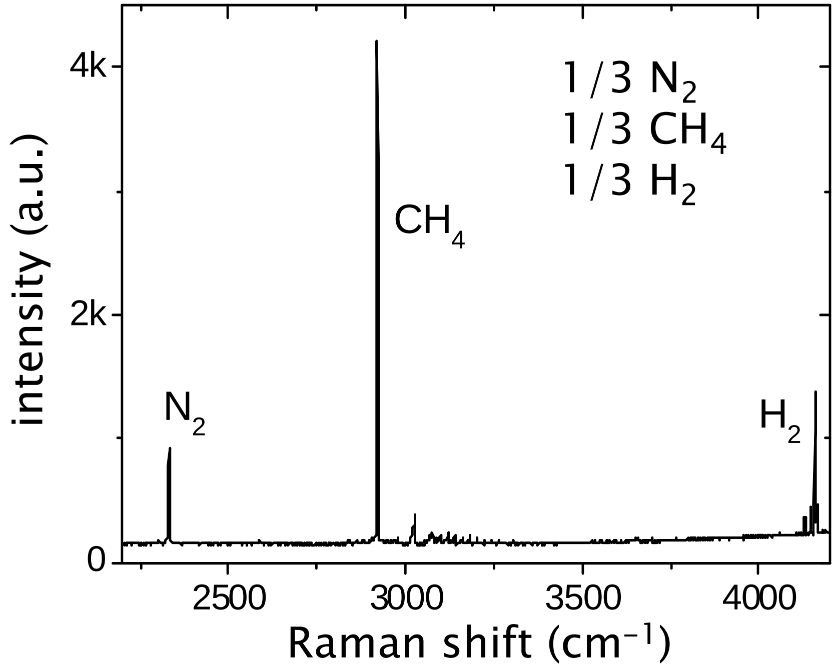
Instrumentation in Raman spectroscopy, part 2: how to calibrate your spectrometer.

Jean Dubessy, Marie-Camille Caumon,
Shiv Sharma, Fernando Rull

Introduction

- Raman spectroscopy provides information on:
  - Molecules or minerals and their physical-chemical environment
  - Quantities or proportions of each compound
  - Geometry (crystal)
  - Spatial arrangement



- Expected information:
  - Number of peaks
  - Peak position (Raman shift, cm^{-1})
  - Peak intensity (relative or absolute)
  - Spatial positioning (x, y, z)

Introduction

- Required to know:
  - Spectral resolution
  - Raman shift wavenumber accuracy and precision
  - Intensity response of the device used (spectrometer, optics, sampling system)
  - Confocality (z: axial resolution)
  - Spatial resolution (x, y: lateral resolution)
- Depend on:
  - Optics (mirrors, objectives, optical geometry)
  - Spectrometer (grating, detector, focal length of the spectrometer, slit and confocal apertures)
  - Excitation wavelength (laser)
  - Time
  - Temperature

Must be determined at least once but more often depending on:
- Time stability of the device
- Required precision and accuracy

Outline

1. Raman shift wavenumber calibration:
   - Detector
   - Laser
2. Raman intensity calibration:
   - spectrometer response
   - cross section
3. Spectral resolution
4. Confocality: axial resolution
5. Spatial resolution : lateral resolution

Outline

1. Raman shift wavenumber calibration:
    - Detector
    - Laser
2. Raman intensity calibration:
    - spectrometer response
    - cross section
3. Spectral resolution
4. Confocality: axial resolution
5. Spatial resolution : lateral resolution

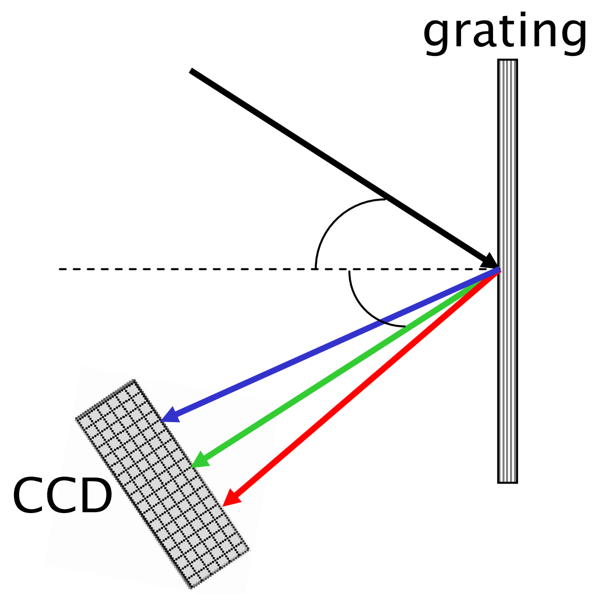
1. Raman shift wavenumber

- Raman shift wavenumber $\overline{\nu_{R,j}}$ depends on laser wavelength:

$$\lambda_{R,j} = \frac{1}{\overline{\nu_{R,j}^{abs}}} = \frac{1}{\overline{\nu_0} - \overline{\nu_{R,j}}}$$

$$\overline{\nu_{R,j}} = \frac{1}{\lambda_0} - \frac{1}{\lambda_{R,j}}$$

- Raman wavelength $\lambda_{R,j}$ scattering by grating :



Parameters to be known:

- CCD pixels' correspondence to wavelength and grating position
- Exact laser wavelength

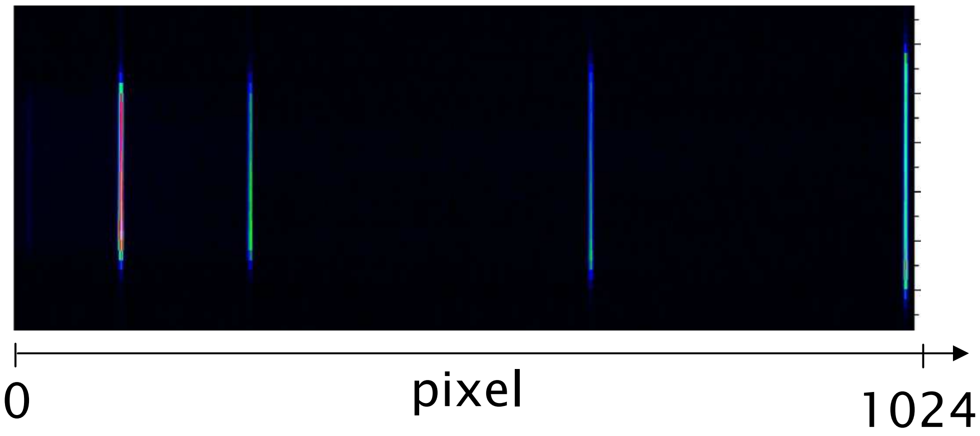
1. Raman shift wavenumber

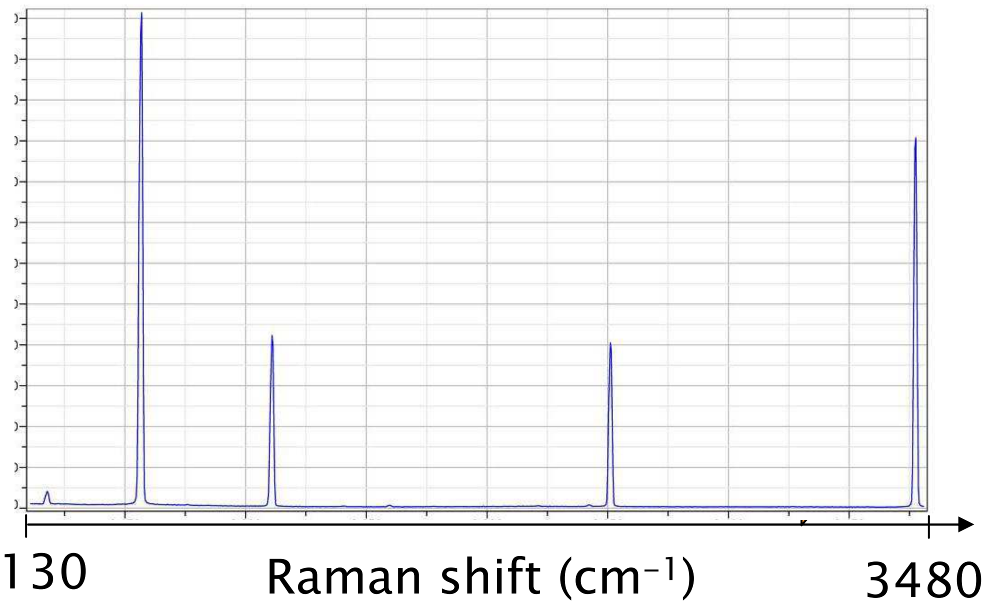
The scattered beam highlights the CCD along the largest dimension:

CCD image of a
Ne lamp emission

?

Raman spectrum
of a Ne lamp





1. Raman shift wavenumber

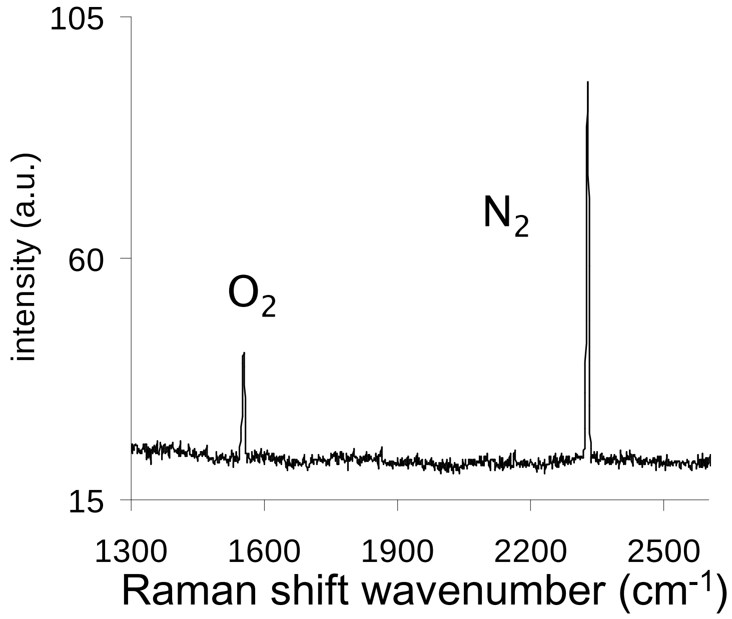
- Correlation curve: one pixel position ↔ one wavenumber
- For each grating position and each laser wavelength
- Usually done at the time of installation but can vary with:
  - Mechanical drift (e.g. grating rotation by a sine bar)
  - Room temperature variations

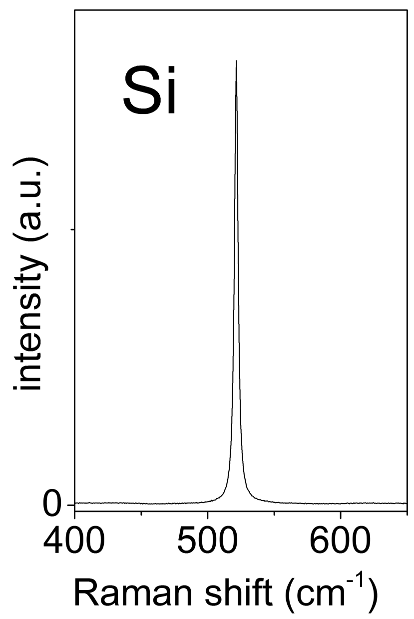
⇒ Depending on the required accuracy, must be checked every day or before each measurement.

- How to proceed:
  1. Determine the required accuracy ($<$ or $>$ 1 cm^{-1})
  2. Determine the Raman shift range to calibrate (full range or reduced window)
  3. Select the relevant standard sample(s)
  4. Record standard's spectrum (! collection geometry)
  5. Modify the correlation curve parameters if necessary

1. Raman shift wavenumber

- Low accuracy (> 1 cm^{-1}) and/or full range:
  - Silicon wafer (520.7 ± 0.5 cm^{-1})
  - Air: O_2 (1555 ± 1 cm^{-1}) and N_2 (2332 ± 1 cm^{-1})
  - Laser (0 cm^{-1})
  - Organic compounds (e.g. cyclohexane, polystyrene)

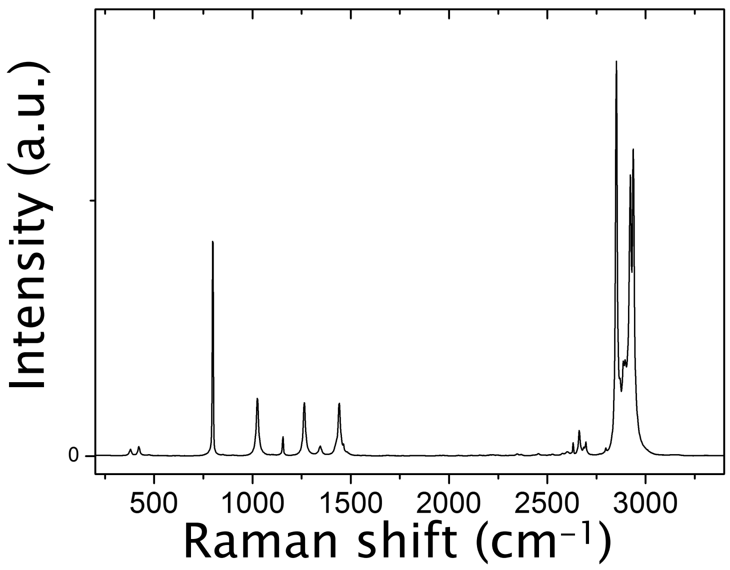




Modify (slightly) the correlation curve parameters to fit the exact peak position.

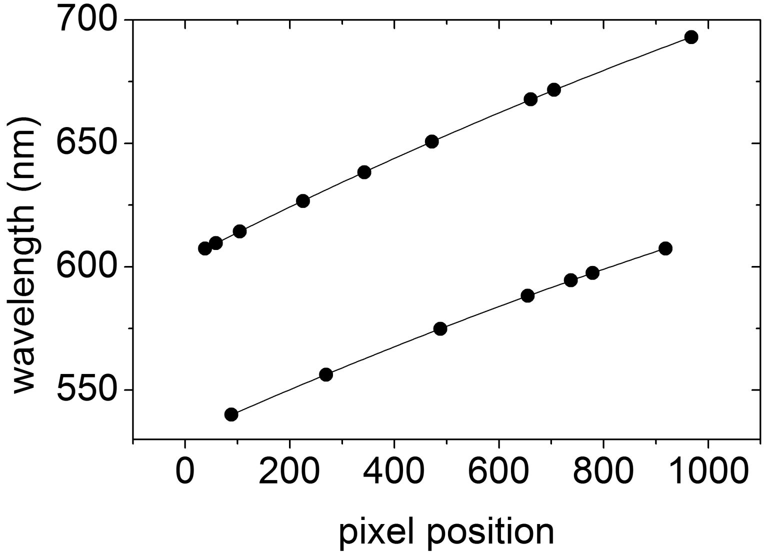
1. Raman shift wavenumber

Cyclohexane Raman spectrum:



Cyclohexane Raman peaks' positions (cm^{-1}) from ASTM E 1840-96:

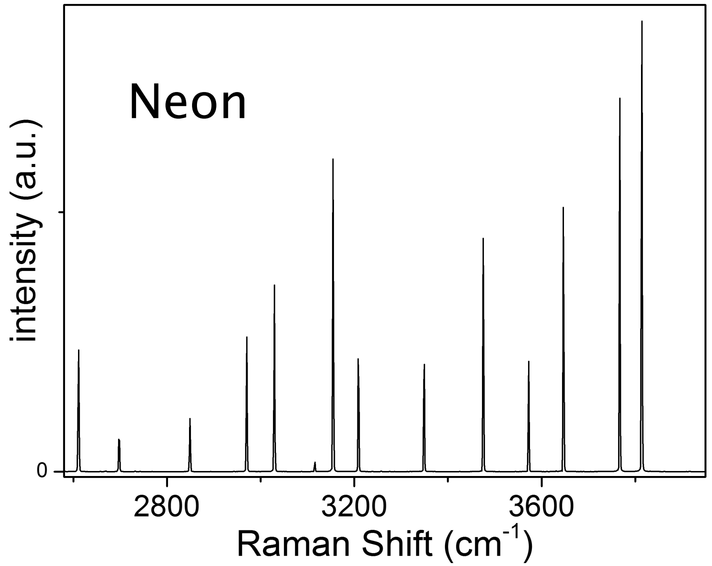
284.1 ± 0.78	1444.4 ± 0.30
426.3 ± 0.41	2664.4 ± 0.42
801.3 ± 0.96	2852.9 ± 0.32
1028.3 ± 0.45	2923.8 ± 0.36
1157.6 ± 0.45	2938.3 ± 0.51
1266.34 ± 0.94	

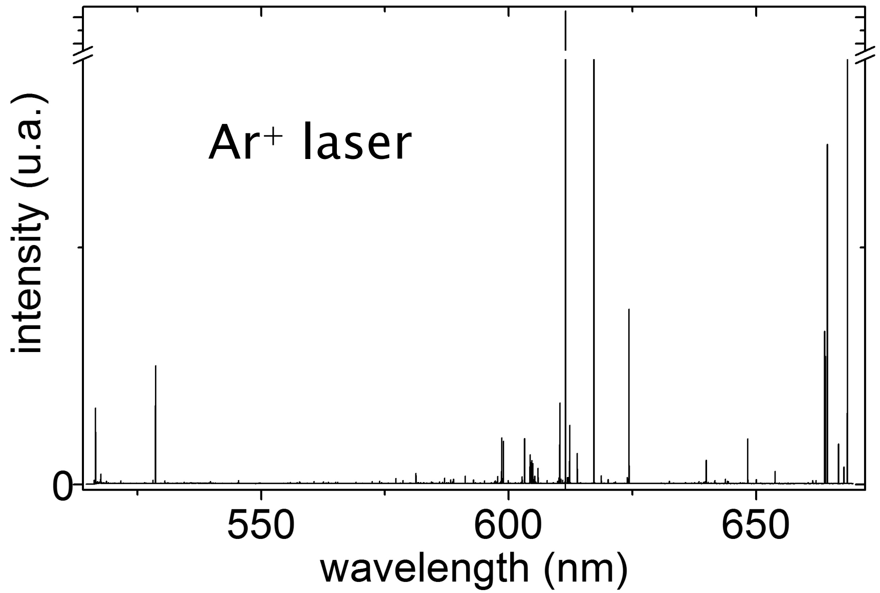


Correlation curves obtained from cyclohexane using a multiplexed VPH grating.

1. Raman shift wavenumber

- High accuracy (< 1 cm^{-1}):
  - Ne, Ar, Hg, etc. lamps
  - Gas laser atomic emission lines





How to proceed:

1. Fit the standard peaks (Lorentzian)
2. Correlate the measured peak positions to the expected ones

Accuracy close to the spectrometer spectral resolution can be reach.

1. Raman shift wavenumber

Laser wavelength

- Gas lasers: atomic emission stable over a long period of time and known with an accuracy ~1pm (0.04 cm^{-1} at 500 nm)
- Solid and semi-conductor lasers: less stable with time

  ⇒ emission wavelength must be checked (and corrected)

How to proceed:

1. Calibrate the Raman shift wavenumber (detector)
2. Select a relevant standard sample (organic compounds)
3. Record the spectrum of the standard
4. Modify the laser wavelength to reach the best correspondence between the measured and expected peak positions of the standard.

Outline

1. Raman shift wavenumber calibration:
    - Detector
    - Laser
2. Raman intensity calibration:
    - spectrometer response
    - cross section
3. Spectral resolution
4. Confocality: axial resolution
5. Spatial resolution : lateral resolution

2. Raman intensity

The scattered Raman intensity I_{Raman}:

$$I_{Raman} \propto P_{laser} \times \underbrace{[vibrator]_{scattering\ volume}}_{?} \times \underbrace{\sigma_{vibrator}}_{?} \times 1/\lambda_{R,j}^{4} \times \underbrace{R_{instrument}}_{\text{To be determined.}}$$

$R_{instrument}$: instrument response function

Depends on optics, grating, filters, wavelength, detector, polarisation, objectives.

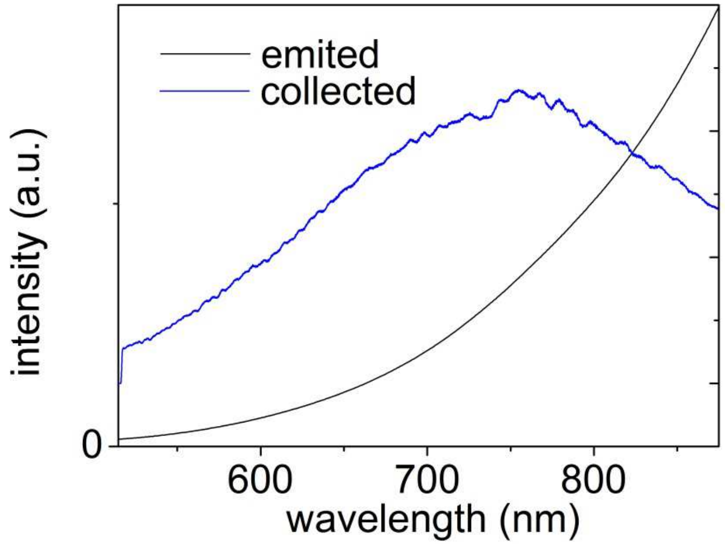
→ One response function for each experimental configuration.
Should not vary with time.

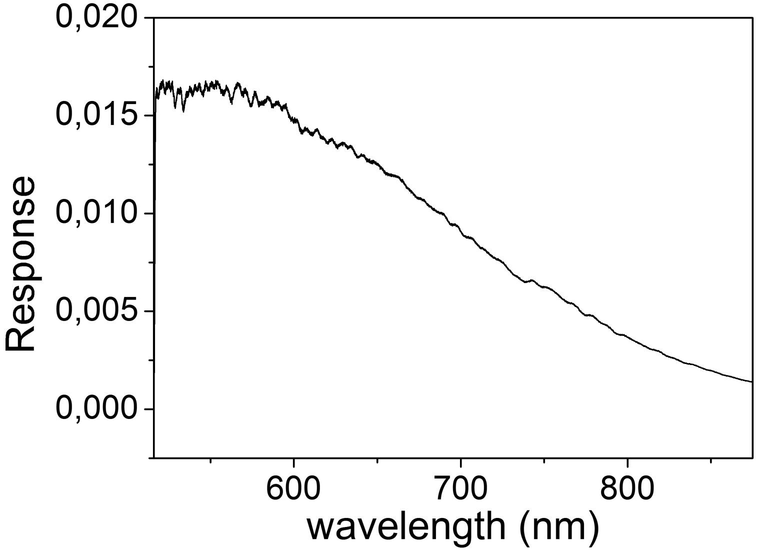
How to proceed:

1. Configure the spectrometer as for samples (grating, filters, objective, etc.).
2. Chose a standard source.
3. Record the spectrum of the standard.
4. Calculate the instrument response (automatically or manually).

2. Raman intensity

- Instrument response $R = I_{measured}/I_{true}$ *vs.* λ.



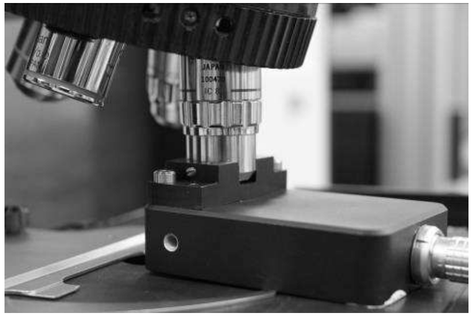


Standard source:

White lamp (tungsten): do not reproduce sample positioning

Luminescent standards: laser wavelength and temperature dependants

Example of a system to ensure a reproducible positioning of the source:

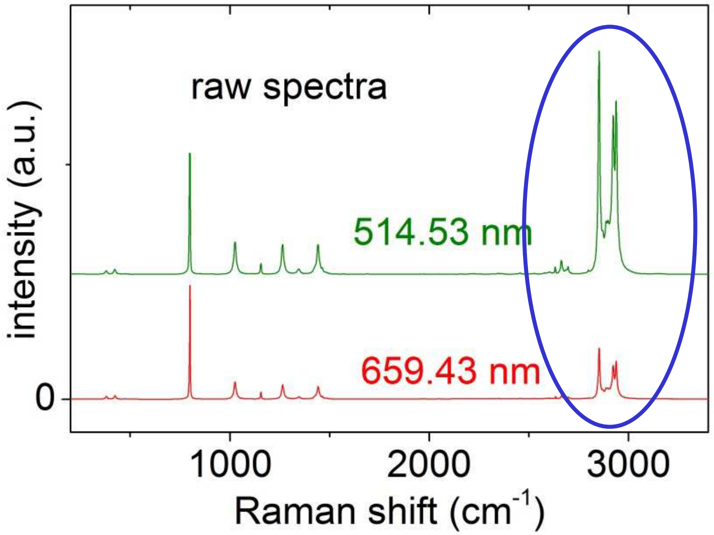


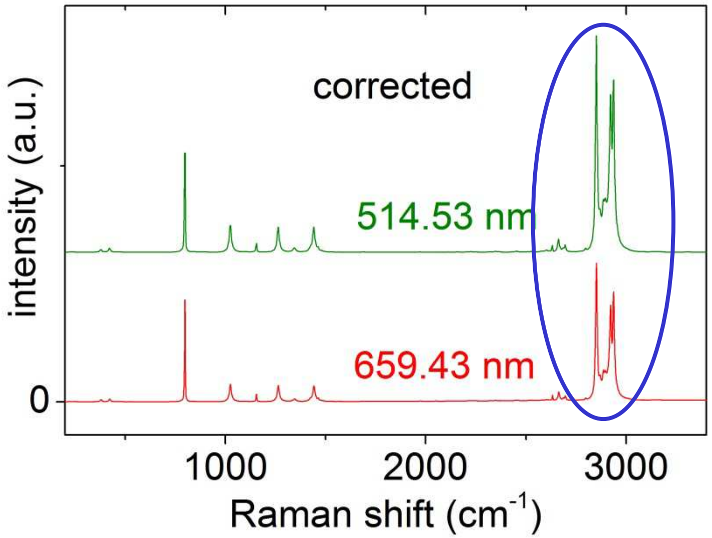
HCA Kaiser Optical Systems, Inc.

2. Raman intensity

- When to measure instrument response?
  - To compare spectra of one sample recorded
    - on different spectrometers
    - using different lasers (! λ^4)
  - To determine true σ Raman cross section

Ex: cyclohexane with 2 ≠ lasers:





2. Raman intensity

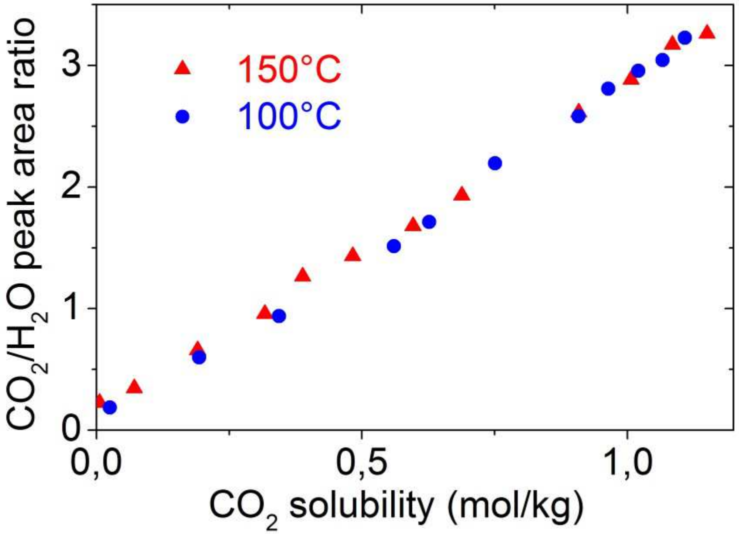
- Semi-quantitative measurements: internal standard
- First require to record calibration curves

$I_{Raman} \propto P_{laser} \times [\text{vibrator}]_{\text{scattering volume}} \times \sigma_{vibrator} \times 1/\lambda_{R,\,j}^{4} \times R_{instrument}$

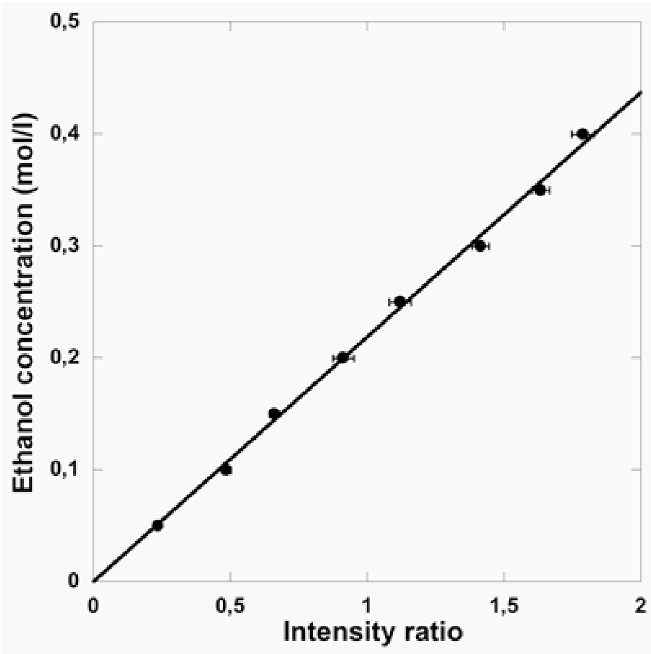
$I_A/I_B = ([A] \times \sigma^*_A)/([B] \times \sigma^*_B)$

with σ^*_A (and σ^*_B) $= \sigma_A \times R_{instrument} \times 1/\lambda_{R,\,A}^{4}$

(effective Raman cross section of A)



CO_2 solubility (mol/kg) in water.
Internal standard: water



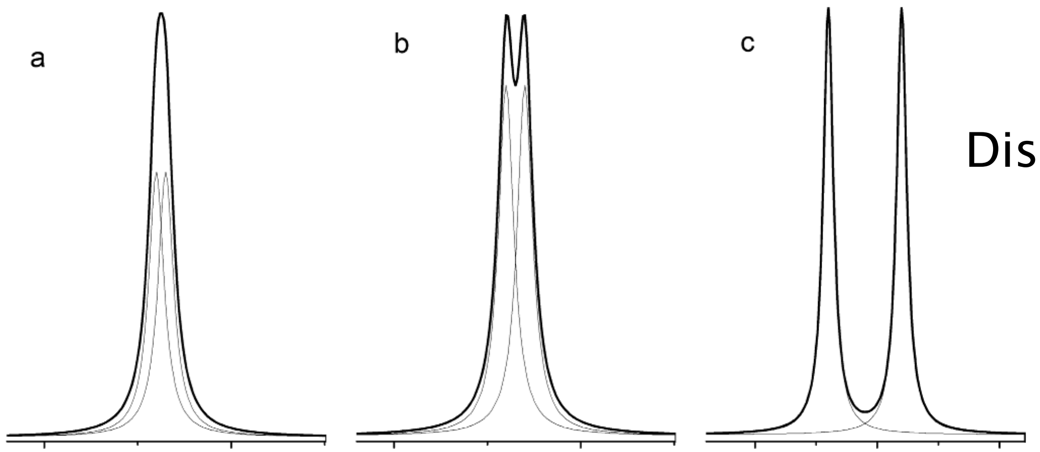
From Isabelle Daniel

Outline

1. Raman shift wavenumber calibration:
   - Detector
   - Laser
2. Raman intensity calibration:
   - spectrometer response
   - cross section
3. Spectral resolution
4. Confocality: axial resolution
5. Spatial resolution : lateral resolution

3. Spectral resolution

- Spectral resolution: ability of the spectrometer to separate two peaks.



Distance between 2 peaks ≥ 2FWHM

a: unresolved
b, c: resolved

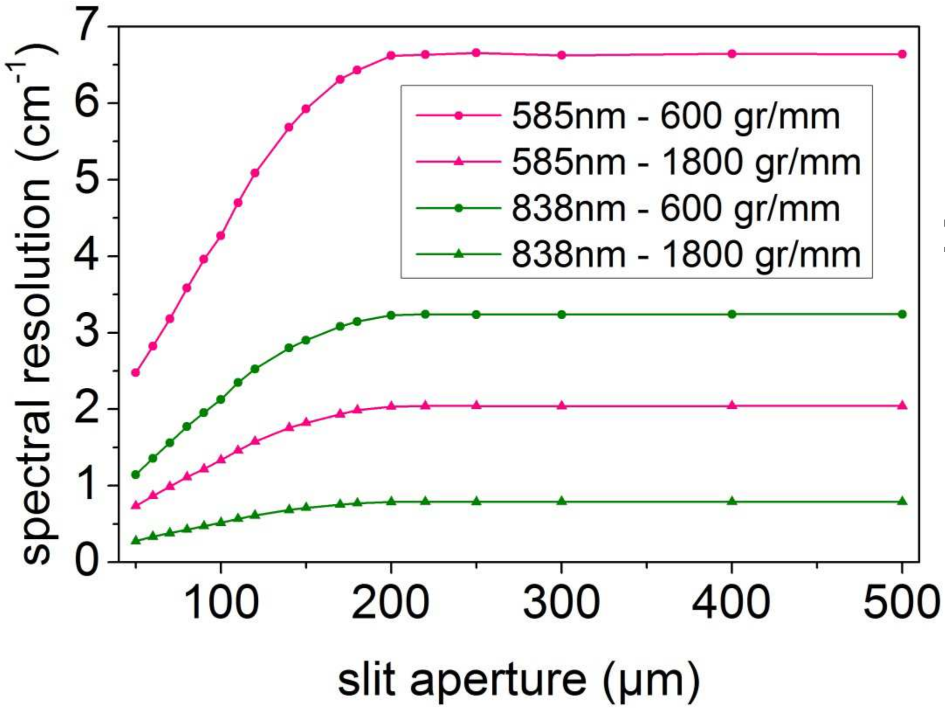
- Depends on:
  - Wavelength
  - Grating (no of grooves/mm)
  - CCD (no and size of pixels)
  - Focal length of the spectrometer
  - Entrance slit aperture
  - Natural bandwidth of the peak

3. Spectral resolution

How to proceed:

1. Highlight the spectrometer with lamp (Ne, Hg, Ar, Kr) (bandwidth < 0.01nm)
2. Record the spectrum of the lamp in the desired configuration (slit, grating, wavenumber, etc.)
3. Fit the peak (Lorentzian) => spectral resolution = FWHM

Stable over time: must be determined only once.



Spectral resolution is improved by:

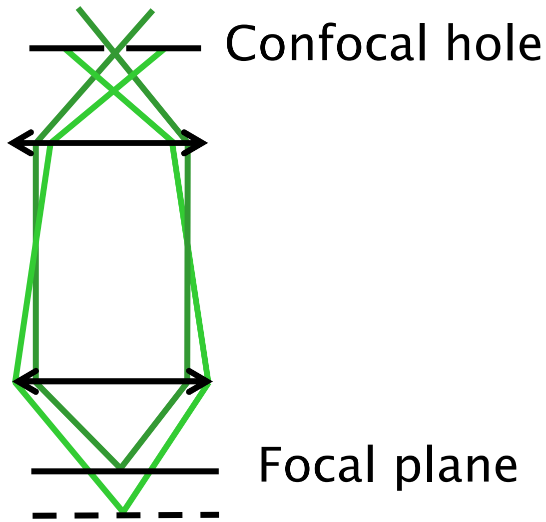
- decreasing slit aperture
- increasing grating grooves density
- increasing wavelength

Outline

1. Raman shift wavenumber calibration:
    - Detector
    - Laser
2. Raman intensity calibration:
    - spectrometer response
    - cross section
3. Spectral resolution
4. Confocality: axial resolution
5. Spatial resolution : lateral resolution

4. Confocality: axial resolution

- Confocality : selectivity along the axial direction
- Only for microspectrometers
- Depends on:
  - N.A. of the objective
  - Laser wavelength
  - Confocal hole aperture



- It is an indicator of laser optical alignment.

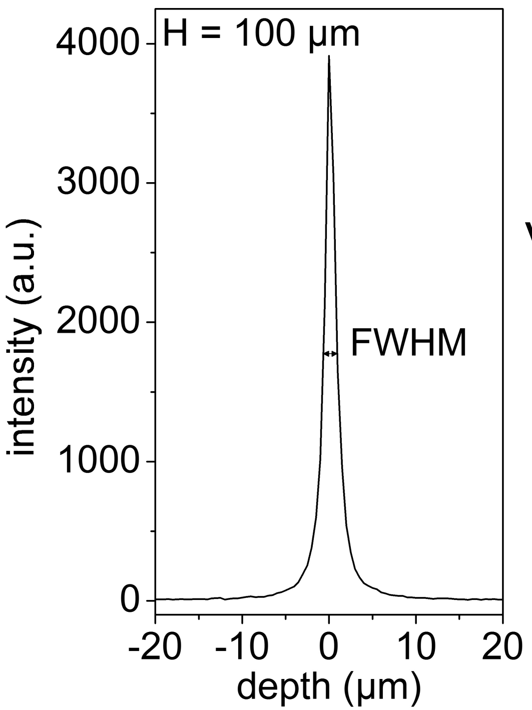
→ Must be frequently checked!

4. Confocality: axial resolution

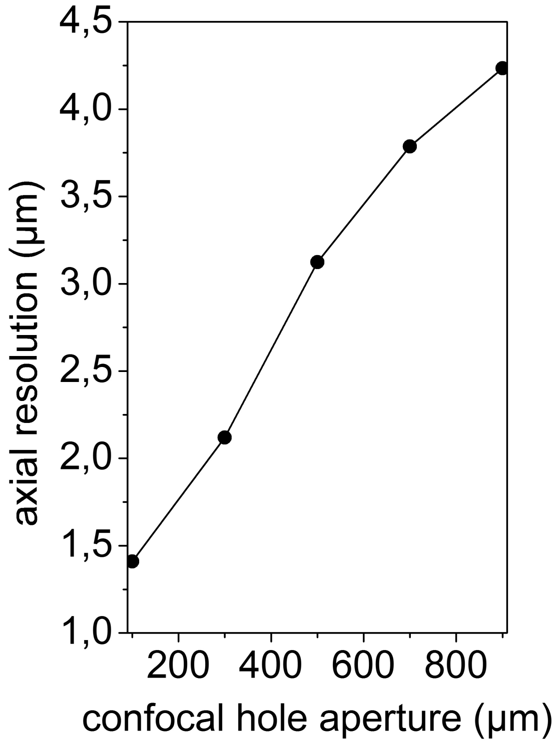
- How to proceed:

1. Illuminate a Si wafer with laser (520.7 ± 0.5 cm^{-1})
2. Record Si spectrum as a function of depth and confocal hole aperture
3. Plot the peak intensity *vs.* depth for each hole aperture:

   axial resolution = FWHM of depth profiling peak.
4. Compare the curves of axial resolution and relative intensity *vs.* confocal hole aperture with anterior ones.



Varying confocal hole aperture

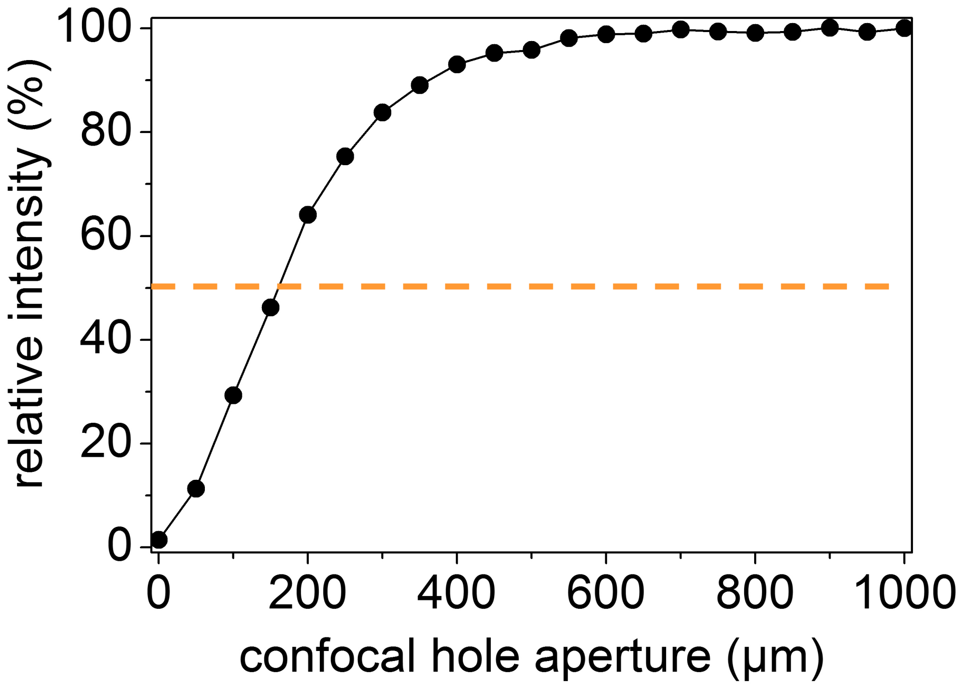


4. Confocality: axial resolution

- How to proceed:

1. Illuminate a Si wafer with laser (520.7 ± 0.5 cm^{-1})
2. Record Si spectrum as a function of depth and confocal hole aperture
3. Plot the peak intensity *vs.* depth for each hole aperture:

   axial resolution = FWHM of depth profiling peak.
4. Compare the curves of axial resolution and relative intensity *vs.* confocal hole aperture with anterior ones.



Outline

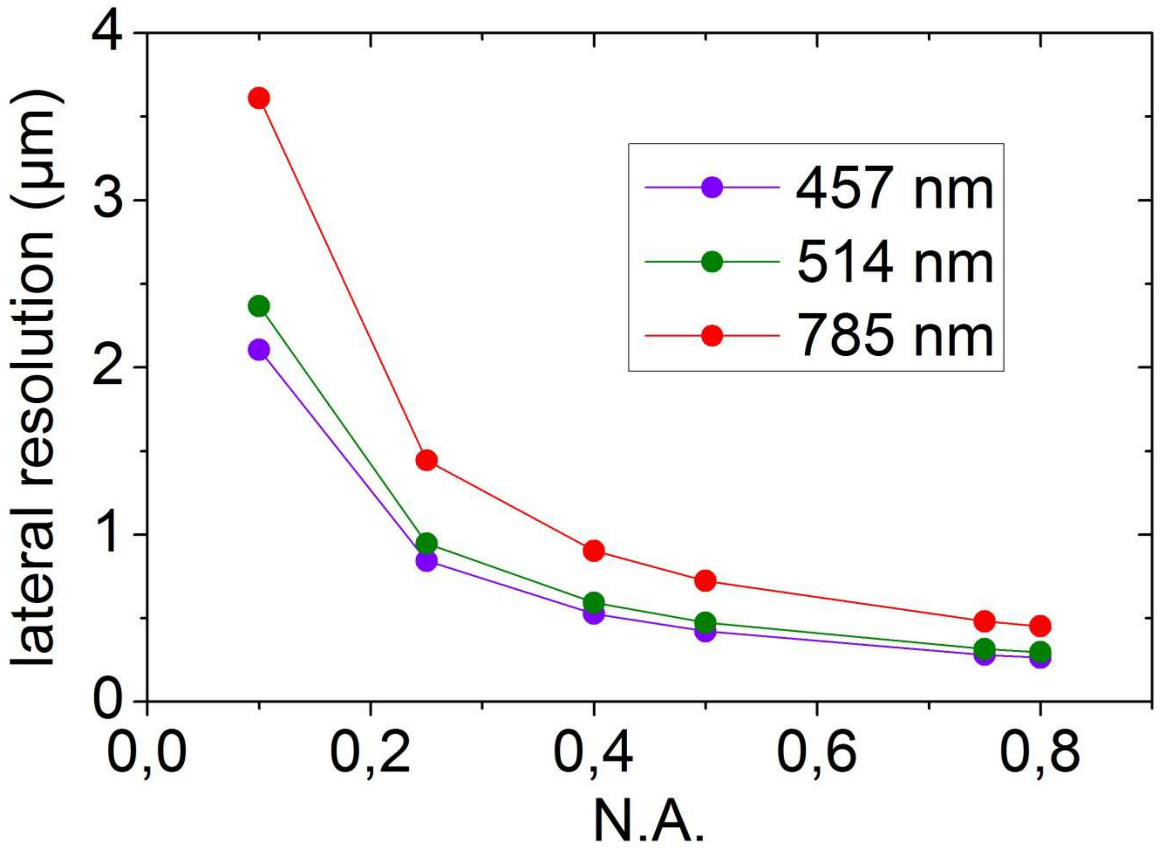
1. Raman shift wavenumber calibration:
    - Detector
    - Laser
2. Raman intensity calibration:
    - spectrometer response
    - cross section
3. Spectral resolution
4. Confocality: axial resolution
5. Spatial resolution : lateral resolution

5. Spatial resolution: lateral resolution

- Indicates the minimum surface size that can be individually analyzed.
- Limited by light diffraction (resolving power of a confocal microscope):

$\delta_{xy} = 0.46\lambda/\text{N.A.}$

=> Depends on wavelength and N.A. of objectives.



Summary

1. Raman shift wavenumber calibration
2. Raman intensity calibration
3. Spectral resolution
4. Confocality
5. Spatial resolution

- Useful standards:
  - Atomic emission lamps (Ne, Ar, etc.)
  - Si wafer
  - Organic compounds (cyclohexane, polystyrene, etc.)