Lecture 23 — Vibrational (IR) Spectroscopy of Diatomics

Reading: Engel 4th ed., Chapter 8 (Sections 8.4–8.5)

Learning Objectives

- State and apply selection rules for vibrational transitions of diatomics
- Interpret the fundamental absorption band of a diatomic molecule
- Determine force constants from IR spectral data
- Predict isotope effects on vibrational frequencies
- Use group theory to predict IR and Raman activity of polyatomic vibrations

1. Vibrational Selection Rules

Gross Selection Rule

The molecule must have a **dipole moment that changes during the vibration**:

$$\left(\frac{d\mu}{dx}\right)_{x=0} \neq 0$$

- **IR active**: HCl, CO, NO (heteronuclear diatomics)
- **IR inactive**: H₂, N₂, O₂ (homonuclear — no dipole change)

> [!NOTE] **Concept Check 23.1** For a vibration to be IR active, the dipole moment must change during the motion. In CO_2, the asymmetric stretch is IR active, but the symmetric stretch is not. Briefly explain why based on the dipole moment.

Specific Selection Rule (Harmonic Approximation)

$$\boxed{\Delta v = \pm 1}$$

Only the **fundamental** transition ($v = 0 \to 1$) is allowed.

With Anharmonicity

The selection rule relaxes slightly:

- $\Delta v = \pm 1$: **fundamental** (strong)
- $\Delta v = \pm 2$: **first overtone** (weak)
- $\Delta v = \pm 3$: **second overtone** (very weak)

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2. The Fundamental Absorption Frequency

$$\tilde{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (\text{cm}^{-1})$$

This gives the center of the fundamental absorption band.

Force Constant from IR Data

$$k = (2\pi c \tilde{\nu}_0)^2 \mu = 4\pi^2 c^2 \tilde{\nu}_0^2 \, \mu$$

Typical Values

Molecule	$\tilde{\nu}_0$ (cm⁻¹)	k (N/m)	Bond type
HF	4138	966	Single (strong)
HCl	2991	516	Single
HBr	2649	412	Single
HI	2309	314	Single
CO	2170	1902	Triple
NO	1904	1595	~2.5
N_2	2359	2294	Triple

Trends:

- Stronger bonds → higher k → higher $\tilde{\nu}$
- Lighter atoms → smaller μ → higher $\tilde{\nu}$
- The C–H stretch (~3000 cm⁻¹) is a diagnostic region in organic IR

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3. Isotope Effects on Vibrational Frequencies

Since k is unchanged by isotopic substitution:

$$\frac{\tilde{\nu}'}{\tilde{\nu}} = \sqrt{\frac{\mu}{\mu'}}$$

Example: HCl → DCl

$$\mu_{\text{HCl}} = \frac{(1.008)(34.97)}{35.98} = 0.9796 \text{ u}$$

$$\mu_{\text{DCl}} = \frac{(2.014)(34.97)}{36.98} = 1.904 \text{ u}$$

$$\frac{\tilde{\nu}_{\text{DCl}}}{\tilde{\nu}_{\text{HCl}}} = \sqrt{\frac{0.9796}{1.904}} = 0.717$$

$$\tilde{\nu}_{\text{DCl}} = 0.717 \times 2991 = 2145 \text{ cm}^{-1}$$

Experimental: 2145 cm⁻¹ — excellent agreement!

> [!NOTE] **Concept Check 23.2** When hydrogen in HCl is replaced by deuterium to form DCl, the vibrational frequency decreases. Based on the reduced mass μ, explain why heavier isotopes lead to lower vibrational frequencies.

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4. Raman Spectroscopy

The Raman Effect

In Raman spectroscopy, monochromatic light (ν_0) is scattered by a sample. Most photons scatter elastically (**Rayleigh scattering**), but a small fraction exchange energy with molecular vibrations:

- **Stokes lines**: $\nu_{\text{scattered}} = \nu_0 - \nu_{\text{vib}}$ (molecule gains energy)
- **Anti-Stokes lines**: $\nu_{\text{scattered}} = \nu_0 + \nu_{\text{vib}}$ (molecule loses energy)

Raman Selection Rule

A vibration is Raman active if the **polarizability** changes during the vibration:

$$\left(\frac{d\alpha}{dx}\right)_{x=0} \neq 0$$

- **Raman active**: H_2, N_2, O_2 (homonuclear diatomics — polarizability changes!)
- All diatomic molecules are Raman active (for the stretch)

Comparison: IR vs. Raman

Feature	IR	Raman
Selection rule	Dipole must change	Polarizability must change
Homonuclear diatomics	Inactive	Active
Heteronuclear diatomics	Active	Active
Mutual exclusion (centrosymmetric)	u modes only	g modes only
Intensity	Absorption	Scattering (weaker)

Mutual Exclusion Rule (from Symmetry)

For molecules with an inversion center (i): **no vibration is both IR active and Raman active.** This is a direct consequence of group theory — g and u representations are mutually exclusive.
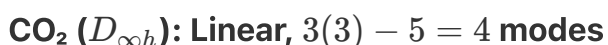
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5. IR and Raman Activity of Polyatomic Molecules

Using the group theory results from Week 6, we can predict activity for each normal mode.

H₂O (C_{2v}): $\Gamma_{\text{vib}} = 2A_1 + B_2$

Mode	Symmetry	z?	x^2, y^2, z^2?	IR?	Raman?
Symmetric stretch	A_1	✓ (z)	✓ (x^2, y^2, z^2)	✓	✓
Bend	A_1	✓ (z)	✓ (x^2, y^2, z^2)	✓	✓
Asymmetric stretch	B_2	✓ (y)	✓ (yz)	✓	✓

All three modes are both IR and Raman active (no inversion center → no mutual exclusion).

CO₂ ($D_{\infty h}$): Linear, $3(3) - 5 = 4$ **modes**

Mode	Symmetry	IR?	Raman?
Symmetric stretch	Σ_g^+	✗	✓
Asymmetric stretch	Σ_u^+	✓	✗
Bend (×2)	Π_u	✓	✗

Mutual exclusion rule holds perfectly.

Key Equations Summary

Equation	Expression
Vib. selection rule (harmonic)	$\Delta v = \pm 1$
Fundamental frequency	$\tilde{\nu}_0 = \frac{1}{2\pi c}\sqrt{k/\mu}$
Force constant from IR	$k = 4\pi^2 c^2 \tilde{\nu}_0^2 \mu$
Isotope effect	$\tilde{\nu}'/\tilde{\nu} = \sqrt{\mu/\mu'}$
Raman shift (Stokes)	$\Delta\tilde{\nu} = \tilde{\nu}_0 - \tilde{\nu}_{\mathrm{vib}}$
IR active	$d\mu/dx \neq 0$
Raman active	$d\alpha/dx \neq 0$

Recent Literature Spotlight

"Using Computational Chemistry Activities to Promote Learning in an Undergraduate Physical Chemistry Course" *T. E. Simos, et al.*, Journal of Chemical Education, **2020**, 97, 3014–3023. DOI

This paper describes how computational chemistry tools can be used to teach students about rovibrational spectroscopy of diatomic molecules. Students calculate Morse potential parameters, rotational constants, and vibration-rotation coupling constants — connecting the theoretical framework of this lecture to real spectroscopic data and developing intuition for how quantum mechanics predicts molecular spectra.

Practice Problems

1. **Force constant.** The fundamental vibrational frequency of $^{14}N^{16}O$ is 1904 cm⁻¹. Calculate the force constant and classify the bond order.

2. **Isotope substitution.** Predict $\tilde{\nu}$ for $^{15}N^{16}O$ and $^{14}N^{18}O$. Which isotope substitution causes a larger shift?

3. **Activity prediction.** For SO_2 (C_{2v}, $\Gamma_{\text{vib}} = 2A_1 + B_2$), predict which modes are IR active and which are Raman active. Is the mutual exclusion rule expected to hold?

Next lecture: Vibration-Rotation Spectra & Anharmonicity