 + A\Lambda\Sigma$ (more on this later)

For $A > 0$, “Regular” state

For $A < 0$, “Inverted” state

$^{2}\Pi_{1/2}$  $^{2}\Pi_{3/2}$
3.2. Interaction of $\Lambda$ and $\Sigma$

- This interaction is key to modeling the influence of spin on the electronic state structure.

When $\Lambda \neq 0$, $S \neq 0$, they combine to form a net component of $\Omega$.

$\Lambda \neq 0 \Rightarrow$ an associated magnetic field due to net current about the axis. This field interacts with spinning electrons.

$\Rightarrow$ Spin-orbit coupling (spin-splitting of energy levels)

Comments:
- Models are only approximations.
- Coupling may change as $J$ ranges from low to high values.
3.2. Interaction of Λ and Σ

Examples

\[ \begin{align*}
\Delta^3 & \leftrightarrow S = 1, \Lambda = 2, \Omega = 3 (\Sigma = 1) \\
\Delta^3 & \leftrightarrow S = 1, \Lambda = 2, \Omega = 2 (\Sigma = 0) \\
\Delta^3 & \leftrightarrow S = 1, \Lambda = 2, \Omega = 1 (\Sigma = -1)
\end{align*} \]

Electronic energies

\[ T_e = T_0 + A\Lambda\Sigma \]

Energy without interaction

Spin-orbit coupling constant, generally increases with molecular weight and the number of electrons

\[ \begin{align*}
\Delta^3 & \leftrightarrow S = 1, \Lambda = 2, \Sigma = 1,0,-1 \\
T_e &= T_0 + A(2)\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}
\end{align*} \]

Sample constants

- \( A_{BeH} \approx 2 \text{ cm}^{-1} \)
- \( A_{NO} \approx 124 \text{ cm}^{-1} \)
- \( A_{HgH} \approx 3600 \text{ cm}^{-1} \)
- \( A_{OH} \approx -140 \text{ cm}^{-1} \)

Notes:
1. The parameter \( Y \) is often specified, where \( Y = A/B_v \)
2. Values for \( A \) given in Herzberg, Vol.I

Now, consider Hund’s cases where \( S \neq 0 \)
3.3. Hund’s case a

- $\Lambda \neq 0, S \neq 0, \Sigma = S, S-1, \ldots, -S$

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

$$\Omega = \Lambda + S, \Lambda + S - 1, \ldots, |\Lambda - S|$$

$$J = \Omega, \Omega + 1, \ldots$$

P, Q, R branches for each value of $\Omega$.

Example:

$^2\Pi \Rightarrow \Omega = 3/2$ and $1/2$, two electronic sub-states

- a total of $2 \times 3 = 6$ branches

Recall

$$A = \frac{h}{8\pi^2 I_A c}, B = \frac{h}{8\pi^2 I_B c}$$

Not to be confused with spin-orbit constant
3.4. Hund’s case b

- Applies when spin is *not* coupled to the A-axis
  - E.g., 1. For $\Lambda = 0$, $\sum S$ is not defined, must use $\vec{S}$
  2. At high $J$, especially for hydrides, even with $\Lambda \neq 0$

Allowed $J$: $J = N+S$, $N+S-1$, ..., $N-S$, $J \geq 0$ only

For this case, $\vec{S}$ and $\vec{N}$ couple directly,
3.4. Hund’s case b

Example – O₂

Ground state X³Σ has three J’s for each N!

<table>
<thead>
<tr>
<th>N</th>
<th>J = N + 1</th>
<th>J = N</th>
<th>J = N − 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>J = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>J = 2</td>
<td>J = 1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>J = 3</td>
<td>J = 2</td>
<td>J = 1</td>
</tr>
</tbody>
</table>

Notes:

- Split rotational levels for N > 0
- Each level has a degeneracy of 2J + 1, and a sum of Hönl-London factors of 2J + 1
- Minimum J is |N−S|
- In N = 0 level, only spin is active (S = 1), this is the minimum value of J
3.5. Λ – doubling

- Further complexity in the energy levels resulting from Λ-doubling
  - Different coupling with nuclear rotation (\( \vec{N} \) and \( \vec{\Lambda} \) interaction)
    - The two orientations of \( \vec{\Lambda} \) (± Λ along the A-axis) have slightly different energies
    
    \[
    F(J) \rightarrow F_c(J) \text{ and } F_d(J)
    \]

- By definition, \( F_c(J) > F_d(J) \) (c,d replaced by e,f in some literature)
- Lambda doubling usually results in a very small change in energy, affecting Boltzmann distribution only slightly.
- Change of parity between Λ-doubled states – reduces the accessible fraction of molecules for a given transition (due to selection rules)
4. Quantitative absorption

- Review of Beer’s law and spectral absorption as interpreted for molecules with multiplet structure

  - Beer’s Law
    \[
    \left( \frac{I}{I^0} \right)_v = \exp(-k_vL)
    \]

  - For two-level system
    \[
    k_v = S_{12}\phi(v) = \left( \frac{\pi e^2}{m_e c} \right) n_1 f_{12} \left( 1 - \exp\left( -\frac{hv}{kT} \right) \right) \phi(v)
    \]

    Integrated absorption intensity [cm\(^{-1}\)s\(^{-1}\)]

  For a complex, multiple level system, we have 2 quantities to specify:
  - Boltzmann fraction?
  - Oscillator strength for a specific transition?
4. Quantitative absorption

Boltzmann fraction

\[ n_1 = n_i \frac{n_1}{n_i} \]

\[ n_i = \text{the total number density of species } i \]
\[ n_1/n_i = \text{the fraction of species } i \text{ in state/level 1} \]

Quantum numbers:
- \( n \) – electronic
- \( v \) – vibrational
- \( \Sigma \) – spin
- \( \Lambda \) – orbital
- \( J \) – total angular momentum
- \( N \) – nuclear rotation
- \( c \) or \( d \) – \( \Lambda \)-component

We will illustrate this in the next lecture!
4. Quantitative absorption

- Oscillator strength
  - Strength of a *specific*, single transition (i.e., from *one* of the J" substrates to a specific J' substrate), $f_{J''J'}$.

\[
 f_{12} = f_{(m,v'',J'')(n,v',J')} = f_{J''J'} \\
 = f_{el} \times q_{v''v'} \times \frac{S_{J''J'}}{2J''+1}
\]

**Notes:**

- $\sum_{v'} q_{v''v'} = 1$
- $\sum_{J'} S_{J''J'} = (2J''+1)[(2S+1)\delta]$, $\delta = 1$ for $\Sigma-\Sigma$, otherwise $\delta = 2$ (\Lambda-doubling).
- $[(2S+1)\delta] = 4$ for OH's $A^2\Sigma \leftrightarrow X^2\Pi$ system.
- $\sum_{v',J''} f_{J''J'} = [(2S+1)\delta]f_{el}$ sum is $f_{el}$ for a single J" substate.
4. Quantitative absorption

Oscillator strength

Remarks

1. Band oscillator strength \( f_{v''v'} = f_{el} q_{v''v'} \rightarrow \) often is tabulated
   e.g., \( f_{00} = 0.001 \) (OH \( A^2\Sigma \leftarrow X^2\Pi \))

2. \( f_{J''J'} = f_{v''v'} \left( \frac{S_{J''J'}}{2J''+1} \right) \)
   e.g., if only P and R are allowed \( S_{J''J'}^P = J'', S_{J''J'}^R = J''+1 \)

3. In some cases, an additional "correction term" \( T_{J''J'} \) is used, e.g., in OH
   \( f_{J''J'} = f_{v''v'} \left( \frac{S_{J''J'}}{2J''+1} \right) T_{J''J'}, T_{J''J'} \text{ always near 1} \)

4. In terms of A-coefficient
   \[
   f_{v''v'} = \left( \frac{m_e c \lambda^2}{8 \pi^2 e^2} \right) A_{v''v'} \left( \frac{g_e'}{g_e''} \right) 
   = \frac{g_e'}{g_e''} f_{v''v''}
   \]
Next: Case Study of Molecular Spectra

- Ultraviolet: OH