Raman: it’s not just for noodles anymore

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Outline - Lecture 1

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■ 2. Theory
   ■ Role of polarizability; mathematical models
   ■ Depolarization ratio
   ■ Temperature correction

■ 3. System instrumentation/common techniques
   ■ Components
   ■ FT-Raman
   ■ Raman microscopy
Outline - Lecture 2

4. Other Raman techniques
   - High pressure Raman spectroscopy
   - Surface enhanced Raman (SERS)

5. Vibrations and peak identification

6. Case studies
   - Silicates
   - Borates
   - Germanates
   - Other glass examples

7. References
1. Introduction
Introduction

The graph on the left shows a good summary of the capabilities and kinds of Raman spectrometry. Just follow each quadrant and the different topics it includes.

(From: www.spectroscopynow.com/coi/cda/detail.cda?page=3&id=1882&type=EducationFeature&chId=6)
History

- 1900: Studies on scattering of light
- 1910: Prediction of the Raman effect
- 1920: Discovery of the Compton effect
- 1930: Discovery of the Raman effect
- 1930: Notions on the use of the Raman effect for chemical analyses
- 1940: Double monochromator Raman grating spectrometer
- 1950: Resonance Raman spectra
- 1960: First laser Raman spectra
- 1970: Stimulated Raman effects
- 1970: Hyper Raman spectra
- 1980: Basic principles of Raman microscopy
- 1980: Surface-enhanced Raman scattering
- 1980: FT-Raman spectroscopy with NIR excitation
- 1990: First use of CCD detectors for Raman spectroscopy
- 2000: 

Invention of the CCD
Advantages of Raman

- Selection rules allow for some vibrations (normally symmetric) to be seen only by Raman spectroscopy.
- Measurements of depolarization ratios yield information about molecular symmetry.
- Only a small sample area is needed (laser spot).
- Water is a weak Raman scatterer, allowing for the use of aqueous solutions. Can also sample through glass container walls.
- The region $4000 \text{ cm}^{-1}$ to $50 \text{ cm}^{-1}$ can be covered in a single scan without changing gratings, splitters, detectors, etc.
Disadvantages of Raman

- Laser source is needed, which can cause local heating/decomposition.
- Can cause fluorescence.
- More difficult to obtain rotational and ro-vibrational spectra with high resolution.
- Way more expensive: 150-200 k$ vs. 40-60 k$ for FTIR.
Figure 1: Mechanisms of various light-scattering processes. (a) Rayleigh, (b) non-resonance Raman, (c) pre-resonance Raman, (d) resonance Raman and (e) resonance fluorescence
Stokes/Anti-Stokes

Note that the transitions (scattering) take $10^{-14}$ seconds or less!
As you can see, the Stokes peaks correspond to lower photon frequencies and lower energies. The anti-Stokes side is symmetric but corresponds to higher frequencies and energies. The Stokes lines are stronger because the population of molecules at $\nu=0$ is much larger than at $\nu=1$ by the Maxwell-Boltzmann distribution law.
2. Theory
Some classical Raman theory

Let light $E = E_0 \cos 2\pi V_0 t$ shine on a diatomic molecule. The induced dipole moment is

$$P = \alpha E = \alpha E_0 \cos 2\pi V_0 t.$$  Here $\alpha$ is the polarizability of the molecule.

If the molecule is vibrating with frequency $V_m$ then the displacement (nuclear) is given by

$$q = q_0 \cos 2\pi V_m t.$$  For small amplitudes, we consider $\alpha$ as a linear function of $q$, so

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 + \ldots$$

Then the combined equations yield

$$P = \alpha E_0 \cos 2\pi V_0 t = \alpha_0 E_0 \cos 2\pi V_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi V_0 t =$$

$$\alpha_0 \cos 2\pi V_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi V_0 t \cdot \cos 2\pi V_m t =$$

$$\alpha_0 \cos 2\pi V_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \left[ \cos \left\{ 2\pi \left( V_0 + V_m \right) t \right\} + \cos \left\{ 2\pi \left( V_0 - V_m \right) t \right\} \right]$$
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\]

Anti-Stokes

Stokes
In actual molecules, the nice linear relationship does not hold since both $P$ and $E$ are vectors. Then the equation must be written as

$$
\begin{bmatrix}
P_x \\
P_y \\
P_z \\
\end{bmatrix} =
\begin{bmatrix}
\alpha & \alpha & \alpha \\
\alpha & \alpha & \alpha \\
\alpha & \alpha & \alpha \\
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix}
$$

The matrix is called the polarizability tensor. We can plot $\alpha_i$ ($\alpha$ in the i direction) in all directions we get a 3D surface. Conventionally we plot $1/\sqrt{\alpha_i}$ instead, and get a polarizability ellipsoid.
CO$_2$ Polarizability ellipsoids

Raman active

IR active

IR active
Scattering

- Classically, the observed intensity of Raman scattering is proportional to

\[ I_R = \mu (\nu_0 \pm \nu_j)^4 \alpha_j^2 Q_j^2 \]

where \( \nu_0 \) is the laser light frequency, \( \nu_j \) is the frequency of the \( j^{th} \) mode, \( Q_j \) the displacement, and \( \alpha \) is the polarizability of that mode. Note the dependence on the fourth power of the laser light, typical for dipole scattering.
The depolarization ratio is defined as the ratio of the light scattered at 90 degrees that is perpendicular ($I_y$) to the light that is parallel ($I_\parallel$) with respect to the incident light.

The incident laser light is already polarized. But the scrambler is required because monochromator gratings show different efficiencies for the different polarizations.
Depolarization ratio

Since the ratio is defined as \( \rho_p = \frac{I_y}{I_z} \), and it can be shown that this is related to the polarizability matrix by

\[
\rho_p = \frac{3g^s + 5g^a}{10g^0 + 4g^s},
\]

where

\[
g^0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2
\]

\[
g^s = \frac{1}{3}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2\right]
\]

\[
g^a = \frac{1}{2}\left[(\alpha_{xy} + \alpha_{yx})^2 + (\alpha_{yz} + \alpha_{zy})^2 + (\alpha_{xz} + \alpha_{zx})^2\right]
\]

In normal Raman scattering, \( g^a = 0 \) from symmetry. For totally symmetric vibration, we then get \( 0 \leq \rho_p < \frac{3}{4} \), while for non-totally symmetric vibration \( \rho_p = \frac{3}{4} \).
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where

$$g^0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2$$

$$g^s = \frac{1}{3}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]$$

$$+ \frac{1}{2}[(\alpha_{xy} + \alpha_{yx})^2 + (\alpha_{yz} + \alpha_{zy})^2 + (\alpha_{zx} + \alpha_{xz})^2]$$

$$g^a = \frac{1}{2}[(\alpha_{xy} - \alpha_{yx})^2 + (\alpha_{xz} - \alpha_{zx})^2 + (\alpha_{yz} - \alpha_{zy})^2]$$

In normal Raman scattering, $g^a = 0$ from symmetry. For totally symmetric vibration, we then get $0 \leq \rho_p < \frac{3}{4}$, while for non-totally symmetric vibration $\rho_p = \frac{3}{4}$. 

Depolarization ratio
In the spectrum on the left you see the totally symmetric vibrations of CCl$_4$ (459 cm$^{-1}$) and the non-totally symmetric modes (314 and 218 cm$^{-1}$), taken in a 90° scattering geometry. The values of $\rho_0$ were 0.02 for the first case (459 cm$^{-1}$; note ratio of peaks), and 0.75 for the other two peaks, as expected.

Though usually done with liquids and gases, depolarization measurements can be done in solids by suspending them in a material with a similar index.
$\text{CCl}_4$ modes and Raman

Animation from

http://fy.chalmers.se/~brodin/MolecularMotions/CCl4molecule.html
Temperature correction

- The thermal population factor can mask peaks or bands in the low-frequency region of the spectrum. The corrected (reduced) Raman intensity can be calculated from

\[
I_{\text{reduced}} = \frac{I_{\text{observed}}}{\exp \left[ -\frac{\hbar \omega}{kT} \right] + 1}
\]

- This needs to be done before any peak assignments are made
Temperature correction

- The effect of the temperature correction can be seen at left, where the most dramatic change occurs at low wavenumbers.
3. System components and common techniques
Simplified Raman spectrometer layout
For a long time the most common laser for a Raman system was the Ar:ion laser, which provided multiple lines (wavelengths). Cost was significant, however, as were maintenance costs. Nowadays the selection is much greater: Gas Ion, HeNe, DPSS 532 nm, Solid-state visible lasers, NIR Diode, High power fibre linked, UV lasers.

The key is what laser can minimize the fluorescence signal of the sample. On the left we see a sample irradiated with green light (too fluorescent); red light (still too much), and NIR (785 nm; just right).
Exercise

- Which of the following lasers would yield best results when measuring weak Raman signals, and approximately by how much?
  - Green argon line (514.5 nm) vs. blue argon line (488 nm):
  - Nd:YAG fundamental (1064 nm) vs. diode laser (785 nm):
EXERCISE

Which of the following lasers would yield best results when measuring weak Raman signals, and approximately by how much?

- Green argon line (514.5 nm) vs. blue argon line (488 nm):
  \[
  \frac{514.5}{488} = \frac{4}{4} = 1.24
  \]

- Nd:YAG fundamental (1064 nm) vs. diode laser (785 nm):
  \[
  \frac{1064}{785} = \frac{4}{4} = 3.37
  \]
The most common spectrograph arrangement is the Czerny-Turner, shown on the right. The mirrors are used as collimators, and the turret contains planar reflective gratings.
For higher resolution and rejection of unwanted (read Rayleigh) wavelengths, one can use a double or triple monochromator. This adds to the price and diminishes the overall light signal.
CCD Detectors

- Most of the current dispersive Raman set-ups are now equipped with multichannel two-dimensional CCD detectors. The main advantages of these detectors are the high quantum efficiency, the extremely low level of thermal noise (when effectively cooled), low read noise and the large spectral range available. Many CCD chips exist, but one of the most common spectroscopy sensor formats is the 1024 x 256 pixel array.
Advantages and disadvantages of FT-Raman

- Use of NIR lasers greatly reduces fluorescence problem
- Relatively inexpensive (less so lately!)
- High resolution, high throughput
- Collects Stokes and Anti-Stokes simultaneously
- Can be attached to an IR instrument

But...
- Black body emissions at higher temp swamp Raman
- Lower scattering intensity due to use of NIR ($\nu^4$ effect)
- Absorptions in the NIR
- Slow (tens of minutes in some systems)
Michelson interferometer
FT-Raman schematic

- Focusing Mirror
- LN₂ Cooled Ge Detector
- Dielectric Filters
- Spatial Filters
- Fixed Mirror
- Beam Splitter
- Sample
- 200mm Lens
- Parabolic Collection Mirror
- Nd/YAG Laser With Line Filter
1λ, Zero path difference

If there is a zero path difference (ZPD) between the two arms of the interferometer, then the waves will recombine and add constructively. The detector will then see a modulated, bright beam coming out of the interferometer.

Note that we are only considering one scattered wavelength!
1λ, Single interferogram
2\lambda, Sum of interferograms

![Graph showing intensity vs. optical path difference with labeled peaks at \lambda, 3\lambda, \lambda + 3\lambda]
EXERCISE

\[ \sin(x) + \sin(3x) + \sin(5x) \]

\[ \sin(x) + \sin(3x) + \sin(5x) + \sin(7x) + \sin(9x) + \sin(11x) \]

\[ \sin(x) + \sin(3x) + \sin(5x) + \sin(7x) + \sin(9x) + \ldots + \sin(21x) \]

What would the interferogram of a large number of wavelengths look like?
EXERCISE

What would the interferogram of a large number of wavelengths look like?

Sin(x) + Sin(3x) + Sin(5x)

Sin(x) + Sin(3x) + Sin(5x) + Sin(7x) + Sin(9x) + Sin(11x)

Sin(x) + Sin(3x) + Sin(5x) + Sin(7x) + Sin(9x) + … + Sin(21x)

<-Calculated for first 100 odd sine terms

From FTIR-->
Raman microscopes
Microscope schematic
Conventional vs. Confocal
Raman microscopy

**Figure 4.** Small cuprite crystals of micrometre size interspersed in the glass matrix of red opaque disc-shaped beads: back-scattered image.

**Figure 5.** Raman spectra of cuprite (Cu$_2$O) in the red disc-shaped beads 2B19B and 2B14: excitation wavelength $\lambda = 514.5$ nm.

Characterisation of inorganic pigments in ancient glass beads by means of Raman microspectroscopy, microprobe analysis and X-ray diffractometry

N. Welter,¹ U. Schüssler² and W. Kiefer¹
7. References

- **Handbook of Raman Spectroscopy**, I.R. Lewis, H.G.M. Edwards, eds. (Marcel Dekker, 2001)
- Website of J. Yvon.
7. References

