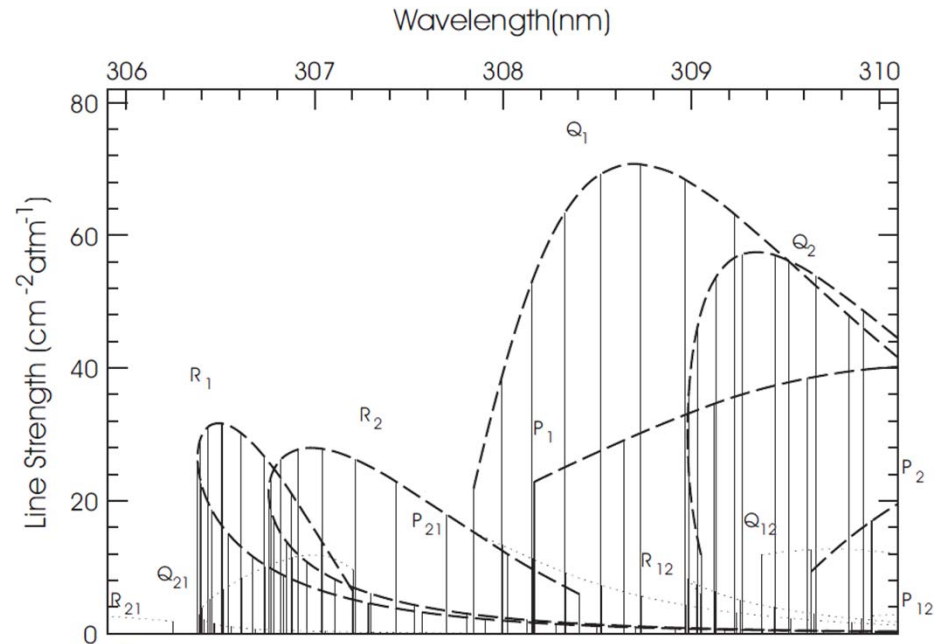# Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 3: Electronic Spectra, Bond Diss. Energy

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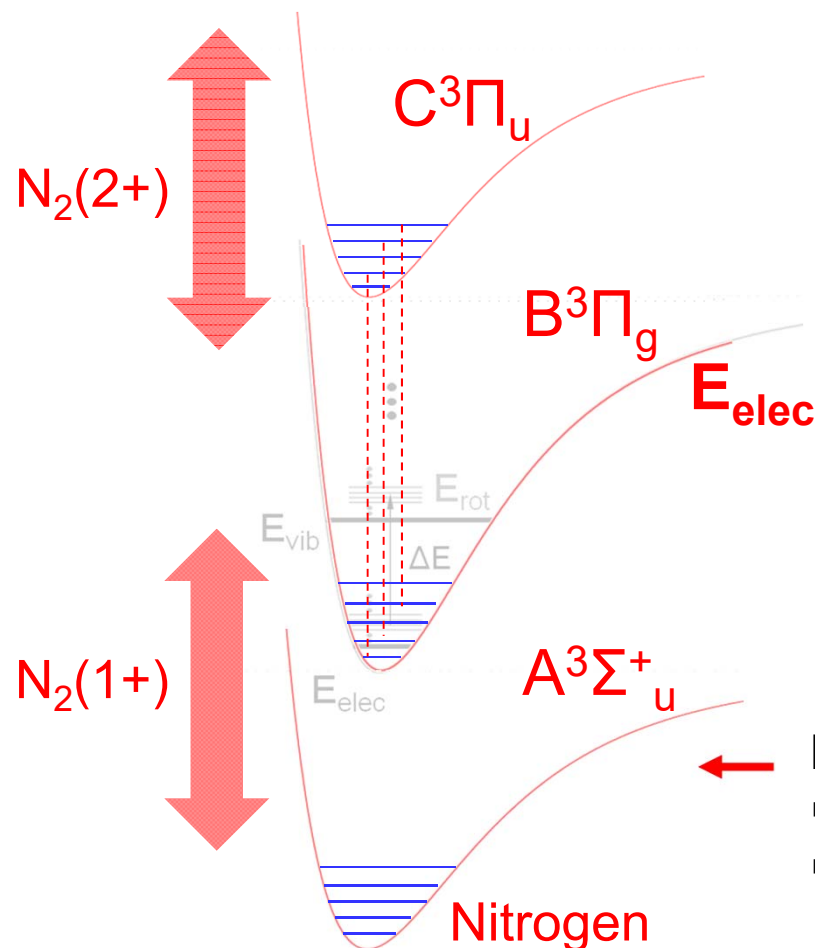5. Analysis summary
6. Dissociation Energies

OH line strengths for a selected region of the $A^2\Sigma^+\leftarrow X^2\Pi(0,0)$ band at 2000K

An example of what we need to calculate

1. Potential energy wells

■ Electronic transitions

Recall: Lecture 1 – Line, Band, System

$C^3\Pi_u$

$N_2(2+)$

$B^3\Pi_g$

E_{elec}

E_{rot}

E_{vib} ΔE

$N_2(1+)$

E_{elec}

$A^3\Sigma^+_u$

Nitrogen

System:
■ Transitions between different potential energy well
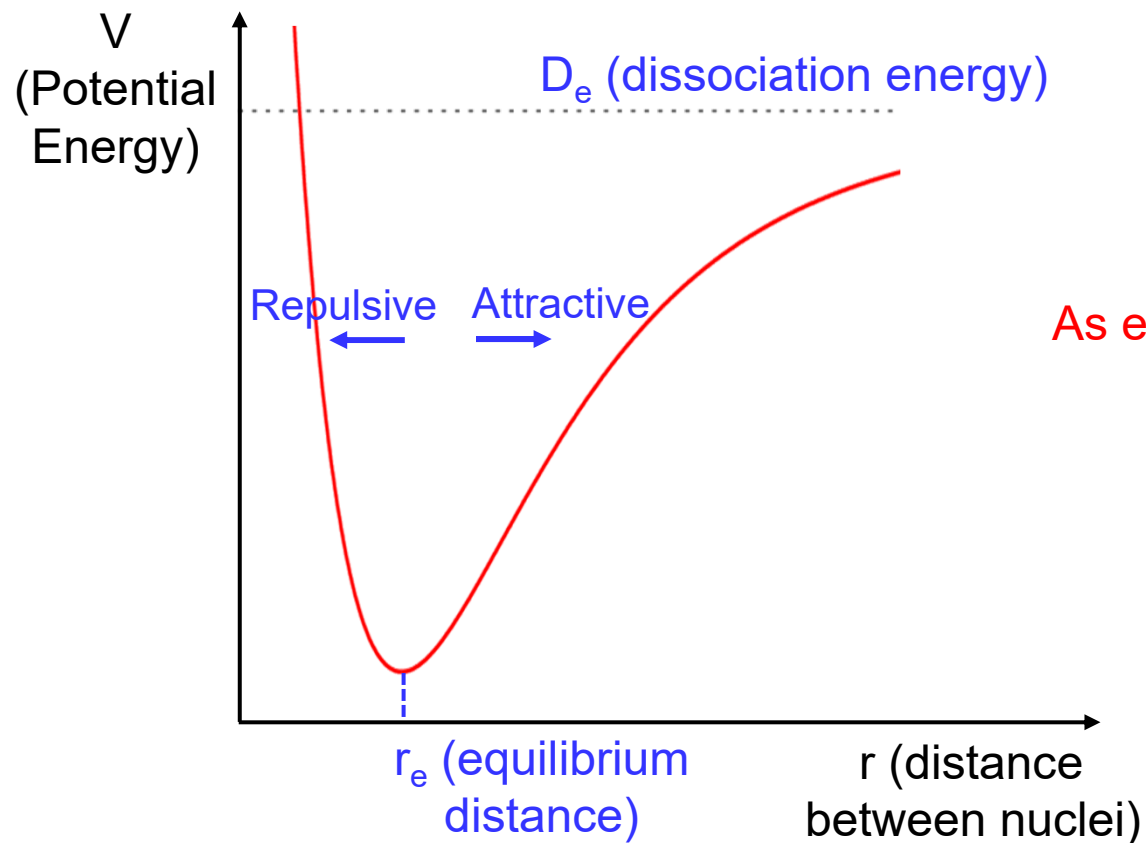
↓

Depends on electronic configuration

✎ Note: Both homonuclear and heteronuclear can have electronic spectra, in contrast w/ rotational and rovibrational spectra

← Example: N_2
■ First positive SYSTEM: $B^3\Pi_g \rightarrow A^3\Sigma^+_u$
■ The ground (lowest energy) state is $X^1\Sigma^+_g$

1. Potential energy wells

- Electronic force and potential energy

V (Potential Energy)

D_e (dissociation energy)

Repulsive   Attractive

r_e (equilibrium distance)

r (distance between nuclei)
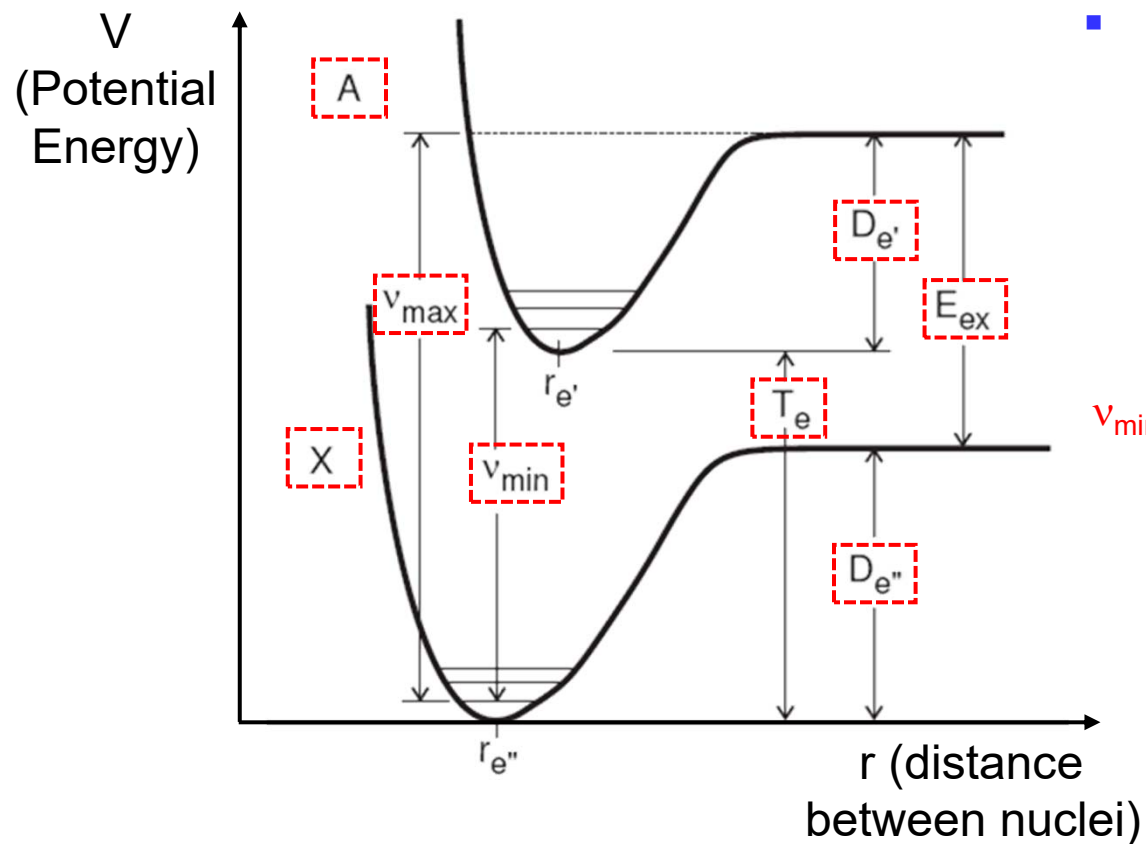
Force $F = -\dfrac{dV}{dr}$

As electronic configurations change

Potential well changes shape

1. Potential energy wells

- Electronic force and potential energy

Example:
- Potential energy wells for N_2

V (Potential Energy)

A
$D_{e'}$
E_{ex}
v_{max}
$r_{e'}$
T_e
X
v_{min}
$D_{e''}$
$r_{e''}$

r (distance between nuclei)

A   First excited state

X   Ground electronic state

T_e Energy of A-state w/ respect to ground state

v_{min}, v_{max} Extremes of photon energies for discrete absorption from v"=0

E_{ex} Difference in electronic energy of atomic fragments

D_e Dissociation energy

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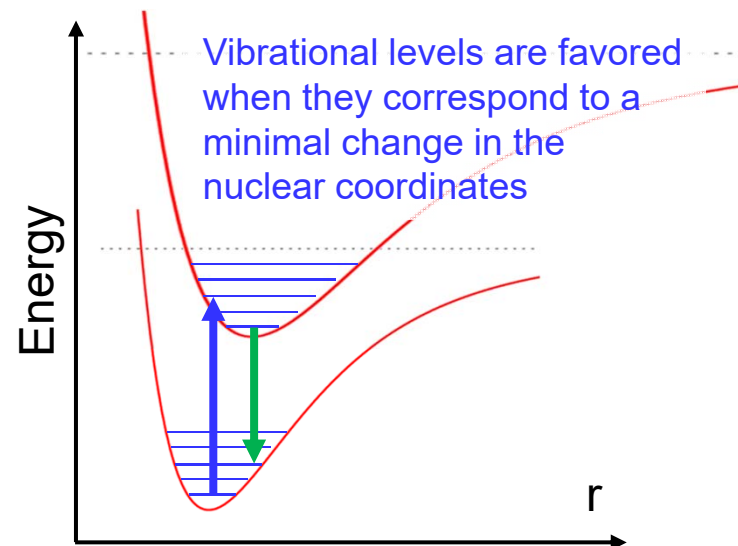
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1. Potential energy wells

- Characteristic event times

  - $\tau_{elec} \approx 10^{-16} s$ time to move/excite electrons

  - $\tau_{vib} \approx 10^{-13} s$ characteristic time for vibration

  - $\tau_{coll} \approx 10^{-12} s$ duration of collision

  - $\tau_{rot} \approx 10^{-10} s$ characteristic time for rotation

  - $\tau_{emiss} \approx 10^{-6} - 10^{-8} s$ "radiative lifetime" – average time a molecule (or atom) spends in an excited state before radiative emission

- Frank-Condon Principle

  As $\tau_{elec} << \tau_{others}$, the molecule's vibration and rotation appear "frozen" during electronic transition

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

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

  Energy

  r

- When $\tau_{coll} \approx \tau_{vib}$ ⟹ Increased probability of V-T energy transfer
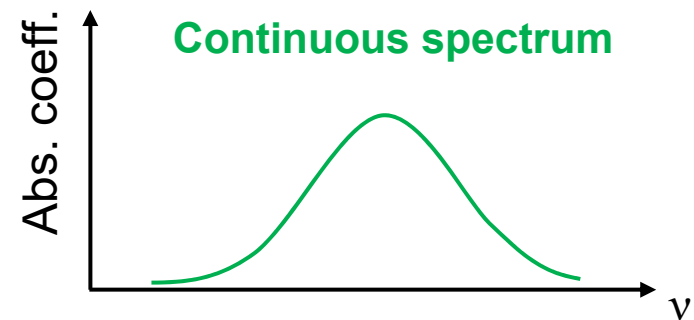
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2. Types of spectra
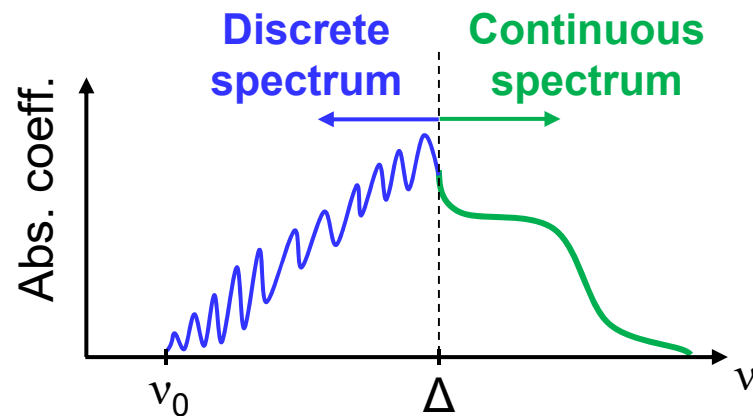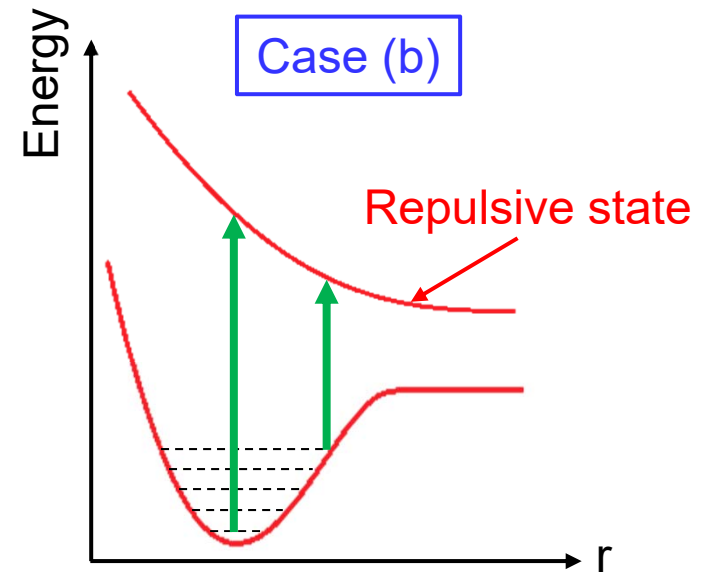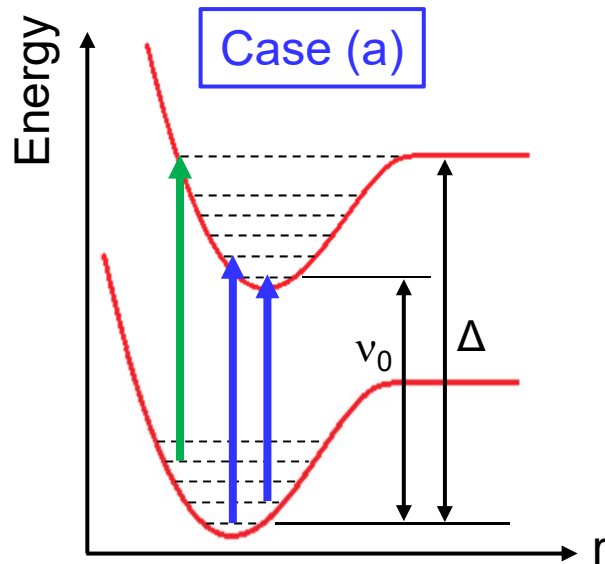
- Discrete

  - $r_e' \approx r_e''$

  - Franck-Condon Principle:

    r ≈ const. in absorption and emission

  - Vibrationally excited molecules (v≠0) spend more time near the <u>edges of the potential well</u>, so that transitions to and from these locations will be favored
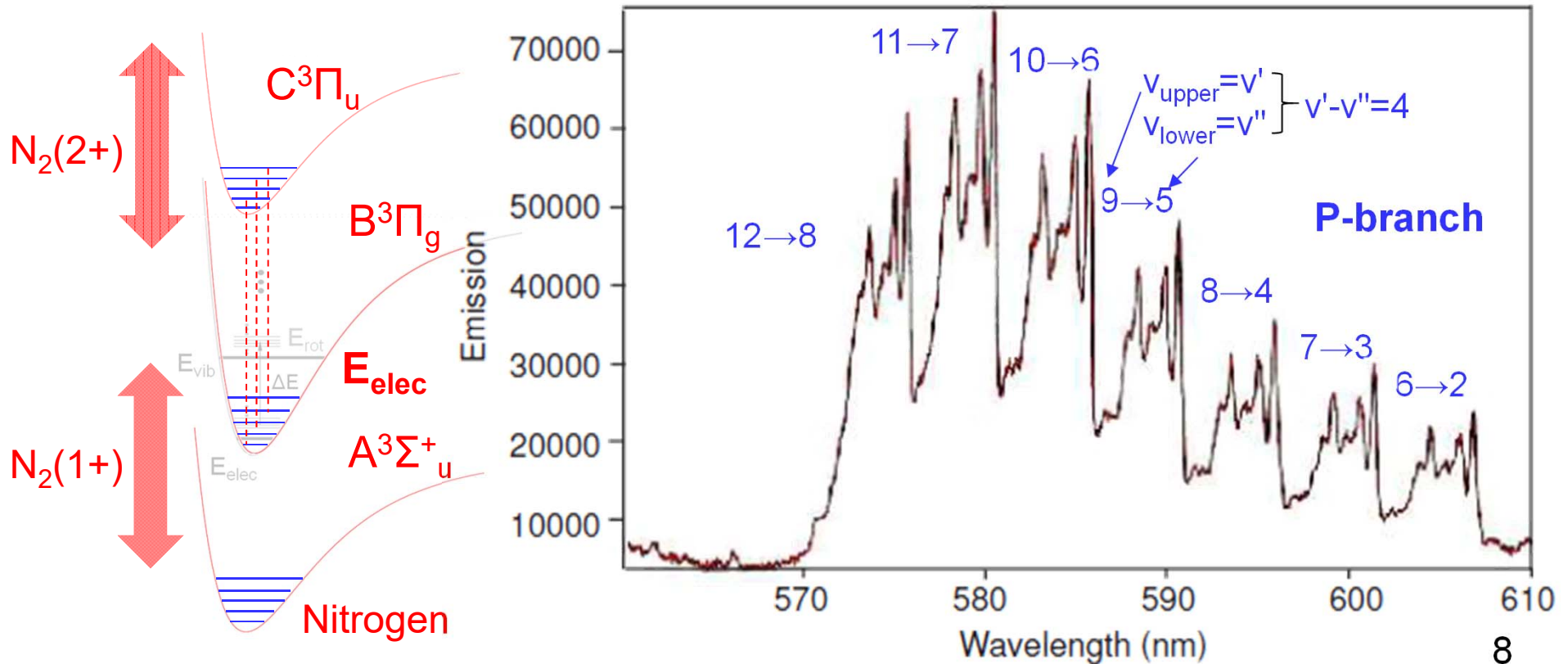
  - Lowest v" levels are most populated
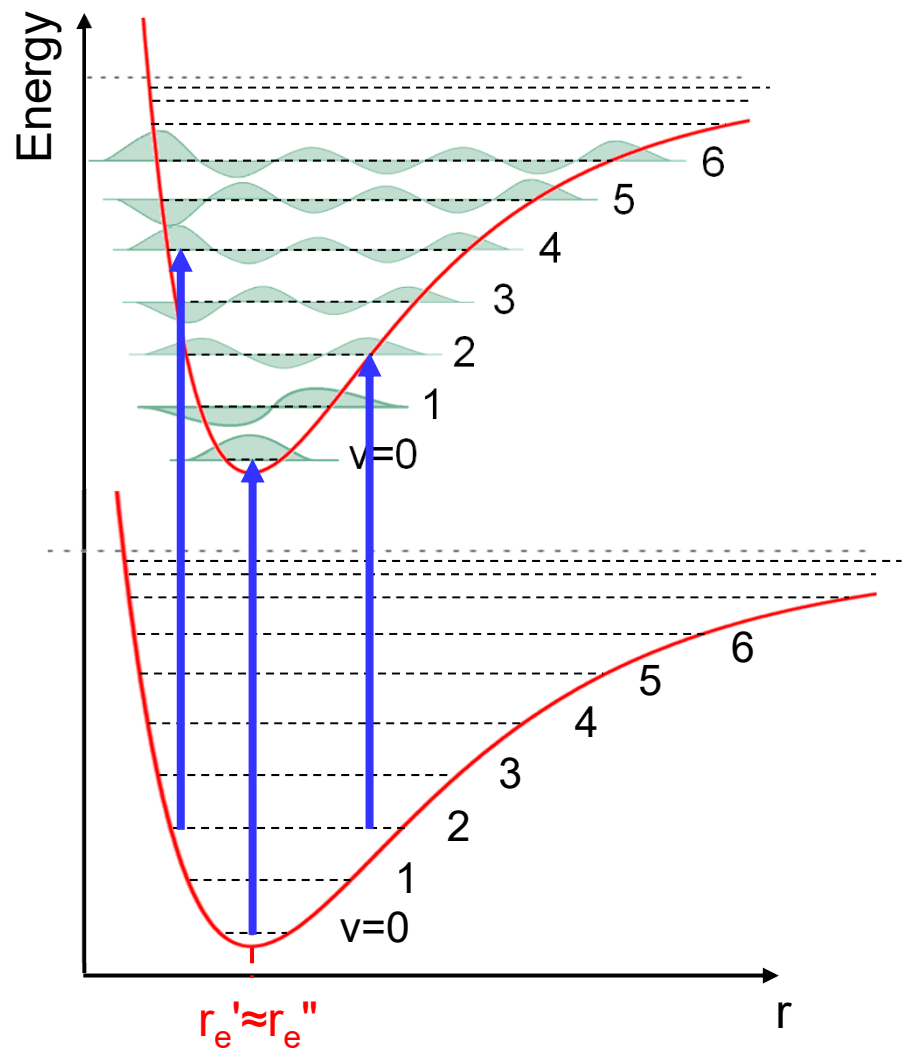
2. Types of spectra

- Continuum

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 <u>rotational analysis</u> to understand the band structure?

3. Rotational analysis

- Fortrat Parabola

Upper: $T' = T_{rot} + T_{vib} + T_{elec}$

$$= F(J') + G(v') + T'_{elec}$$

$$= BJ'(J'+1) + \omega_e(v'+1/2) - \omega_e x_e (v'+1/2)^2 + T'_{elec}$$

$\underbrace{\phantom{BJ'(J'+1) + \omega_e(v'+1/2) - \omega_e x_e (v'+1/2)^2 + T'_{elec}}}_{C' \text{ (const. for rot. analysis in a single band)}}$

Lower: $T'' = T_{rot} + T_{vib} + T_{elec}$

$$= F(J'') + \underbrace{G(v'') + T''_{elec}}_{C''}$$

C=C'-C"

$$T' - T'' = BJ'(J'+1) - BJ''(J''+1) + C$$

$$T = T' - T'' = am^2 + bm + C$$

$$where \quad m = \begin{cases} -J & \text{for P branch} \quad a = B' - B'' \\ J+1 & \text{for R branch} \quad b = B' + B'' \end{cases}$$

Bandhead $\dfrac{dT}{dm} = 2am + b = 0$

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

Note:
1. $r_e' > r_e''$, B' < B", a<0, bandhead in R branch
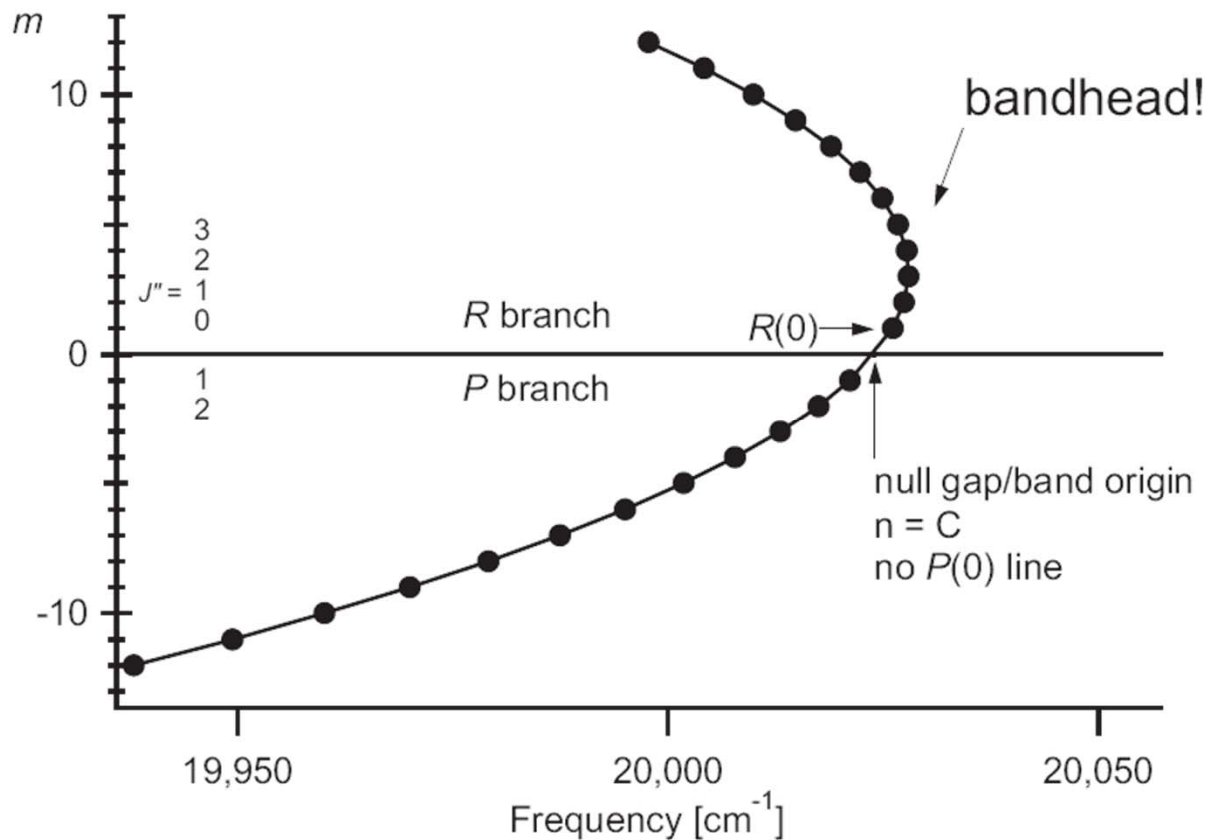2. $r_e' < r_e''$, B' > B", a>0, bandhead in P branch

Example: O_2
- $X^3\Sigma^-_g$ ground state: B"=1.44cm^{-1}
- $A^3\Pi^-_u$ upper state: B'=1.05cm^{-1}

$$m_{bandhead} = \frac{2.49}{2 \times 0.39} \approx 3$$

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3. Rotational analysis

- Fortrat Parabola

$$T = T' - T'' = am^2 + bm + C \qquad m = \begin{cases} -J & \text{for P branch} \qquad a = B' - B'' \\ J + 1 & \text{for R branch} \qquad b = B' + B'' \end{cases}$$

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 ($A^3\Pi_{0+u} - X^1\Sigma^+_g$) in $^{35}Cl_2$

➡ Find B_e', B_e'', r_e', r_e'', and the null gap frequency ν_0

ν, cm^{-1}

18147.85
18147.81
18147.71
18147.60
18147.22
18146.91
18146.66
18146.25
18145.93
18145.42
18145.02
18144.41
18143.94
18143.23
18142.69
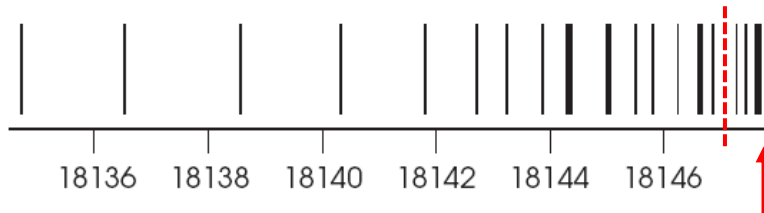18141.87
18140.34
18138.64
18136.76
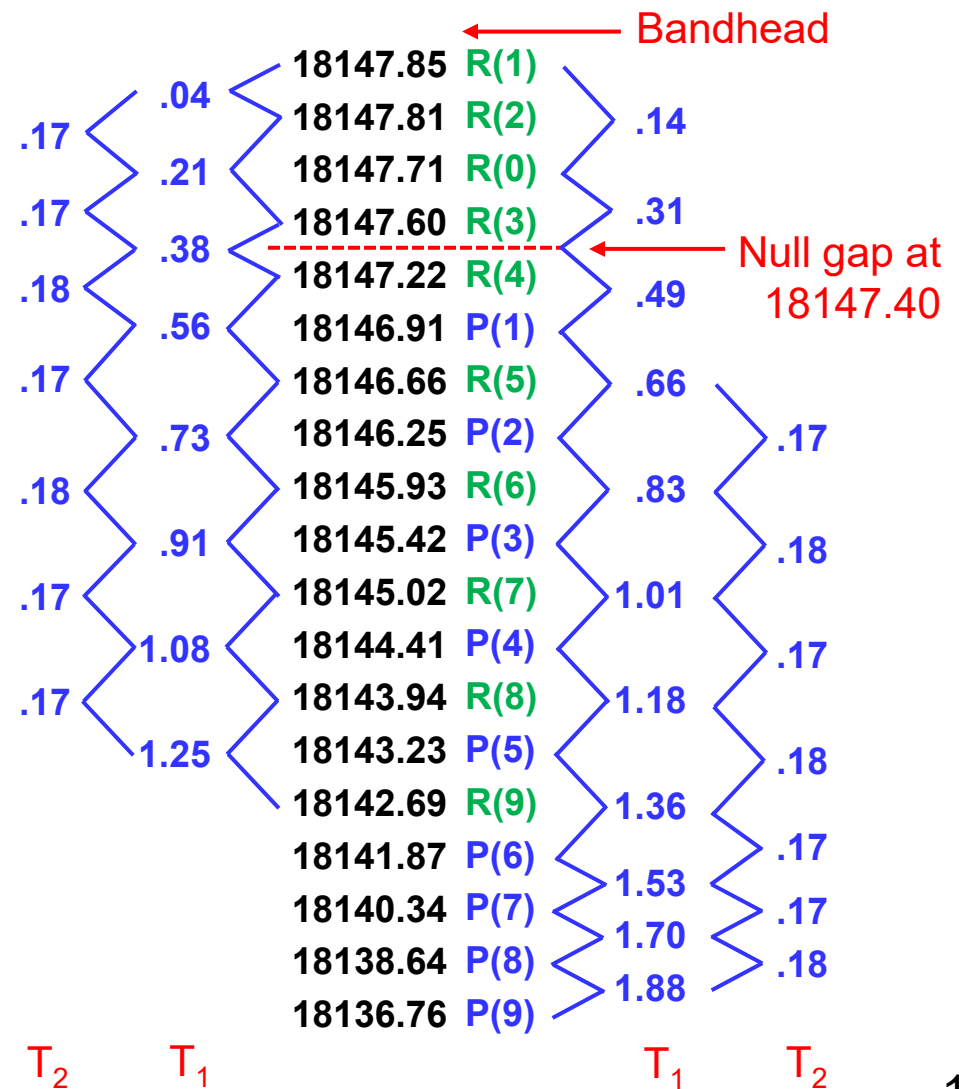
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3. Rotational analysis

- Fortrat Parabola

Example:
Rotational analysis of electronic spectra

Find B_e', B_e'', r_e', r_e'', and the null gap frequency ν_0

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

Note: All T_2 are negative!

Bandhead

.17	.04	18147.85 R(1)
		18147.81 R(2)	.14
	.21	18147.71 R(0)
.17		18147.60 R(3)	.31
	.38	18147.22 R(4)
.18		18146.91 P(1)	.49
	.56	18146.66 R(5)
.17		18146.25 P(2)	.66
	.73	18145.93 R(6)	.17
.18		18145.42 P(3)	.83
	.91	18145.02 R(7)	.18
.17		18144.41 P(4)	1.01
	1.08	18143.94 R(8)	.17
.17		18143.23 P(5)	1.18
	1.25	18142.69 R(9)	.18
		18141.87 P(6)	1.36
		18140.34 P(7)	1.53 .17
		18138.64 P(8)	1.70 .18
		18136.76 P(9)	1.88

Null gap at 18147.40

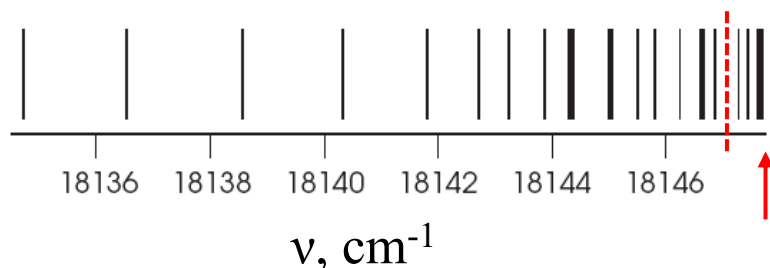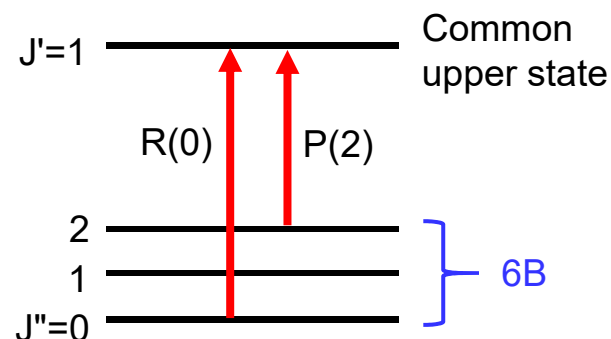T_2 T_1 T_1 T_2

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3. Rotational analysis

- Fortrat Parabola

Example:
Rotational analysis of electronic spectra

Find B_e', B_e'', r_e', r_e'', and the null gap frequency ν_0

ν, cm^{-1}

1. $\nu_0 = 18147.40$ cm^{-1}
2. $2a = T_2 = -0.173$ cm^{-1} = 2(B'-B")
3. Use common states to get B"
4. Solve for r', r" from B' and B"

Could also have used common lower states to get B'

J'=1 _____ Common upper state

R(0)   P(2)

2 _____
1 _____ } 6B
J"=0 _____

$R(0) = 18147.71, P(2) = 18146.25$

$R(0) - P(2) = 1.46$

$B'' = 1.46 / 6 = 0.243 cm^{-1}$

$B' = B'' + a = 0.157 cm^{-1}$

$B_e'' = 0.2438, \alpha_e = 0.0017$

$\Rightarrow B_0'' = 0.2438 - 0.0008 = 0.243$

$B_e' = 0.158, \alpha_e = 0.003$

$\Rightarrow B_0' = 0.158 - 0.0015 \approx 0.157$

$T_e = 18310.5, r_e'' = 1.988 \overset{o}{A}, r_e' = 2.47 \overset{o}{A}$

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4. Vibrational analysis

- ■ Band origin data

  Vibrational analysis can be used to determine information regarding ω_e, x_e

  Absorption → information on upper states
  Emission → information on lower states

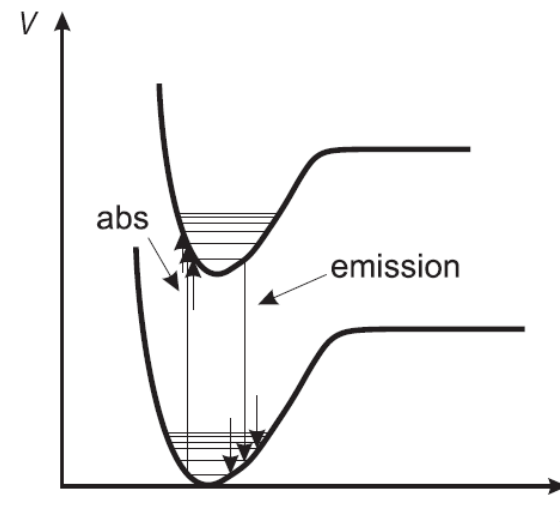 Tables of band origin values

- ■ Deslandres Table

  Recall: $G(\mathrm{v}) = \omega_e(\mathrm{v}+1/2) - \omega_e x_e(\mathrm{v}+1/2)^2$

  $$G(1)-G(0) = \omega_e - 2\omega_e x_e$$
  $$G(2)-G(1) = \omega_e - 4\omega_e x_e$$
  $$\bigg\}\, 2\omega_e x_e$$

Column analysis for ω_e', $\omega_e x_e'$

Row analysis for ω_e'', $\omega_e x_e''$

$2\omega_e x_e'$ 〈 $\omega_e' - 2\omega_e x_e'$ 〈
$\omega_e' - 4\omega_e x_e'$ 〈

v' \ v''	0	1	2	3
0	$\nu_{0,0}$	$\nu_{0,1}$	$\nu_{0,2}$	$\nu_{0,3}$
1	$\nu_{1,0}$			
2	$\nu_{2,0}$			
3	$\nu_{3,0}$			

$\omega_e'' - 2\omega_e x_e''$ $\omega_e'' - 4\omega_e x_e''$

$2\omega_e x_e''$

4. Vibrational analysis

- Deslandres Table

Transition v' ← v"	Energy required to observe transition	1st difference	2nd difference
0 ← 0	$T_e + 1/2\omega_e' - 1/4\omega_e x_e' - 1/2\omega_e'' + 1/4\omega_e x_e''$		
		$\omega_e' - 2\omega_e x_e'$	
1 ← 0	$T_e + 3/2\omega_e' - 9/4\omega_e x_e' - 1/2\omega_e'' + 1/4\omega_e x_e''$		$2\omega_e x_e'$
		$\omega_e' - 4\omega_e x_e'$	
2 ← 0	$T_e + 5/2\omega_e' - 25/4\omega_e x_e' - 1/2\omega_e'' + 1/4\omega_e x_e''$		$2\omega_e x_e'$
		$\omega_e' - 6\omega_e x_e'$	
3 ← 0	$T_e + 7/2\omega_e' - 49/4\omega_e x_e' - 1/2\omega_e'' + 1/4\omega_e x_e''$		$2\omega_e x_e'$
		$\omega_e' - 8\omega_e x_e'$	
4 ← 0	$T_e + 9/2\omega_e' - 81/4\omega_e x_e' - 1/2\omega_e'' + 1/4\omega_e x_e''$		

| v' \ v"		0	1	2	3	4
			20	**20**		
		1480	**1460**	**1440**		
0		29647.5	28167.5	26707.5	25267.5	
1	**40** **760**	30407.5	28927.5	27467.5	26027.5	24607.5
2	**40** **720**	31127.5	29647.5	28187.5	26747.5	25327.5
3	**40** **680**	31807.5	30327.5	28867.5	27427.5	26007.5
4	**640**	32447.5	30967.5	29507.5		
5			31567.5	30107.5	28667.5	
6				30667.5	29227.5	27807.5
7					29747.5	28327.5

Band origin data from an emission spectrum

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5. Analysis summary
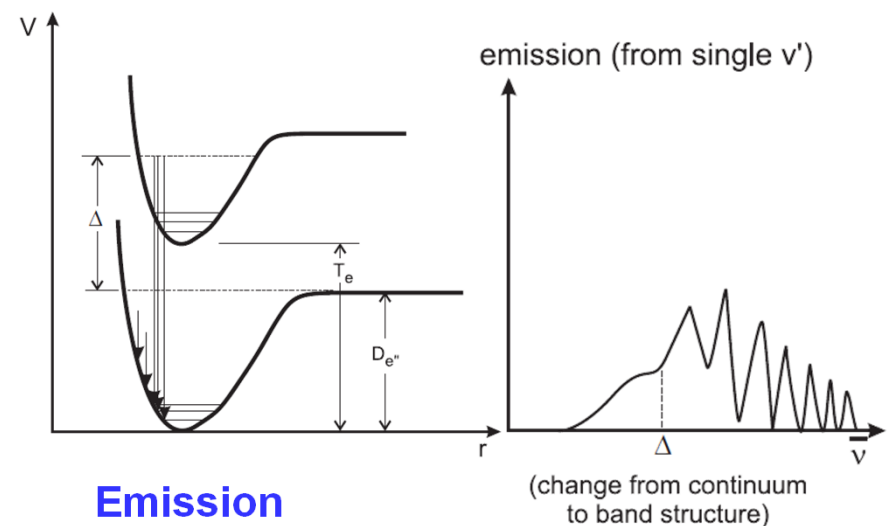
- Analysis techniques and related fundamental quantities

Analysis	Parameters
Rotational analysis	B_e, α_e, D_e, β_e
Vibrational analysis	ω_e, $\omega_e x_e$
Emission analysis	D_e'', $G(v'')$
Absorption analysis	D_e', T_e, $G(v')$

- Typical analyses
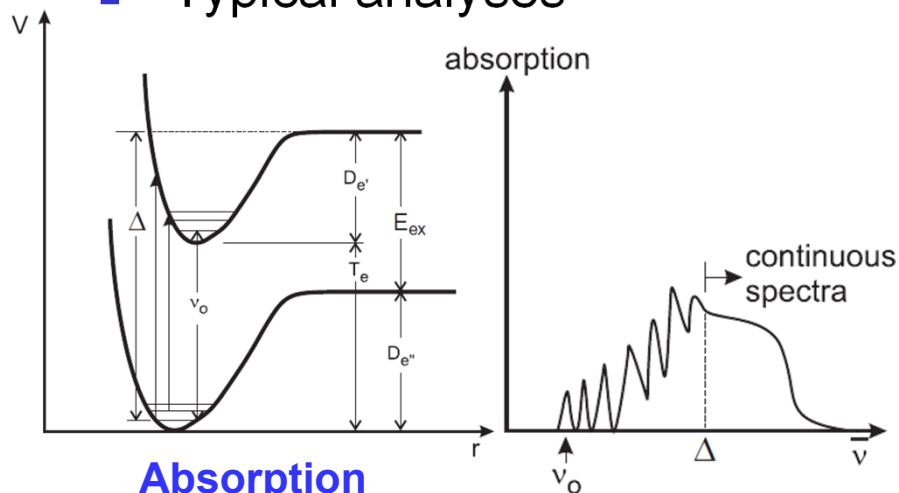
Absorption
1. Band origin → $G(v')$
2. $\nu_0 = T_e + G(v') - G(v'') \rightarrow T_e$
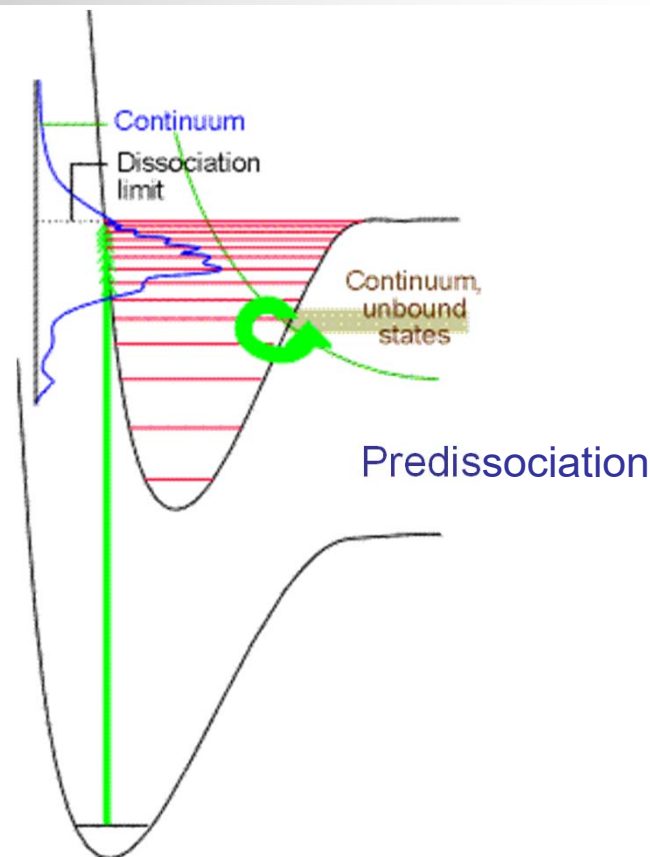3. $\Delta + G(v'') = T_e + D'_e \rightarrow D'_e$

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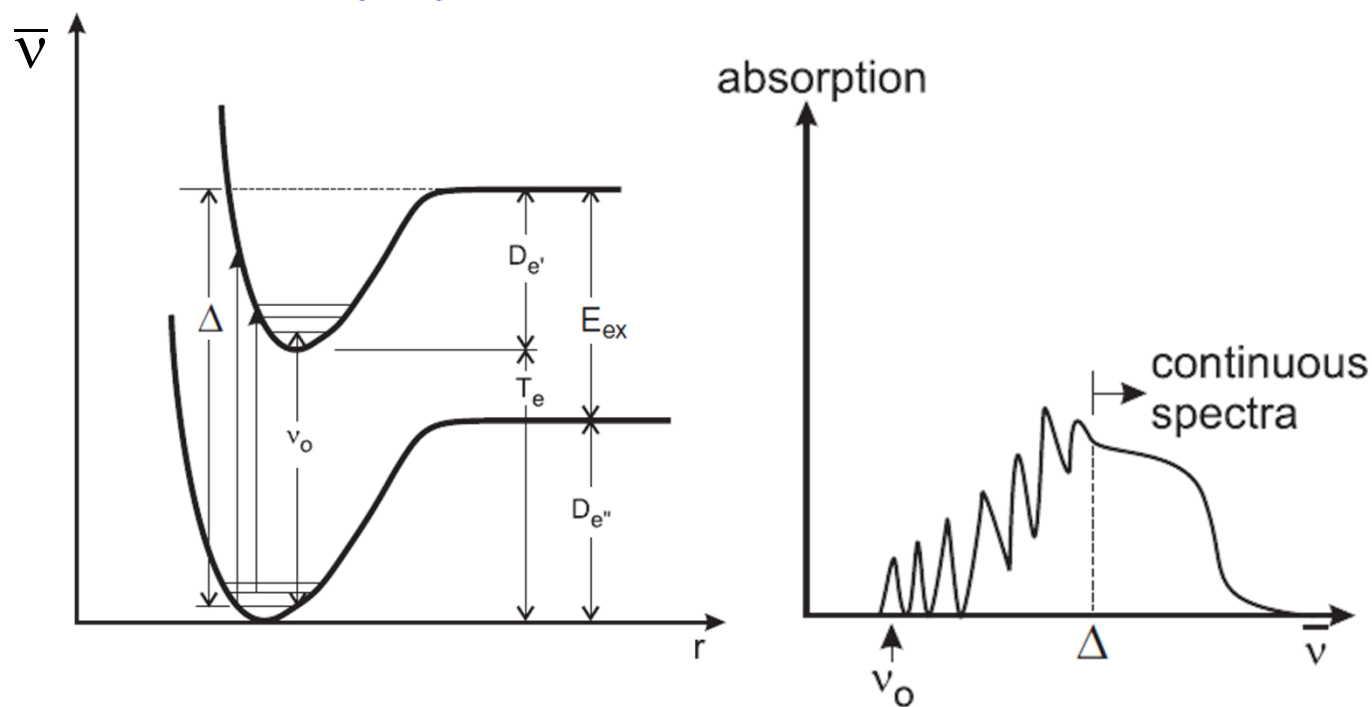
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6. Bond Dissociation Energies

1. Absorption and emission analysis

2. Birge-Sponer method

3. Thermochemical approach

4. Working example

Continuum

Dissociation limit

Continuum, unbound states

Predissociation

6. Bond dissociation energies

- Absorption

Absorption $\rightarrow D_e'$, T_e, $G(v')$

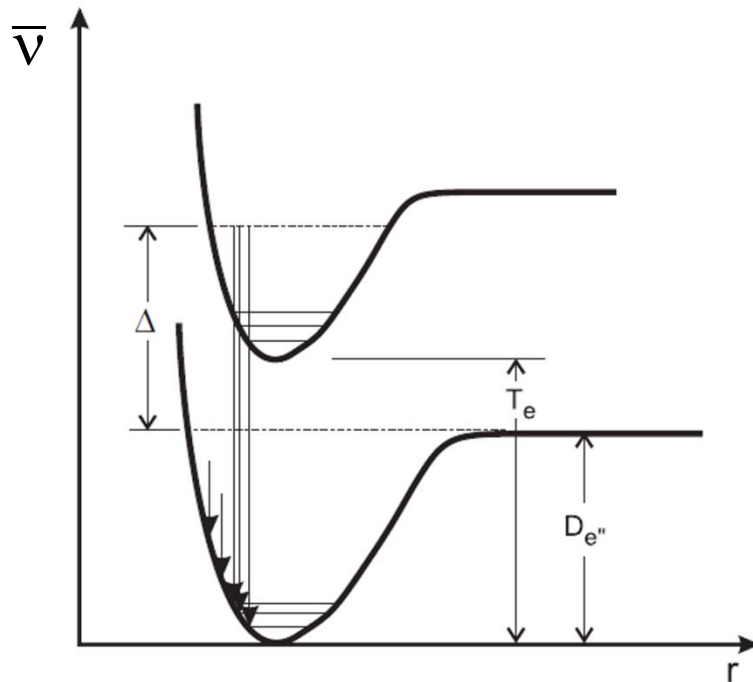1. Band origin $\rightarrow G(v')$ $\longleftarrow$ Enter in Deslandres Table
2. $\overline{\nu}_0 = T_e + G(v') - G(v'') \rightarrow T_e$
3. $\Delta + G(v'') = T_e + D'_e \rightarrow D'_e$

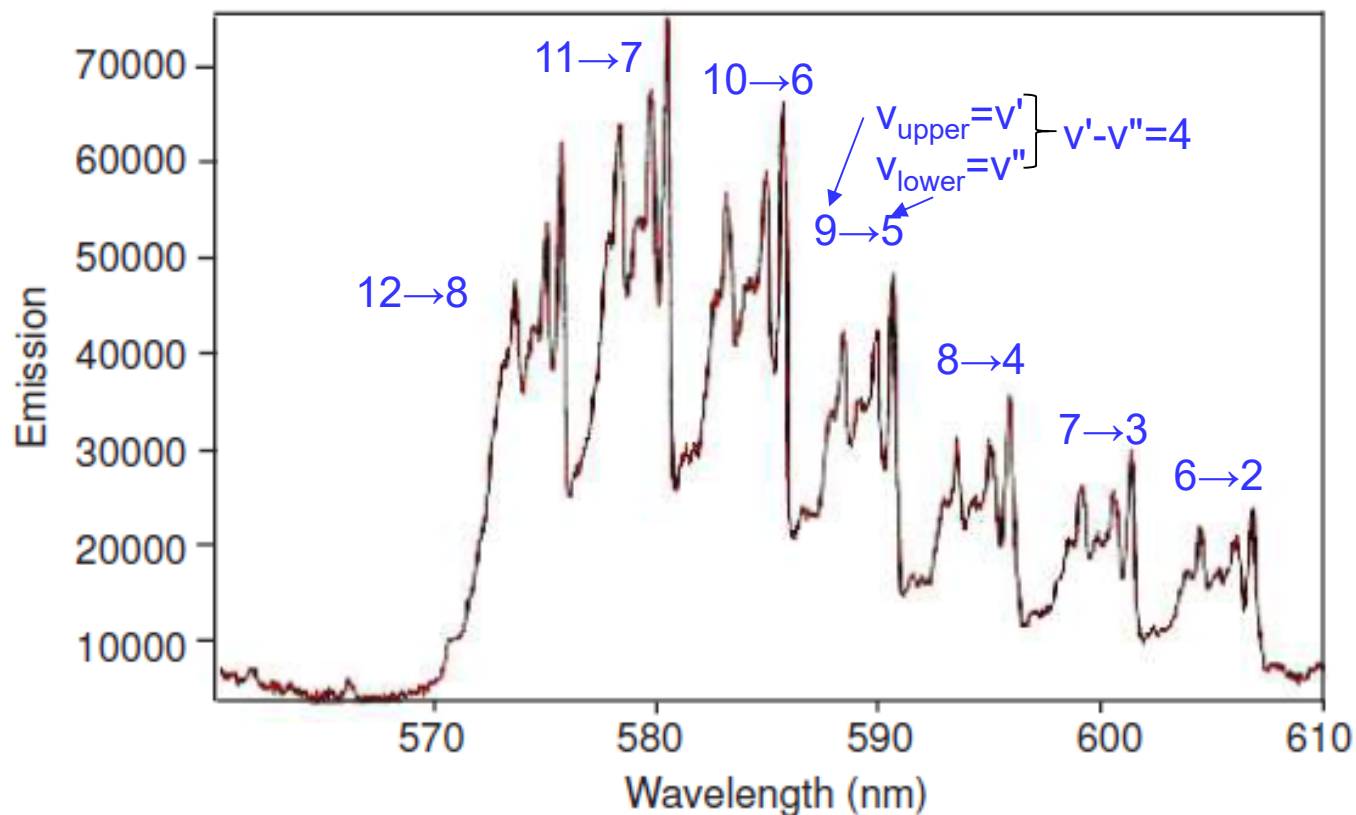# 6.1. Absorption and emission

- Emission

Emission → D_e'', G(v')

emission (from single v')

(change from continuum to band structure)
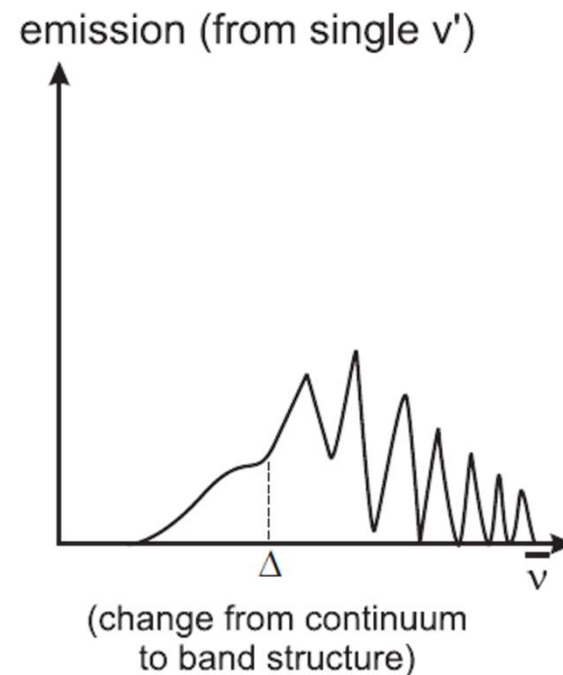
1. Band origin from fixed v' → G(v'') ⟵ Enter in Deslandres Table
2. $D''_e + \Delta = T_e + G(v') \rightarrow D''_e$
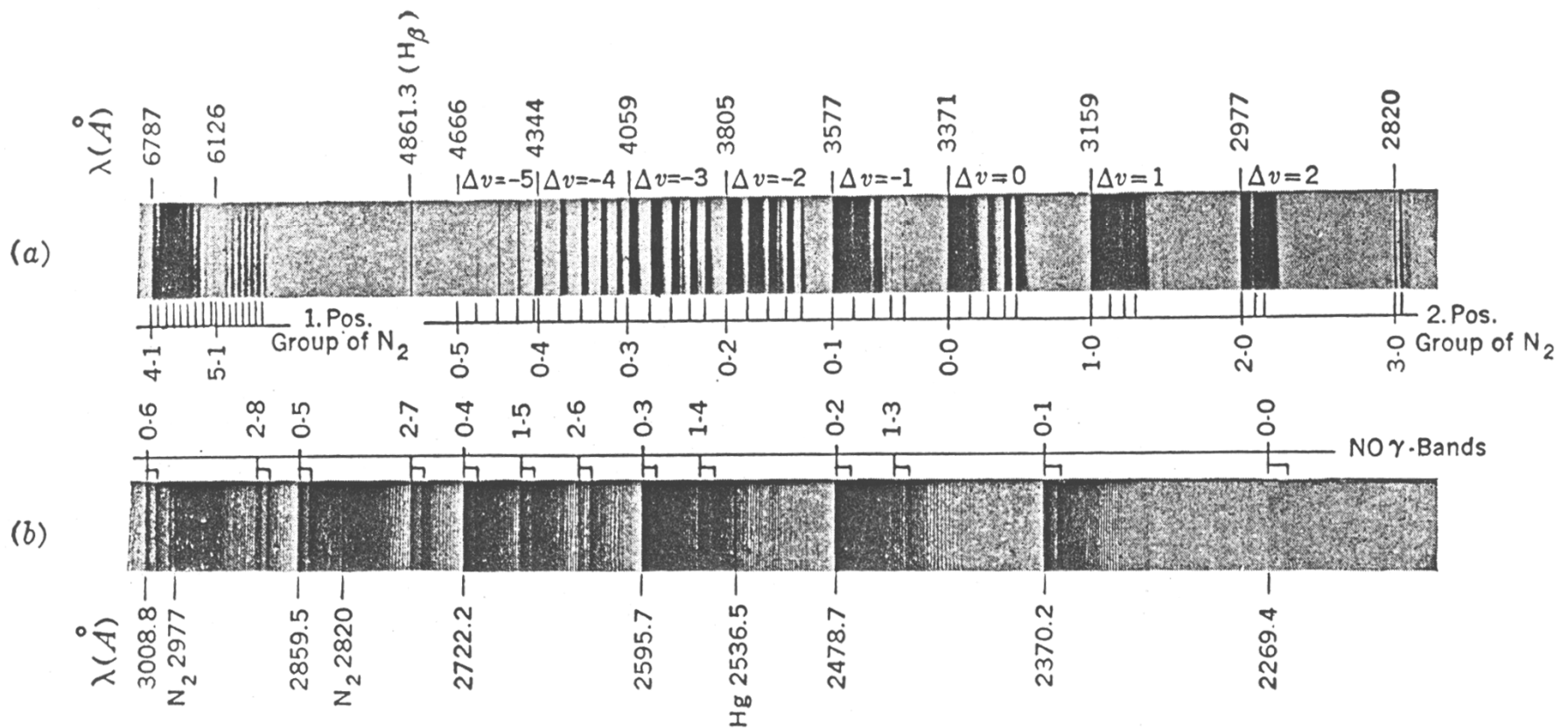
6.1. Absorption and emission

- Emission

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

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
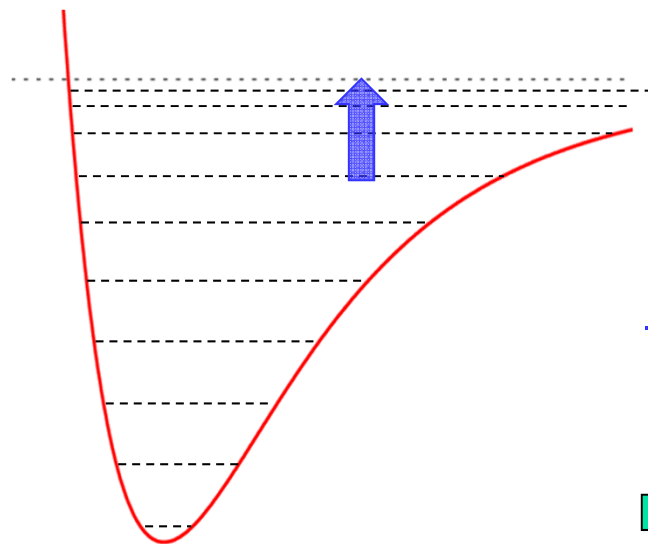
- Determine dissociation energies

Dissociation energies

$\Rightarrow$
- [Thermodynamics]   Heats of formation and reaction
- [Kinetics]   Rates of reaction

Birge-Sponer method
- Spectroscopic parameters $\Longrightarrow$ Dissociation energies

Constant anharmonicity

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

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

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

$$\Delta G(v) = G(v+1) - G(v) = \underbrace{-2\omega_e x_e v}_{a} + \underbrace{(\omega_e - 2\omega_e x_e)}_{b}$$

$\Rightarrow$ $\Delta G(v) = av + b$ Linear dependence on v!

6.2. Birge-Sponer method
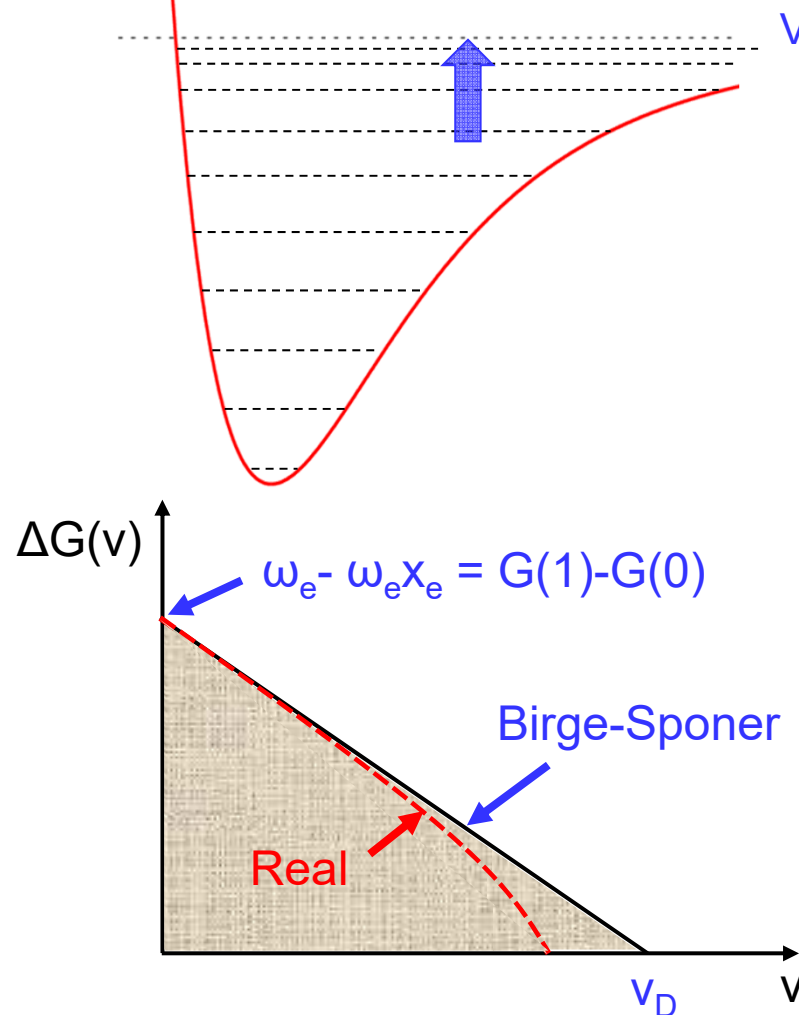
- Determine dissociation energies

Vibrational level spacing → 0 in the limit of dissociation

$\Delta G(\mathrm{v}) = a\mathrm{v} + b = 0$ @ dissociation

$$\mathrm{v}_D = -\frac{b}{a} = \frac{\omega_e}{2\omega_e x_e} - 1$$

$$D_e = \omega_e(\mathrm{v}_D + 1/2) - \omega_e x_e(\mathrm{v}_D + 1/2)^2$$

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

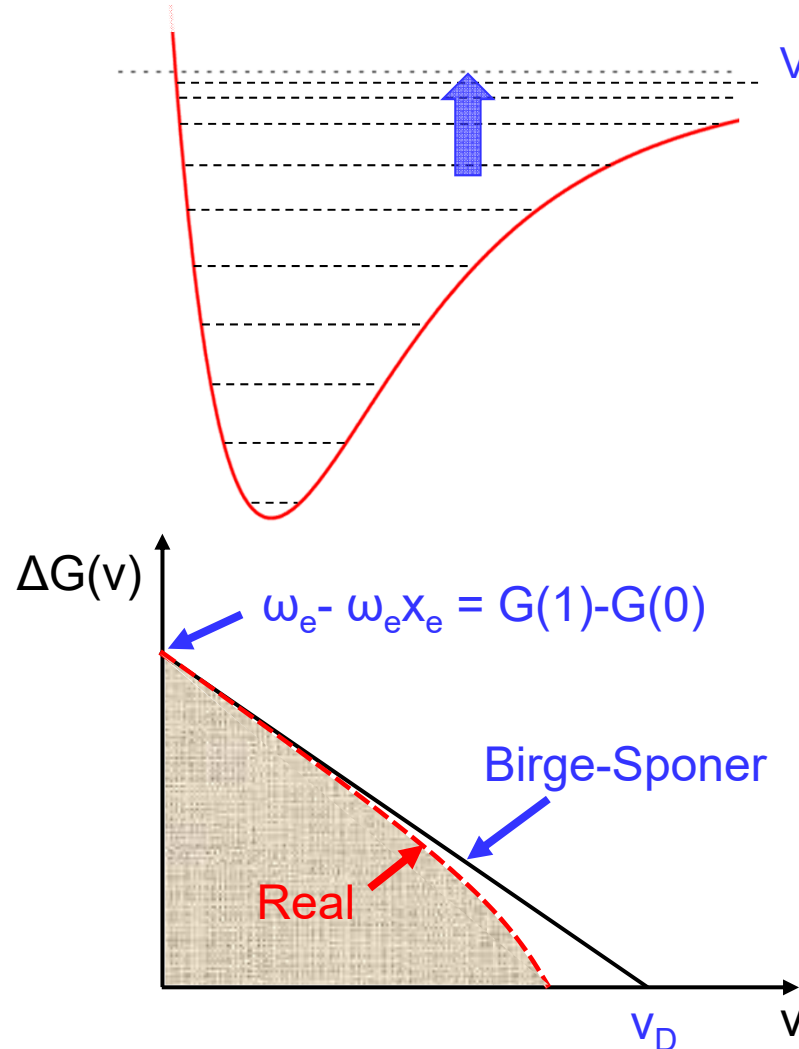$\propto$ Area under curve

$\Delta G(\mathrm{v})$

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

Birge-Sponer

Real

v_D

v

Real case: anharmonicity increases near dissociation limit

Birge-Sponer overpredicts D_e

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6.2. Birge-Sponer method

- Determine dissociation energies

Vibrational level spacing → 0 in the limit of dissociation

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

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

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

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

$\propto$ Area under curve

$\Delta G(v)$

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

Birge-Sponer

Real

v_D

v

Example: HCl

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

$\Rightarrow v_D = 27.7 \rightarrow 27$

$\Rightarrow D_e = 513 kJ/mole$

Actual:

$D_e = 427 kJ/mole$

Overpredicts by ~20%

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6.3. Thermochemical approach

- Determine dissociation energies

E.g., $I_2 \rightarrow 2I$

$$K_p = \frac{P_I^2}{P_{I_2}}$$

$$\frac{d\left(\ln K_p\right)}{dT} = \frac{\Delta H}{RT^2} \quad \text{where} \quad \Delta H = \sum v_i H_i = H_{prod} - H_{react} = D_e + 2\int_I \hat{c}_p dT - \int_{I_2} \hat{c}_p dT$$
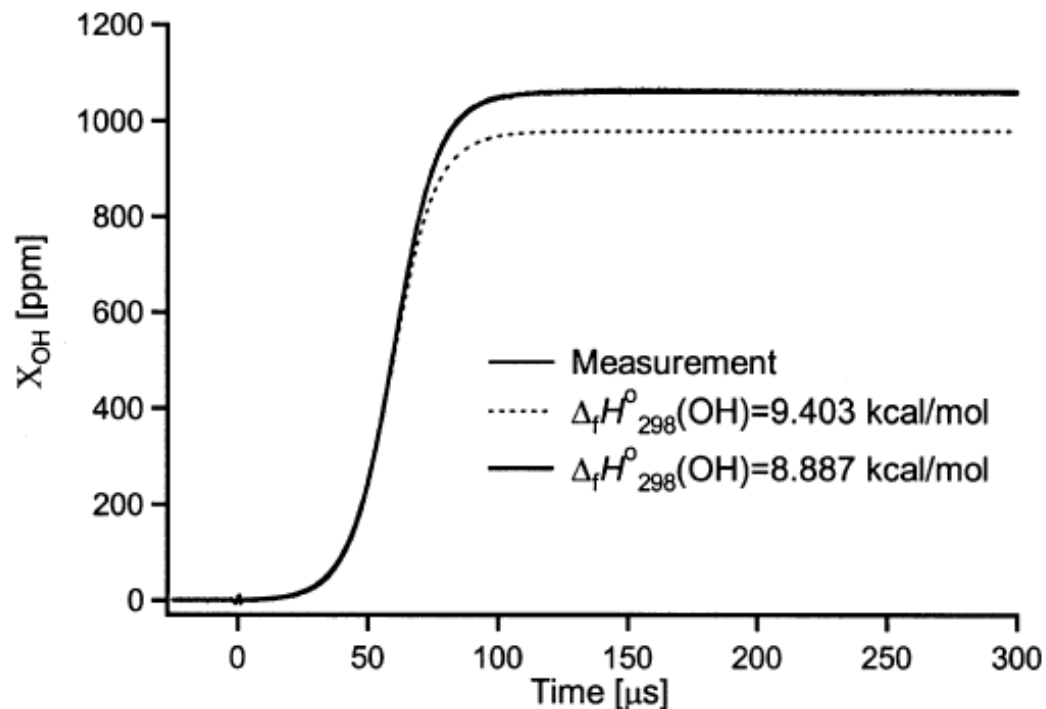
Measurements of partial pressures $\Rightarrow$ $K_p(T)$ $\Rightarrow$ $\Delta H, \boxed{D_e''}$

Measured spectroscopically (e.g., by laser absorption)

6.4. Working example

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



Experimentally measured and modeled
OH mole fraction time histories.

- T_5=2590K, P_5=1.075atm, mixture: 4002ppm H_2/3999ppm O_2/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 $\Delta_f H^0_{298}$(OH) from 9.403 to 8.887kcal/mol

6.4. Working example

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

Experimentally derived values for $\Delta_f H^0_{298}$(OH).
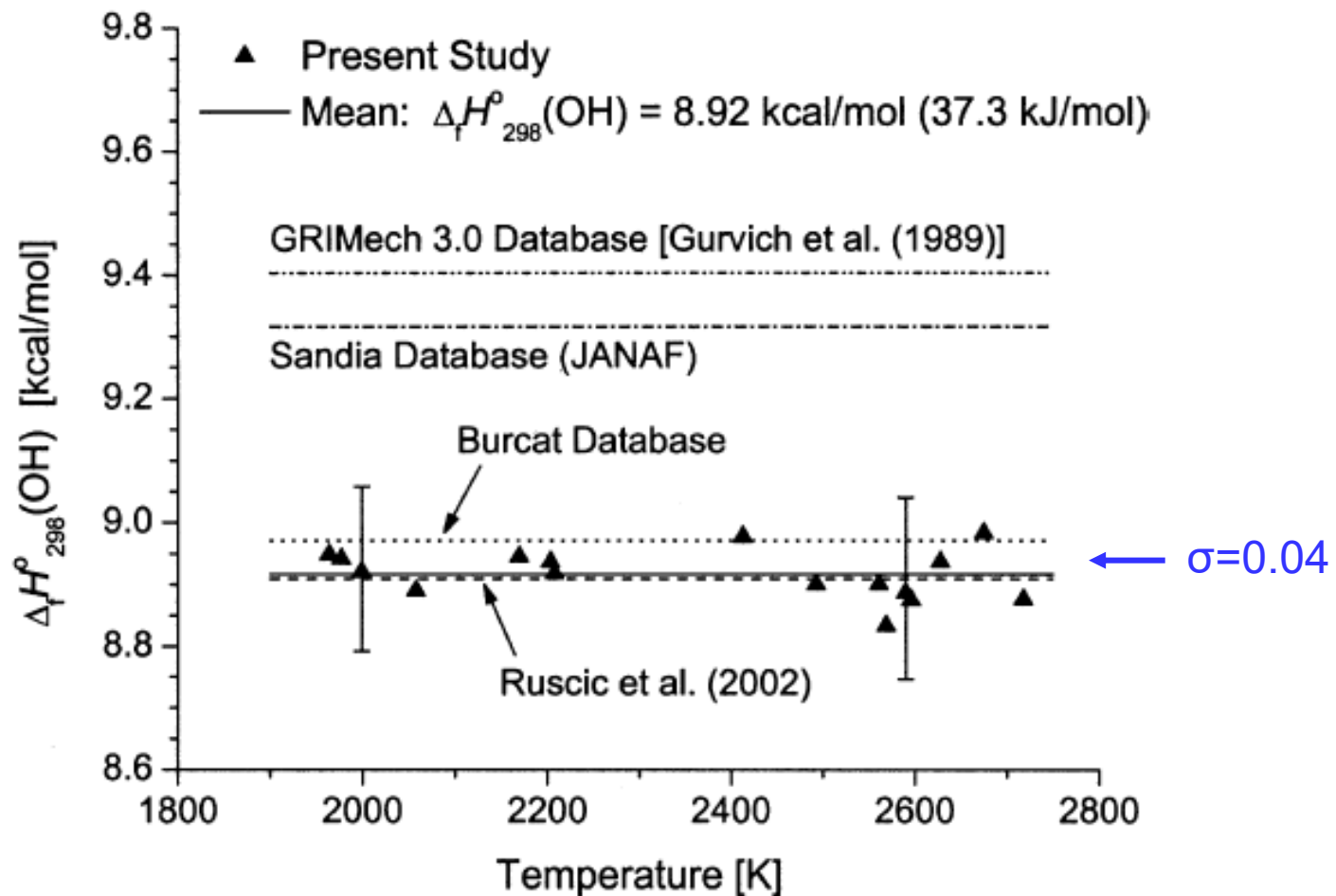
Next: Polyatomic Molecular Spectra

- ❖ Rotational Spectra
- ❖ Vibrational Bands, Rovibrational Spectra