Applications of Group Theory to Spectroscopy

Vibrational Spectroscopy

- Raman & IR Apparatus and Concept
- Selection Rules (Allowedness)
- Symmetry of Vibrational Modes
- Normal mode analysis
- Raman, Resonance Raman, CARS
- Electron Energy Loss Spectroscopy (EELS)

(Rotational Spectroscopy: not to be covered in class)

Comparison between IR and Raman

light scattering is a 2 photon event!
Comparison between IR and Raman light scattering is a 2 photon event:

Virtual energy states

Vibrational energy states

Infrared absorption
Rayleigh scattering
Stokes Raman scattering
Anti-Stokes Raman scattering

2 Kinds of Light Scattering

1) Elastic: "Rayleigh"
   \[ \hbar^2 \rightarrow \hbar^2 + \delta \]

2) Inelastic: "Raman" (1928)
   \[ \hbar^2 \rightarrow \hbar^2 + \Delta \]

\( \delta \) = vib or rot frequency of sample

Infrared Vibrational Spectroscopy


Dispersive (dual beam)

FTIR: Fourier Transform InfraRed

Michelson interferometer

An FTIR interferogram converts wavelength into mirror position (i.e., energy into time). The central peak is at the ZPD position (“Zero Path Difference”) where the maximum amount of light passes through the interferometer to the detector.

The interferogram is then fast Fourier transformed (FFT) back into the wavelength regime: i.e., the IR absorbance spectrum.
**FTIR Advantages**

- **Speed**: all frequencies measured simultaneously, FT-IR scans in sec. rather than several minutes. **Felgett Advantage**.

- **Sensitivity**: Sensitivity dramatically improved with FT-IR. The detectors are much more sensitive. Optical throughput is much higher (Jacquinot Advantage, better S/N). Fast scans enable co-addition of several scans (signal averaging).

- **Internally Calibrated**: HeNe laser used as internal wavelength calibration (Connes Advantage).

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**Raman Spectroscopy**

Raman: Scattering of visible light with loss (or gain) of frequency corresponding to vibrational quanta.

![Raman Spectroscopy Diagram](image)
Monochromator

CCD Camera (main detector)

PMT (alternative detector)

Motorized Gratings
600 g/mm
1200 g/mm
2400 g/mm

Raman Microscope

Triple Spectrograph

CCD

Nikon TE300

GWU 240-500 nm

Ti:Sapphire 700-1100 nm

Millenia V4 532 nm

Dye laser 605-700 nm

Tunable He/Ne laser
Raman Sample Handling

(a) Capillary
(b) Cylinder
(c) NMR Tube
(d) Pellet

Sealed or Flow Spin Spin or Stir Spin

(e) Low Temperature
(f) Electrochemical
(g) Microscope

Pump Liq. N₂ Cu crystal

Small sample of e.g., frozen solution Matrix

Electrode or Bulk Small area, e.g., single crystal

Raman Spectroscopy

Argon \( \text{Ar} \)
CW Lasers

Krypton \( \text{Kr} \)
Inter-\text{Ar} Inter-\text{Kr}

Excimer N₂ \( \text{N}_2 \)
N₂F \( \text{N}_2\text{F} \)
Dye Lasers

Pulsed Lasers

λ (nm)

0.05–15 W, 3–53 ps pulses at 3–10 kHz

0.25–200 mW, 0.01–1 mW pulses, 0.05–10 µs at 0.05–50 kHz

0.1–10 W, 3–100 ps pulses, 0.05–10 µs at 0.05–10 kHz

0.1–10 W, 3–100 ps pulses, 0.05–10 µs at 0.05–10 kHz

pumped by Nd:YAG Laser

340
514
1064

Molecular Vibrations: 3N-6 (5) Rule

For N atom molecule, there are:

3N-6 Normal Modes for Non-Linear
3N-5 Normal Modes for Linear

i.e. 3 coord. for each atom
- 3 translations
- 3 rotations (2 for Linear)

The Lost Rotation:

rotation

Infrared Absorption Selection Rule

IR Selection Rule: For any IR absorption, the vibrational excitation must change the dipole moment of the molecule in order for radiation absorption to occur.

i.e. $\text{H-Cl}$ $\nu_{\text{as}} = 2886 \text{ cm}^{-1}$

$\text{H-H}$ $\nu_{\text{IR}}$ not observed (Raman at $4400 \text{ cm}^{-1}$)

$\text{H$_2$O}$ $\nu_{\text{IR}}$ at $4400 \text{ cm}^{-1}$
Infrared Absorption Selection Rule

The Dipole Moment ($M$) must change during vibration

\[ M \neq 0 \]

\[ M = \int \psi_{es} \hat{M} \psi_{gs} \, dx \]

where \( \psi_{es} \) = vibrational Excited State Wave Function

\( \psi_{gs} \) = Ground State Wave Function = Arg Symm.

\( \hat{M} \) = Dipole Moment Operator = \( (x, \hat{y}, \hat{z}) \)

Group Theory View of Selection Rules

For Integrals over all space,

Only functions with Arg Symmetry

(i.e. Totally Symmetric)

Will have Non-Zero Integrals!
Group Theory View of Selection Rules

All \( f^2(x) \) will/must include an \( A_{1g} \) (totally symmetric) function.

Infrared Absorption Selection Rule

The Dipole Moment (\( M \)) must change during vibration

\[
M = \int \Psi_x \hat{M} \Psi_z \, dx
\]

where \( \Psi_x \) = vibrational excited state wave function
\( \Psi_z \) = ground state wave function = \( A_{1g} \) sym.
\( \hat{M} \) = Dipole Moment Operator = \( (\vec{x}, \vec{y}, \vec{z}) \)

The ground vibrational state is always totally symmetric (\( A_{1g} \)):
i.e., the atoms aren’t “moving” (sorta…)

And dipole moments are just vectors:
i.e., they transform as \( x, y \) and \( z \).
Infrared Absorption Selection Rule

The Dipole Moment ($M$) must change during vibration

\[ M = \int \psi_e^* \mathbf{M} \psi_e \, d\mathbf{r} \]

where \( \psi_e \) = vibrational Excited State Wavefunction
\( \mathbf{M} \) = Dipole Moment Operator = \( \left( \hat{x}, \hat{y}, \hat{z} \right) \)

In GT terms: must contain an \( A_{1g} \) to be non-zero:

\[ \Gamma \otimes A_{1g} \otimes \Gamma = \Gamma \]

i.e., \( \Gamma \times A_{1g} = \Gamma \)

Raman vs. Infrared Selection Rules

Infrared absorption: (1 photon process)

Raman Scattering: (2 photon process)

The polarizability tensor goes as the quadratics of \( xyz \).
**Vibrational Selection Rules**

Selection Rules:

IR active modes must have IrrReps that go as \(x, y, z\).

Raman active modes must go as quadratics \((xy, xz, yz, x^2, y^2, z^2)\).

(Raman is a 2-photon process: photon in, scattered photon out)

---

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>(D_{3h})</th>
<th>(E)</th>
<th>(2C_3)</th>
<th>(3C_2)</th>
<th>(3\sigma_v)</th>
<th>(2\sigma_h)</th>
<th>(3\sigma_v)</th>
<th>(R_z)</th>
<th>(R_y)</th>
<th>(R_x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1')</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(x^2 + y^2, z^2)</td>
</tr>
<tr>
<td>(A_2')</td>
<td>1</td>
<td>1</td>
<td>(-1)</td>
<td>1</td>
<td>1</td>
<td>(-1)</td>
<td>1</td>
<td>1</td>
<td>(-1)</td>
<td>(R_z)</td>
</tr>
<tr>
<td>(E')</td>
<td>2</td>
<td>(-1)</td>
<td>0</td>
<td>2</td>
<td>(-1)</td>
<td>0</td>
<td>((x, y))</td>
<td>(x^2 - y^2, xy))</td>
<td>((x^2, y^2))</td>
<td></td>
</tr>
<tr>
<td>(A_1'')</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(-1)</td>
<td>(-1)</td>
<td>(-1)</td>
<td>1</td>
<td>(-1)</td>
<td>(-1)</td>
<td>(z)</td>
</tr>
<tr>
<td>(A_2'')</td>
<td>1</td>
<td>1</td>
<td>(-1)</td>
<td>(-1)</td>
<td>(-1)</td>
<td>1</td>
<td>(-1)</td>
<td>1</td>
<td>(-1)</td>
<td>(z)</td>
</tr>
<tr>
<td>(E'')</td>
<td>2</td>
<td>(-1)</td>
<td>0</td>
<td>(-2)</td>
<td>1</td>
<td>0</td>
<td>((R_x, R_y))</td>
<td>((xz, yz))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Vibrational Selection Rules

Selection Rule Summary:

IR active modes must have IrrReps that go as x, y, z.

Raman active modes must go as quadratics (xy, xz, yz, x^2, y^2, z^2)

<table>
<thead>
<tr>
<th>D_{3h}</th>
<th>E</th>
<th>2C_3</th>
<th>3C_2</th>
<th>σ_h</th>
<th>2S_3</th>
<th>3σ_v</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1'</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>x^2 + y^2, z^2</td>
</tr>
<tr>
<td>A_2'</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>R_z</td>
</tr>
<tr>
<td>E'</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>(x, y)</td>
</tr>
<tr>
<td>A_1''</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>(x^2 - y^2, xy)</td>
</tr>
<tr>
<td>A_2''</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>z</td>
</tr>
<tr>
<td>E''</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>(R_x, R_y)</td>
</tr>
</tbody>
</table>

The Centrosymmetric Rule

If a molecule has an inversion center (i.e., is “centrosymmetric”), then no vibration can be both IR and Raman allowed (active, absorbing).

x, y, z symmetries must have
\[ \chi_i = -1 \] (for IR activity)

Quadratic symmetries must have
\[ \chi_i = +1 \] (for Raman activity)
The Centrosymmetric Rule: CO₂

- Symmetric stretch
- Antisymmetric stretch

R
- Has a center of inversion
- none are BOTH IR and Raman active

IR

Normal Modes of H₂O

For H₂O (because the H's are light), stretching frequencies are much higher than bending frequencies.
i.e., very little mixing of stretches and bends;
∴ we can consider stretches and bends separately.

Accounting Rule: stretches/bends behave as double headed arrows, counted individually only if they stay in the same place after symmetry operation.

<table>
<thead>
<tr>
<th>C₂v</th>
<th>E</th>
<th>C₂</th>
<th>σ₁(xz)</th>
<th>σ₁'(yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B₂</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

Both O-H Stretches: \( \Gamma_{O-H} = 2 \cdot 0 \cdot 0 \cdot 2 = A_1 + B_2 \) => z & y

H₂O Bend: \( \Gamma_8 = 1 \cdot 1 \cdot 1 \cdot 1 = A_1 \) => z
### Normal Modes of H_2O

<table>
<thead>
<tr>
<th>C_{2v}</th>
<th>E</th>
<th>C_2</th>
<th>σ_v(xz)</th>
<th>σ_v′(yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A_2</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B_1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B_2</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Both O-H Stretches: \( \Gamma_{\text{O-H}} \) | 2 0 0 2 | = A_1 + B_2 => z & y  
H_2O Bend: \( \Gamma_\theta \) | 1 1 1 1 | = A_1 => z

**Diagram:**

- A_1: 3657 cm\(^{-1}\)
- B_2: 3756 cm\(^{-1}\)
- A_1: 1595 cm\(^{-1}\)

### Symmetry Effects on Infrared Active Vibrations

Sulfate (SO_4^{2-}) can be ligated in several ways:

- **Non-coordinated:** T_d
- **Unidentate:** C_3v
- **Bidendate:** C_{2v}
  - M' & M same atom, chelated: "\( \eta^2-\)"
  - M' & M different, bridging: "\( \mu^-\)"
Symmetry Effects on Infrared Active Vibrations

Consider only S-O stretches (↔)

<table>
<thead>
<tr>
<th>C₃ᵥ</th>
<th>E</th>
<th>2C₃</th>
<th>3σ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

Γ₃-O | 4 | 1 | 2 | All S-O Stretches

Accounting Rule: stretches are double headed arrows, counted individually only if they stay on the same bond.

Irreducible Representations (IrR): Γ

Order = 1+2+3 = 6 = h

# of A₁ = 1/h (1*1*4 + 2*1*1 + 3*1*2) = 1/6 (12) = 2 A₁
# of A₂ = 1/h (1*1*4 + 2*1*1 + 3*-1*2) = 1/6 (0) = 0 A₂
# of E = 1/h (1*2*4 + 2*-1*1 + 3*0*2) = 1/6 (6) = 1 E
Symmetry Effects on Infrared Active Vibrations

Thus, $\Gamma_{S-O} = 2A_1 + E$ for $C_{3v}$ (unidentate)

$A_1$ and $E$ are both IR active (i.e., z and (xy))

Therefore: 3 IR bands expected for $C_{3v}$ unidentate $SO_4^{2-}$

ICBST: For $T_d$ symmetry, only 1 IR Active stretch,

For $C_{2v}$ symmetry, 4 IR Active stretches.

$SO_4^{2-}$ can be ligated in several ways:

- Non-coordinated: $T_d$
- Unidentated: $C_{3v}$
- Bidentate: $C_{2v}$

M & M’ same atom: chelated, “η”
M & M’ different: bridging, “μ”

For S-O stretches (1000 – 1200 cm$^{-1}$):

“Descent in Symmetry”
1 IR Band $\Rightarrow$ Non-coordinated ($T_d$)
3 IR bands $\Rightarrow$ Unidentate ($C_{3v}$)
4 IR bands $\Rightarrow$ Bidentate ($C_{2v}$)
Symmetry Effects on Infrared Active Vibrations

$\text{SO}_4^{2-}$ can be ligated in several ways:

- Non-coordinated: $T_d$
- Unidentated: $C_{3v}$
- Bidentate: $C_{2v}$

M & M’ same atom: chelated, “η²-”
M & M’ different: bridging, “μ-”

There exist "correlation tables" for this kind of "descent in symmetry", which is easier than re-figuring out the local symmetry point group and allowed IR or Raman transitions.

E.g.,
http://www.staff.ncl.ac.uk/j.p.goss/symmetry/Correlation.html

GT & Vibrational Spectroscopy: cisplatin

Consider $\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}_2$ vs. $\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}_2$.

$\text{cis} \rightarrow$ Space Nonane (more labile)

Cis-Pt(NH$_3$)$_2$Cl$_2$ is "cisplatin", a potent anti-cancer drug.

(Trans form completely inactive)
GT & Vibrational Spectroscopy: Cisplatin

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_{(xz)}$</th>
<th>$\sigma_{(yz)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

\[ E \quad C_2 \quad \sigma_{(xz)} \quad \sigma_{(yz)} \]

\[ z \quad x^2, y^2, z^2 \quad x, R_x \quad xy, yz \]

\[ \frac{1}{4} \left( \sum_{B_{1g}} A \right) = \frac{1}{4} \left( 2(0) + 0 + 0 + 2(0) \right) = 0 \]

\[ \frac{1}{4} \left( \sum_{B_{2g}} A \right) = \frac{1}{4} \left( 2(0) + 0 + 0 + 2(0) \right) = 0 \]

... etc. for $B_1$ & $B_2$

\[ \begin{bmatrix} 2 & 0 & 0 \end{bmatrix} = A_1 + B_2 \]

But actually there is a little bit of Pd motion, too.

symmetric stretch

anti-symmetric stretch (w.r.t. $C_2$ or $\sigma_{yz}$)
GT & Vibrational Spectroscopy: Cisplatin

\[
\Gamma_{M-Cl} = 2 \quad 0 \quad 0 \quad 0 \quad 0 \quad 2 \quad 0 \quad 2 = A_{1g} + B_{2u}
\]

Raman Active

IR Active

GT & Vibrational Spectroscopy: Pd(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}

1 band in IR

2 bands in IR
IR Stretches for Metal Carbonyls

<table>
<thead>
<tr>
<th>Complex</th>
<th>Point group</th>
<th>Symmetries of CO stretching modes</th>
<th>IR active modes</th>
<th># IR bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(CO)₆</td>
<td>Oᵥ</td>
<td>A₁ᵥ, Eᵥ, T₁ᵤ</td>
<td>T₁ᵤ</td>
<td>1</td>
</tr>
<tr>
<td>M(CO)₂X</td>
<td>C₄ᵥ</td>
<td>A₁, A₁, B₁, E</td>
<td>A₁, A₁, E</td>
<td>3</td>
</tr>
<tr>
<td>trans-M(CO)₄X₂</td>
<td>D₄h</td>
<td>A₁₂, B₁₂, E₂</td>
<td>E₂</td>
<td>1</td>
</tr>
<tr>
<td>cis-M(CO)₄X₂</td>
<td>C₂ᵥ</td>
<td>A₁, A₁, B₁, B₂</td>
<td>A₁, A₁, B₁, B₂</td>
<td>4</td>
</tr>
<tr>
<td>fac-M(CO)₃X₃</td>
<td>C₃ᵥ</td>
<td>A₁, E</td>
<td>A₁, E</td>
<td>2</td>
</tr>
<tr>
<td>mer-M(CO)₃X₃</td>
<td>C₂ᵥ</td>
<td>A₁, A₁, B₁</td>
<td>A₁, A₁, B₁</td>
<td>3</td>
</tr>
</tbody>
</table>
Polyatomic Vibrations: Normal Modes

Normal Modes: (NM)
1. are symmetry adapted, internal motions of atoms within a molecule.
2. For a molecule vibrating in a NM, all atoms vibrate at same frequency but at different amplitudes.
3. All vibrational motion can be represented as a linear combination of NMs.
4. NMs are independent, stationary states. A molecule in one NM is isolated, stays in that NM.
5. NMs can be represented by Int. Rep. of molecule’s Point Group.

Normal Coordinates: Vectors on each atom describing the motion of those atoms in that NM.

Naming Normal Modes

\[ \nu_1 \text{ highest frequency Ag (totally sym) mode} \]
\[ \nu_2 \text{ highest frequency Ag ( asymmetric) vibration} \]
\[ \nu_3 \text{ highest frequency Bending mode} \]
\[ \nu_4 \text{ highest frequency out-of-plan (2-fold degrees) bending mode} \]

Exception for Triatomics: \( \nu_2 \) is bending mode.

Usually: \( \nu_{\text{asym}} > \nu_{\text{sym}} > \nu_{\text{bending}} \)
GT & Cartesian Coordinate Analysis

When Stretching or Bending Modes Mix, Full Analysis is necessary:

1) Put Cartesian Coordinates on each nucleus. (3N total, N = # nuclei)
2) Form Reducible Rep. from #1
3) Find Ir. Rep. which make up #2
4) Subtract Translations and Rotations from #3:
   non-linear: $x, y, z, R_x, R_y, R_z$
   linear: $x, y, z, R_x, R_y$
5) This leaves $3N - 6$ (5 for linear) Normal Vibrational Modes.

GT & Cartesian Coordinate Analysis

What are the Normal Modes of some molecule?

E.g.

$$E = 3N - 6$$

$C_{2h}$ 3N Cartesians

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$G_e$</th>
<th>$G_i$</th>
<th>$G_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_g$</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_u$</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

$$3N = 12 \hspace{1cm} 0 \hspace{1cm} 0 \hspace{1cm} 4 = 4 A_g + 2 B_g + 2 A_u + 4 B_u$$

Rotations = $A_g + 2 B_g$

Translations = $A_u + 2 B_u$

$\therefore$ 3N - 6 Vibrations = $3 A_g + A_u + 2 B_u$

Raman IR IR
GT & Cartesian Coordinate Analysis

But what are these vibrations (i.e., 3 \( A_u \), \( A_u \), and 2 \( B_u \))?

\( A_u \) is easy. By inspection:

\( A_u \) is anti-sym. w.r.t. \( \sigma \Rightarrow \text{out-of-plane motion} \)

(remember, center of mass must be preserved or it becomes a translation/rotation!)

GT & Cartesian Coordinate Analysis

For the 3 \( A_g \) and 2 \( B_u \), let us use Bond Stretch Vectors and Angles as a starting basis set:

The 3 \( A_g \) are linear combinations of:

- \( N-F \) Symmetric Stretch
- \( N=N \) Stretch
- \( N-N \) Symmetric Bonding
GT & Cartesian Coordinate Analysis

For the 3 Ag and 2 Bu, let us use Bond Stretch Vectors and Angles as a starting basis set:

But in all cases, the extent of mixing ("coupling") is NOT available from GT.

Alternative Method: Projection Operators

E  C₂ i ᵄᵣ
Bₜ =  1  -1  -1  1

form a projection operator:

\[ \hat{P}_{Bu}(F, M) = \frac{F_{A} - F_{B}}{2} \]
\[ \hat{P}_{Bu}(E, M) = \frac{E_{A} - E_{B}}{2} \]
\[ \hat{P}_{Bu}(\theta) = \frac{\theta_{1} - \theta_{2}}{2} \]

So again, the 2 Bu vibrations are a combination of the N-F asymmetric stretch and the asymmetric bend (θ₁ - θ₂).
Extent of Mode Mixing

1) Only Normal Coordinate Analysis can tell. Not G.T.

2) Large $\Delta V$ keeps high energy stretches and low energy bends with little mixing.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\Delta V$</th>
<th>$\nu$</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$</td>
<td>1523 cm$^{-1}$</td>
<td>80% N-N (Brp $\nu$ 1570)</td>
<td></td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1018</td>
<td>50% N-F, 35% Bond, 15% N-N</td>
<td></td>
</tr>
<tr>
<td>$A_2''$</td>
<td>603</td>
<td>50% N-F, 50% Bond</td>
<td></td>
</tr>
</tbody>
</table>

IR $A_2$ 364 100% out of plane bend

IR $A_2'$ 990 90% N-F stretch

IR $A_2''$ 423 90% Asym. bend

Short, Short Cut

1) Form $\Gamma_{xyz}$

2) For each Sym Op, write down # of unmoved atom, $\Gamma_{um}$

3) $\Gamma_{tot} = \Gamma_{xyz} \otimes \Gamma_{um}$

   = $\Gamma_{trans} + \Gamma_{rot} + \Gamma_{vib}$

   = $\Gamma_{xyz} + \Gamma_{R_x, R_y, R_z} + \Gamma_{vib}$
A Short, Short Cut

\[ \begin{array}{c|cccc} \hline \text{O}_{3h} & E & 2C_2 & 3C_2 & \sigma_h \ \\ \hline A_1' & 1 & 1 & 1 & 1 \\ A_2' & 1 & -1 & 1 & -1 \\ E & 1 & 1 & 0 & 1 \\ A_1'' & 1 & 1 & -1 & -1 \\ A_2'' & 1 & -1 & -1 & 1 \\ E'' & 2 & 1 & 0 & 0 \\ \hline \end{array} \]

\[ \Gamma_{\text{tot}} = a_1' + a_2' + 3e' + 2a_3'' + e'' \]

\[ \begin{array}{c|cccc} \hline \text{B}_3 \text{Cl}_3 & C_3 \beta-\text{Cl} \\ \hline \imp{3y_2} \ \\ \imp{3y_2} \ \\ \imp{3y_2} \ \\ \imp{3y_2} \ \\ \end{array} \]
### Vibrational Group Frequencies

<table>
<thead>
<tr>
<th>Group</th>
<th>Compound Class</th>
<th>Frequency Range (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>Alkanes</td>
<td>2965-2850</td>
</tr>
<tr>
<td></td>
<td>-CH₃</td>
<td>1450</td>
</tr>
<tr>
<td></td>
<td>-CH₂</td>
<td>1380</td>
</tr>
<tr>
<td></td>
<td>Alkenes</td>
<td>3095-3010</td>
</tr>
<tr>
<td></td>
<td>Alkynes</td>
<td>700-1000</td>
</tr>
<tr>
<td>C=C</td>
<td>Alkanes</td>
<td>700-1200</td>
</tr>
<tr>
<td>C=O</td>
<td>Ketones</td>
<td>1725-1765</td>
</tr>
<tr>
<td></td>
<td>Aldehydes</td>
<td>1740-1720</td>
</tr>
<tr>
<td></td>
<td>Carbonic Acids</td>
<td>1725-1760</td>
</tr>
<tr>
<td></td>
<td>Esters</td>
<td>1750-1730</td>
</tr>
<tr>
<td></td>
<td>Amides</td>
<td>1700-1620</td>
</tr>
<tr>
<td></td>
<td>Anhydrides</td>
<td>1850-1800</td>
</tr>
<tr>
<td>C=O</td>
<td>Any</td>
<td>1300-1000</td>
</tr>
<tr>
<td>-O-H</td>
<td>Alcohols, isolated</td>
<td>3650-3590</td>
</tr>
<tr>
<td></td>
<td>Alcohols, H-bonded</td>
<td>3400-3200</td>
</tr>
<tr>
<td></td>
<td>Carbonic Acids</td>
<td>3300-2500</td>
</tr>
<tr>
<td>-N-H</td>
<td>Primary Amines</td>
<td>~3500</td>
</tr>
<tr>
<td></td>
<td>Secondary Amines</td>
<td>3500</td>
</tr>
<tr>
<td>C≡N</td>
<td>Nitriles</td>
<td>2260-2240</td>
</tr>
</tbody>
</table>

---

**Warning:** Group vibrations do not represent the normal modes of the whole molecule.

Beware of mixing:

\[
\begin{align*}
\nu_{\text{C-H}} &= 3372 \text{ cm}^{-1} \\
\nu_{\text{C≡N}} &= 2264 \text{ cm}^{-1} \\
\delta \text{ (predicted)} &= 1406 \\
\delta \text{ (measured)} &= 1381 \\
\end{align*}
\]

Not Electronic Effect (i.e., rehybridization)

Mixing with νC=C
Complications: Coupling of Normal Modes

If two normal modes have the same symmetry, then they can mix ("Fermi Coupling")

Example: CO$_2$ shows a F.C. between $D'_1$ and $2D'_2$

$A''_g$, \((E)^2\rightarrow A'_g\)

Group Vibrations: If one uses Gr. Vib as an Approx. Basis Set for the Normal Modes, one will speak of "coupling" of different Gr. Vib. These "couplings" can occur only between Gr. Vib. of the Same Symm.

Harmonic vs. Anharmonic Oscillators

Potential energy of form $\frac{1}{2}kx^2$ with Translational energy.

$E_n = (n + \frac{1}{2})h\nu$

Equilibrium separation $x_0$ represents the equilibrium separation between the nuclei.

Energy vs. internuclear separation graph showing $D_0$ and $D_2$. Copyright 2000 B.M. Tossell.
Harmonic vs. Anharmonic Oscillators

Second kind of anharmonicity: mixtures of normal modes. e.g., combinations, overtones, difference bands.

The sym. of a Combination, Difference or Overtone Band is the direct Product of the Ir. Rep. of its constituents.

Example: $\text{BF}_3$ ($D_3h$ Point Group)

- $\tilde{\nu}_1 = A_1^\prime$ (IR inactive)
- $\tilde{\nu}_2 = A_2^\prime$ (IR active)
- $\tilde{\nu}_3 = E^\prime$ (IR active)

$\tilde{\nu}_1 + \tilde{\nu}_2 = A_1^\prime \oplus E^\prime = A_2^\prime$ (IR active)

$2\tilde{\nu}_2 = A_2^\prime \oplus A_2^\prime = A_1^\prime$ (IR inactive)

$3\tilde{\nu}_2 = A_2^\prime \oplus A_2^\prime \oplus A_2^\prime = A_1^\prime$ (IR active)

Even if symmetry allowed, Anharmonic bands are usually weak.

Normal Coordinate Analysis

For Polyatomic Vibrations, observed frequencies are functions of all inter-atomic Interactions.

In principle, $D$ should be able to yield these interactions (force constants).

In Practice, never enough $D$ observed and Analysis is intrinsically difficult.
Normal Coordinate Analysis

Problem: Relating coordinate systems of kinetic energy of atoms with that of interaction.

1. Pick set of Internal Coordinates
   - $F_{11} = \text{force along } L_1$
   - $F_{12} = \text{force between } L_1 \text{ and } L_2$
   - $F_{13} = \text{force between } L_1 \text{ and } \theta$
   - $F_{22} = \text{force along } L_2$
   - $F_{33} = \text{force along } \theta$

2. From bond lengths, distances and masses, rules exist to construct a “Geometry” Matrix, $G$. (See Wilson or Nakamoto)

Molecular Vibrations: The Theory of Infrared and Raman Vibrational, by E. B. Wilson, J. C. Decius, P. C. Gross
Infrared Spectra of Inorganic and Coordination Compounds, by K. Nakamoto

Normal Coordinate Analysis

3. ICBST

$$\left| G E - \lambda \right| = 0 \quad \text{for all } \lambda$$

where $\lambda_n = \left[ \begin{array}{c} \lambda_1 \cr \lambda_2 \cr \lambda_3 \end{array} \right]$ and $\lambda_n = \frac{\lambda_n}{2 \pi}$

and $F = \left[ \begin{array}{c} F_{ii} \cr F_{ij} \cr \vdots \end{array} \right] = \text{Force Matrix}$

$F_{ii}$ = force constant along coord. $i$

$F_{ij}$ = coupling between $i$ and $j$

(GF = distance x force = energy)
Normal Coordinate Analysis

GF matrices seldom are solvable due to lack of sufficient $\nu$ so we make simplifications or we calculate potentials from ab initio or DFT:

- **Generalized Valence Force Field (GVF)**
  
  \[ F_{ij} = 0 \quad \text{if} \quad i = \text{stretch and } j = \text{bend} \]

- **Urey-Bradley Field (UBF)**
  
  \[ F_{ij} = 0 \quad \text{if} \quad i \neq j \quad \text{for non-atomic nuclei} \]
  
  Keeps $F_{ij}$ for inter-atomic repulsions

- **Valence Bond Force Field (VBF)**
  
  \[ F_{ij} = 0 \quad \text{if} \quad i \neq j \]
  
  (only stretches and bends)

Example: GVFF

But even 16 force constants out-numbers the number of observables considerably!
Applications of Group Theory to Spectroscopy

Vibrational Spectroscopy

Raman & IR Apparatus and Concept

Selection Rules (Allowedness)

Symmetry of Vibrational Modes

Return to vibrations and normal mode analysis

Raman, Resonance Raman, CARS

Electron Energy Loss Spectroscopy (EELS)

Rotational Spectroscopy

Complications: Anharmonicity

The Harmonic Oscillator

\[ V = \frac{1}{2} k (x - a)^2 \]

Hook's Law

\[ \epsilon_n = \hbar \nu (n + \frac{1}{2}) \]

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

ICBST: For a HO, only \( \Delta n = \pm 1 \) is IR allowed.
Complications: Anharmonicity

The Harmonic Oscillator

Bonds can never break for any HO!

For any non-HO, \( |\Delta n| > \pm 1 \) are allowed (but weak).
Complications: Anharmonicity

Morse Potential hard to solve Schroedinger Eqn.
Easier to do a Cubic Perturbation:

\[ V = \frac{1}{2} k(x) - \lambda (x)^3 \quad \text{if } \lambda \ll k \]

\[ E_n = \hbar \omega \left( n + \frac{1}{2} \right) - \hbar \lambda \chi_k \left( n + \frac{1}{2} \right)^2 \]

\( \chi_k \) = 1st order anhar. correction

\( k \) = force constant (Hook’s Law)
\( \lambda \) = cubic correction

Consequences of Anharmonicity:

Coupling of Normal Modes

**Fundamentals** — Excitation of a single Normal Mode

**Overtones** — Multiple Excitation of one N.M.

**Combinations** — Excitation of 2 or more N.M.

**Difference** — Changes an excited molecule from 1 N.M. to a 2nd.

**Fermi Coupling** — Mires and Splits two N.M. of same symmetry and similar frequency.
Consequences of Anharmonicity: 
Coupling of Normal Modes

- Fundamentals : \( n=0 \rightarrow n'=1 \) \( \Delta E=\hbar v \)
- "Hot" Bands : \( n=1 \rightarrow n'=n\pm 1 \) \( \Delta E=\hbar v \)
- Overtones : \( n=0 \rightarrow n'=2,3,... \) \( \Delta E=2\hbar v, 3\hbar v,... \)
- Combination Bands : \( n_1=0, n_2=0 \rightarrow n_1'=1, n_2'=1 \) \( \Delta E=\hbar v_1+\hbar v_2 \)

Consequences of Anharmonicity: 
Coupling of Normal Modes

The sym. of a Combination Difference or Overtone Band is the direct Product of the Sym. Rep. of its constituents.

Example: \( BF_3 \) (D_3h Point Group)

\[ \begin{align*}
\vec{v}_1 &= A_1' \text{ (IR inactive)} \\
\vec{v}_2 &= A_2'' \text{ (IR active)} \\
\vec{v}_3 &= E' \text{ (IR active)}
\end{align*} \]

\[ \begin{align*}
\vec{v}_1 + \vec{v}_3 &= A_1' \oplus E' = E' \text{ (IR active)} \\
2 \vec{v}_2 &= A_2'' \oplus A_2'' = A_2'' \text{ (IR inactive)} \\
3 \vec{v}_2 &= A_2'' \oplus A_2'' \oplus A_2'' = A_2'' \text{ (IR active)}
\end{align*} \]

Even if symmetry allowed, coupled bands are usually weak.
Consequences of Anharmonicity: Coupling of Normal Modes

The Force Constant

Force Constant, $k$, measures the curvature of the bottom of the potential energy well. $k$ is a measure of the stiffness of internal motions.

$$k \approx \left( \frac{\partial^2 V}{\partial \vec{r}^2} \right)_{\vec{r}=0}$$

Units: $10^5$ dynes/cm $\equiv 1$ millidynes/Å $\equiv 144$ kcal/mol

- Triple bonds: Stretching $K$ 18-13 md/Å
- Double " " 12-8
- Single " " 8-1
- Bending Modes $\sim 1$ md-Å/rad$^2$
Sinclair’s Monofilament (a la Larry Niven)

aka Shigawire (Dune by Frank Herbert), monomolecular filament (Johnny Mnemonic by William Gibson) and The Space Elevator (of Arthur C. Clarke)

What’s the ultimate strength of a monomolecular chain of macroscopic length?

Assume \( r_{cc} = 1.5 \text{ Å} \)
Assume chain breaks if \( r_{cc} > 2 \text{ Å} \)
Assume \( K = 10 \text{ mol}^{-1} \text{ Å}^{-1} = 1.9 \times 10^{4} \text{ cm}^{2} \text{ mol}^{-1} \text{ Å}^{-1} \)

\( 1 \text{ meter chain} = (1.5 \times 10^{-10} \text{ mol C-C})^{-1}(6 \times 10^{33})^{-1} = 10^{-45} \text{ mol} \)

\[ \begin{align*}
\text{Stretches 1 meter to 1.5 meters breaks chain.} & \quad \text{How much energy?} \\
(1.4 \times 10^{6} \text{ mol Å}) (10^{17} \text{ mol}^{-1}) (5 \times 10^{9} \text{ Å}) & = 70 \text{ calories} \\
& \sim 280 \text{ J}
\end{align*} \]

How much force to break?
\[ \frac{280 \text{ J}}{0.5 \text{ m}} = 560 \text{ N} \sim 100 \text{ Lbf} \]
Strength of 1 cm² rope?
\[ \frac{10^{14} \text{ nm}^{2} \text{ cm}^{-2}}{1 \text{ nm}^{2} / \text{ chain}} \sim 10^{16} \text{ Lbf} \]
\( (= 5 \times 10^{6} \text{ Empire State Buildings}) \)

Isotope Effects on Vibrations

Remember the problem in polyatomics of not enough frequencies vs. too many force constants?

Isotopic labeling gives you more observables, but same force constants.
Isotope Effects on Vibrations

Correlations between k and Physical Properties

Caveat: There is no simple relationship between 

$k$ and either bond length or bond strength. 

(the shape of the bottom does not dictate the 
position or the shape of the top!)

In general, however, for a series of related 
crystals, there is a correlation.
Correlations between $k$ and Physical Properties

**Badger's Rule:**

$$(R - \delta)^3 = \frac{a}{K}$$

- $R$: Bond length
- $\delta$: Factor for size/strain

i.e. Bond length and $k$ correlate inversely.

**Lippincott's Rule:**

$$D_e = \frac{K R}{R_{\text{constant}}}$$

- $D_e$: Dissociation energy
- $K$: Constant $= 6.3 \text{ a.u.}$

i.e. Bond strength and $k$ correlate.

**Graph:**

- Title: Badger's Rule
- X-axis: $r_{\text{CO}}$ (Å)
- Y-axis: $K_{\text{CO}}$ (eV Å$^{-3}$)
- Data points for CO adsorbed on Pt and Ir as a function of electrode potentials.

- Legend:
  - X: uncoordinated
  - O: atop Pt
  - ●: hollow Pt
  - ●: atop Ir
  - △: atop Pd
  - ▲: hollow Pd
Correlations between k and Physical Properties

Badger’s Rule applied to Fe-O stretches in heme and non-heme oxygenases

\[ v \text{ (cm}^{-1}\text{)} \]
\[ r_{Fe-O} \text{ (Å)} \]
\[ \frac{1}{\sqrt{v^2}} \text{ (cm}^2\text{)} \]

Force Constant

Lippincott’s Rule for diatomics
Effects of Metal Ion Coordination on $\nu$

Metal or Lewis acid coordination lowers observed $\nu$ if ligand has $\pi^*$ electron density (back donation $\pi^* \rightarrow \sigma^*$).

- $\text{N}_2(gas)$ at 2331 cm$^{-1}$, $\text{M}^N\text{N}$ at 2100-2000 cm$^{-1}$
- $\text{C}_2(gas)$ at 1620 cm$^{-1}$, $\text{M}^\text{O}\text{O}$ at 1500-1100 cm$^{-1}$
- $\text{CO}_2(gas)$ at 2144 cm$^{-1}$, $\text{M}^\text{C}=\text{O}$ at 2050-1800 cm$^{-1}$
- $\text{M}^\text{X}=\text{O}$ at 1700-1500 cm$^{-1}$

Similar for $\text{CN}^-$, $\text{N}=\text{O}$, $\text{P}=\text{O}$, $\text{S}=\text{O}$, $\text{X}=\text{O}$.

Comparison between IR and Raman

Light scattering is a 2 photon event:
Raman vs. Infrared Selection Rules

Infrared absorption:
(1 photon process)

\[ \bar{\mu} = \left( \frac{\mu_x}{\mu_y} \right) \]

Average for random orientation

Raman Scattering:
(2 photon process)

The polarizability tensor goes as the quadratics of xyz.

\[ \bar{\kappa} = \left( \kappa_{xx} \kappa_{yy} \kappa_{zz} \right) \]

Depolarization Ratio

\[ \rho = \frac{I_1}{I_2} = \frac{\kappa_{xx}^2 + \kappa_{yy}^2 + \kappa_{zz}^2}{4 \kappa_{xx}^2 + 4 \kappa_{yy}^2 + 4 \kappa_{zz}^2} \]

Rotational invariants

\[ \text{TRACE: } \lambda = \frac{1}{3} \sum \kappa_i \]

\[ \text{ANISOTROPY: } \lambda_1 = \frac{1}{2} \sum (\kappa_{xx} - \kappa_{yy}) + 2 \sum (\kappa_{xy} \kappa_{yx}) \]

\[ \text{ASYMMETRY: } \lambda_2 - 3 \sum (\kappa_{xx} - \kappa_{yy}) \]

Figure 4

Polarization properties of IR absorption and Raman scattering. The dipole moment is a vector quantity, and polarization information is lost if the molecules are randomly oriented. The polarizability change, however, is a tensor quantity and even for randomly oriented molecules, symmetry information can be obtained by analyzing the scattered light into components parallel and perpendicular to the incident light vector. This information is contained in the rotational invariants of the tensor, which determine the depolarization ratio.

2 Kinds of Light Scattering

1) Elastic: "Rayleigh"

Information about structure of liquids and size of macromolecules

2) Inelastic: "Raman" (1928)

\[ h(\omega + \delta \omega) \]

\( \delta \omega \) is vib. or rot. frequency of sample

Complements I.R. absorption spectroscopy.
Raman Spectroscopy: Stokes v. Anti-Stokes

CCl₄
Ar⁺ laser at 488 nm

\[ \rho_{v=0} \gg \rho_{v=1} \Rightarrow \text{Anti-Stokes} \ll \text{Stokes} \]
Raman Spectroscopy

Molecular Origin of Raman Spectra
- Photon-Molecule Inelastic Collision

\[ E \]
\[ \text{Oscillating electric field} \]
\[ v_0 \]
\[ \text{Diatomic molecule} \]
\[ \text{Scattered radiation} \]
\[ v_0 - v_{0,v'} \]
\[ P = \alpha \times E \]
\[ \text{Polarizability} \]

(b) Stretching Vibration
Polarizability Ellipsoid
Polarizability Component

Raman Selection Rule

The polarizability (i.e., induced dipole created by the electromagnetic radiation field) must change during the excited vibration.

Consider \( N_2 \)

\[ v_0 \]
\[ \text{compressed} \]
\[ \text{extended} \]
\[ \text{equilibrium} \]

\( v_0 \) change Polarizability \( \Rightarrow \) Raman Active
\( \text{does not change Dipole} \) \( \Rightarrow \) IR Inactive
Raman Selection Rule

Polarizability:

\[ \alpha_{pq} = \sum_{n=0}^{\infty} \left( \langle \Psi_0 | \hat{u}_p | \Psi_n \rangle \langle \Psi_n | \hat{u}_q | \Psi_0 \rangle \right) \frac{E_n - E_0}{E_n} \propto \nu_{\text{raman}}^{1/2} \]

The polarizability goes as the quadratics within any point group.
And the polarizability is frequency dependent (more later).

Raman Scattering Intensities

\[ I_{\text{scatt}} = \frac{1}{2} I_0 \left( \frac{\nu - \nu_0}{\nu_0} \right)^2 \left( \frac{\alpha_{pq}}{\nu_0} \right)^2 \]

where:

\[ \hat{D} = \vec{D} \cdot \vec{E} \]

Impressed Dipole 

Polarizability 

Imposed Field 

Sponge analogy:

reason sky is blue!
Raman Scattering Intensities: 
Kramers-Heisenberg-Dirac Equation (!)

The polarizability is a function of photon frequency:

\[
\langle \chi_{ij} \rangle_{eg} = \frac{i}{\hbar} \sum_{k} \left[ \frac{m_{ij}^{ex} \mu_{i}^{ex}}{v_k - v_0 + \delta} + \frac{m_{ij}^{ex} \mu_{i}^{ex}}{v_k + v_0 - v_0 + \delta} \right]
\]

\(i, j = x, y, z, g\)  
\(g\) = ground vibrational state  
\(e\) = excited vibrational state  
\(v_0\) = incident photon frequency  
\(v_0\) = excited electronic states (all φ)  
\(v_0\) = vibrational frequency of \(e\)  
\(M_i\) = transition Moment in \(i\) direction  
\(\delta\) = small damping factor

Thus the polarizability, and therefore \(I_{\text{raman}}\) increase as:

1. Increases in strength of coupling of electronic-excited states with both ground and vibrationally excited states.

2. Closeness of incident radiation to actual electronic transition: "Resonant enhancement"  
i.e., "Resonance Raman Spectroscopy"
Relative Intensities of Raman Scattering

<table>
<thead>
<tr>
<th>Type</th>
<th>$I_{\text{scat}} / I_{\text{incident}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence</td>
<td>1 – 0.01</td>
</tr>
<tr>
<td>Rayleigh</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>Raman Fundamentals (Stokes)</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>Raman Overtones (Stokes)</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Raman Anti-Stokes Fundamentals</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Resonance Raman</td>
<td>$10^{-2}$ to $10^{-4}$</td>
</tr>
<tr>
<td>Surf. Enhanced Raman</td>
<td>&gt;1 (multiple scatters)</td>
</tr>
</tbody>
</table>

"Resonance" Raman when $\nu_0 \approx \nu_r$. Enrichments of $10^6$ possible. Only vibrations coupled to $\nu_r$ enhanced. Note: Enhancement very dependent on choice of $\nu_r$.

Raman Scattering Cross-Section

$$\frac{d\sigma}{d\Omega} = \frac{\text{scattered flux/unit solid angle}}{\text{incident flux/unit solid angle}}$$

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega}$$

<table>
<thead>
<tr>
<th>Process</th>
<th>Cross-Section of</th>
<th>$\sigma$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>absorption</td>
<td>UV</td>
<td>$10^{-18}$</td>
</tr>
<tr>
<td>absorption</td>
<td>IR</td>
<td>$10^{-21}$</td>
</tr>
<tr>
<td>emission</td>
<td>Fluorescence</td>
<td>$10^{-19}$</td>
</tr>
<tr>
<td>scattering</td>
<td>Rayleigh</td>
<td>$10^{-26}$</td>
</tr>
<tr>
<td>scattering</td>
<td>Raman</td>
<td>$10^{-29}$</td>
</tr>
<tr>
<td>scattering</td>
<td>RR</td>
<td>$10^{-24}$</td>
</tr>
<tr>
<td>scattering</td>
<td>SERRS</td>
<td>$10^{-15}$</td>
</tr>
<tr>
<td>scattering</td>
<td>SERS</td>
<td>$10^{-16}$</td>
</tr>
</tbody>
</table>

$\sigma(\nu_{ex}) = \text{target area presented by a molecule for scattering}$

Table adapted from Aroca, Surface Enhanced Vibrational Spectroscopy, 2006
Resonance Raman Scattering

Advantages:
1. Affected only by chromophore (usually the metal center)
2. Sensitive to small structural changes
3. Unaffected by medium (e.g., H$_2$O, powders, glasses, …)
4. High sensitivity ($\mu$M)

Disadvantages:
1. Affected only by the chromophore!
2. Fluorescence often interferes (impurities, …)
3. Thermal and photo-stability can be problematic.
4. Analysis usually by empirical correlations.

Uses of Resonance Raman Scattering

1. Materials available only in low concentrations (> $\mu$M)
   Especially biological chromophores.
   Probes changes only near the chromophore.
   Often hard to assign bands except empirically (e.g., fingerprinting oxidation states).

2. Assignment of Electronic Spectra
   if one already knows the vibration modes,
   then the coupling between the electronic absorbance bands and the vibrational modes
   can assign electronic states.
Bioinorganic Applications of Resonance Raman

Bioinorganic systems with chromophores, e.g.,
1. Heme proteins
2. Photosynthetic reaction centers & antennae
3. Rhodopsin & vision pigments (non metallic)
4. Fe & Cu enzymes (often near UV)

Types of information obtained:
 a. Type of ligands (but selective, not all necessarily)
 b. Oxidation state of metal (indirectly, marker bands)
 c. Comparisons between proteins
    and synthetic analogs, or among proteins
 d. Dynamics (down to ps) of photoinduced rxns.

Resonance Raman of Heme Proteins

Oxidation State Marker
- Fe(III) : $\nu_4 \sim 1375$ cm$^{-1}$
- Fe(II) : $\nu_4 \sim 1360$ cm$^{-1}$
- Fe(IV) : $\nu_4 \sim 1380$ cm$^{-1}$
But note (Fe(II)NO,CO $\nu_4 \sim 1375$ cm$^{-1}$)

Spin State and Core-Size Marker
- Low-Spin: $\nu_3 \sim 1580-1590$ cm$^{-1}$
Resonance Raman Scattering: Heme Proteins

NO Binding to Ferric Hemoproteins Studied by UV-RR (244 nm)

Met-Hb

Met-Hb-^{15}NO

Met-Hb-^{15}NO

Difference Spectrum

Resonance Raman of Hb

5145\text{Å} laser

4579\text{Å} laser
Resonance Raman Scattering: Heme Proteins

Low Frequency Raman Scattering: Lattice Vibrations

Whole molecules within a crystal will vibrate and partially rotate with respect to one another: lattice vibrations and librations. a.k.a. “phonons”. Very low energy (big masses). Very hard to do far-IR (<600 cm⁻¹), not hard to do Raman.
Surface Enhanced Raman Scattering: SERS

- SERS is a surface sensitive technique that results in the enhancement of Raman scattering by molecules adsorbed on rough metal surfaces or nanoparticles.

- The enhancement factor can be as much as $10^{12}$, which allows the technique to be sensitive enough to detect single molecules (through heroic efforts, multiple scatters per molecule over time).

How Does SERS Work?

- SERS substrates commonly used
  Silver (Ag), gold (Au) and copper (Cu)
  The energy required to generate plasmons matches the Raman light source

- Surface preparations
  Largest enhancements for rough surfaces of 10 – 100 nm
Origins of SERS

A. Electromagnetic field enhancement mechanism
- excitation of surface plasmon
- tends to form spatially localized “hot areas” for adsorbates
- the magnitude of enhancement \( \sim 10^6 \text{-} 10^7 \) times for single Ag np
- \( \sim 10^8 \) for the gap between two coupled particles

B. Chemical enhancement
- due to specific interactions, forming charge-transfer complexes
- the magnitude of chemical enhancement \( \sim 10\text{-}100 \) times

Conductive Ag or Au nanofeatures concentrate oscillating electric field from light through plasmon resonance. Even greater concentration of field at “hot spots” at small radii of curvature (sharp points)

CARS: Coherent Anti-Stokes Raman Spectroscopy

Raman = 2 photon process (1 laser + 1 scattered)

CARS = 4 photon Process (3 laser + 1 scattered)

non-linear optical effect, lasers must be very high flux (short pulsed)

1. When \( \nu_a - \nu_b = \text{real vibration } \nu \), molecules are driven into \( \nu=1 \) state.
2. Then laser A photons (at \( \nu_a \)) drive \( \nu=1 \) molecules back to \( \nu=0 \), with emission of \( \nu + \nu_a \). This is called stimulated anti-Stokes Raman.

CARS is \( \sim 10^6 \) more efficient than Raman.
EELS

Electron Energy Loss Spectroscopy

Each edge sits on the tails of the preceding edges -> Backgrounds are large

Table 38.1. Characteristics of the Principal Energy-Loss Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy loss (eV)</th>
<th>$\theta_q$ (mrad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phonons</td>
<td>~0.02</td>
<td>5–15</td>
</tr>
<tr>
<td>Inter/intra-band transitions</td>
<td>5–25</td>
<td>5–10</td>
</tr>
<tr>
<td>Plasmons</td>
<td>~5–25</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Inner-shell ionization</td>
<td>~10–1000</td>
<td>1–5</td>
</tr>
</tbody>
</table>

Element specific, but not as easy as XPS, AES or EDX

HREELS: High resolution EELS - surface vibrational spectra

Advantage of EELS: Sensitive to light elements (O, N, C in metal alloys)
High spatial resolution
High Resolution EELS (HREELS)

Figure 18.1 Schematic of a high-resolution electron energy loss spectrometer that employs a double-pass monochromator (M1,M2) and rotatable analyzer (AN) (see text).

HREELS

Figure 18.11 HREELS spectra of an HF cleaned surface under best cleaning conditions (trace a) compared to the spectrum of a heavily hydrocarbon contaminated sample after vacuum annealing for 5 minutes to 750°C.
HREELS Selection Rule

For electron to lose/gain energy from scattering off of an adsorbate, it must interact with a surface charge or dipole. Only adsorbate dipoles perpendicular to metallic surface will be felt by incoming e-.

adsorbate

metal surface

image dipole

No net surface dipole!

HREELS of Adsorbates

Electron energy loss spectra for acetylene on Pd (110) for specular and off-specular scattering.
HREELS of Adsorbates

HREELS of ethylene on a 3.4 \times 10^{10} \text{ atoms/cm}^2 coverage of Pt on Al_{2}O_{3} film: (a) clean; (b) ethylene 165 K; (c) ethylene at 325 K.\textsuperscript{13}

Spherical Top: All Three Moments of Inertia are Equal
\[ I_x = I_y = I_z \]

Symmetrical Top: \[ I_x = I_y \neq I_z \]

Asymmetrical Top: \[ I_x \neq I_y \neq I_z \]

Rigid Rotor Approx.: Bond lengths and angles are independent of Rotational Excitation.
(i.e. Centrifugal Distortion Ignored)

Rotations Spectra: Selection Rules

FIR/Microwave:
1) Molecule must have Dipole Moment
   (Rotations cannot induce change in Dip. Mom. otherwise)
2) For Rigid Rotor, \( \Delta J = \pm 1 \)

Rot. Raman:
1) Polarizability must be anisotropic
   (Rot. cannot change Polarizability otherwise)
   i.e. \( \text{No } C_3, C_4 \ldots \) (\( C_2 \) okay)
2) For Rigid Rotor: \( \Delta J = \pm 2 \)
Rotational Spectra: Linear Rigid Rotor

\[ E_J = \hbar B J(J+1) \quad (J_B = \text{Bose-Einstein}) \]

\[ B = \frac{1}{\hbar^2} \quad I = \frac{L^2}{2} \]

Limitations:

J \rightarrow J+1 \quad \Delta D = 2B(J+1) \quad \text{IR - Microwave}

J \rightarrow J+2 \quad \Delta \nu = B(4J+3) \quad \text{Raman}

Rotational Spectra Informational Content

1. Gives very accurate \( I_{xx,yy,zz} \)

2. Band Distance & Angles

3. Fingerprinting of Gases

4. Torsional Barrier to Rotations

5. Accuracy Dipole Moments

Limitations:

1. Simple Molecules only
2. High Energy \( > \text{1.1 cm}^{-1} \quad (30,000 \text{ MHz}) \)

K. S. Suslick, 2013