Spectroscopy: Lecture 5

Application of Raman Spectroscopy: Characterization of Chemical Bondings

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Outlines

- History of Raman Effect and Scattering of Light
- Selection Rules of Raman & Infrared spectroscopy
- Depolyrization Ratio of Raman lines
- Molecular Vibrations
- Effect of Isotopes on Vibrational Frequencies
- Micro-Raman Instrumentation within Raman spectroscopy Laboratory within HIGP
- Remote Raman Instrument
- Geological Applications of Raman Spectroscopy
  - (i) Fluid Inclusions
  - (ii) Structure of Silicate glasses
  - (iii) Mineral Identifications in Thin Sections
  - (iv) Effect of High Pressure on Minerals
- Summary
The Raman Effect

First published observation:
"A new type of Secondary Radiation"
C. V. Raman and K. S. Krishnan
Nature, 121, 501, March 31, 1928

Nobel Prize in Physics 1930

$\nu_o = \text{frequency of incident beam}$

$\nu_m = \text{vibrational frequency of molecule}$


Raman Spectrum

- \( \nu_0 - \nu_m \) Stokes Raman
- \( \nu_0 \) Rayleigh
- \( \nu_0 + \nu_m \) Anti-Stokes Raman
In the Raman spectra the information about vibrations of molecules is obtained in visible part of the spectrum as a difference from the energy of the visible laser excitation.

Raman spectra is complementary to IR spectra but the selection rules are different. For IR activity requires change in the permanent dipole moment.
**Raman Activity – Classical Approach**

Electric field of an electromagnetic wave of frequency $\nu_0$:

$$ E = E_0 \cos 2\pi\nu_0 t \quad \text{(i)} $$

$\alpha$ = Molecular polarizability

$$ p = \alpha E = \alpha E_0 \cos 2\pi\nu_0 t \quad \text{(ii)} $$

Where the polarizability $\alpha$ is defined as the ratio of the induced dipole moment of an atom or molecule to the electric field that produces this dipole moment.

Polarizability can be expressed as:

$$ \alpha = \alpha_0 + \sum_i \left( \frac{\delta\alpha}{\delta Q_i} \right) \Delta Q_i + \text{higher order terms} \quad \text{(iii)} $$

Where $\alpha_0$ is the polarizability of non-vibrating molecule; and $\Delta Q_i$ is the internuclear distortion accompanying the motion of normal vibration $i$.

$\delta\alpha/\delta Q_i$ = Change in polarizability due to normal vibration $i$.

Since molecule is vibrating

$$ \Delta Q_i = Q_0 \cos 2\pi\nu_i t \quad \text{(iv)} $$

$$ p = \alpha_0 E_0 \cos 2\pi\nu_0 t + E_0 Q_0 \sum_i \left( \frac{\delta\alpha}{\delta Q_i} \right) \cos 2\pi\nu_0 t \cos 2\pi\nu_i t $$

or

$$ p = \alpha_0 E_0 \cos 2\pi\nu_0 t + E_0 Q_0 \sum_i \left( \frac{\delta\alpha}{\delta Q_i} \right) \left[ \cos 2\pi (\nu_0 - \nu_i) t + \cos 2\pi (\nu_0 + \nu_i) t \right] \quad \text{(v)} $$

If $\delta\alpha/\delta Q_i$ is not zero, the vibration will be Raman active

According to classical theory Intensity of both the Stokes and anti-stokes Raman lines $\alpha (\delta\alpha/\delta Q_i)^2$

However, the intensity of anti-stokes lines is much lower than the stokes Raman lines. This observation can be explained on the basis of quantum mechanics.

Distribution of Molecules

If the sample is in thermal equilibrium, the relative numbers of molecules in states of different energy will be given by the Boltzmann distribution:

\[
\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-\frac{\Delta E_v}{kT}}
\]

- \(N_0\): number of atoms in the lower vibrational state
- \(N_1\): number of atoms in the higher vibrational state
- \(g_0\): degeneracy of the lower vibrational state (number of orbitals of the same energy)
- \(g_1\): degeneracy of the higher vibrational state
- \(\Delta E_v\): energy difference between these two vibrational states
- \(k\): Boltzmann's constant
- \(T\): temperature in Kelvin

The ratio of the intensities of anti-Stokes Raman to that of Stokes Raman lines will be:

\[
I_{\text{anti-Stokes}} / I_{\text{Stokes}} = \left(\frac{v_0 + v_i}{v_0 - v_i}\right)^4 e^{-hv/kT}
\]
Consider a light ray along the Z axis of a Cartesian coordinate system with its polarization parallel to the Y axis. If the Raman scatter is observed along the X direction with polarization parallel to Y direction, the intensity will be given by Plaezek's theorem as

\[ I_{\parallel} = \frac{16\pi^3 h (\nu_0 - \nu)^4 g}{135c \nu (1 - e^{-h\nu/kT})} N (45\alpha'^2 + 4\gamma'^2) I_o \]  

where \( I_o \) is the intensity of the exciting light at the wavenumber \( \nu_0 \), \( \nu \) the wavenumber of the Raman scatter, \( N \) the number of scattering molecules, and \( g \) a factor of degeneracy. The factors \( \alpha'^2 \) and \( \gamma'^2 \) are defined by the derivative of the polarizability as

\[ \alpha'^2 = \frac{1}{3} (\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz}) \]

\[ \gamma'^2 = \frac{1}{2} \left[ (\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{yy} - \alpha'_{zz})^2 + (\alpha'_{zz} - \alpha'_{xx})^2 + 6 (\alpha'_{xy}^2 + \alpha'_{yz}^2 + \alpha'_{zx}^2) \right]. \]

For the scattered light polarized parallel to the Z direction, the intensity becomes

\[ I_{\perp} = \frac{16\pi^3 h (\nu_0 - \nu)^4 g}{135c \nu (1 - e^{-h\nu/kT})} N 3\gamma'^2 I_o \]

At a given wavenumber \( \nu \) and for fixed experimental conditions, therefore,

\[ I_{\parallel} \sim 45\alpha'^2 + 4\gamma'^2 \]  
\[ I_{\perp} \sim 3 \gamma'^2. \]

Depolarization Ratio \((\rho) = I_{\perp}/I_{\parallel}\)

For a totally symmetric vibration \( \gamma' = 0 \), \( \rho = 0 \)
For totally antisymmetric vibration \( \alpha'^2 = 0 \), and \( \rho = 3/4 \)
Vibration of a Diatomic Molecule

Newtonian mechanics

Molecular vibrations can be treated using Newtonian mechanics, to calculate the correct vibration frequencies. The basic assumption is that each vibration can be treated as though it corresponds to a spring. In the harmonic approximation the spring obeys Hooke’s law: the force required to extend the spring is proportional to the extension. The proportionality constant is known as a force constant, \( k \).

\[
Q(t) = A \cos(2\pi \nu t)
\]

\[
\nu = \left(\frac{1}{2\pi}\right) \left(\frac{k}{\mu}\right)^{1/2}
\]

\( A \) is the maximum amplitude of the vibration coordinate \( Q \), and \( \mu \) is the reduced mass of the molecule and is given by

\[
\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}
\]

In the case of isotope substitution in the molecule, the force constant remains the same and the frequency will change because of increase in the mass of the atoms. For example in the case of hydrogen molecule

\[
\nu_{\text{H-H}} = 4160.2 \text{ cm}^{-1} \text{ and } \nu_{\text{D-D}} = 2989.5 \text{ cm}^{-1}
\]

Isotope substitution is often used for identifying the atoms involved in a vibrational mode of a molecule in the gas phase, liquid, glasses and crystalline solids.
Diatomic Molecules

\( \text{N}_2, \text{O}_2, \text{H}_2 \) (Homopolar diatomic Molecules)

\( \text{Cl}_2, \text{Br}_2, \text{I}_2 \)

\( \text{CO}, \text{NO} \) (Heteropolar diatomic molecules)

Homopolar diatomic XX Molecules (\( \text{D}_{\infty h} \)) the vibration is along the chemical bond and is only Raman active.

\[
\nu(\text{N}_2) = 2330.7; \quad \nu(\text{O}_2) = 1556; \quad \nu(\text{H}_2) = 4160.2 \text{ cm}^{-1}
\]

Heteropolar diatomic XY molecule (\( \text{C}_{\infty h} \)) the vibration is both Raman and infrared active.

\[
\nu(\text{CO}) = 2145; \quad \text{NO} = 1877 \text{ cm}^{-1}
\]
Normal Vibrational modes of XY₂ Molecules

The vibration types or species are designated according to symmetry operations which they represent as following:

A Symmetric with respect to principal axis of symmetry
B Anti-symmetric with respect to principal axis of symmetry
E Doubly degenerate vibrations
T or F Triply degenerate vibrations

Subscripts:

g & u Symmetric or anti-symmetric with respect to a center of symmetry*
1 and 2 Symmetric or anti-symmetric with respect to a rotational axis (Cₚ) or rotational-reflection axis (Sₚ) other than the principal axis or in those point group with one symmetric axis with respect to plane of symmetry.

Superscripts:

Prime (') and double prime (''')
Symmetric or antisymmetric with respect to a plan of symmetry

* g and u are taken from the German words grade and ungrade meaning even or uneven

\[ \Gamma_{C_{2v}} = 2A₁(R, IR) + B₂(R, IR) \]

H₂O; NO₂

\[ ν₁ (A₁) \]

Symmetric stretch

3600; 1330 cm⁻¹

\[ ν₂ (A₁) \]

Symmetric bending

1650; 828 cm⁻¹

\[ ν₃ (B₂) \]

Anti-symmetric stretch

3760; 1228 cm⁻¹
Normal Vibrational Modes of CO₂ Molecule

\( \nu_1 \) (Raman Active) 1337* cm\(^{-1}\)

\( \nu_3 \) (IR Active) 2349 cm\(^{-1}\)

\( \nu_2 \) (IR Active) 667 cm\(^{-1}\)

* \( \nu_1 \) and 2\( \nu_2 \) produce a Fermi resonance doublet at 1285 and 1388 cm\(^{-1}\)
Normal Vibrational modes of $XY_4$ Molecules

$\Gamma_{Td} = A_1(R) + E(R) + 2T_2(R,IR)$

$CCl_4$: $\nu_1 = 459; \nu_2 = 218; \nu_3 = 762; \nu_4 = 314 \text{ cm}^{-1}$

$CBr_4$: $\nu_1 = 269; \nu_2 = 127; \nu_3 = 665; \nu_4 = 127 \text{ cm}^{-1}$

$CH_4$: $\nu_1 = 2914; \nu_2 = 1526; \nu_3 = 3020; \nu_4 = 1306 \text{ cm}^{-1}$

(1 atm gas)

$SiO_4^{4-}$: $\nu_1 = 819; \nu_2 = 340; \nu_3 = 956; \nu_4 = 527 \text{ cm}^{-1}$
For geological, planetary and materials science research, the Raman spectroscopy Laboratory within SOEST at UH has the following fully Raman spectrographs:

Cofocal Micro-Raman spectrometer with *SPEX TRIPLEMATE* spectrograph and CCD detector is also available. The *SPEX* micro-Raman system can use various excitation lines of existing Ar and Kr-ion lasers.

*Kaiser Raman RXN1™* Microprobe equipped with 785 nm laser excitation. The microscope is also equipped with optical imaging accessories.

*Renishaw inVia Raman* microscope equipped with 830, 514.5 and 244 nm laser excitation. The microscope is also equipped with optical imaging accessory.

In addition Planetary Science on the 5th Floor of Post building also has

*WiTec alpha300* Micro-Raman system equipped with 532 and 632.5 nm lasers.
Confocal Micro-Raman System with Diamond Anvil Cell

Laser excitation wavelengths
488, 514.5 nm (Ar⁺); 671.5, 752.5 nm (Kr⁺)

Kaiser RAMAN RXN1™ Microprobe
Schematics of Kaiser Raman Spectrometer with Microprobe Attachment

- Invictus Near IR Diode Laser 785 nm
- CCD Detector
- Computer
- Spectrograph
- Fiber-optic Probe Head
- FO Cables
- FO cables To spectrometer & laser
- Raman Microscope
Renishaw *InVia* Micro-Raman system

- Laser Excitation Wavelengths Available
  - 244 nm (UV), 514.5 nm (Green) & 830 nm (NIR)
Raman Spectroscopy of Fluid Inclusions

- In synthetic Fe-free basaltic glasses containing CO$_2$, CO fluid inclusions
- In synthetic quartz sample containing CaCl$_2$.xH$_2$O
- CH$_4$ inclusions in olivine crystals

Fluids released from the subducting oceanic lithosphere are generally accepted to cause mantle wedge peridotite melting that produces arc magmas. These fluids have long been considered to be dominated by highly oxidized H$_2$O and CO$_2$ as inferred from erupted arc lavas. This inference is also consistent with the geochemistry of peridotite xenoliths in some arc basalts. We will discuss application of micro-Raman spectroscopy of abundant CH$_4$ + C+H$_2$ fluid inclusions in olivine of a fresh orogenic harzburgite in the Early Paleozoic Qilian suture zone in Northwest China.
## Synthesis conditions for C-O-H fluid bearing Fe-free Baslatic glasses

<table>
<thead>
<tr>
<th>Wt%</th>
<th>Sample</th>
<th>Ptot (MPa)</th>
<th>Temperature (°C)</th>
<th>P(H2) (bars)</th>
<th>H2O (FTIR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ = 54.8</td>
<td>KB3</td>
<td>210</td>
<td>1225</td>
<td>27</td>
<td>0.27</td>
</tr>
<tr>
<td>Al₂O₃ = 21.1</td>
<td>KB8</td>
<td>197</td>
<td>1250</td>
<td>56</td>
<td>1.09</td>
</tr>
<tr>
<td>MgO = 8.1</td>
<td>KB5</td>
<td>210</td>
<td>1225</td>
<td>27</td>
<td>1.09</td>
</tr>
<tr>
<td>CaO = 12.9</td>
<td>KB16</td>
<td>300</td>
<td>1250</td>
<td>40</td>
<td>1.51</td>
</tr>
<tr>
<td>Na₂O = 3.2</td>
<td>KB10</td>
<td>320</td>
<td>1250</td>
<td>62</td>
<td>1.66</td>
</tr>
<tr>
<td>Na¹³CO₃ = 1</td>
<td>KB12</td>
<td>313</td>
<td>1250</td>
<td>17</td>
<td>2.52</td>
</tr>
</tbody>
</table>

*Y. Morziet et al., Chemical Geology, 264 (2009) 58-70.*
Micro-photograph of synthetic Fe-free basaltic glass in equilibrium with COH fluid phase with X60 objective*

<table>
<thead>
<tr>
<th>Sample</th>
<th>H$_2$O (FTIR)</th>
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<tr>
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</tbody>
</table>

Near IR spectra of OH & H2O in synthetic basalt glasses*

The 4500 cm\(^{-1}\) band is assigned to the combination of stretching and bending of structurally bonded OH and the band at 5200 cm\(^{-1}\) to the combination of stretching and bending modes of H2O molecule.

NMR & Raman spectra of fluid inclusions*

KB3: $X(\text{H}_2\text{O}) = 0.004 \pm 0.004$; $X(\text{^{13}CO}_2) = 0.746 \pm 0.021$

KB5: $X(\text{H}_2\text{O}) = 0.044 \pm 0.004$; $X(\text{^{13}CO}_2) = 0.720 \pm 0.021$

KB16: $X(\text{H}_2\text{O}) = 0.071 \pm 0.004$; $X(\text{^{13}CO}_2) = 0.614 \pm 0.015$

Micro-photograph of fluid inclusion CaCl$_2$.xH$_2$O in Quartz at Various Temperatures

A = Antarcticite (CaCl$_6$.6H$_2$O); L = Liquid; V=Vapor

M. Baumgartner and R. J. Bakker, Chemical Geology, 206, 335-344 (2009)
Raman spectra of a fluid inclusion CaCl$_2$.xH$_2$O

Antarcticite (CaCl$_6$.6H$_2$O)
Raman spectra of fluid inclusions in olivine crystals in Harzburgite from North-West China

Confocal micro-Raman spectroscopy of Minerals in Thin Sections

Patricia Fryer¹, Toshio Nozaka², Shiv K. Sharma¹, Pavel Zinin¹ and the IODP Expeditions 304/305/ Scientific Shipboard Party

¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, USA
²Okayama University, Okayama, Japan
To study serpentinized mantle peridotite rocks beneath the Mid-Atlantic Ridge.
Actual rock types recovered from gray region were the opposite, i.e. “relatively anhydrous gabbro with lesser serpentinized peridotite.”
Alteration Characteristics and Rock Types Recovered at IODP Hole 1309D

Expedition 304
- Gabbro
- Olivine gabbro
- Oxide gabbro
- Troctolite
- Peridotite
- Dunitic troctolite
- Leucocratic gabbro

Expedition 305
- Gabbro
- Olivine-bearing gabbro
- Olivine gabbro
- Oxide gabbro
- Troctolite
- Dunitic troctolite
- Leucocratic gabbro
- Microgabbro

Fresher below ~800 m except where heavily veined
Serpentinization Textures in Olivine Gabbro from IODP Site 1309

width of view 5.5 mm, plain-polarized light

width of view 700 µm, cross-polarized light
Raman Spectra of the 3 Main Serpentine Phases:

(Raman spectra from Rinaudo and Gastaldi (2003), Can Min., 41, 883-890.)

Antigorite, $(\text{Mg}_{2.25}, \text{Fe}_{0.75}^{2+})\text{Si}_2\text{O}_5(\text{OH})_4$: Monoclinic
Chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$: Monoclinic; Orthorhombic
Lizardite, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$: Triclinic
Micro-Raman Spectrum of Tremolite Corona in Olivine Gabbro at IODP Site 1390
Thin section #283: U1309D-80R-1W, 110-114cm
Micro-Raman Spectrum of Chlorite Corona in Olivine Gabbro at IODP Site 1390 Thin Section #283: U1309D-80R-1W,110-114

Chlorite (Fe, Mg, Al)$_6$(Si, Al)$_4$O$_{10}$(OH)$_8$
Micro-Raman Spectrum of Plagioclase in Olivine Gabbro, IODP Site 1390
Thin Section #283: U1309D-80R-1W,110-114
Micro-Raman Spectral Mapping of Serpentinized Olivine Grain in Olivine Gabbro at IODP Site 1390 Thin section #281: U1309D-88R-4W, 132-135cm

Blue = Water Bands 
(3663 cm\(^{-1}\))

Green = Olivine 
(823 & 855 cm\(^{-1}\))

Light Orange = Serpentine 
(690 cm\(^{-1}\))
Raman Spectra of Silicate Minerals & of Isochemical Glasses

- Raman spectra of quartz and silica glass at high temperature
- Raman spectra of ortho-silicate M2SiO4 minerals and isochemical glasses (Where M = Mg, Fe \(^{2+}\))
- Raman spectra of pyro-silicate (melilite) crystals and isochemical glasses
- Raman spectra of pyroxene crystals and isochemical glasses
- Raman spectra of glasses along the join M\(_2\)O-SiO\(_2\)
Effect of Heating on Raman Spectrum of $\alpha$-Quartz Crystal
Effect of Heating on Raman Spectrum of Silica Glass

![Raman Spectrum Graph]

- T=1013 K
- SiO₂ Glass
- Intensity (a.u.)
- Raman Shift (cm⁻¹)
- Multiplied by: x1, x10, x10, x10, x1

(Chart showing spectral shifts and heating effects on silica glass.)
Raman Spectra of Mg_2SiO_4 (FO) & Fe_2SiO_4 (FA) Xtal & Glasses
Raman Spectra of Glasses along the Join Fa-Fo
Raman Spectra of Melilite crystals & Glasses

Raman spectra of Al-containing Melilite crystals & Glasses
Effect of T’-O Bond Length on the Intensity of T-O\(^-\) Raman Line in Melilite Xtals
Raman spectra of Pyroxene Xtnals & Glasses

Raman Spectra of CaFeSi$_2$O$_6$ xtal & Glass
Raman Spectra of SiO$_2$- $x$M$_2$O Glasses
M= 5 - 10%

Raman Spectra of SiO$_2$-xM$_2$O Glasses
M= 15 - 20%

Summary

Raman spectroscopy can be used to learn about fluid inclusions in synthetic and natural minerals and glasses.

Raman spectra fingerprints of minerals can be used for positively identifying minerals in thin sections as well as for obtaining mineral maps.

Raman spectroscopy has been useful in understanding structure of silicate melts and glasses.
Reading:

• Franc C. Hawthorne (Editor) Spectroscopy Methods in Mineralogy and Geology. *Reviews in Mineralogy*, 18, pp.698 (1988)
• Raman-IR Mineral Data Bases
  [http://minerals.gps.caltech.edu/files/raman/](http://minerals.gps.caltech.edu/files/raman/) (CalTech)
  [http://rruff.info/](http://rruff.info/) (University of Arizona)