

# 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
- 

## 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, H<sub>2</sub>O — heteronuclear diatomics and most polyatomics
- **Inactive:** H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> (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<sub>4</sub> (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  $\Gamma_{J'} \otimes \Gamma_{\text{translation}} \otimes \Gamma_J \supseteq$  totally symmetric.

## Specific Selection Rules

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

## 2. The Rotational Spectrum

### Transition Frequencies

For  $J \rightarrow J + 1$ :

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

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

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

### 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:

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

[!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.,  $\text{H}^{35}\text{Cl}$  vs.  $\text{H}^{37}\text{Cl}$ ):

- The force constant  $k$  is unchanged (same electronic structure)
- The reduced mass  $\mu$  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	$r_e = \sqrt{h / (8\pi^2 c \mu B)}$

## 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  $3.863\text{ cm}^{-1}$ . 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  $J_{\text{max}}$  and predict which rotational transition will be most intense.
- 

*Next lecture: Vibrational (IR) Spectroscopy of Diatomics*