

Lecture 22 — Rotational (Microwave) Spectroscopy

Reading: Engel 4th ed., Chapter 8 (Sections 8.1–8.3)

Learning Objectives

- State the selection rules for pure rotational transitions and justify them from symmetry
 - Predict and interpret rotational (microwave) spectra of diatomic molecules
 - Determine rotational constants and bond lengths from spectral data
 - Account for centrifugal distortion
 - Explain population effects and predict the most intense spectral line
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1. Conditions for Rotational Spectroscopy

Gross Selection Rule

A molecule must have a **permanent electric dipole moment** to absorb or emit microwave radiation via rotational transitions.

- **Active:** HCl, CO, NO, H₂O — heteronuclear diatomics and most polyatomics
- **Inactive:** H₂, N₂, O₂, CO₂ (symmetric stretch) — homonuclear diatomics and some symmetric modes

[!NOTE] **Concept Check 22.1** Why must a molecule have a permanent dipole moment to exhibit a pure rotational spectrum? Would you expect to observe a rotational spectrum for *CH*₄ (methane)?

Symmetry Perspective

The transition dipole moment $\langle J', m'_J | \hat{\mu} | J, m_J \rangle$ is nonzero only if the direct product of representations contains the totally symmetric representation. Since $\hat{\mu}$ transforms as a translation (*x*, *y*, or *z*), we need $\Gamma_{J'} \otimes \Gamma_{\text{translation}} \otimes \Gamma_J \supseteq \text{totally symmetric}$.

Specific Selection Rules

$$\Delta J = \pm 1, \quad \Delta m_J = 0, \pm 1$$

2. The Rotational Spectrum

Transition Frequencies

For $J \rightarrow J + 1$:

$$\tilde{\nu}_{J \rightarrow J+1} = \frac{E_{J+1} - E_J}{\hbar c} = B[(J+1)(J+2) - J(J+1)] = 2B(J+1)$$

The pure rotational spectrum consists of **equally spaced lines** separated by $2B$:

Transition	$\tilde{\nu}$ (cm^{-1})
$J = 0 \rightarrow 1$	$2B$
$J = 1 \rightarrow 2$	$4B$
$J = 2 \rightarrow 3$	$6B$
$J = 3 \rightarrow 4$	$8B$

Measuring B from the Spectrum

The spacing between adjacent lines is $2B$. A single measurement gives:

$$B = \frac{\tilde{\nu}_{J \rightarrow J+1}}{2(J+1)}$$

From B , we get the bond length:

$$r_e = \sqrt{\frac{\hbar}{8\pi^2 c \mu B}}$$

[!NOTE] **Concept Check 22.2** In the rotational spectrum of a rigid diatomic molecule, the lines are equally spaced by $2B$. If the bond length of the molecule were to increase, how would the spacing between these lines change?

3. Centrifugal Distortion

Real molecules are not perfectly rigid — as J increases, centrifugal force stretches the bond, increasing I and decreasing the effective B .

Corrected Energy Levels

$$E_J = BhcJ(J + 1) - DhcJ^2(J + 1)^2$$

where D is the **centrifugal distortion constant** (small, positive).

$$D = \frac{4B^3}{\tilde{\nu}^2}$$

Effect on the Spectrum

Lines at high J are shifted to **lower frequency** relative to the rigid rotor prediction:

$$\tilde{\nu}_{J \rightarrow J+1} = 2B(J + 1) - 4D(J + 1)^3$$

4. Intensities and the Boltzmann Distribution

Population of Level J

$$N_J \propto (2J + 1) \exp\left(-\frac{BhcJ(J+1)}{k_B T}\right)$$

- $(2J + 1)$: degeneracy factor (increases with J)
- Exponential: Boltzmann factor (decreases with J)

These competing effects create a **maximum** in population at:

$$J_{\max} = \sqrt{\frac{k_B T}{2Bhc}} - \frac{1}{2}$$

Spectral Envelope

The most intense line in the rotational spectrum corresponds to the transition originating from the most populated level J_{\max} .

Worked Example: HCl at 300 K

$$B = 10.59 \text{ cm}^{-1}$$

$$J_{\max} = \sqrt{\frac{(1.381 \times 10^{-23})(300)}{2(10.59)(6.626 \times 10^{-34})(3 \times 10^{10})}} - \frac{1}{2} \approx 3$$

The strongest absorption line is the $J = 3 \rightarrow 4$ transition at $\tilde{\nu} = 8B = 84.7 \text{ cm}^{-1}$.

5. Isotope Effects

For isotopic substitution (e.g., H³⁵Cl vs. H³⁷Cl):

- The force constant k is unchanged (same electronic structure)
- The reduced mass μ changes
- The rotational constant changes: $B \propto 1/\mu$

$$\frac{B'}{B} = \frac{\mu}{\mu'}$$

Isotopic splitting is often observed in high-resolution microwave spectra and can be used to determine precise bond lengths.

Key Equations Summary

Equation	Expression
Selection rule	$\Delta J = \pm 1$
Transition frequency	$\tilde{\nu} = 2B(J + 1)$
Line spacing	$2B$
Centrifugal distortion	$\tilde{\nu} = 2B(J + 1) - 4D(J + 1)^3$
Population maximum	$J_{\max} \approx \sqrt{k_B T / (2Bhc)} - 1/2$
Bond length	$r_e = \sqrt{\hbar / (8\pi^2 c \mu B)}$

Recent Literature Spotlight

"Detection of Two Interstellar Polycyclic Aromatic Hydrocarbons via Spectral Matched Filtering" *B. A. McGuire, R. A. Loomis, A. M. Burkhardt, K. L. K. Lee, C. N. Shingledecker, et al.*, *Science*, **2021**, 371, 1265–1269. [DOI](#)

Using Green Bank Telescope observations of the Taurus Molecular Cloud, the authors identified interstellar 1- and 2-cyanonaphthalene through rotational spectroscopy. Each detection relied on matching observed microwave transition frequencies to the rotational constants predicted by quantum mechanics — the same $E_J = BJ(J + 1)$ energy levels derived in this lecture for rigid rotors.

Practice Problems

1. **Microwave spectrum.** The first line in the rotational spectrum of $^{12}\text{C}^{16}\text{O}$ appears at 3.863 cm^{-1} . Calculate (a) B , (b) I , and (c) r_e .
 2. **Isotope effect.** Predict the rotational constant B for $^{13}\text{C}^{16}\text{O}$ given $B(^{12}\text{C}^{16}\text{O}) = 1.931 \text{ cm}^{-1}$.
 3. **Most populated level.** For CO at 300 K ($B = 1.931 \text{ cm}^{-1}$), find J_{\max} and predict which rotational transition will be most intense.
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Next lecture: Vibrational (IR) Spectroscopy of Diatomics