Introduction to Crystal Symmetry and Raman Spectroscopy

José A. Flores Livas

Thursday 13th December, 2012
Outline

Introduction to Raman spectroscopy

Symmetry of crystals and normal modes

Experimental set-up

Calculation of Raman intensities

Example: Raman intensities for Wurtzite-ZnO
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First, what is ... ?

Symmetry
Symmetry is when one shape becomes exactly like another if you flip, slide or turn it. The simplest type of symmetry is “reflection” (mirror symmetry). An “orthogonal” transformation varying orientation.

Spectroscopy
The Science concerned with the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic radiation.

Raman spectroscopy
Spectroscopic technique used to observe vibrational, rotational, and optical quasiparticles in matter.
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Applications

Raman Spectroscopy is used for

✓ Identification of phases (minerals, and composition of materials).
✓ Identification of crystalline polymorphs (Olivine, andalusite, etc).
✓ Measurement of stress in solids, at nanoscale (nanotubes).
✓ High-pressure and High-temperature in-situ studies possible.
✓ Water content of silicate glasses and minerals, liquid phase, etc.
✓ Suitable for biological samples in native state.
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![Identification of real pearls](image1)

![In-situ measurement of Minerals in marine soils](image2)
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![Identification of real pearls](Image)

*In-situ* measurement of Minerals in marine soils

![Graph of Raman Shift vs Wavenumber](Image)
In-situ planetary Raman spectroscopy

Instruments are small enough to fit in a human hand, it is now feasible to apply Raman spectroscopy as a field tool for geology and planetary exploration.\(^1\)

On Mars Surveyor 2003, 2005 and curiosity 2009 missions Spectra were obtained from rocks and soils Martians. Detailed mineralogy information identified trace of minerals and water.\(^2\)


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Spectroscopy of matter with photons

- Incident light
- Reflected
- Transmission
- Scattered light

Mie particles
Rayleigh Particles
Brillouin Acoustic phonons, molecular translations
Raman Quasiparticles: o-phonons, Magnons, etc.
Raman spectroscopy in dates:

1871 Lord Baron-Rayleigh (elastic scattering\textsuperscript{3}) $I \propto 1/\lambda^4$.

1923 Inelastic light scattering is predicted by Adolf Smekal.\textsuperscript{4}

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First measure of an inelastic scattered light (1928)
Origin of the Raman scattering

A exciting wave (electromagnetic radiation) induce a polarization of matter. The induced dipole moment (or its density) is proportional to the electric field of the wave:

$$\vec{P}_\omega(t) = \alpha(\omega) \vec{E}_0 e^{-i\omega t},$$

where $\alpha$ is the (complex) tensor of polarizability (susceptibility). The electronic contribution $\alpha$ depends on the positions $Q$ of the atomic nuclei.

$$\vec{P}_\omega(t, Q) = [\alpha(\omega, Q) I_0 + \frac{\partial \alpha(\omega, Q)}{\partial Q} I_0 Q + \frac{1}{2} \frac{\partial^2 \alpha(\omega, Q)}{\partial Q^2} I_0 Q^2 + ...] \vec{E}_0 e^{-i\omega t}$$

For example the polarizability of the H$_2$ molecule, changes for different inter-atomic distances (see in following slides).
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Origin of the Raman scattering

For a periodic motion of the nuclei with the frequency $\Omega$,

$$Q(t) = Q_m e^{-i\Omega t} + Q_p e^{-i\Omega t},$$

The electric susceptibility splits into a static and a dynamic $Q$-dependent part. The leading terms of the induced moment are,

$$\vec{P}_\omega(t, Q) \approx \alpha(\omega, Q) I_0 \vec{E}_0 e^{-i\omega t} + \frac{1}{2} \frac{\partial \alpha(\omega, Q)}{\partial Q} I_0 \vec{E}_0 [Q_p e^{-i(\omega-\Omega)t} + Q_m e^{-i(\omega+\Omega)t}],$$

containing the unmodified frequency $\omega$, and the sidebands: $\omega - \Omega$ (stokes) and $\omega + \Omega$ (anti-Stokes).
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Selection rules of vibrational modes

Rule of thumb: symmetric = Raman active, asymmetric = IR active
Polarisability tensor matrix

Since $\vec{P}$ and $\vec{E}$ are both vectors, in general for molecules and crystals the correct expression is:

$$
\begin{bmatrix}
P_x \\
P_y \\
P_z
\end{bmatrix} = 
\begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
$$

We plot polarisability ellipsoid: $1/\sqrt{\alpha_i}$

$$
I_{ij} = \int \psi_0 \alpha_{ij} \psi_1 d\Omega \sim \int \psi_0 \chi_i \chi_j \psi_1 d\Omega
$$

$\alpha_{ij} (ij = x, y, z)$ are the components of the polarizability tensor

The transition is Raman active if:

$$
I_{ij} \neq 0
$$
Energy diagrams of scattered light

**Excited electronic states**

- **Virtual states**
  - $\omega$
  - $\omega_i$
  - $\omega_i + \omega_s$

**Electronic ground state**

- **Infrared**
- **Rayleigh**
- **Stokes**
- **anti-Stokes**
- **Fluorescence**

**Excited state**

- **~Linear Raman**
  - $\omega_i$
  - $\omega_i - 2\omega_s$

**Ground state**

- **Resonance Raman**
  - $\omega_i - \omega_s$
- **Hyper-Raman**
  - $2\omega - \omega_s$
- **Coherent anti-Stokes Raman**
  - $\omega_{CARS}$
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Crystal symmetry

Ordered state in which positions of the atom are repeated periodically in space

Translations

14 cells of Bravais

Set of group operations

32 Point group

All symmetry operations + motif

230 crystals

32 Point group

<table>
<thead>
<tr>
<th>Triclinic</th>
<th>Monoclinic</th>
<th>Trigonal (Rhombohedral)</th>
<th>Tetragonal</th>
<th>Hexagonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>C2</td>
<td>2</td>
<td>C3</td>
<td>3</td>
<td>C4</td>
</tr>
<tr>
<td>Ci</td>
<td>C5</td>
<td>m</td>
<td>C3h</td>
<td>3</td>
<td>C4h</td>
</tr>
<tr>
<td>C2h</td>
<td>mm2</td>
<td>2/m</td>
<td>C3v</td>
<td>3m</td>
<td>C4v</td>
</tr>
<tr>
<td>D_2</td>
<td>222</td>
<td>D_3</td>
<td>32</td>
<td>3m</td>
<td>D_4</td>
</tr>
<tr>
<td>D_2h</td>
<td>mmm</td>
<td></td>
<td></td>
<td></td>
<td>D_4h</td>
</tr>
</tbody>
</table>

Symmetry operations

<table>
<thead>
<tr>
<th>Symmetry element</th>
<th>International (Hermann-Mauguin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity</td>
<td>1</td>
</tr>
<tr>
<td>Rotation axes</td>
<td>n = 1, 2, 3, 4, 6</td>
</tr>
<tr>
<td>Mirror planes</td>
<td>m</td>
</tr>
<tr>
<td>⊥ to n-fold axis</td>
<td>m, m_n</td>
</tr>
<tr>
<td>∥ to n-fold axis</td>
<td>m_n, m'</td>
</tr>
<tr>
<td>bisecting (∠2,2)</td>
<td>m_d, m'_</td>
</tr>
<tr>
<td>Inversion</td>
<td>T_1</td>
</tr>
<tr>
<td>Roto inversion axes</td>
<td>n = 1,2,3,4,6</td>
</tr>
<tr>
<td>Translation</td>
<td>t_n</td>
</tr>
<tr>
<td>Screw axes</td>
<td>n_k</td>
</tr>
<tr>
<td>Glide planes</td>
<td>a, b, c, n, d</td>
</tr>
</tbody>
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Phonon symmetry in crystals

The phonon symmetry description in crystals is given by the analysis of the eigenvector \( \{ e(\kappa|k_i) \} \), obtained from the dynamical matrix:

\[
\{ D_{\alpha\beta}(\kappa\kappa'|k) \}
\]

Is the displacement pattern of the atoms vibrating in the mode \( (k_i) \). Knowledge of the forms of these eigenvectors and of their transformation properties under the symmetry operations is often useful for the solution of certain types of lattice dynamical problems.\(^7\) Among:

- Selection rules for processes such as two-phonon lattice.
- Absorption and the second-order Raman effect (or higher order).
- Phonon-assisted electronic transitions.

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The phonon symmetry description in crystals is given by the analysis of the eigenvector \( \{ e(\kappa|\mathbf{k}i) \} \), obtained from the dynamical matrix:

\[
\{ D_{\alpha\beta}(\kappa\kappa'|\mathbf{k}) \}
\]

Is the displacement pattern of the atoms vibrating in the mode \((\mathbf{k}i)\). Knowledge of the forms of these eigenvectors and of their transformation properties under the symmetry operations is often useful for the solution of certain types of lattice dynamical problems.\(^7\) Among:

- Selection rules for processes such as two-phonon lattice.
- Absorption and the second-order Raman effect (or higher order).
- Phonon-assisted electronic transitions.

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Character table: IR, Rmn and H-Raman modes

and choose space group and Wyckoff Positions of the atoms: 1a and 2d, spgrp 164

<table>
<thead>
<tr>
<th>Point group</th>
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<th>-1</th>
<th>-3</th>
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Symmetry operation

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<td>A_{2g}</td>
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<td>E_{g}</td>
<td>$\Gamma_3^+$</td>
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<td>A_{1u}</td>
<td>$\Gamma_1^-$</td>
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<td>-</td>
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<tr>
<td>Raman</td>
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<th>Matrix form</th>
<th>Geometrical interpretation</th>
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<td>x,y,z</td>
<td>(1 0 0)</td>
<td>1</td>
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<tr>
<td>2</td>
<td>-y,-x,z</td>
<td>(0 -1 0)</td>
<td>$3'$, 0,2</td>
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<td>3</td>
<td>-3+y,-x,z</td>
<td>(-1 -1 0)</td>
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</table>
Assignment of normal modes

The Bravais lattice is hP (primitive hexagonal) Point Group: D3d^3

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<tr>
<th>mode</th>
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<th>symmetry operation no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<th>6</th>
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<td>0.0</td>
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<td>1.0</td>
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<tr>
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<td>2 is an inversion</td>
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<td>0.0</td>
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<td>0.0</td>
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Label:
- Operations
- acoustic
- Eu
- A2u
- Alg
- Eg
Mulliken symbols

**A, B** Non-degenerate (single) mode: one set of atom displacements. Subscripts g and u: symmetric or a-symmetric to inversion $-1$.

**E** Doubly degenerate mode. Two sets of atom displacements. Superscripts ’ and “: symmetric or anti-symmetric to a $m$.

**T** Triply degenerate mode. Three sets of atom displacements. Subscripts 1 and 2: symmetric or anti-symmetric to $m$ or $C_n$. 

---

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On summary for Raman scattering

1. Synthesis and experimental XRD
2. Crystal structure
3. Theoretical structure
4. Crystal prediction ask Max!
5. Raman scattering measurements
   - I got peaks... or something...
   - do you have A or B?
   - A: Single crystal and high performance Raman exp. you are happy!
   - B: Polycrystalline and standard Raman exp. you still having only peaks...
6. Selection rule determination at the Brillouin zone centre (3 methods)
    - Space group and W. positons Mechanical representation
    - IR, Raman and Hyper Raman modes!
    - From selection rule Raman tensor matrix
8. Zone centre Phonon calculation
   - Ab-initio calculation of Raman tensor matrix.
   - Compare results from both ways. But careful with theoretical drawbacks, and the underlying physics of the experiment.
# Table of contents

- Introduction to Raman spectroscopy
- Symmetry of crystals and normal modes
- Experimental set-up
- Calculation of Raman intensities
- Example: Raman intensities for Wurtzite-ZnO
Experimental set-up

- **Mirror**
- **Laser** (electric power $10^3$ Watt)
- **Sample**
- **Collimating lens**
- **Notch filter**
- **Monochromators and slits**
- **Spectrograph, CCD, etc.**

**Violet (mercury lamp)**
- 4358 Å, 22933 (1/cm)

**Green (ionised Ar)**
- 4880 Å, 20492 (1/cm)

**Red (laser He-Ne)**
- 6328 Å, 15803 (1/cm)

**Infra-red (laser Nd-YAG)**
- 10640 Å, 9392 (1/cm)
Experimental geometry: Porto notation

Raman intensity

\[ I \propto (\alpha_{\alpha\beta})^2 \]

Directions of the propagation of incident (i) and scattered (s) light

Directions of the polarisation of incident (i) and scattered (s) light

**Geometry**

Backscattering (180°)

**Sample**

\[ k_i (E_i, E_s) k_s \]

\( (q_x, 0, 0) \)

**Laser**

\[ \bar{X}(YY)X \]

\[ \bar{X}(YZ)X \]

\[ \bar{X}(ZZ)X \]

\[ E_i \parallel E_s \]

\[ E_i \parallel / E_s \]

\[ E_i \parallel / / E_s \]

\[ \alpha_{YY} \]

\[ \alpha_{YZ} \]

\[ \alpha_{ZZ} \]

\[ \alpha_{\alpha\beta}^n \]

n: X= LO and Y,Z = TO

**Polarisation**

Right angle

\[ k_i = k_s + q, \text{ E is always } \perp \text{ to } k \]
Example for cubic crystals

Polarisability matrix or Raman tensor

\[
\begin{align*}
T_d(\bar{4}3m) & = \\
\begin{pmatrix}
(a & \cdot & \cdot) \\
\cdot & (a & b) \\
\cdot & \cdot & (b & -2b)
\end{pmatrix} \\
(a & \cdot & \cdot) \\
\cdot & (b & \cdot) \\
\cdot & \cdot & (d & \cdot)
\end{pmatrix}
\end{align*}
\]

Geometry

Sample

Laser

Polarisation

Porto

Mode

Backscattering

(180°)

\[q = (0, 0, q_z)\]

\[q = (q_x, 0, q_z)\]
Table of contents

Introduction to Raman spectroscopy

Symmetry of crystals and normal modes

Experimental set-up

Calculation of Raman intensities

Example: Raman intensities for Wurtzite-ZnO
Using Kramers-Kroing relation

Born and Huang derived\(^8\) an expression which reduces the computation of the integral Raman intensities to the evaluation of the imaginary part of the linear Raman susceptibility.\(^9\)

\[
I_{i,\gamma\beta} = \frac{2\pi\hbar(\omega_L - \omega_i)^4}{c^4\omega_i} \left[n(\omega_i) - 1\right]\left(\alpha_{i,\gamma\beta}\right)^2, \quad (1)
\]

polarisation along \(\gamma\), and field along \(\beta\), for the \(i\)-mode, \(\omega_L\) is the laser frequency of excitation source, and the Bose occupation number

\[
n(\omega) - 1 = \left[1 - e^{\left(\frac{-\hbar\omega_i}{k_B T}\right)}\right]^{-1}
\]

where \(\omega_i\) the frequency of mode \(i\) and \(k_B\) the Boltzmann constant. The Raman susceptibility tensor \((\alpha_{i,\gamma\beta})\) is then, defined as

Calculation of Raman intensities

\[ \alpha_{i,\gamma\beta} = \frac{\sqrt{\Omega}}{4\pi} \sum_{n\gamma i} R_{i\alpha\beta, n\gamma} e_{i\gamma} M_n^{-1/2} \], \quad R_{i\gamma\beta, n\nu} = \frac{\partial \epsilon_{\gamma\beta}(\omega_L)}{\partial u_{i\nu}}. \]

\(M_n\) mass, \(e_{i\gamma}\) eigenvector and \(\Omega\) unit cell volume. Two cases: a) For single crystal Eq. 1 is applicable. b) For poly-crystal, an average (using the ellipsoid) of intensity.\(^{10}\) Reduced intensity for polarised \(\parallel\) and depolarised \(\perp\) light (backscattering) is,

\[ I_{i\parallel}^{\text{poly}} \sim (\omega_L - \omega_i)^4 \left[ 1 + n(\omega_i)/30\omega_i \right] \left[ 10G_i^{(0)} + 4G_i^{(2)} \right] , \]

\[ I_{i\perp}^{\text{depol}} \sim (\omega_L - \omega_i)^4 \left[ 1 + n(\omega_i)/30\omega_i \right] \left[ 5G_i^{(1)} + 3G_i^{(2)} \right] , \]

\[ I_{i,\text{sum}}^{\text{reduced}} = I_{i\parallel}^{\text{poly}} + I_{i\perp}^{\text{depol}} \quad \text{and} \quad I_i^{\text{ratio}} = \frac{I_{i\parallel}^{\text{poly}}}{I_{i\perp}^{\text{depol}}} \]

\(^{10}\)Poilblanc et Crasnier, ”Spectroscopies Infrarouge et Raman“ (2006).
Calculation of Raman intensities

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On summary for the *ab initio* calculation:

Third-order derivatives of the energy can be calculated

- DFPT for $\chi +$ Frozen phonon (finite differences).
- DFPT using $(2n + 1)$ theorem. The $th$ derivative of energy depends only on derivatives up to order $n$ of the charge density.
- DFPT + second-order response to electric field.
- Finite electric fields + frozen phonon.

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Calculation of Raman intensities

Example: Raman intensities for Wurtzite-ZnO
The case of Wurtzite-ZnO

Example for a single crystal of wurtzite

Hexagonal system:

\[ P6_3mc \]

\[ C_{6v}^4 \]

Raman tensor

\[
\begin{pmatrix}
  a & . & . \\
  . & a & . \\
  . & . & b \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
  d & . & . \\
  . & d & . \\
  . & . & . \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
  . & . & c \\
  . & . & . \\
  . & . & c \\
\end{pmatrix}
\]

Zinc

Oxygen

Polar: LO-TO splitting

Non-polar: no LO-TO splitting

Displacement \parallel c-axis

A and B modes

Displacement \perp c-axis

E modes

Right angle

\[ k_s \]

\[ k_i \]
Polycrystalline Wurtzite-ZnO

Exp.
Polycrystalline sample of ZnO measured at room temperature (green excitation).

Sim.
Ab-initio calculation using DFT with pseudopotentials, plane-wave code. LDA calculations. k-mesh of 16x16x16. Optimized volume: \(a = 3.198, \ c = 5.166\)
Linera-response phonon calculation within DFPT. ABINIT

Experiment: Marcel Schumm
PhD. Thesis at Julius Maximilians Universitat.
Single crystal of ZnO aligned on X(YX)Z

Exp.

Sim.
Our work

Note the ratio between intensities

2 order

437

101

440

91
Single crystal of ZnO aligned on X(YY)Z

**Exp.**

*Porto et al. Phys. Rev. 142, 570-574 (1966)*

**Sim.**

*Our work*
General comments

✓ IR: induced dipole moment due to the change in the atomic positions.
✓ Raman: induced dipole moment due to deformation of the e-shell.
✓ Simultaneous IR and Raman, only in non-centrosymmetric structures.

Further reading

• Transformation of polarizability tensors.
• Disorder effects on Raman peaks.
• Temperature dependence of the Raman scattering.
• Phonon lifetimes and linewidths ($\Gamma_i$).
• Fröhlich interactions (shape of response) anharmonic effects.
• Fluctuations of the spin density: Magnon.

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