Lectures in Spectroscopy

Raman Spectroscopy

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My sincere acknowledgments to


- Many other free & copyright internet resources.
1. Introduction
   - Raman Scattering

2. Rotational Raman spectroscopy
   - Linear Molecules
   - Symmetric Top Molecules

3. Vibrational Raman spectroscopy
   - Vibrational Raman
   - Vibrational+Rotational Raman
   - Mutual Exclusion
   - Hyper-Raman scattering

4. Raman spectrometer
Scattering in Molecules

- **Interaction of photons ($\nu_0$) with molecules:**
  1. Elastic (Rayleigh) scattering: Most molecules.
  2. Inelastic (Raman) scattering: Very few molecules

Frequency/Energy shift (1928: CV Raman & KS Krishnan)

Raman Scattering

- Lower freq. ($\nu = \nu - \Delta \nu$) ⇒ Stoke’s lines.
- Higher freq. ($\nu = \nu + \Delta \nu$) ⇒ Anti-Stoke’s lines.
- Raman shift $\Delta \nu$ (around $10 - 4,000 \text{ cm}^{-1}$).
- Original freq. $\nu$ ⇒ Rayleigh lines.


Classical Theory: Raman Scattering

- **Molecule in electric field 'E':**
  Electric field of radiation distorts the electron distribution.
  Polarization of charged particles \( P = \alpha E \),
  \( \alpha \): Polarizability of the molecule.

- For an incident radiation of freq. \( \nu_0 \),
  change in electric field \( E = E_0 \cos(2\pi\nu_0 t) \).

- Vibrational motion of the molecule
  \( Q = Q_0 \cos(2\pi\nu_m t) \),
  for normal coordinate \( Q \) with vibrational freq. \( \nu_m \).

- Polarizability due to vibrations/rotations
  \( \alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 \, Q + \cdots H.O. \).

- Effective Polarization:
  \[ P = \left[ \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 \, Q_0 \cos(2\pi\nu_m t) \right] \, E_0 \cos(2\pi\nu_0 t). \]
Classical Theory: Raman Scattering...

\[ P = \alpha_0 E_0 \cos(2\pi \nu_0 t) \]
\[ + \frac{1}{2} \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 E_0 \left[ \cos 2\pi (\nu_0 + \nu_m) t + \cos 2\pi (\nu_0 - \nu_m) t \right]. \]

- First term: original freq. \( \nu_0 \) (Rayleigh line)
- Second term: higher freq. \( \nu_0 + \nu_m \) (Raman anti-Stokes line)
- Third term: lower freq. \( \nu_0 - \nu_m \) (Raman Stokes line)

Change in polarizability for \( CO_2 \)

symmetric stretch  bend  asymmetric stretch.

Symmetric vibrations: Raman active (but IR inactive)
Asymmetric vibrations: very weak in Raman (negligibly small)
Quantum Theory: Raman Scattering

- **Drawback in classical theory**: Gave frequency shifts, but not able to find intensities.
- **Duality**: Radiation as particle/photon & wave.
  - Molecules interact with photon/particle $h\nu_0$.
  - Moves to virtual state by absorbing some energy. & Return to original state by emitting radiation.
- **No. photon scattering $\propto$ Size of bonds.**
  - Mostly, frequency of emitted radiation is same to the frequency of incident radiation: Rayleigh/elastic scattering.
  - Small fraction of radiation with high/low frequency than incident frequency (gains/looses energy): Raman scattering.
  - If molecule gains energy, scattered photon freq. $\nu_0 - \nu_m$: Stokes lines
  - If molecule looses energy, scattered photon freq. $\nu_0 + \nu_m$: anti-Stokes lines.
Quantum Theory: Raman Scattering...

- Intensity depends on initial population.
- Power $P_s = I_0 \times \sigma_R$ (Incident Int. & Raman cross-section)
- Boltzmann distribution $\Rightarrow \frac{I_s}{I_{as}} = \exp \frac{h\nu_m}{kT}$.

(or) $\frac{I_s}{I_{as}} = \left(\frac{\nu_0 - \nu_m}{\nu_0 + \nu_m}\right)^4 \exp \frac{h\nu_m}{kT}$.
Rotational Raman spectroscopy

**Linear Molecules**

Rotational energy changes due to Raman scattering!

- Rotational energy $\epsilon_J = BJ(J + 1) \text{ cm}^{-1}$, $J = 0, 1, 2, \ldots$
- Selection rule $\Delta J = 0, \pm 2$!
  
  Jump in the level due to additional scattered energy.
  (Symmetry of the polarizability: end-over-end rotations)
- Rotational energy change $\tilde{\nu} = \Delta \epsilon_J = \epsilon_{J+2} - \epsilon_J = B(4J + 6)$.
- When molecules gains energy or scattered photon looses energy $\Rightarrow$ Stokes lines with lower frequencies than $\tilde{\nu}_0$.
  
  Freq. of Stokes spectral lines $\tilde{\nu} = \tilde{\nu}_0 - B(4J + 6)$.
- When molecules looses energy or scattered photon gains energy $\Rightarrow$ anti-Stokes lines with higher frequencies than $\tilde{\nu}_0$.
  
  Freq. of anti-Stokes spectral lines $\tilde{\nu} = \tilde{\nu}_0 + B(4J + 6)$.
- Freq. of Raman spectra $\tilde{\nu} = \tilde{\nu}_0 \pm B(4J + 6)$, $J = 0, 1, 2, \ldots$
Rotational Raman spectra for Linear Molecules

Transitions giving
Stokes lines

\( J \)

\( j \)

Transitions giving
Anti-Stokes lines

(a)

\[ 4B \]

\[ 6B \]

Stokes lines

\( \nu \) cm\(^{-1} \)

Anti-Stokes lines
Symmetric Top Molecules

- Rotational energy $\epsilon_{JK} = BJ(J + 1) + (A - B)K^2 \text{ cm}^{-1}$, Here $J = 0, 1, 2, ..., K = 0, \pm 1, \pm 2, ...$
- Selection rule $\Delta K = 0 \& \Delta J = 0, \pm 1, \pm 2$ !!
  Jump in the level due to additional scattered energy.
  (Rotation about molecular axis & its perpendicular axis)
- Rotational energy change
  \[ \bar{\nu} = \Delta \epsilon_R = \epsilon_{J+1} - \epsilon_J = 2B(J + 1) \quad (\text{for } \Delta J = 1: \text{ R branch}) \]
  \[ \bar{\nu} = \Delta \epsilon_S = \epsilon_{J+2} - \epsilon_J = B(4J + 6) \quad (\text{for } \Delta J = 2: \text{ S branch}) \]
- Two Frequency bands for Raman lines:
  \[ \bar{\nu}_R = \bar{\nu}_0 \pm 2B(J + 1) \text{ cm}^{-1}. \]
  \[ \bar{\nu}_S = \bar{\nu}_0 \pm B(4J + 6) \text{ cm}^{-1}. \]
- Spectral lines spacing: $2B$ for R branch Raman lines.
  Spectral lines spacing: $4B$ for S branch Raman lines.
Rotational Raman spectra for Symmetric Top molecule

(a) $\Delta J = +1$ transitions

(b) $\Delta J = +2$ transitions

(c) Complete spectrum
Vibrational Raman spectra

- Degrees of freedom (normal modes): Anharmonic vibrations.
- Vibrational energy $\epsilon_v = (v + \frac{1}{2}) \bar{\nu}_e - (v + \frac{1}{2})^2 x_e \bar{\nu}_e$ cm$^{-1}$.
  Here $v = 0, 1, 2, ...$ ($\bar{\nu}_e$ equilibrium oscillation freq.)
- Selection rule $\Delta v = \pm 1, \pm 2, \pm 3, ...$!!!
  Jump in the level due to additional scattered energy.
- Raman spectra are very weak, so only $\Delta v = \pm 1$.
  (overtones, combination & hot bands are negligible)
- Vibrational energy change $\Delta \epsilon = \epsilon_1 - \epsilon_0 = \bar{\nu}_e (1 - 2x_e)$ cm$^{-1}$.
- Freq. of Raman lines $\bar{\nu} = \bar{\nu}_0 \pm \bar{\nu}_e (1 - 2x_e)$ cm$^{-1}$.
- Population in $v \geq 1$ is very less, so anti-Stokes lines are very weak than Stokes lines.
Vibrational+Rotational Raman spectra

- Energy for Raman spectra with vibration+rotation
  \[ \epsilon_{Jv} = (v + \frac{1}{2}) \bar{\nu}_e - (v + \frac{1}{2})^2 x_e \bar{\nu}_e + BJ(J + 1) \text{ cm}^{-1}. \]
  Here \( v = 0, 1, 2, \ldots \) & \( J = 0, 1, 2, \ldots \)

- Selection rule \( \Delta v = \pm 1 \) & \( \Delta J = 0, \pm 2! \)

- For \( \Delta v = 1 \) & \( \Delta J = 0 \): Q branch Stokes lines
  \[ \Delta \epsilon = \bar{\nu}_e (1 - 2x_e) \text{ cm}^{-1} \]
  \[ \bar{\nu}_Q = \bar{\nu}_0 - \bar{\nu}_e (1 - 2x_e) \text{ cm}^{-1}. \]

- For \( \Delta v = 1 \) & \( \Delta J = 2 \): S branch Stokes lines
  \[ \Delta \epsilon_{Jv} = \bar{\nu}_e (1 - 2x_e) + B(4J + 6) \text{ cm}^{-1} \]
  \[ \bar{\nu}_S = \bar{\nu}_0 - \bar{\nu}_e (1 - 2x_e) - B(4J + 6) \text{ cm}^{-1}. \]

- For \( \Delta v = 1 \) & \( \Delta J = -2 \): O branch Stokes lines
  \[ \Delta \epsilon_{Jv} = \bar{\nu}_e (1 - 2x_e) - B(4J + 6) \text{ cm}^{-1} \]
  \[ \bar{\nu}_s = \bar{\nu}_0 - \bar{\nu}_e (1 - 2x_e) + B(4J + 6) \text{ cm}^{-1}. \]
Rotational+Vibrational structure of Raman Stokes lines of diatomic molecule with vibrational frequency $\tilde{\nu}_e (1 - 2x_e)$. 
Mutual Exclusion: Raman spectra

- Raman scattering & IR: two different processes.
- Some molecular vibrations are active in both IR & Raman.
- Several vibrations can be active either in Raman or IR.
- Molecules with centre of symmetry: Raman active (polarizability), IR inactive (no change in dipole moment) ⇒ Mutual exclusion
- Molecules without centre of symmetry shall be active in both IR & Raman.
Comparison: IR and Raman transitions!

Virtual energy states

Vibrational energy states

Infrared absorption
Rayleigh scattering
Stokes Raman scattering
Anti-Stokes Raman scattering
IR and Raman offers complementary techniques!

<table>
<thead>
<tr>
<th>Raman</th>
<th>IR</th>
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</thead>
<tbody>
<tr>
<td>Weak signal intensity</td>
<td>High background (absorption)</td>
</tr>
<tr>
<td>Low background (scattering) (once Rayleigh component is removed)</td>
<td>More bands ...</td>
</tr>
<tr>
<td>Low Raman signal of water and glass (important for biological samples, etc..)</td>
<td>... but Complex spectra</td>
</tr>
<tr>
<td>$\Delta \nu$ shift independent of $\lambda_{inc}$, the lines are narrower</td>
<td>Infrared sources and detectors</td>
</tr>
<tr>
<td>Possibility to work in UV-Vis-Near IR region (good sources and detectors)</td>
<td>Characteristic signature of species</td>
</tr>
<tr>
<td>Characteristic signature of species</td>
<td>Applicable to gas, liquid and solid samples</td>
</tr>
<tr>
<td>Can also access range not available for IR (e.g. 100-700 cm$^{-1}$)</td>
<td></td>
</tr>
</tbody>
</table>
Hyper-Raman scattering (HRS) effect

- A modified version of Raman scattering!
- Inelastic second harmonic scattering of photons.

- Sum frequency generation: A coherent process involving two incident fields (with frequencies $\nu_1$ & $\nu_2$ and wave vectors $k_1$ & $k_2$) produce a single field with frequency $\nu_1 + \nu_2$ and wave vector $k_1 + k_2$.
- Hyper-Rayleigh scattering: Elastic scat. for $\nu_1 = \nu_2$ & $k_1 = k_2$.
- Hyper-Raman scattering: Inelastic form of Hyper-Rayleigh scattering!!
Hyper-Raman scattering (HRS) effect...

- Hyper-Raman scattering: Inelastic scattering of incident photons (with frequency $\nu_1 = \nu_2 = \nu$) into photons of two different frequencies $2\nu \pm \Delta \nu$!

- HRS Stokes lines: $\nu_S = \nu_1 + \nu_2 - \Delta \nu$.
- HRS anti-Stokes lines: $\nu_{AS} = \nu_1 + \nu_2 + \Delta \nu$.

$\Delta \nu$ depends on the usual scattering of molecular vibrations.

- HRS effect is usually very weak, but has aspects which make it interesting for Raman spectroscopy.
- HRS can provide vibrational information on molecules where ordinary Raman Scattering is suppressed due to symmetry issues.
Basic Raman spectrometer

- light source
- sample
- filter
- Spectral selection and recording
Schematic: Basic Raman spectrometer
**Schematic: Basic Raman spectrometer**

- **Sample**
  - $L_1$
- **Source of monochromatic radiation**
- **Sample device**
  - $L_2$
- **Dispersing system**
- **Monochromator**
- **Detection device**
  - **Detector** → **Recorder**
Basic Raman spectrometer

A Raman Spectrometer

Detector

UV laser unit

Mirror

Sample
Several variants of Raman spectrometers...

To enhance the sensitivity (ex. surface-enhanced Raman), improve the spatial resolution (Raman microscopy), very specific information (resonance Raman), etc.

- Spontaneous Raman spectroscopy
- Surface-enhanced Raman spectroscopy (SERS)
- Resonance Raman spectroscopy
- Surface-enhanced resonance Raman spectroscopy (SERRS)
- Angle-resolved Raman spectroscopy
- Transmission Raman spectroscopy
- Tip-enhanced Raman spectroscopy (TERS)
- Stand-off remote Raman

- Many hand-held Raman spectrometers!
Few Applications of Raman spectra

- Characteristic Raman frequencies → Material composition
- Changes in frequency of Raman peaks → Stress/strain
- Polarizations of Raman peak → Crystallographic orientation and symmetry
- Width of Raman peak → Crystallinity
- Intensity of Raman peak → Amount of material
Summary

From the present series of lectures, we have learned the principle, explicit description and detailed analyses of transitions in molecules due to Raman scattering by including the vibrational and rotational effects!
Thank You