Dalian ROA Lectures
June-July 2010
Lecture 2

Basic Theory and Measurement of Raman Scattering

Invariants, Depolarization Ratios, Scattering
Geometries and Instrumentation

Outline

• Classical Theory of Raman Spectroscopy
• Quantum Mechanical Theory
• Scattering Intensity Invariants
• General Scattering Intensities and Polarization
• Far-From-Resonance Scattering Intensities and Polarization Ratios
• Measurement of Raman Scattering
Classical Theory of Raman Scattering – Simple Version

Classical Theory

\[ E = E_0 \cos 2\pi \nu_0 t \]  
Fluctuation with time of incident electromagnetic wave (laser beam)

\[ \mu \text{ (or } P) = \alpha E = \alpha E_0 \cos 2\pi \nu_0 t \]  
Induced electric dipole moment (P or \( \mu \)) in irradiated molecule; \( \alpha \) is the polarizability

\[ l = \frac{16\pi^4}{3c^3} \nu_0^4 \mu_0^2 \]  
Classical expression for average rate of total scattered radiation

\[ Q_k = Q_k^0 \cos 2\pi \nu_k t \]  
Normal mode of vibration in molecule at frequency \( \nu_k \) with amplitude \( Q_k^0 \)

\[ \alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k + \cdots \]  
Polarizability is changed by vibration

\[ \alpha E = \mu \text{ (or } P) = \alpha_0 E + \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k E \]  
Induced dipole is linear function of normal mode for small amplitude vibration
Classical Theory, continued

\[ aE = \mu \text{ (or } P) = \alpha_0 E + \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k E \]

Substitute time dependence of \( E \) and \( Q_k \):

\[ \mu = \alpha_0 E_0 \cos 2\pi \nu_0 t + E_0 Q_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 \cos 2\pi \nu_0 t \cos 2\pi \nu_k t \]

Apply trigonometric identity for product of two cosines

\[ \mu = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} E_0 Q_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 \left[ \cos 2\pi (\nu_0 + \nu_k) t + \cos 2\pi (\nu_0 - \nu_k) t \right] \]

Rayleigh scattering  Anti-Stokes scattering  Stokes Raman scattering

Failure of Classical Theory

Classical theory correctly predicts that Raman scattering should be weaker than Rayleigh scattering and that there is a simple linear dependence of Raman scattering on incident intensity and on sample concentration. With classical theory, Stokes/anti-Stokes intensity ratio is predicted to be

\[ \left[ (\nu_0 - \nu_k)/(\nu_0 + \nu_k) \right]^4 \]

However, Boltzmann distribution will be major factor in determining relative Stokes and anti-Stokes intensity. The excited vibrational state will be only thermally populated, and Stokes intensity will be much larger than anti-Stokes.
Classical Theory of Raman Scattering – Tensor Version

Polarizability Tensors

\[ \mathbf{\mu} = \alpha \mathbf{E} \]

\[ \mu_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \]
\[ \mu_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \]
\[ \mu_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \]

Expression for induced dipole moment can be written in terms of Cartesian components

Matrix equation for \( \mathbf{\mu} \):
\[ \begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \]

Polarizability tensor is usually symmetric

\[ \alpha_{xy} = \alpha_{yx} ; \quad \alpha_{yz} = \alpha_{zy} ; \quad \alpha_{xz} = \alpha_{zx} \]
Quantum Mechanical Theory

• Full quantum mechanical treatment of Raman spectroscopy has been derived with time-dependent perturbation theory.
• Expressions for polarizability tensors involve sums over excited electronic states.
• Polarizability is divided into isotropic and anisotropic parts:

\[ \alpha = \alpha^s + \alpha^a \]

\[ \alpha^s = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \]

\[ \alpha^a = \frac{1}{2}\left( (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2) \right)^{1/2} \]

Polarizability derivative \((\partial\alpha/\partial Q)_0\) is denoted \(\alpha'\).

\[ I = \text{constant} \frac{(v_0 + v_{mn})^4}{v_{mn}} \frac{NI_0}{1 - \exp(-h v_{mn}/kt)} \left[ 45(\alpha'^s)^2 + 13(\alpha'^a)^2 \right] \]

\[ \frac{I_{\text{Stokes}}}{I_{\text{anti-Stokes}}} = \left( \frac{v_0 - v_{mn}}{v_0 + v_{mn}} \right)^4 \exp(h v_{mn}/kt) \quad \text{for } m \rightarrow n \text{ transition, far from resonance} \]

Stokes and Anti-Stokes Raman Spectra

Figure 1-9  Raman spectrum of CCl₄ (488.0 nm excitation).
Classical Theory with Polarizability Tensors

\[ I(\omega_0, \omega) = k'_0 \omega_s^4 \left( \mu'_i \right)^2 \sin^2 \theta \]

Intensity from induced electric dipole moment as function of scattering angle

\[ \mu'_i(t) = \sum_\rho \alpha_{\rho p}(t) E^{(0)}_\rho(t) = \alpha_{\rho p}(t) E^{(0)}_\rho(t) \]

Induced electric dipole moment in explicit Cartesian summation or implied summation over x, y and z of repeated Greek indices

\[ E^{(0)}_\rho(t) = E^{(0)}_{\rho,0} \cos \omega_t \quad \alpha_{\rho p}(t) = \alpha_{\rho p,0} + \left( \frac{\partial \alpha_{\rho p}}{\partial Q_a} \right)_{Q_0=0} Q_a \cos \omega_t \]

\[ \mu'_i(t) = \alpha_{a,\rho,0} E^{(0)}_{\rho,0} \cos(\omega_0 t) + \left( \frac{\partial \alpha_{\rho p}}{\partial Q_a} \right)_{Q_0=0} Q_a E^{(0)}_{\rho,0} \cos(\omega_0 t) \cos(\omega_t) \]

\[ \mu'_i(t) = \alpha_{a,\rho,0} E^{(0)}_{\rho,0} \cos(\omega_0 t) + \frac{1}{2} \left( \frac{\partial \alpha_{\rho p}}{\partial Q_a} \right)_{Q_0=0} Q_a E^{(0)}_{\rho,0} [\cos(\omega_0 - \omega_t) t + \cos(\omega_0 + \omega_t) t] \]

Quantum Mechanical Theory of Raman Scattering - Simple Version
General Quantum Mechanical Theory

Master scattering intensity as a function in incident and scattered complex polarization vectors and a complex polarizability

\[ I(\vec{e'}, \vec{e}) = 90K \left| \vec{e'}^* \vec{\alpha}_{\alpha\beta} \vec{e}^\beta \right|^2 \quad K = \frac{1}{90} \left( \frac{\omega_0^2 \vec{\mu}_\alpha \vec{E}^{(0)}}{4\pi R} \right)^2 \]

General quantum mechanical complex polarizability in terms of second order perturbation theory for the interaction of the molecule with incident and scattered photons

\[
\left( \vec{\alpha}_{\alpha\beta} \right)_{\mu\nu} = \frac{1}{\hbar} \sum_{j, m, n} \left[ \frac{\langle \hat{\Psi}_m | \hat{\mu}_\alpha | \hat{\Psi}_j \rangle \langle \hat{\Psi}_j | \hat{\mu}_\beta | \hat{\Psi}_n \rangle + \langle \hat{\Psi}_m | \hat{\mu}_\beta | \hat{\Psi}_j \rangle \langle \hat{\Psi}_j | \hat{\mu}_\alpha | \hat{\Psi}_n \rangle}{\omega_m - \omega_0 - i\Gamma_j} \right] \frac{\omega_m + \omega_0 + i\Gamma_j}{\omega_j}
\]

\[
\hat{\mu}_\alpha = -\epsilon x \sum_j r_{j\alpha}
\]

Invariants of the Raman Polarizability Tensor

There are three invariants of the polarizability that are independent of the orientation of the molecule relative to the incident and scattered radiation.

Isotropic invariant \(\alpha^2 = \frac{1}{9} \text{Re} \left[ (\vec{\alpha}_{\alpha\alpha})^* (\vec{\alpha}_{\beta\beta})^* \right] \)

Symmetric anisotropic invariant

\[
\beta_S (\vec{\alpha})^2 = \frac{1}{2} \text{Re} \left[ 3 (\vec{\alpha}_{\alpha\alpha})^* (\vec{\alpha}_{\beta\beta})^* - (\vec{\alpha}_{\alpha\alpha})^* (\vec{\alpha}_{\beta\beta})^* \right] \]

Antisymmetric anisotropic invariant

\[
\beta_A (\vec{\alpha})^2 = \frac{1}{2} \text{Re} \left[ 3 (\vec{\alpha}_{\alpha\alpha})^A (\vec{\alpha}_{\beta\beta})^A \right] \]

The symmetric and antisymmetric parts of the Raman polarizability tensor are defined as

\[
(\vec{T}_{\alpha\beta})^S = \frac{1}{2} \left[ (\vec{T}_{\alpha\beta}) + (\vec{T}_{\beta\alpha}) \right] \quad (\vec{T}_{\alpha\beta})^A = \frac{1}{2} \left[ (\vec{T}_{\alpha\beta}) - (\vec{T}_{\beta\alpha}) \right] \]
General Scattering Intensities and Polarization Ratios

Right Angle Scattering Intensity Incident Linearly Polarized Radiation

Scattering intensity for light incident along the Z-axis polarized linearly in the X-direction (vertical) and scattered along the Y-axis polarized in the Z-direction, perpendicular to incident polarization direction.

\[
I^x_Z (90^\circ) = 2K \left[ 3\beta_s (\hat{\alpha})^2 + 5\beta_s (\hat{\alpha})^2 \right]
\]

Same scattering geometry and polarization above except the scattered radiation is now polarized in the X-direction parallel to the incident polarization direction.

\[
I^x_X (90^\circ) = 2K \left[ 45\alpha^2 + 4\beta_s (\hat{\alpha})^2 \right]
\]

Depolarization ratio

\[
\rho (90^\circ) = \frac{I^x_Z (90^\circ)}{I^x_X (90^\circ)} = \frac{3\beta_s (\hat{\alpha})^2 + 5\beta_s (\hat{\alpha})^2}{45\alpha^2 + 4\beta_s (\hat{\alpha})^2}
\]
Right Angle Scattering Intensity
Incident Unpolarized Radiation

Scattering intensity for unpolarized light incident along the Z-axis and scattered along the Y-axis polarized in the Z-direction.

\[ I^U_Z(90^\circ) = I^X_Z(90^\circ) + I^Y_Z(90^\circ) = 2K\left[6\beta_s(\bar{\alpha})^2 + 10\beta_A(\bar{\alpha})^2\right] \]

Same scattering geometry and polarization above except the scattered radiation is now polarized in the X-direction.

\[ I^U_X(90^\circ) = I^X_X(90^\circ) + I^Y_X(90^\circ) = 2K\left[45\alpha^2 + 7\beta_s(\bar{\alpha})^2 + 5\beta_A(\bar{\alpha})^2\right] \]

Depolarization ratio

\[ \rho_n(90^\circ) = \frac{I^U_X(90^\circ)}{I^U_X(90^\circ)} = \frac{6\beta_s(\bar{\alpha})^2 + 10\beta_A(\bar{\alpha})^2}{45\alpha^2 + 7\beta_s(\bar{\alpha})^2 + 5\beta_A(\bar{\alpha})^2} \]

Backscattering Intensity with
Dual Circularly Polarized Radiation

Scattering intensity for incident circularly polarized light incident backscattered with the same sense of circular polarization.

\[ I^R_R(180^\circ) = I^L_L(180^\circ) = 2K\left[6\beta_s(\bar{\alpha})^2\right] \]

Backscattering geometry with opposite circular polarization for the incident and scattered radiation

\[ I^R_L(180^\circ) = I^L_R(180^\circ) = 2K\left[45\alpha^2 + 7\beta_s(\bar{\alpha})^2 + 5\beta_A(\bar{\alpha})^2\right] \]

Reversal ratio is defined as the ratio of co-rotating to contra-rotating circular polarization scattering intensities

\[ R(180^\circ) = \frac{I^R_R(180^\circ)}{I^R_L(180^\circ)} = \frac{I^L_L(180^\circ)}{I^R_R(180^\circ)} = \frac{6\beta_s(\bar{\alpha})^2}{45\alpha^2 + 7\beta_s(\bar{\alpha})^2 + 5\beta_A(\bar{\alpha})^2} \]
Backscattering Intensity with Circularly Polarized and Unpolarized Radiation

Backscattering intensity for incident right or left circular and scattered unpolarized radiation

\[
I_U^R(180^\circ) = I_R^R(180^\circ) + I_L^R(180^\circ) = I_L^L(180^\circ) = I_R^R(180^\circ) + I_L^R(180^\circ) = 2K\left[45\alpha^2 + 7\beta_S(\alpha)^2 + 5\beta_A(\alpha)^2\right]
\]

There is no depolarization or reversal ratio for combing unpolarized and circularly polarized radiation in a scattering intensities

Another ratio used for dual circular polarization measurements is the degree of circular polarization measurement defined as

\[
\kappa_C(180^\circ) = \frac{I_R^R(180^\circ) - I_L^R(180^\circ)}{I_R^R(180^\circ) + I_L^R(180^\circ)} = \frac{5\beta_S(\alpha)^2 - 45\alpha^2 - 5\beta_A(\alpha)^2}{45\alpha^2 + 7\beta_S(\alpha)^2 + 5\beta_A(\alpha)^2}
\]

Isolation of Raman Tensor Invariants

All three Raman tensor invariants can be isolated if Raman intensity is combined from at least two different scattering angle geometries, for instance right angle and backscattering geometries. From expressions defined above

\[
\alpha^2 = \frac{1}{90K}\left[I_X^X(90^\circ) - \frac{2}{3}I_R^R(180^\circ)\right]
\]

\[
\beta_S(\alpha)^2 = \frac{1}{12K}I_R^R(180^\circ)
\]

\[
\beta_A(\alpha)^2 = \frac{1}{20K}\left[I_R^R(180^\circ) - 2I_Z^X(90^\circ)\right]
\]

Note the backscattering with dual circular polarization states yields the isolated symmetric anisotropic tensor invariant.

Far-From Resonance Scattering Intensities and Polarization Ratios

There are only two invariants of the polarizability in the Far From Resonance (FFR) approximation:

- **Isotropic invariant**
  \[ \alpha^2 = \frac{1}{9} \alpha_{\alpha\alpha} \alpha_{\beta\beta} \]

- **Anisotropic invariant**
  \[ \beta(\alpha)^2 = \frac{1}{2} (3\alpha_{\alpha\beta}^2 - \alpha_{\alpha\alpha} \alpha_{\beta\beta}) \]

There is no antisymmetric anisotropic invariant.
Intensities and Depolarization Ratios in the FFR Approximation

\[ \rho_l(90^\circ) = \frac{I_Z^x(90^\circ)}{I_X^x(90^\circ)} = \frac{3\beta(\alpha)^2}{45\alpha^2 + 4\beta(\alpha)^2} \quad 0 < \rho_l(90^\circ) < 3/4 \]

\[ \rho_n(90^\circ) = \frac{I_Z^l(90^\circ)}{I_X^l(90^\circ)} = \frac{6\beta(\alpha)^2}{45\alpha^2 + 7\beta(\alpha)^2} \quad 0 < \rho_n(90^\circ) < 6/7 \]

\[ R(180^\circ) = \frac{I_R^l(180^\circ)}{I_L^l(180^\circ)} = \frac{I_R^l(180^\circ)}{I_L^R(180^\circ)} = \frac{6\beta(\alpha)^2}{45\alpha^2 + \beta(\alpha)^2} \quad 0 < R(180^\circ) < 6 \]

\[ R^C(180^\circ) = \frac{I_R^l(180^\circ) - I_L^R(180^\circ)}{I_R^l(180^\circ) + I_L^R(180^\circ)} = \frac{5\beta(\alpha)^2 - 45\alpha^2}{45\alpha^2 + 7\beta(\alpha)^2} \quad -1 < R^C(180^\circ) < 5/7 \]

Relationships Between Polarization Ratios Far From Resonance

Conversions between polarizations ratios is easily achieved in the FFR approximation.

Between the two right angle linear depolarization ratios

\[ \rho_n(90^\circ) = \frac{2\rho_l(90^\circ)}{1 + \rho_l(90^\circ)} \quad \rho_l(90^\circ) = \frac{\rho_n(90^\circ)}{2 - \rho_n(90^\circ)} \]

Between circular and linear depolarization ratios

\[ R(180^\circ) = \frac{2\rho_l(90^\circ)}{1 - \rho_l(90^\circ)} \quad R^C(180^\circ) = \frac{3\rho_l(90^\circ) - 1}{1 + \rho_l(90^\circ)} \]

Measurement of Raman Spectra

History

Discovered in 1928 by Sir Chandrasekhra Venkata Raman, using sunlight as a source, telescope as a collector, his eyes as a detector.

Subsequent mercury sources replaced by lasers in 1962

Photographic plates replaced by photomultiplier tubes by 1953

Double and triple monochromators introduced in 1960s; holographic gratings in 1968

FT-Raman, array detectors, Raman microscopes more recent
Raman’s Spectrograph on display at the First Asian Spectroscopy Conference at the Indian Institute of Science, Bangalore, India
Advantages in Analytical Applications

• Very small samples, even without microscopes (e.g., single very small crystals, single grains of powder, individual polymer filaments, 1 nL liquid samples)
• Samples can be oriented
• Raman scattering from water is weak, enabling studies of aqueous samples
• High pressure or temperature cells can be used in situ in reactors
Disadvantages in Analytical Applications

• Interference from fluorescence, often from trace impurities, can obscure Raman spectrum of major component (UV or near-IR excitation can reduce this problem)
• Laser excitation can lead to photochemistry in the focused laser beam
• Multiphoton processes may alter the spectrum

Photon Molecule Interactions
Raman Active Vibrations

Change in polarizability ellipsoids during vibrations of CO$_2$

Raman Active Vibrations

Changes in polarizability ellipsoid during vibrations of H$_2$O
## Comparison of Raman and IR Intensities

**Table 1.1. Characteristic Wavenumbers and Raman and Infrared Intensities of Groups in Organic Compounds**

<table>
<thead>
<tr>
<th>Vibration*</th>
<th>Region (cm(^{-1}))</th>
<th>Intensity(^b)</th>
<th>Raman</th>
<th>Infrared</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(O–H)</td>
<td>3650–3000</td>
<td>w</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>v(N–H)</td>
<td>3500–3300</td>
<td>m</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>v(≡C–H)</td>
<td>3300</td>
<td>w</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>v(==C–H)</td>
<td>3100–3000</td>
<td>s</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>v(–C–H)</td>
<td>3000–2800</td>
<td>s</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>v(–S–H)</td>
<td>2600–2550</td>
<td>s</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td>v(C==N)</td>
<td>2255–2220</td>
<td>m–s</td>
<td>s–0</td>
<td></td>
</tr>
<tr>
<td>v(C==C)</td>
<td>2250–2100</td>
<td>vs</td>
<td>w–0</td>
<td></td>
</tr>
<tr>
<td>v(C==O)</td>
<td>1820–1680</td>
<td>s–w</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td>v(C==C)</td>
<td>1900–1500</td>
<td>vs–m</td>
<td>0–w</td>
<td></td>
</tr>
<tr>
<td>v(C==N)</td>
<td>1680–1610</td>
<td>s</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>v(N==N), aliphatic substituent</td>
<td>1580–1550</td>
<td>m</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
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Polarization of Light by Scattering

\[
\begin{align*}
\nu_{\text{C} - \text{O} - \text{C}} & : 1150-1060 \, \text{w} \quad \text{s} \\
\nu_{\text{C} - \text{O} - \text{C}} & : 970-800 \, \text{s-m} \quad \text{w-0} \\
\nu_{\text{Si} - \text{O} - \text{Si}} & : 1110-1000 \, \text{w-0} \quad \text{vs} \\
\nu_{\text{Si} - \text{O} - \text{Si}} & : 550-450 \, \text{vs} \quad \text{w-0} \\
\nu_{\text{O} - \text{O}} & : 900-845 \, \text{s} \quad \text{0-w} \\
\nu_{\text{S} - \text{S}} & : 550-430 \, \text{s} \quad \text{0-w} \\
\nu_{\text{Se} - \text{Se}} & : 330-290 \, \text{s} \quad \text{0-w} \\
\nu_{\text{C}(\text{aromatic}) - \text{S}} & : 1100-1080 \, \text{s} \quad \text{s-m} \\
\nu_{\text{C}(\text{aliphatic}) - \text{S}} & : 790-630 \, \text{s} \quad \text{s-m} \\
\nu_{\text{C} - \text{Cl}} & : 800-550 \, \text{s} \quad \text{s} \\
\nu_{\text{C} - \text{Br}} & : 700-500 \, \text{s} \quad \text{s} \\
\nu_{\text{C} - \text{I}} & : 660-480 \, \text{s} \quad \text{s} \\
\delta_{\text{C}(\text{CC})}, \text{aliphatic chains} & : 400-250 \, \text{s-m} \quad \text{w-0} \\
\text{C}_{\text{w}} n = 3, \ldots, 12 & : 2495/n \\
\text{n} > 12 & \\
\text{Lattice vibrations in} & : 200-20 \, \text{vs-0} \quad \text{s-0} \\
\text{molecular crystals} & \\
\text{(liberations and translational} & \\
\text{vibrations)} & \\
\end{align*}
\]

Source: Reprinted from B. Schrader, Angew. Chem. 12, 882 (1973), with permission of Verlag Chemie, GMBH, Weirheim, Germany.

\*\nu, stretching vibration; \delta, bending vibration; \nu_{s}, symmetric vibration; \nu_{as}, antisymmetric vibration.

\*\nu_{s}, very strong; s, strong; m, medium; w, weak; 0, very weak or inactive.

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Figure 1.2. Polarization of light by scattering. In the experiment shown, unpolarized radiation propagates along \( z \), and polarized radiation is observed along \( y \).
Depolarization Ratio

\[ \rho = \frac{I_\perp}{I_\parallel} \]

\[ \rho = \frac{3(\alpha^a)^2}{45(\alpha^s)^2 + 4(\alpha'^a)^2} \]

\( \alpha^s \) is non-zero only for totally symmetric vibrations.

For non-totally symmetric vibrations, \( \rho = \frac{3}{4} \)

For totally symmetric vibrations, \( 0 \leq \rho < \frac{3}{4} \)

Irradiation of sample from y-direction with plane polarized light, with the electric vector in the z-direction
Instrumentation for Conventional Raman Spectroscopy

- Excitation source (generally a CW laser)
- Sample illumination and scattered light collection system
- Sample holder
- Monochromator or spectrograph
- Detection system (detector, amplifier, output device)

- Scattering efficiency for Raman is $1 \times 10^{10}$ photons!
- Need extremely high intensity source, spectrometer with high degree of discrimination against stray light, extremely sensitive detection system able to detect small numbers of photons over dark background

Typical Dispersive Raman System

Figure 2-1: Schematic diagram of a typical dispersive Raman system. (Reproduced with permission from Ref. 1)
Excitation Sources

• CW gas lasers
  (Ar, Kr, Ne, N₂ (337.1 nm UV, pulsed), CO₂ (9-11 μm IR, CS/pulsed), excimer XeCl, 308 nm UV, pulsed)

• Dye lasers

• Solid-state lasers
  Ruby (694.3 nm, pulsed), Nd:YAG (1064-nm near-IR, CW/pulsed), Diode (3500-380 cm⁻¹ IR, CW/pulsed)

• Pulsed Nd:YAG
  laser harmonics (532 nm, 355 nm, 266 nm) for time-resolved and UV resonance Raman applications

Table 2.1. Results from Argon and Krypton CW Lasers*

<table>
<thead>
<tr>
<th>Argon</th>
<th>Krypton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>Typical Output</td>
</tr>
<tr>
<td>4545</td>
<td>1.0</td>
</tr>
<tr>
<td>4579</td>
<td>1.0</td>
</tr>
<tr>
<td>4638</td>
<td>1.0</td>
</tr>
<tr>
<td>4727</td>
<td>2.5</td>
</tr>
<tr>
<td>4765</td>
<td>6.0</td>
</tr>
<tr>
<td>5017</td>
<td>6.4</td>
</tr>
<tr>
<td>5287</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Some lines require special optics.
*Outputs were obtained with Spectra Physics 171-18.

CW Gas Lasers

These lasers require high voltage input and water cooling. Wavelength is given in Ångstroms, output in watts.
Argon-Ion & Krypton-Ion Pumped Dyes

**Figure 2-4** Output powers and wavelengths obtainable from a Spectra-Physics Model 375 dye laser pumped by an argon-ion and krypton-ion laser. (Reproduced with permission.)

Solid-State Lasers

**Figure 3-9: Schematic of the Millennia IIa Laser Head**
Sample Illumination

Proper focusing of laser and efficient collection of scattered radiation required to detect very weak Raman scattering.

Laser focuses to ~1mm; F-number ($F = f/D$) of collection lens should be small for large light-gathering power and should be matched to $F$-number of monochromator (usually two lenses are used, a short focal length, low $F$-number to collect the largest solid angle, and the second to $F$-match the monochromator).

Collection optics with elliptical collection mirror

Figure 2-6 Collection optics with an elliptical collection mirror. FL, focusing lens; S, sample; ES, entrance slit.
Ellipsoidal collection system

![Diagram of ellipsoidal collection system](image)

Figure 2.3. Ellipsoidal collection system.

Monochromator

![Diagram of monochromator](image)

Spex Model 1403/4 Double Monochromator
Monochromator

Spex Model 1877 Triple Monochromator: large stray light rejection, allows observation of bands very close to Rayleigh line

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Monochromator

Fig. 3. Optical layout of an on-axis, low-f-number holographic monochromator (courtesy of Kaiser Optical).
Detection: Photon Counting

In photomultiplier tube, photocathode emits electrons when struck by photon; series of dynodes each emit a number of secondary electrons when struck by electron; anode collects electrons as output signal.

Detection: Photodiode array

Multichannel detector, 2.5 cm long with 1024 silicon photodiodes, each 25 μm wide, 2.5 mm high. Dispersed radiation striking detector causes charge pattern to develop that is related to intensity of radiation in focal plane.

Intensifier (multichannel plate) in front of detector increases sensitivity by ~10^4.
Detection: CCD

The CCD (charge-coupled device) is an optical array detector consisting of a two-dimensional array of silicon diodes. CCDs have low readout noise and high quantum efficiency and sensitivity over wide wavelength range (100-1000 nm).

Frequency Calibration

- Internal standards to obtain ~1 cm\(^{-1}\) accuracy
- Laser plasma lines (detune laser and scatter from melting point tube)
- Neon emission lines from neon lamp
- Indene (vacuum distilled and sealed in capillary)
Frequency Calibration

\[ I = K(ν) \times A(ν) \times ν^4 \times I_0 \times J(ν) \times C \]

where \( I \) is intensity of Raman line, \( K(ν) \) is overall spectrometer response, \( A(ν) \) is self-absorption of medium, \( ν \) is frequency of scattered radiation, \( I_0 \) is intensity of incident radiation, \( J(ν) \) is a molar scattering parameter and \( C \) is the concentration of the sample. \( ν^4 \) term dominates if other terms do not differ appreciably—higher frequency laser beam yields stronger Raman signal.

Absolute intensity is extremely difficult to determine, but relative amount of sample in a solution can be determined from the relative intensity of a Raman band. Prepare a working curve from known samples containing fixed amount of non-interacting internal standard (such as ClO_4^- for aqueous solutions, strong Raman band at 928 cm\(^{-1}\)). Sample relative intensity given by:

\[ I_{rel} = \frac{K(ν) \times A(ν) \times ν^4 \times J(ν) \times C}{K(ν') \times A(ν') \times ν'^4 \times J(ν') \times C'} \]

Primes refer to internal standard

\[ I_{rel} = \text{constant} \times C \]
### Sampling Techniques

- **A**
  - Gas cell with external resonating mirrors for multiple passes of laser beam

- **B**
  - Capillary cell for liquids

- **C**
  - Cylindrical cell for liquids

- **D**
  - KBr pellet for solids

### Sampling Techniques for Colored Compounds

- Methods to avoid local heating from absorption of laser beam
  - Line focus with cylindrical lens, C, focuses beam on sample, S, over 10 to 25 mm instead of a few microns
  - Rotating cylindrical cell: centrifugal force drives liquid to outer part of cell. Laser is focused near the wall to minimize self-absorption of Raman scattered light
Sampling of Colored Solids

Rotating device for solid samples

Apparatus for making ring-shaped powder pellets (can obtain spectra from 1mg sample)

High Temperature Raman Cell
Low Temperature Raman Cells

Figure 2-20 (a) Simple low-temperature Dewar cell. (b) Mini-bulb configuration.

Sample Spinner for 180° Scattering

Figure 2-21 Sample spinner for 180° (or oblique) illumination: (a) Complete system with evacuated Pyrex jacket (J) surrounding the sample tube. S, cold (or warm) gas such as N₂ is passed through J to control the sample temperature. L₁, L₂, and M are lenses and a mirror; C is the sample chuck. (b) Details of the sample chuck. O, split nylon cone; P, knurled aluminum nut attached to aluminum body of chuck; Q, spinner shaft. (Reproduced with permission from Ref. 56.)
Special Cells

- High Temperature
- High pressure/high temperature
- Polymerization cell
- Electrochemical cell

Raman Difference Spectra

Figure 2-23 Divided rotating cell connected to a Spex 1475 difference/ratio generator. (Reproduced with permission.)
Fiber-Optic Probe

FT-Raman Spectroscopy

Quartz beam splitter, solid state laser, backscattering collection, Rayleigh line filter before interferometer (holographic notch filter, OD > 6 at laser frequency), InGaAs or high purity Ge detector.

Can measure down to 70 cm\(^{-1}\) Stokes shift.

FT-Raman spectroscopy solves problems of fluorescence and sample degradation by excitation in the near-IR. Interferometric optics achieve multiplex measurement.
FT-Raman

Figure 3. A) Schematic diagram of an FT-Raman spectrometer (Bruker RFS 100); B) Schematic diagram of the sample compartment
L = laser; RA = Raman; SA = Sample
(Reproduced by permission of Bruker Optik GmbH, D-76275 Ettlingen, Germany)

FT Raman Detectors

Figure 25. Relative instrument response functions for Ge and InGaAs detectors.
Reduction of Fluorescence Background

![Graph showing reduction of fluorescence background.](image)

Figure 2.7. (a) Raman spectrum of anthracene at 514.5-nm excitation. (b) FT-Raman spectrum of anthracene at 1.06-µm excitation.

Performance of FT-Raman

![Graph showing performance of FT-Raman.](image)

Figure 2.6. FT-Raman spectrum of indene at 1.0 W and (a) 2-s and (b) 30-s measurement time.
Accurate subtraction of spectra is possible with FT-Raman.
(a) 70/30 mixture, toluene/benzene (b) toluene (c) a - b (d) benzene.
Special Techniques

Nonlinear Raman Spectroscopy: with extremely strong laser pulses (~10^9 V cm\(^{-1}\) from Q-switched ruby or Nd-YAG lasers), higher order terms in induced dipole moment become important:

\[
P = \alpha E + \frac{1}{2} \beta E^2 + \frac{1}{6} \gamma E^3 + \cdots
\]

E: strength of applied electric field (laser beam)
\(\alpha\): Polarizability
\(\beta, \gamma\): first and second hyper-polarizabilities

Hyper-Raman Effect

With high intensity pulse at frequency \(v\), scattered radiation contains frequencies \(2v\) (hyper-Rayleigh scattering) and \((2v \pm v_M)\) (Stokes and anti-Stokes hyper-Raman scattering), where \(v_M\) is normal vibration of molecule, caused by two incident photons \((2v)\) of the laser. Different symmetry selection rules apply, and hyper-Raman effect contains all IR active modes.
Stimulated Raman Effect

When electric field of laser exceeds $10^9$ V cm$^{-1}$, stimulated Raman scattering generates strong coherent beam at Stokes frequency ($\nu - \nu_M$), which acts as source to excite ($\nu - 2\nu_M$). Effect is used to generate H$_2$ Raman shifters.

Concentric colored rings observed in stimulated Raman of benzene
Coherent Anti-Stokes Raman Scattering (CARS)

For sample irradiated by two high-energy laser beams at $v_1$ and $v_2$ ($v_1 > v_2$) in colinear direction, beams interact coherently to produce strong scattered light of frequency $2v_1 - v_2$. When $v_2$ is tuned to resonance such that $v_2 = v_1 - v_M$ for Raman active mode of sample at $v_M$, a strong beam at frequency $2v_1 - v_2 = 2v_1 - (v_1 - v_M) = v_1 + v_M$ is emitted. Effect is called CARS. CARS signal is coherent and emitted in one direction and can be observed without monochromator. It is on anti-Stokes side and thus avoids fluorescence. All modes that are Raman active and some inactive Raman and IR modes are active in CARS.

Figure 3-3 Initial apparatus for measuring anti-Stokes emission using a frequency-doubled Nd:YAG pumped dye laser. L is a short focal lens (3-4 cm); S is the sample; I is an iris for spatially filtering the two exciting beams; F is a wideband interference filter; D is the detector (usually a PIN diode); M is a monochromator (not usually necessary). Not shown are the PAR-160 box car integrator, chart recorder, and dye laser scan drive used to record spectra. (Reproduced with permission from Ref. 1.)
Photoacoustic Raman Spectroscopy (PARS)

Two laser beams, \( \nu_p \) (pump beam) and \( \nu_S \) (Stokes beam) impinge on gaseous sample, interact when \( \nu_p - \nu_S = \nu_M \) for Raman active mode. The Stokes beam is amplified and the pump beam is attenuated. The vibrationally excited molecules lose excitation to translational energy, changing the pressure in the cell, which can be detected with a microphone. In this case there is no Rayleigh line, and low energy rotational lines can be studied.

Figure 3.4 Schematic representation of the photoacoustic Raman scattering (PARS) process. (a) A simple energy level diagram illustrating the Raman interaction that occurs in the PARS process; (b) Basic elements of the PARS experimental arrangement. The pump beam is attenuated and the Stokes beam is amplified by the stimulated Raman process that takes place when the beams overlap in the gas sample cell. For each Stokes photon created by the Raman process, one molecule is transferred from the lower state to the upper state of the transition. Collisions relax these excited molecules producing a pressure change that is detected by a microphone. (Reproduced with permission from Ref. 4.)

Figure 3.5 Photoacoustic Raman spectra of CO2 at a pressure of 107 torr. The resolution line spacing is about 3 cm⁻¹. Laser powers of the pump and Stokes beams were 33 mW and 120 mW, respectively. (Reproduced with permission from Ref. 4.)
Resonance Raman Spectroscopy

Ni (OEP) at three different excitations, within B, Q₀ and Q₁ bands. Excitation within B produces polarized modes, within Q₀ produces depolarized modes and within Q₁ produces anomalously polarized modes.
Raman Excitation Profile

- Plot of Raman intensity vs exciting laser wavelength
- Provides information on electronic excited states
- Provides information on symmetry of molecular vibration

Raman Microscopy

Figure 11.1. Scheme of a Raman microspectrometer equipped with a multichannel detector.
Fig. 11. Schematic diagram of the filtered Kaiser commercial fiber-coupled Raman microscope.