FT-Raman Spectroscopy at Dalhousie University

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Instrument available for use as part of the
IRM Facilities for Materials Characterization

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FT-Raman set-up

- Nicolet NXR 9650 FT-Raman spectrometer, 2013 installation
- Key features:
  - Nd:YVO_4 1064 nm laser
  - two detectors:
    - InGaAs
    - Ge (inc. sensitivity)
  - spectral range: 4000 cm^{-1} to 50 cm^{-1}
  - up to 1 cm^{-1} resolution
  - variable temperature cell (-150 to 150 °C)
  - depolarization accessory

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Advantage of this set-up

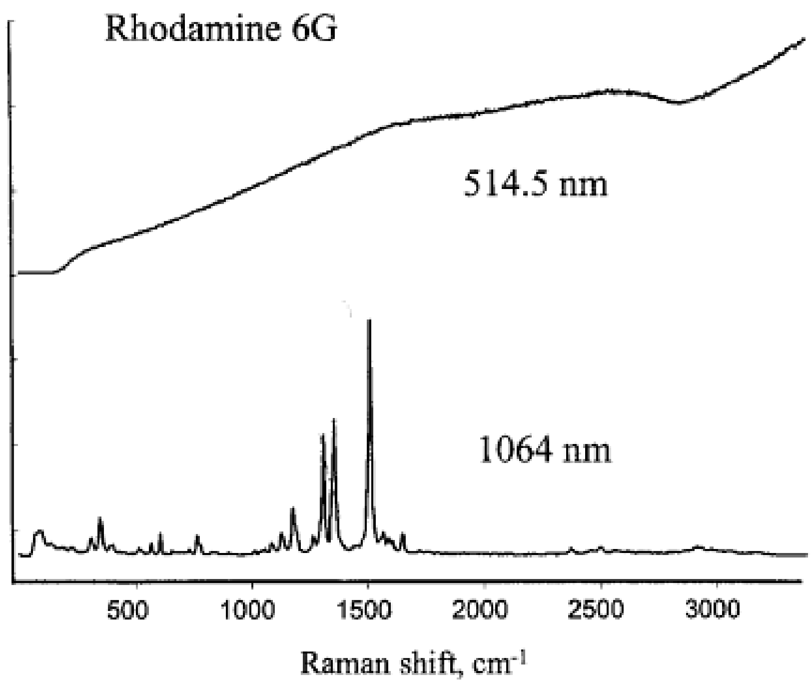

Figure 1.5 from Raman Spectroscopy for Chemical Analysis by Richard L. McCreery highlighting the effect of laser power on signal.

- High energy lasers excite valence e^- to an excited state (e^*) where on relaxation, energy can be released as fluorescence.
- However, the 1064 nm laser does not fully excite e^- and hence reduces fluorescence.
- **Result: Raman signal, with much improved baseline.**

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Sample morphologies

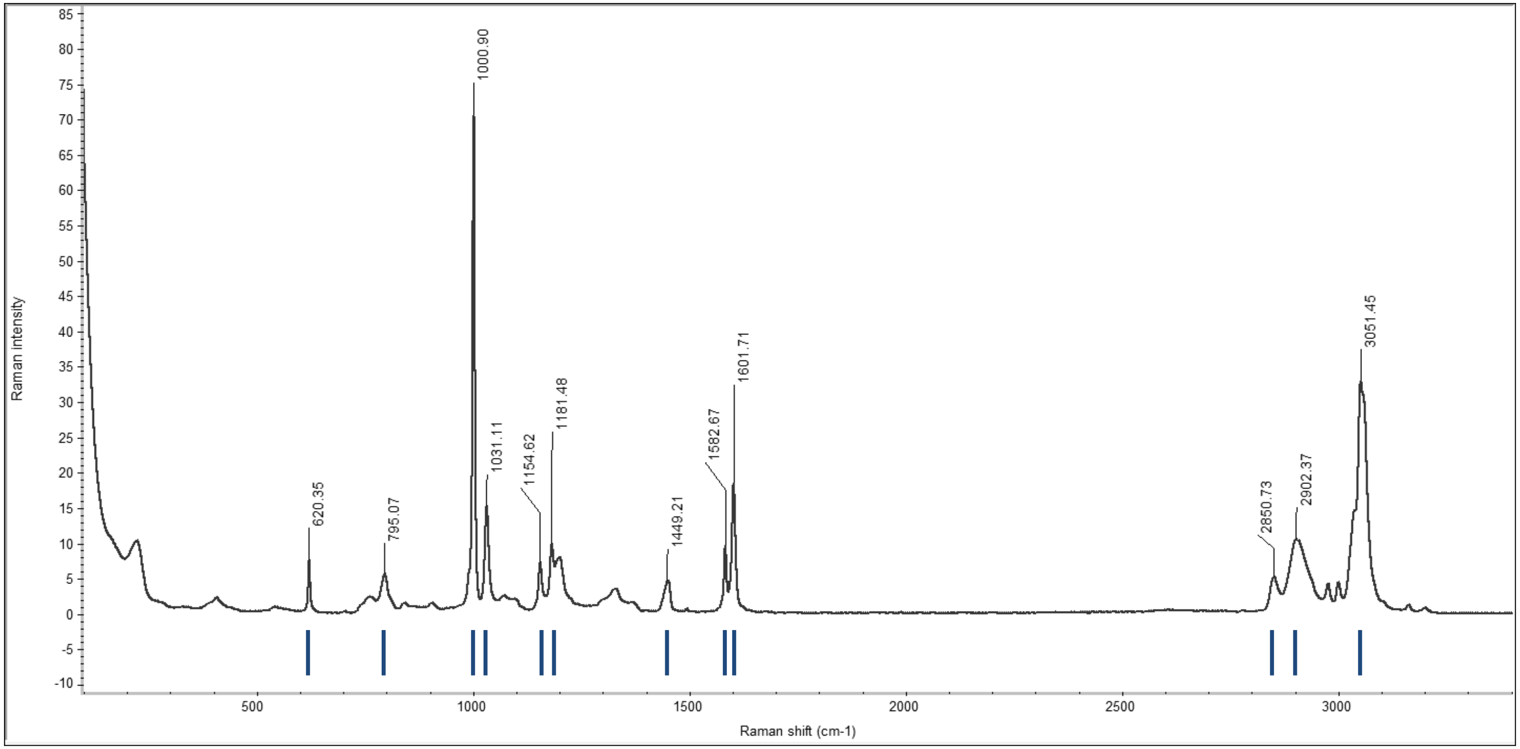
- Sample sizes for analysis can be a few milligrams up to tens of grams.
- Sample morphology for FT-Raman are solid, liquid, and gel samples.
  - Solid samples include powders, glasses, metals, crystals, and films.
- Air sensitive samples can be analyzed in sealed NMR or melting point tubes.
- Various sample holders are available to easily mount prepared samples
- After FT-Raman analysis, the sample is recoverable and can be used for further experiments.

Applications

- Raman spectroscopy is a good complement to infrared spectroscopy and has similar applications:
  - Materials science
    - Composition analysis, vibrational spectroscopy, phase transitions
  - Pharmaceuticals
    - Polymorphs, crystallinity, phase transitions
  - Geology/mineralogy
    - Gemstone ID, phase transitions
  - Petrochemistry
    - Polymer characterization
  - Semiconductors
    - Purity, doping effects
  - And many more including arts, archeology, nuclear science, biological science

Instrument validation - 1

- Polystyrene is used as a standard material for signal observation
  - Good agreement (blue lines; key peaks) with ASTM protocols[1]



[1]ASTM E1840: Raman Shifts Standards for Spectrometer Calibration

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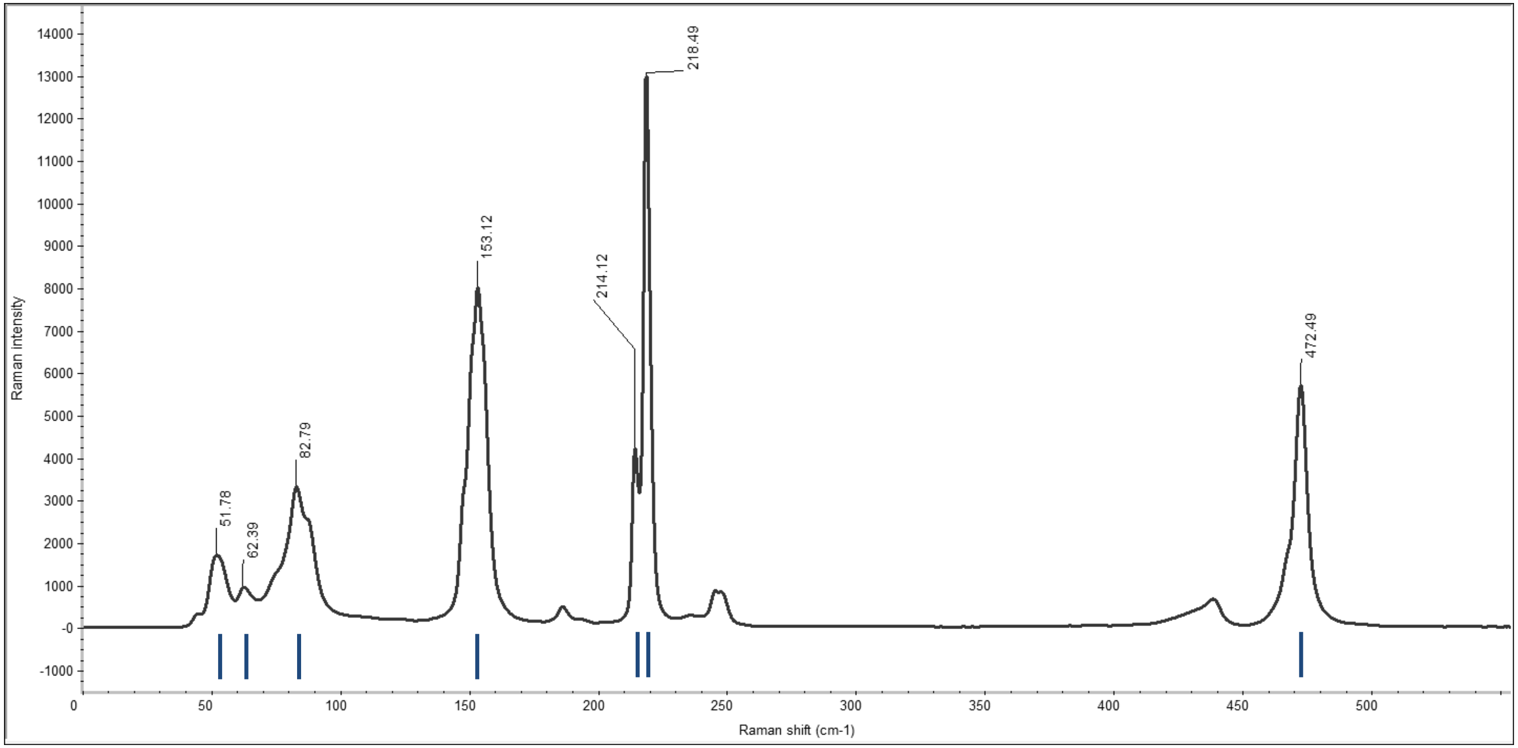
Instrument validation - 2

- Sulfur was also used as a standard material for signal observation
  - Good agreement (blue lines; key peaks) with ASTM protocols[1]



[1]ASTM E1840: Raman Shifts Standards for Spectrometer Calibration

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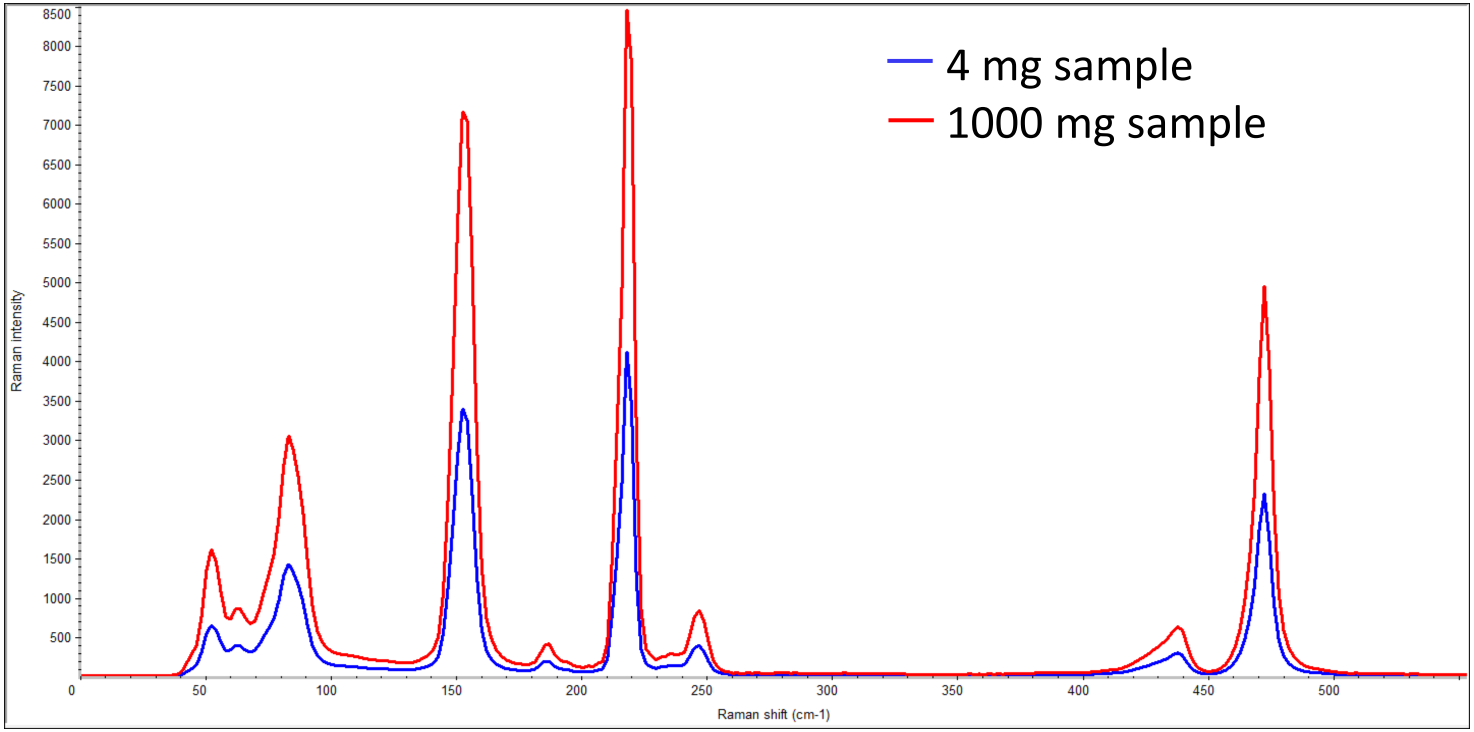
Instrument validation - 3

- The signal-to-noise sensitivity of the instrument was investigated by measuring a 4 mg sulfur sample
  - Smaller signal compared with bulk sulfur, but still well above noise of the instrument.



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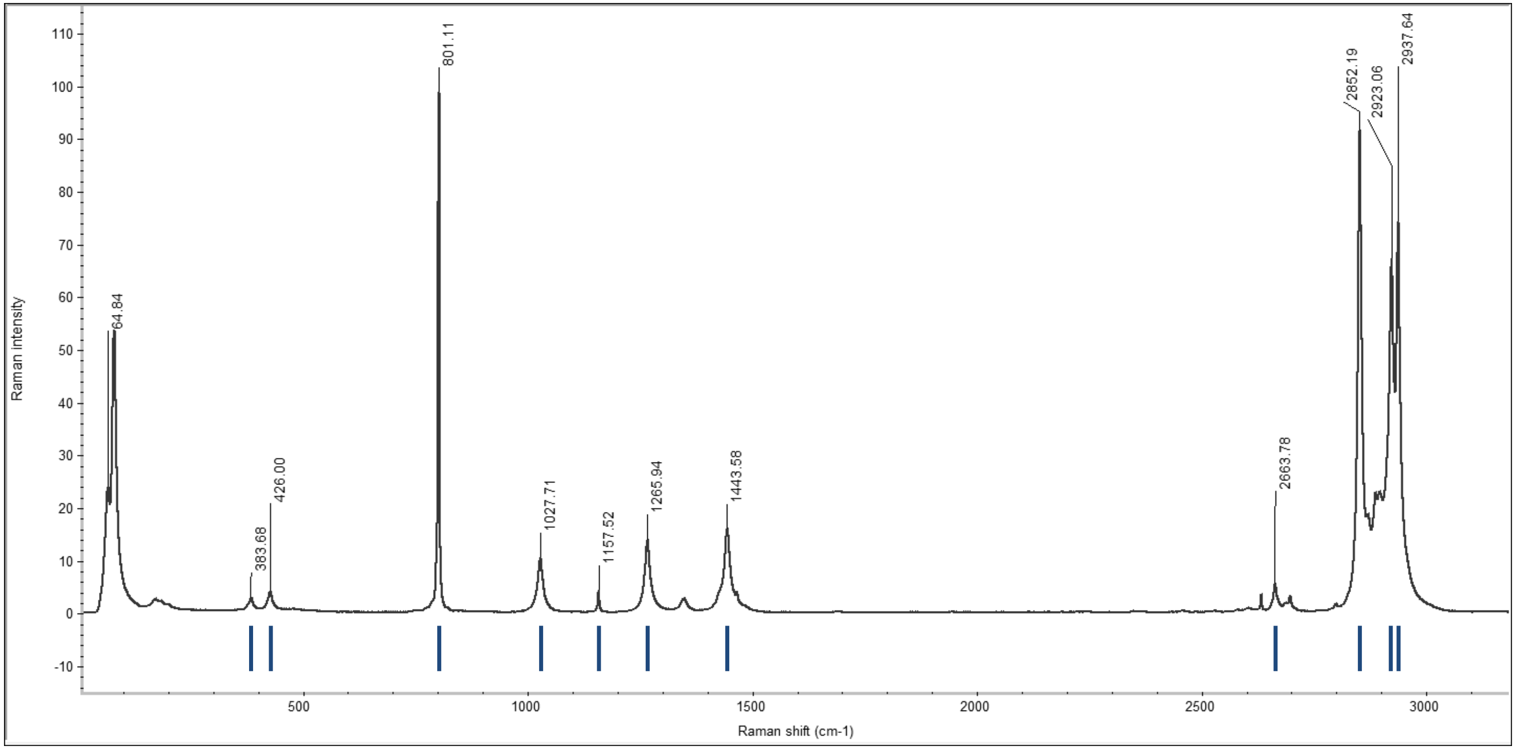
Instrument validation - 4

- Cyclohexane was also used as a standard material for signal observation
  - Good agreement (blue lines; key peaks) with ASTM protocols[1]



[1]ASTM E1840: Raman Shifts Standards for Spectrometer Calibration

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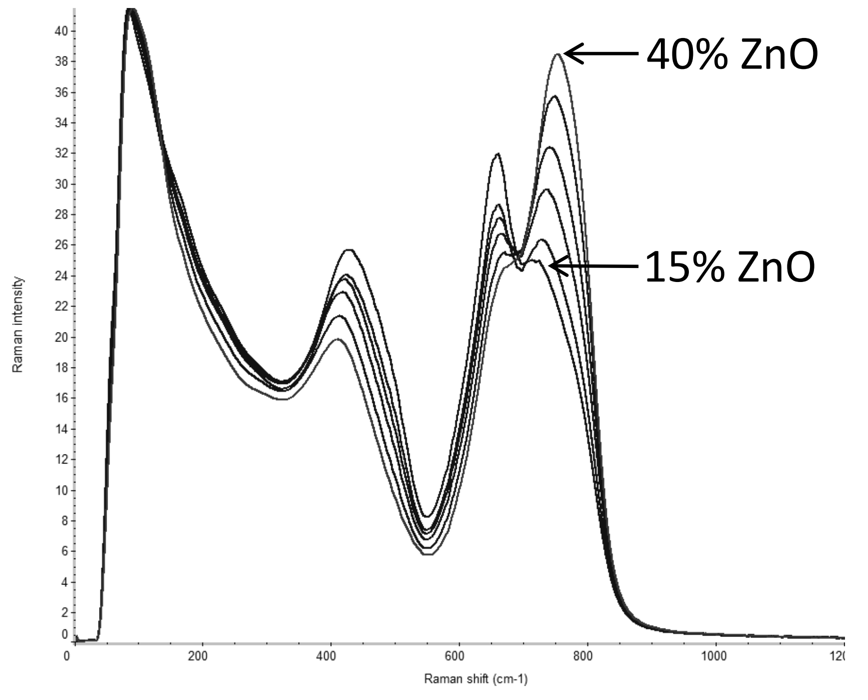
Experimental case: glasses

- A series of glasses containing ZnO/TeO_2 were analyzed by FT-Raman[2]
- As the amount of ZnO is increased from 15% to 40%:
  - Peaks at 425 cm^{-1} and 625 cm^{-1} decrease while peak at 775 cm^{-1} increases
  - Characteristic of telluride environment with 3 or 4 oxygen atoms surrounding it[3]



[2]Data unpublished
[3]V. G. Plotnichenko *et al.*, *Optic Letters*, **30**, 1156 (2005)

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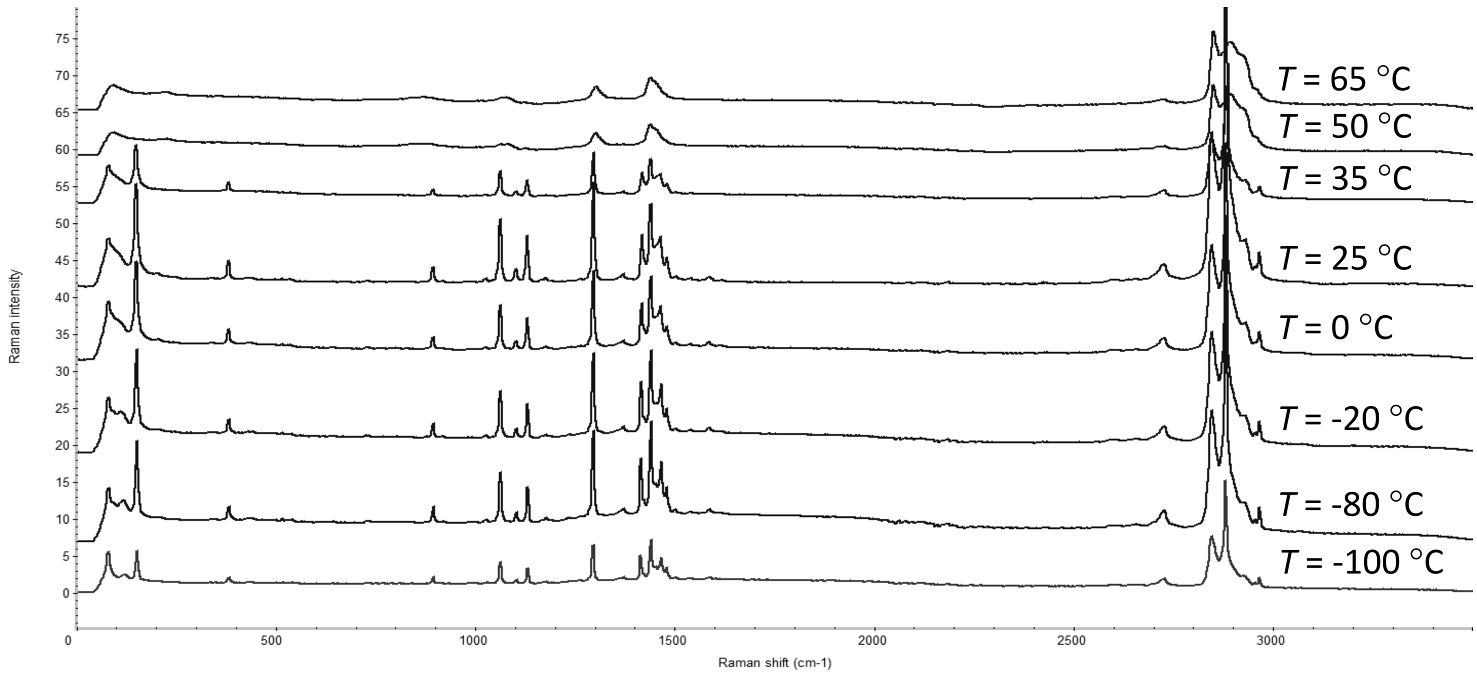
Variable temperature

- Mixture of crystal violet lactone and lauric acid was investigated on cooling[4]
  - Observe gain of crystallinity (sharp signals), characteristic of liquid-to-solid transitions
  - no new phases observed down to -100 °C



[4]Data unpublished, test material

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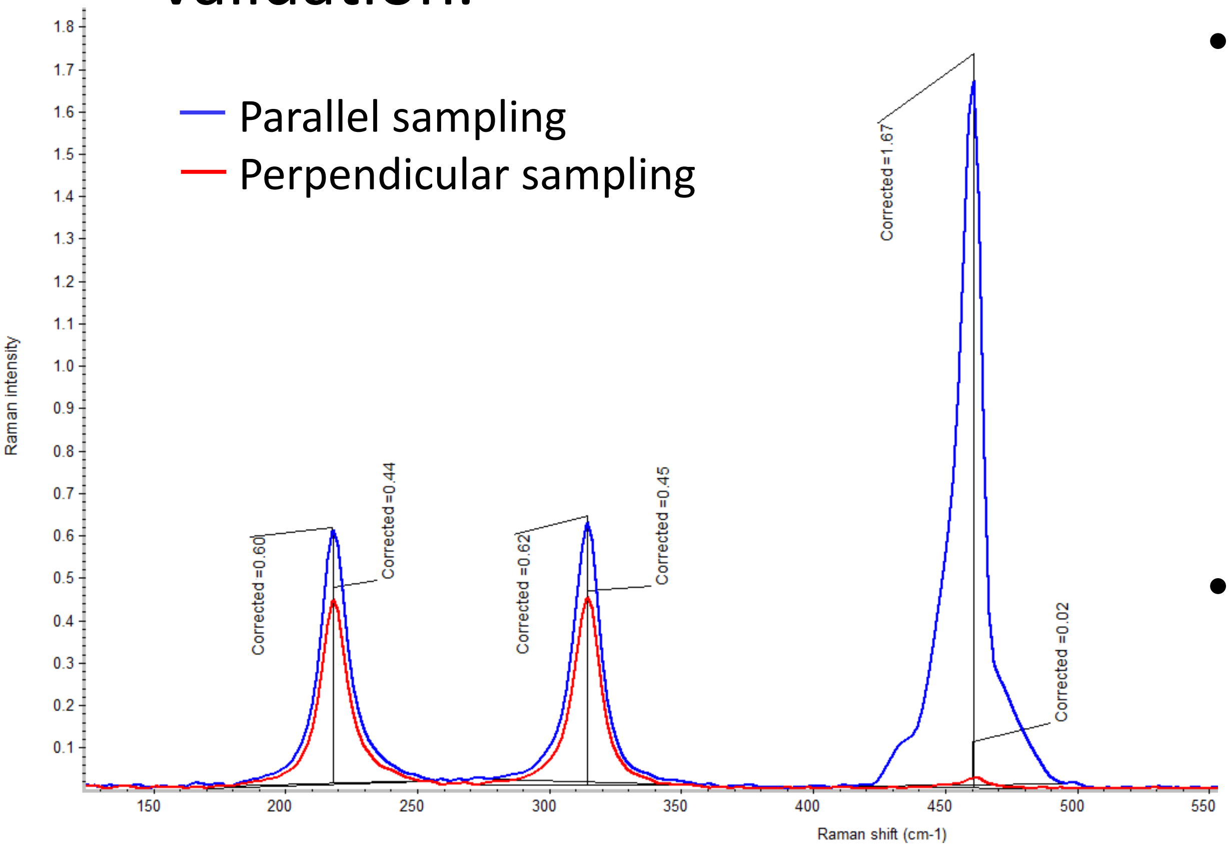
Depolarization

- CCl_4 was used as a standard test for depolarization validation.[5]



- Area ratio of 3 peaks analyzed in parallel and perpendicular configuration:
  - ρ_{220}=0.73
  - ρ_{315}=0.73
  - ρ_{460}=0.01
- Good agreement with reference 5

[5]T. Chakraborty *et al. Spectrochimica Acta, Part A* **62**, 438 (2005).

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