

Lecture 24 — Vibration-Rotation Spectra & Anharmonicity

Reading: Engel 4th ed., Chapter 8 (Sections 8.6–8.8)

Learning Objectives

- Explain the P, Q, and R branch structure of vibration-rotation spectra
 - Derive the combined selection rules for simultaneous vibrational-rotational transitions
 - Extract B , $\tilde{\nu}_0$, and bond length from vibration-rotation band analysis
 - Account for anharmonicity and its spectroscopic consequences
 - Calculate dissociation energies from spectroscopic data using the Birge-Sponer extrapolation
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1. Vibration-Rotation Transitions

In the gas phase, a vibrational transition is always accompanied by a simultaneous rotational transition. The combined selection rules are:

$$\Delta v = \pm 1 \quad \text{and} \quad \Delta J = \pm 1$$

(For molecules with no orbital angular momentum about the bond axis. If $\Lambda \neq 0$, then $\Delta J = 0$ is also allowed.)

Energy of Vibration-Rotation Levels

$$E_{v,J} = \tilde{\nu}_0 \left(v + \frac{1}{2} \right) + BJ(J+1) \quad (\text{in cm}^{-1})$$

(Neglecting anharmonicity, centrifugal distortion, and vibration-rotation coupling.)

2. The P, R, and Q Branches

R Branch ($\Delta J = +1$): $J \rightarrow J + 1$

$$\tilde{\nu}_R(J) = \tilde{\nu}_0 + 2B(J+1), \quad J = 0, 1, 2, \dots$$

Lines appear at **higher frequency** than $\tilde{\nu}_0$.

P Branch ($\Delta J = -1$): $J \rightarrow J - 1$

$$\tilde{\nu}_P(J) = \tilde{\nu}_0 - 2BJ, \quad J = 1, 2, 3, \dots$$

Lines appear at **lower frequency** than $\tilde{\nu}_0$.

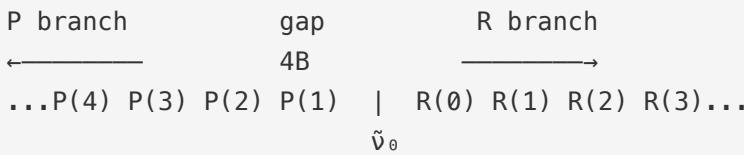
Q Branch ($\Delta J = 0$): Allowed only for certain molecules

$$\tilde{\nu}_Q = \tilde{\nu}_0$$

For diatomic molecules in ${}^1\Sigma$ states (most common), $\Delta J = 0$ is **forbidden**. There is **no Q branch**, and a gap of $4B$ appears at $\tilde{\nu}_0$ between the P and R branches.

[!NOTE] **Concept Check 24.1** In a vibration-rotation spectrum of a typical diatomic molecule, why is there a "gap" where the fundamental vibrational frequency $\tilde{\nu}_0$ should be? What selection rule is responsible for this?

Schematic of the Band



Each line is separated by approximately $2B$ from its neighbor.

3. Determining Molecular Parameters from the Spectrum

Method: Combination Differences

From the R and P branch line positions:

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J) = 4B \left(J + \frac{1}{2} \right)$$

$$\tilde{\nu}_R(J) + \tilde{\nu}_P(J+1) = 2\tilde{\nu}_0$$

These equations allow extraction of B and $\tilde{\nu}_0$ independently.

Vibration-Rotation Coupling

In reality, B differs slightly between $v = 0$ and $v = 1$ because the average bond length changes:

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right)$$

where α_e is the **vibration-rotation coupling constant** (small, positive — typically ~1% of B_e).

This causes the R branch lines to **converge** and P branch lines to **diverge** at high J :

$$\tilde{\nu}_R(J) = \tilde{\nu}_0 + (B_0 + B_1)(J + 1) + (B_1 - B_0)(J + 1)^2$$

$$\tilde{\nu}_P(J) = \tilde{\nu}_0 - (B_0 + B_1)J + (B_1 - B_0)J^2$$

4. Anharmonicity in Spectra

Anharmonic Energy Levels

$$G(v) = \tilde{\nu}_e \left(v + \frac{1}{2} \right) - \tilde{\nu}_e x_e \left(v + \frac{1}{2} \right)^2 + \dots$$

Observed Frequencies

Fundamental ($v = 0 \rightarrow 1$): $\tilde{\nu}_{0 \rightarrow 1} = \tilde{\nu}_e(1 - 2x_e)$

First overtone ($v = 0 \rightarrow 2$): $\tilde{\nu}_{0 \rightarrow 2} = 2\tilde{\nu}_e(1 - 3x_e)$

Second overtone ($v = 0 \rightarrow 3$): $\tilde{\nu}_{0 \rightarrow 3} = 3\tilde{\nu}_e(1 - 4x_e)$

Hot Bands

Transitions from $v = 1$ (thermally populated at high T):

$$\tilde{\nu}_{1 \rightarrow 2} = \tilde{\nu}_e(1 - 4x_e)$$

Hot bands appear at slightly lower frequency than the fundamental.

5. Dissociation Energy: Birge-Sponer Extrapolation

The spacing between adjacent vibrational levels decreases linearly (for Morse potential):

$$\Delta G_{v+1/2} = G(v+1) - G(v) = \tilde{\nu}_e - 2\tilde{\nu}_e x_e (v+1)$$

The dissociation energy is the total of all level spacings:

$$D_0 = \sum_{v=0}^{v_{\max}} \Delta G_{v+1/2} \approx \frac{\tilde{\nu}_e^2}{4\tilde{\nu}_e x_e} - \frac{1}{2} \tilde{\nu}_e (1 - x_e)$$

Graphically: plot ΔG vs. v and sum the area under the curve (until $\Delta G = 0$).

Worked Example: HCl

$$\tilde{\nu}_e = 2991 \text{ cm}^{-1}, x_e = 0.0174$$

$$D_e = \frac{\tilde{\nu}_e}{4x_e} = \frac{2991}{4(0.0174)} = 43,000 \text{ cm}^{-1} = 5.33 \text{ eV}$$

$$D_0 = D_e - \frac{1}{2}\tilde{\nu}_e(1 - x_e) = 43,000 - 1470 = 41,500 \text{ cm}^{-1} = 5.15 \text{ eV}$$

Experimental $D_0 = 4.43$ eV — the Morse model overestimates somewhat, but captures the right order.

[!NOTE] **Concept Check 24.2** What happens to the spacing between vibrational energy levels near the dissociation limit of a molecule? How does this differ from the prediction of the harmonic oscillator model?

6. Summary of Spectroscopic Parameters

All molecular constants can be extracted from high-resolution spectra:

Parameter	Determined from
$\tilde{\nu}_e$	Fundamental + overtone frequencies
x_e	Anharmonicity from overtones
B_e	Rotational structure (line spacing)
α_e	Difference in B_0 and B_1
D	Centrifugal distortion from high- J lines

Parameter	Determined from
r_e	From B_e
k	From $\tilde{\nu}_e$ and μ
D_0	Birge-Sponer extrapolation

Key Equations Summary

Equation	Expression
R branch	$\tilde{\nu}_R = \tilde{\nu}_0 + 2B(J + 1)$
P branch	$\tilde{\nu}_P = \tilde{\nu}_0 - 2BJ$
Band gap	$4B$
Combination differences	$\tilde{\nu}_R(J) - \tilde{\nu}_P(J) = 4B(J + \frac{1}{2})$
Anharmonic fundamental	$\tilde{\nu}_{0 \rightarrow 1} = \tilde{\nu}_e(1 - 2x_e)$
Birge-Sponer	$D_e \approx \tilde{\nu}_e/(4x_e)$

Recent Literature Spotlight

"Rovibrational Spectroscopy of the CH⁺-He Complex in a 4 K Cryogenic Ion Trap" *T. Salomon, J. L. Doménech, P. C. Schmid, E. A. Michael, S. Schlemmer, O. Asvany, Journal of Molecular Spectroscopy, 2021, 377, 111421.* [DOI](#)

This experiment used a cryogenic 22-pole ion trap at 4 K to record the high-resolution rovibrational spectrum of the CH⁺-He complex. The observed transitions between quantized rovibrational states — with rotational fine structure superimposed on vibrational bands — provide a textbook example of the vibration-rotation coupling taught in this lecture.

Practice Problems

1. **Branch analysis.** The following lines are observed in the vibration-rotation spectrum of HBr (in cm⁻¹): P(1) = 2623.2, P(2) = 2606.8, R(0) = 2655.6, R(1) = 2671.7. Determine

$\tilde{\nu}_0$ and B .

2. **Overtone analysis.** For HF, the fundamental is at 3961.6 cm^{-1} and the first overtone at 7750.8 cm^{-1} . Calculate $\tilde{\nu}_e$ and x_e .
 3. **Dissociation energy.** Using your $\tilde{\nu}_e$ and x_e for HF from Problem 2, calculate D_0 via Birge-Sponer extrapolation. Compare to the experimental value of 5.87 eV.
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Next week: The Hydrogen Atom