Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 3: Electronic Spectra, Bond Diss. Energy

1. Potential energy wells
2. Types of spectra
3. Rotational analysis
4. Vibrational analysis
5. Analysis summary
6. Dissociation Energies

**An example of what we need to calculate**
1. Potential energy wells

- Electronic transitions

Recall: Lecture 1 – Line, Band, System

System:
- Transitions between different potential energy well

Example: \( \text{N}_2 \)
- First positive SYSTEM:
  \[
  \text{B}^3\Pi_g \rightarrow \text{A}^3\Sigma^+_u
  \]

Note: Both homonuclear and heteronuclear can have electronic spectra, in contrast with rotational and rovibrational spectra.
1. Potential energy wells

- Electronic force and potential energy

\[ V_{\text{dissociation energy}} \]

\[ F = -\frac{dV}{dr} \]

As electronic configurations change

Potential well changes shape
1. Potential energy wells

- Electronic force and potential energy

Example:
- Potential energy wells for N₂
  - A First excited state
  - X Ground electronic state
  - $T_e$ Energy of A-state w/ respect to ground state
  - $v_{\text{min}}$, $v_{\text{max}}$ Extremes of photon energies for discrete absorption from $v^{\prime\prime}=0$
  - $E_{\text{ex}}$ Difference in electronic energy of atomic fragments
  - $D_e$ Dissociation energy

Note: not to be confused with the rotational distortion const.
### 1. Potential energy wells

#### Characteristic event times

- $\tau_{\text{elec}} \approx 10^{-16} \text{s}$, time to move/excite electrons
- $\tau_{\text{vib}} \approx 10^{-13} \text{s}$, characteristic time for vibration
- $\tau_{\text{coll}} \approx 10^{-12} \text{s}$, duration of collision
- $\tau_{\text{rot}} \approx 10^{-10} \text{s}$, characteristic time for rotation
- $\tau_{\text{emiss}} \approx 10^{-6} - 10^{-8} \text{s}$, “radiative lifetime” – average time a molecule (or atom) spends in an excited state before radiative emission

#### Frank-Condon Principle

- As $\tau_{\text{elec}} \ll \tau_{\text{others}}$, the molecule’s vibration and rotation appear “frozen” during electronic transition

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**Diagram:**

- Vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates.

- Vertical lines between potential wells to represent an electronic transition at constant $r$.

- When $\tau_{\text{coll}} \approx \tau_{\text{vib}}$, increased probability of V-T energy transfer.
2. Types of spectra

- Discrete
  - $r_e' \approx r_e''$

- Franck-Condon Principle: $r \approx \text{const. in absorption and emission}$

- Vibrationally excited molecules ($v \neq 0$) spend more time near the edges of the potential well, so that transitions to and from these locations will be favored

- Lowest $v''$ levels are most populated
2. Types of spectra

- Continuum

Case (a)

Case (b)

Discrete spectrum

Continuous spectrum

Repulsive state

Continuous spectrum
2. Types of spectra

- High-temperature air emission spectra (560-610nm) (part of the \(N_2(1+)\) system \(B^3\Pi_g \rightarrow A^3\Sigma^+_u\))
  - Review multiband structure and apparent bandhead structure
  - Can we make use of rotational analysis to understand the band structure?
3. Rotational analysis

- Fortrat Parabola

**Upper:**

\[ T' = T_{rot} + T_{vib} + T_{elec} = F(J') + G(v') + T'_{elec} = B J'(J'+1) + \omega_e (v'+1/2) - \omega_x (v'+1/2)^2 + T'_{elec} \]

**Lower:**

\[ T'' = T_{rot} + T_{vib} + T''_{elec} = F(J'') + G(v'') + T''_{elec} \]

\[ C'' = C' - C' \]

\[ C' \text{ (const. for rot. analysis in a single band)} \]

\[ T' - T'' = B J'(J'+1) - B J''(J''+1) + C \]

\[ T = T' - T'' = a m^2 + b m + C \]

**Bandhead**

\[ \frac{dT}{dm} = 2a m + b = 0 \]

\[ m_{\text{bandhead}} = -\frac{b}{2a} = \frac{B' + B''}{2(B'' - B')} \]

**Note:**

1. \( r_{e'} > r_{e''}, B' < B'', a < 0, \text{ bandhead in R branch} \)
2. \( r_{e'} < r_{e''}, B' > B'', a > 0, \text{ bandhead in P branch} \)

**Example: O_2**

- \( X^3 \Sigma^- \) ground state: \( B''=1.44 \text{cm}^{-1} \)
- \( A^3 \Pi^- \) upper state: \( B'=1.05 \text{cm}^{-1} \)

\[ m_{\text{bandhead}} = \frac{2.49}{2 \times 0.39} \approx 3 \]
3. Rotational analysis

- Fortrat Parabola

\[ T = T' - T'' = am^2 + bm + C \]

\[ m = \begin{cases} -J & \text{for P branch} \\ J + 1 & \text{for R branch} \end{cases} \]

\[ a = B' - B'' \]

\[ b = B' + B'' \]
3. Rotational analysis

- Fortrat Parabola

Steps for rotational analysis
1. Separate spectra into bands (v', v'"
2. Tabulate line positions
3. Identify null gap and label lines (not trivial)
4. Infer B' and B" from the Fortrat equation or common states

Strategy for labeling the lines:
- If there is a bandhead → lines overlap, more complicated
- If no bandhead → a null gap is obvious, easier
- If bandhead → start from the wings of the parabola and work backwards using a constant second difference
  - 1st difference: \( T_1 = T(m+1) - T(m) \)
  - 2nd difference: \( T_2 = T_1(m+1) - T_1(m) = 2(B'-B'"
  = 2a \)
3. Rotational analysis

- Fortrat Parabola

Example:
Rotational analysis of electronic spectra

Line positions observed:

Rotational spectrum in the 0-0 band of an electronic transition \((A^3Π_{0^+u} \rightarrow X^1Σ^+_g)\) in \(^{35}\text{Cl}_2\)

Find \(B_e', B_e'', r_e', r_e''\), and the null gap frequency \(ν_0\)
3. Rotational analysis

Example: Rotational analysis of electronic spectra

Find $B_e'$, $B_e''$, $r_e'$, $r_e''$, and the null gap frequency $\nu_0$

1. $\nu_0 = 18147.40 \text{ cm}^{-1}$
2. $2a = T_2 = -0.173 \text{ cm}^{-1}$

Note: All $T_2$ are negative!
3. Rotational analysis

Example: Rotational analysis of electronic spectra
Find \( B_e', B_e'', r_e', r_e'' \), and the null gap frequency \( \nu_0 \)

\[
\begin{align*}
\nu_0 &= 18147.40 \text{ cm}^{-1} \\
2a &= T_2 = -0.173 \text{ cm}^{-1} = 2(B'-B'') \\
\text{Use common states to get } B'' \\
\text{Solve for } r', r'' \text{ from } B' \text{ and } B''
\end{align*}
\]

**Could also have used common lower states to get \( B' \)**

\[
\begin{align*}
R(0) &= 18147.71, P(2) = 18146.25 \\
R(0) - P(2) &= 1.46 \\
B'' &= 1.46/6 = 0.243 \text{ cm}^{-1} \\
B' &= B'' + a = 0.157 \text{ cm}^{-1} \\
B_e'' &= 0.2438, \alpha_e = 0.0017 \\
\Rightarrow B_0'' &= 0.2438 - 0.0008 = 0.243 \\
B_e' &= 0.158, \alpha_e = 0.003 \\
\Rightarrow B_0' &= 0.158 - 0.0015 \approx 0.157 \\
T_e &= 18310.5, r_e'' = 1.988 \text{ Å, } r_e' = 2.47 \text{ Å}
\end{align*}
\]
4. Vibrational analysis

- Band origin data

Vibrational analysis can be used to determine information regarding $\omega_e$, $x_e$

Absorption $\rightarrow$ information on upper states

Emission $\rightarrow$ information on lower states

- Deslandres Table

Recall:

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

$G(1) - G(0) = \omega_e - 2\omega_e x_e$

$G(2) - G(1) = \omega_e - 4\omega_e x_e$

<table>
<thead>
<tr>
<th>$v^1$</th>
<th>$v''$</th>
<th>$0$</th>
<th>$1$</th>
<th>$2$</th>
<th>$3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0$</td>
<td></td>
<td>$v_{0,0}$</td>
<td>$v_{0,1}$</td>
<td>$v_{0,2}$</td>
<td>$v_{0,3}$</td>
</tr>
<tr>
<td>$1$</td>
<td></td>
<td>$v_{1,0}$</td>
<td>$\omega_e - 2\omega_e x_e$</td>
<td>$\omega_e - 4\omega_e x_e$</td>
<td></td>
</tr>
<tr>
<td>$2$</td>
<td></td>
<td>$v_{2,0}$</td>
<td>$\omega_e&quot; - 2\omega_e x_e&quot;$</td>
<td>$\omega_e&quot; - 4\omega_e x_e&quot;$</td>
<td></td>
</tr>
<tr>
<td>$3$</td>
<td></td>
<td>$v_{3,0}$</td>
<td>$2\omega_e x_e&quot;$</td>
<td></td>
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</tbody>
</table>
## 4. Vibrational analysis

### Deslandres Table

<table>
<thead>
<tr>
<th>Transition $v' \leftarrow v''$</th>
<th>Energy required to observe transition</th>
<th>$1^{st}$ difference</th>
<th>$2^{nd}$ difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0 \leftarrow 0$</td>
<td>$T_e + 1/2 \omega_e' - 1/4 \omega_e x_e' - 1/2 \omega_e'' + 1/4 \omega_e x_e''$</td>
<td>$\omega_e' - 2\omega_e x_e'$</td>
<td>$2\omega_e x_e'$</td>
</tr>
<tr>
<td>$1 \leftarrow 0$</td>
<td>$T_e + 3/2 \omega_e' - 9/4 \omega_e x_e' - 1/2 \omega_e'' + 1/4 \omega_e x_e''$</td>
<td>$\omega_e' - 4\omega_e x_e'$</td>
<td>$2\omega_e x_e'$</td>
</tr>
<tr>
<td>$2 \leftarrow 0$</td>
<td>$T_e + 5/2 \omega_e' - 25/4 \omega_e x_e' - 1/2 \omega_e'' + 1/4 \omega_e x_e''$</td>
<td>$\omega_e' - 6\omega_e x_e'$</td>
<td>$2\omega_e x_e'$</td>
</tr>
<tr>
<td>$3 \leftarrow 0$</td>
<td>$T_e + 7/2 \omega_e' - 49/4 \omega_e x_e' - 1/2 \omega_e'' + 1/4 \omega_e x_e''$</td>
<td>$\omega_e' - 8\omega_e x_e'$</td>
<td>$2\omega_e x_e'$</td>
</tr>
<tr>
<td>$4 \leftarrow 0$</td>
<td>$T_e + 9/2 \omega_e' - 81/4 \omega_e x_e' - 1/2 \omega_e'' + 1/4 \omega_e x_e''$</td>
<td>$\omega_e' - 10\omega_e x_e'$</td>
<td>$2\omega_e x_e'$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$v''$</th>
<th>0</th>
<th>1480</th>
<th>1460</th>
<th>1440</th>
<th>3</th>
<th>4</th>
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<tbody>
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<tr>
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<td>31807.5</td>
<td>30327.5</td>
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<td>26007.5</td>
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<td>30107.5</td>
<td>28667.5</td>
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<td>29747.5</td>
<td>28327.5</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Band origin data from an emission spectrum
5. Analysis summary

Analysis techniques and related fundamental quantities

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational analysis</td>
<td>$B_e, \alpha_e, D_e, \beta_e$</td>
</tr>
<tr>
<td>Vibrational analysis</td>
<td>$\omega_e, \omega_e \kappa_e$</td>
</tr>
<tr>
<td>Emission analysis</td>
<td>$D_e''', G(v'')$</td>
</tr>
<tr>
<td>Absorption analysis</td>
<td>$D_e', T_e, G(v')$</td>
</tr>
</tbody>
</table>

Typical analyses

**Absorption**
1. Band origin $\rightarrow G(v')$
2. $v_0 = T_e + G(v') - G(v'') \rightarrow T_e$
3. $\Delta + G(v'') = T_e + D_e' \rightarrow D_e'$

**Emission**
1. Band origin $\rightarrow G(v'')$
2. $D''_e + \Delta = T_e + G(v') \rightarrow D''_e$
6. Bond Dissociation Energies

1. Absorption and emission analysis
2. Birge-Sponer method
3. Thermochemical approach
4. Working example
6. Bond dissociation energies

Absorption

Absorption → $D_e'$, $T_e$, $G(v')$

1. Band origin → $G(v')$  [Enter in Deslandres Table]
2. $\bar{v}_0 = T_e + G(v') - G(v'') \rightarrow T_e$
3. $\Delta + G(v'') = T_e + D_e' \rightarrow D_e'$
6.1. Absorption and emission

- Emission

\[ \text{Emission } \rightarrow D_e'', G(v') \]

1. Band origin from fixed \( v' \rightarrow G(v'') \)

2. \( D''_e + \Delta = T_e + G(v') \rightarrow D''_e \)

Enter in Deslandres Table

(emission (from single \( v' \))

(change from continuum to band structure)
6.1. Absorption and emission

Emission

Example: High-temperature air emission spectra (560-610nm)

\[ v_{\text{upper}} = v' \]
\[ v_{\text{lower}} = v'' \]
\[ v' - v'' = 4 \]

\[ 12 \rightarrow 8 \]
\[ 11 \rightarrow 7 \]
\[ 10 \rightarrow 6 \]
\[ 9 \rightarrow 5 \]
\[ 8 \rightarrow 4 \]
\[ 7 \rightarrow 3 \]
\[ 6 \rightarrow 2 \]
6.1. Absorption and emission

- Emission

Example: Band spectrum of an air-filled Geissler tube. (a) Long-wavelength part. (b) Short wavelength part
6.2. Birge-Sponer method

- Determine dissociation energies

**Dissociation energies**
- [Thermodynamics] Heats of formation and reaction
- [Kinetics] Rates of reaction

**Birge-Sponer method**
- Spectroscopic parameters → Dissociation energies
  - Constant anharmonicity

Vibrational level spacing $\rightarrow 0$ in the limit of dissociation

$$G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2$$
$$G(v+1) = \omega_e (v + 3/2) - \omega_e x_e (v + 3/2)^2$$
$$\Delta G(v) = G(v+1) - G(v) = -2\omega_e x_e v + \left(\omega_e - 2\omega_e x_e\right)$$

$$\Delta G(v) = av + b \quad \text{Linear dependence on } v!$$
6.2. Birge-Sponer method

- Determine dissociation energies

Vibrational level spacing → 0 in the limit of dissociation

\[ \Delta G(v) = av + b = 0 \] @ dissociation

\[ v_D = \frac{b}{a} = \frac{\omega_e}{2\omega_e x_e} - 1 \]

\[ D_e = \omega_e (v_D + 1/2) - \omega_e x_e (v_D + 1/2)^2 \]

\[ D_e = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e x_e}{4} \approx \frac{\omega_e^2}{4\omega_e x_e} = \frac{\omega_e}{4x_e} \]

\( \propto \) Area under curve

Real case: anharmonicity increases near dissociation limit
- Birge-Sponer overpredicts \( D_e \)
6.2. Birge-Sponer method

Determine dissociation energies

Vibrational level spacing $\to 0$ in the limit of dissociation

$\Delta G(v) = av + b = 0$ @ dissociation

$D_e = \omega_e v_D + 1/2 - \omega_e x_e (v_D + 1/2)^2$

Example: HCl

$\omega_e = 2990 \text{ cm}^{-1}, x_e = 0.0174$

$\Rightarrow v_D = 27.7 \to 27$

$\Rightarrow D_e = 513 \text{ kJ/mol}$

Actual:

$D_e = 427 \text{ kJ/mol}$

Overpredicts by $\sim 20\%$
6.3. Thermochemical approach

- Determine dissociation energies

E.g., \( I_2 \rightarrow 2I \)

\[
K_p = \frac{P_i^2}{P_{I_2}}
\]

\[
d\left(\ln K_p\right) = \frac{\Delta H}{RT^2} \quad \text{where} \quad \Delta H = \sum v_i H_i = H_{\text{prod}} - H_{\text{react}} = D_e + 2\int c_p dT - \int c_p dT
\]

Measurements of partial pressures

\[ K_p(T) \quad \Delta H, D_e^{''} \]

Measured spectroscopically (e.g., by laser absorption)
6.4. Working example

- A shock tube study of the enthalpy of formation of OH

- $T_5=2590\text{K}, \ P_5=1.075\text{atm}, \ \text{mixture: 4002ppm H}_2/3999\text{ppm O}_2/\text{balance Ar.}$

- The OH concentration is modeled using GRI-MECH 3.0 and the GRI-MECH 3.0 thermodynamics database, with 0.5ppm additional H atoms to match the induction time.

- The fit required a change in $\Delta_f H_{298}^0(\text{OH})$ from 9.403 to 8.887 kcal/mol

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Experimentally measured and modeled OH mole fraction time histories.
6.4. Working example

- A shock tube study of the enthalpy of formation of OH

Experimentally derived values for $\Delta_f H^0_{298}(\text{OH})$.

\[ \text{Present Study} \]
\[ \text{Mean: } \Delta_f H^0_{298}(\text{OH}) = 8.92 \text{ kcal/mol (37.3 kJ/mol)} \]

GRIMech 3.0 Database [Gurvich et al. (1989)]

Sandia Database (JANAF)

Burcat Database

Ruscic et al. (2002)

\[ \sigma = 0.04 \]
Next: Polyatomic Molecular Spectra

- Rotational Spectra
- Vibrational Bands, Rovibrational Spectra