Outline

- A. Theory of Raman Effect
- B. Construction of Raman Spectroscopy
- C. How to USE and ANALYSIS Data
- D. The Microscopy
- E. Mapping and other development
A. Theory of Raman Effect

- A phenomenon, results from the interaction of light and matter
- The effect was predicted in 1923 by Adolf Smekal
- The effect was discovered in 1928 by C. V. Raman
A. Theory of Raman Effect

Elastic Scattering: Rayleigh (Mie-Tyndall) Scattering

Inelastic Scattering: Raman (Brillouin) Scattering
A. Theory of Raman Effect

- **Stokes Raman scattering:** the material absorbs energy and the emitted photon has a lower energy than the absorbed photon.

- **Anti-Stokes Raman scattering:** the material loses energy and the emitted photon has a higher energy than the absorbed photon.

Raman Shift: \( \Delta \nu = \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \)

Raman Microscopy, 1996, G. Turrell & J. Corset
A. Theory of Raman Effect

Like IR, Raman is a kind of vibrational spectroscopy assessing molecular motion.

Routine energy range (wavenumber): 200 - 4000 cm$^{-1}$. (IR is 600-4000cm$^{-1}$)

Selection rules dictate which molecular vibrations are probed. Some vibrational modes are both IR and Raman active. Symmetry dictates which are active in Raman and IR.

Selection rules related to symmetry: symmetric=Raman active, asymmetric=IR active
B. Construction

- 1. Excitation source (Mainly, laser)
- 2. Sample illumination system and light collection optics
- 3. Wavelength selector (Filter or spectrophotometer)
- 4. Detector (Photodiode array CCD or PMT)

http://www.chem.umd.edu/wp-content/uploads/2014/01/RamanSpectroscopy-300x221.jpg
B. Laser source

- **Best suited Laser wavelength** - The correct selection of the laser wavelength can be an important consideration for Raman spectroscopy. With modern equipment, often several laser wavelengths may be employed so as to achieve the best detection of the Raman signal.

  - NIR (near infrared red laser) - 785 nm: Fluorescence less probable; Lower Raman signal.
  - 514 nm (Green): Fluorescence more probable, resonance more likely and higher signal.

- Most Raman spectroscope use high energy laser, which could destroy polymer materials.
B. Commercial equipment

TruScan™ RM Material Verification Analyzer

The TruScan RM Raman spectrometer for raw material identification and finished product inspection delivers reliable analysis in seconds, right at the point-of-need, to decrease sampling costs and increase inventory turns.

DXRxi Raman imaging microscope

Designed to quickly reveal molecular structure, chemical composition and sample morphology, the Raman imaging microscope can provide new insights, identify defects and confirm product quality with a high degree of confidence. By employing the image-centric software interface, users can quickly profile materials through information-rich chemical images.

B. Commercial equipment

RENISHAW Raman Microscopy

Renishaw inVia microscope
High sensitivity ultra low noise RenCam CCD detector
Multiple lasers on hand (514nm, 633nm, 647nm, 785nm)
< 1 cm-1 spectral resolution capability
Supporting sampling accessories such as fiber optic probes
and temperature control stages (liq. He – 300ºC) are available.
Automated XYZ stage with 100nm positioning control

Jobin-Yvon T64000 Raman spectrometer

640 mm focal length: 0.7 cm-1 spectral resolution
CCD detector: high-sensitivity, low noise detector
Confocal micro-Raman setup: lateral resolution about 1 um
Cryostat: for low temperature measurements in macrocamera configuration
Freeze-drying cryostage: for micro-Raman measurements to be carried out from liquid nitrogen temperature up to 600 oC
C. How to use

- Raman Spectroscope is very easy to use, just like normal IR
- Sample could be any form
- Put sample inside as specific instruction
- Scan background
- Scan sample
- Done.
C. Calibration

- Internal Standards: no greater than 1cm$^{-1}$
- Indene: on the order of 0.5cm$^{-1}$
- Laser plasma lines: better than 1cm$^{-1}$
- Ne emission lines: While using Ar-ion laser (energy is higher than 175000cm$^{-1}$)
C. DATA analysis

1. Decomposition of Nylon
2. Spectroscopic analyses of a’ and a crystalline forms of poly(L-lactic acid)
C. Decomposition of Nylon-6,6
C. Decomposition of Nylon-6,6

<table>
<thead>
<tr>
<th>Proposed Nylon 6,6 degradation products</th>
<th>Examples</th>
<th>References</th>
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<tr>
<td>pyrrolyls</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>31</td>
</tr>
</tbody>
</table>
C. Spectroscopic analyses of $\alpha'$ and $\alpha$ crystalline forms of poly(L-lactic acid)

Lattice structure of poly(L-lactic acid)

Difference between 2 crystal forms are significantly small

Above 120°C, $\alpha$ form will occurs
Below 120°C, $\alpha'$ form will occurs
C. Spectroscopic analyses of \( \alpha' \) and \( \alpha \) crystalline forms of poly(L-lactic acid)
C. Spectroscopic analyses of $\alpha'$ and $\alpha$ crystalline forms of poly(L-lactic acid)

Transform of polymer chains accompany with change of vibration and dipole moment. Raman spectroscopy is about vibration and dipole moment, and it is sensitive to symmetric structure.

Raman is sensitive to chain conformation
D. Raman Microscopy

- Refer to Microscope, Raman microscopy just as visible light microscope. However, it could not only use visible light.
- Include laser source, focus lens, mirrors, analyzers and detectors.
D. Raman Microscopy

While excitation source, laser beam, is focused, this high energy beam might burn out normal polymer sample.
Raman imaging methods can be classified in two categories:
1. parallel or direct-imaging
2. series-imaging
E. Imaging

- The **direct imaging** results in the immediate production of a complete 2D image at a chosen wavelength which is characteristic of a molecular compound within the fully illuminated specimen.

- The **series-imaging** require image reconstruction which is achieved either by scanning the sample with a finely focused laser beam or by encoding with a mask the image of the sample illuminated by an expanded laser beam.
As a demonstration of high resolution Raman confocal imaging on mesostructured polymer thin films, both Atomic Force microscopy surface topography and Raman images were conducted on superimposed surface relief gratings with a periodicity of \(~1 \mu m\).
Summary

1. Available for solid, liquid and even gas. No sample preparation, Not interfered by water.
2. Unlike IR, Raman is based on inelastic scattering. Normally regard as a supplemental method of IR.
3. Advantage than IR, Raman spectroscopy is conformational sensitive. Such as spiral conformation of polymer chains.
4. Quickly within seconds and highly specific like chemical fingerprint.
5. Sensitive would not decrease while analyzing very small volume
6. Some high energy excitation source may burn polymer sample.
7. Light source should be selected due to fluorescence of sample might hide the Raman spectrum.
Reference

- Raman Spectroscopy for soft material applications. Maher S. Amer. Wiley
- Laboratory Raman Spectroscopy. Dennis P. Strommen & Kazuo Nakamoto. Wiley
- Raman, Infrared, And Near-Infrared Chemical Imaging. Slobodan Sasic & Yukihiro Ozaki. Wiley
- Raman Imaging, Techniques and Applications. Arnaud Zoubir. Springer
- Spectroscopic and thermal analyses of α0 and a crystalline forms of poly(L-lactic acid). Jeffrey P. Kalish, Kaoru Aou, Xiaozhen Yang, Shaw Lin Hsu. Polymer 52 (2011) 814e821