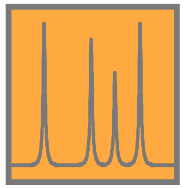
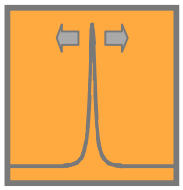
Raman spectroscopy

Information from Raman Spectroscopy



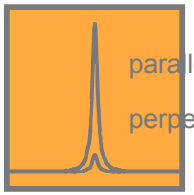
characteristic Raman frequencies → composition of material

e.g. MoS_2, MoO_3



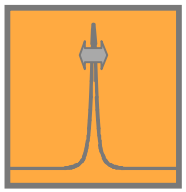
changes in frequency of Raman peak → stress/strain state

e.g. Si 10 cm^{-1} shift per % strain



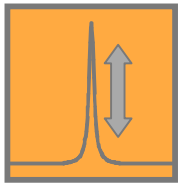
polarisation of Raman peak → crystal symmetry and orientation

e.g. orientation of CVD diamond grains



width of Raman peak → quality of crystal

e.g. amount of plastic deformation



intensity of Raman peak → amount of material

e.g. thickness of transparent coating

Collecting the light

The coupling of a Raman spectrometer with an optical microscope provides a number of advantages:

1) Confocal Light collection

2) High lateral spatial resolution

3) Excellent depth resolution

4) Large solid collection angle for the Raman light

The basic function of a Raman system

- **Deliver the laser to the sampling point**
  - With low power loss through the system
  - Illuminating an area consistent with sampling dimensions
  - Provide a selection/choice of laser wavelengths
- **Collect the Raman scatter**
  - High aperture
  - High efficiency optics
  - High level of rejection of the scattered laser light
- **Disperse the scattered light**
  - Short wavelength excitation requires high dispersion spectrometers
- **Detect the scattered light**
- **Graphically / mathematically present the spectral data**

Laser wavelength selection concerns for classical Raman

As the laser wavelength gets shorter

- Raman scattering efficiency increases
- The risk of fluorescence increases (except deep UV)
- The risk of sample damage / heating increases
- The cost of the spectrometer increases

Raman light source

System basics: lasers

1) UV lasers

2) visible lasers

3) NIR lasers

Common excitation wavelengths

244 nm- biological, catalysts (Resonance Raman)

325 nm- wide bandgap semiconductors

488 nm & 514 nm- semiconductor, catalysts, biological, polymers, minerals & general purpose

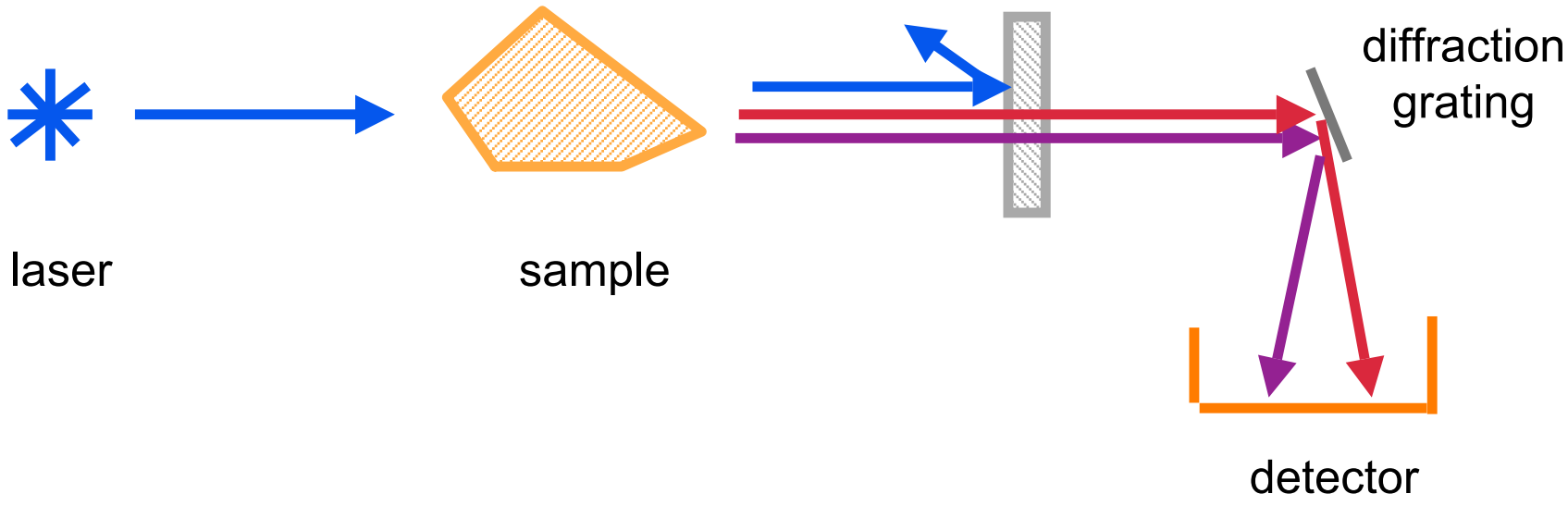
633 nm- corrosion & general purpose

785 nm - polymers, biological & general purpose

830 nm- biological

Generic Raman system flow diagram

- Illuminate a Sample with an Intense Single Frequency Light Source



- Measure the relative frequency shift of the inelastically scattered light

Raman microscopy: Dispersive instrument basics

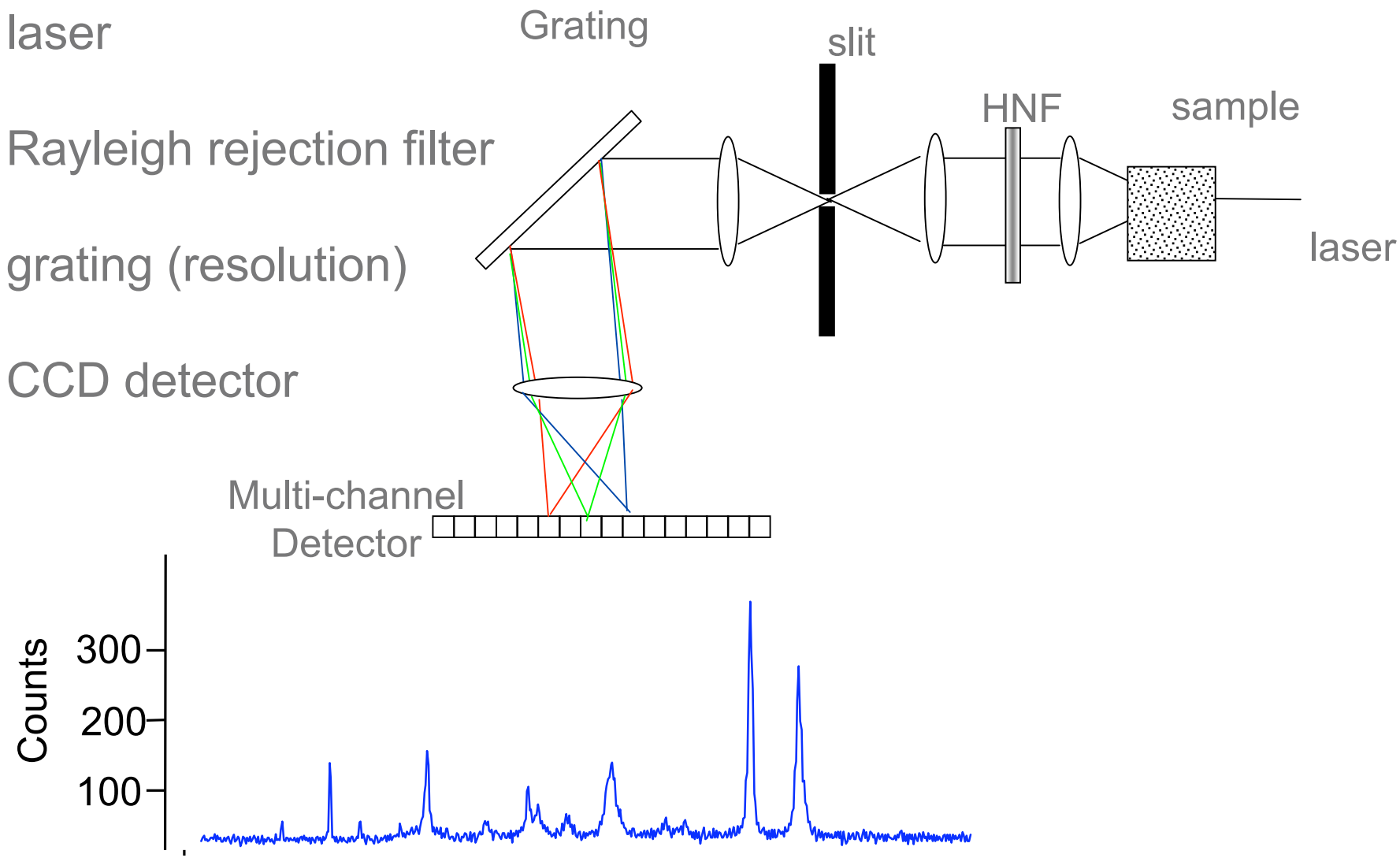
System basics:

1) laser

2) Rayleigh rejection filter

3) grating (resolution)

4) CCD detector



Research Grade MicroRaman Spectrometer

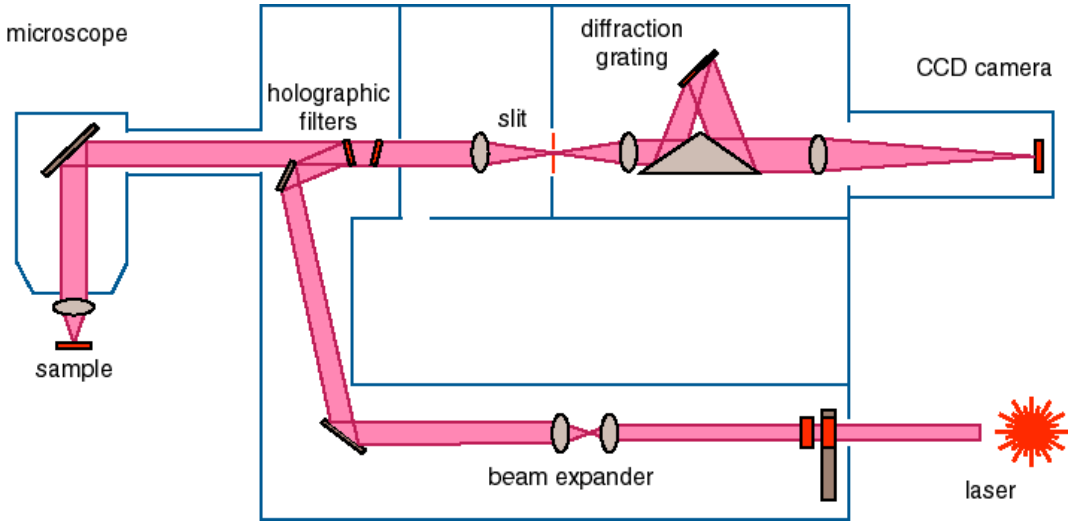
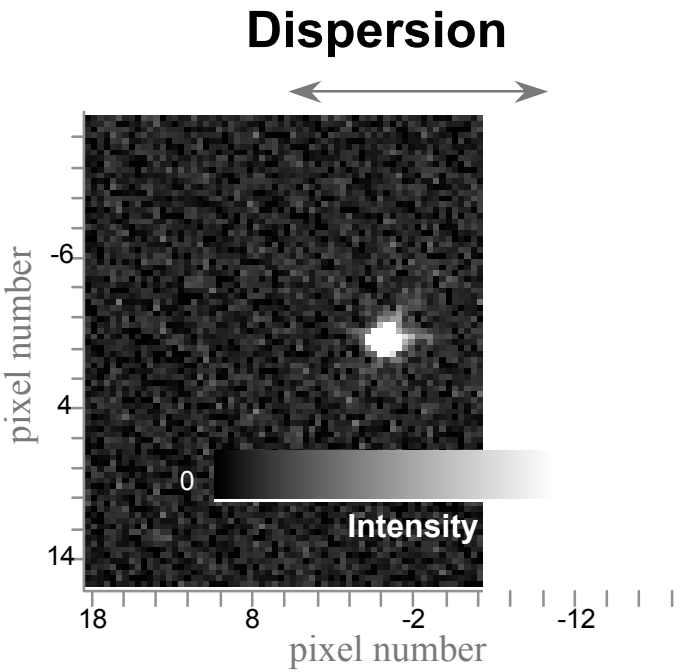


Image of Si 520 cm^{-1} band



The Renishaw Raman spectrometer is an imaging spectrograph

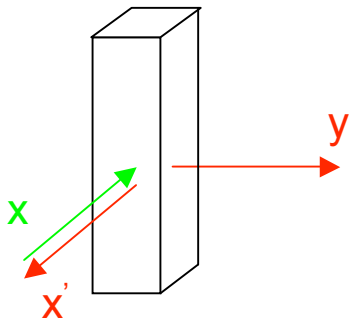
on-axis stigmatic design with a -70 °C Peltier cooled CCD detector. Advanced inverted mode, deep depletion and UV optimized detectors are available as options.

We can easily demonstrate the high quality imaging and system performance advantages as seen in the image of the Si 520 cm^{-1} Raman band on the CCD detector.

Delivering the light

Delivering the light

90 and 180 degree scattering



Porto notation

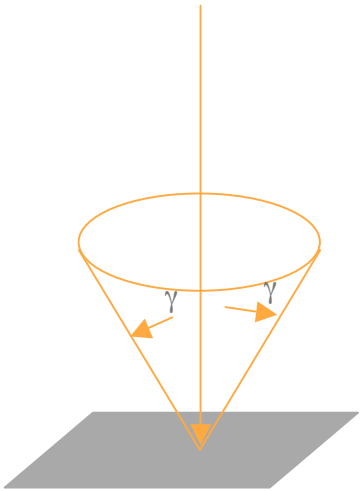
90 degree scattering x(z,z)y and

180 degree scattering x(z,z)x'

excitation direction (excitation polarization,

scattered polarization) scattering direction

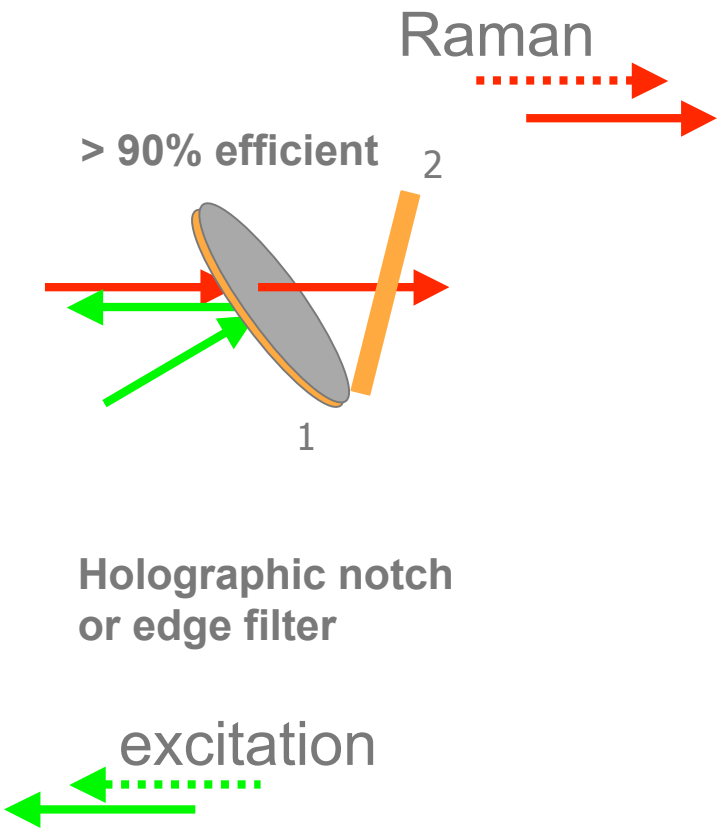
The actual excitation and collection directions are the range of angles 0 to γ



mag	N.A	2*γ(deg)
x5	0.12	11.5
x20	0.4	29
x50	0.75	97.2
x100	0.9	128.3

Delivering the light

Delivering the light (180 degree backscattering)



Raman microscope systems typically operate in with the excitation direction and collected Raman scattering direction separated 180^0. This mode of collection and excitation is referred to as "back-scattering".

Typically back-scattered Raman collection necessitate special optics that operate both as a Rayleigh filter and as a laser mirror. Holographic notch filters and special dielectric mirrors are often the optics of choice, since they minimize laser intensity loss and Raman scattering losses that would otherwise occur when utilizing a partial reflector.

Relative laser excitation efficiency and Raman transmission efficiencies can be easily calculated for most configurations

Delivering the light

Laser focused spot size

The minimum laser focus is determined by:

1. the focusing optic N.A.
2. laser wavefront (distortion or M^2)
3. How the back aperture of the objective is filled

Raman spectroscopy utilizing a microscope for laser excitation and Raman light collection offers that highest Raman light collection efficiencies.

When properly designed, Raman microscopes allow Raman spectroscopy with very high lateral spatial resolution, minimal depth of field and the highest possible laser energy density for a given laser power.

It is important to note that the laser minimum focused spot size is not typically the same size as the coupled Raman scattered spot size.

The minimum laser focused spot size is often compromised by improperly matching the laser size to the back aperture of an objective and by wavefront errors inherent to the laser and introduced by the laser delivery optics.

Laser focused spot size

Without consideration of the laser mode quality and wavefront, or source size the minimum laser focused spot for any optic is described by equation 1:

$$d_l = \frac{1.22 * \lambda}{N.A.}$$

	d_l	
N.A.	514.5	785
0.12	2.72	4.15
0.25	1.31	1.99
0.4	0.82	1.25
0.75	0.44	0.66
0.9	0.36	0.55

Minimum laser focus

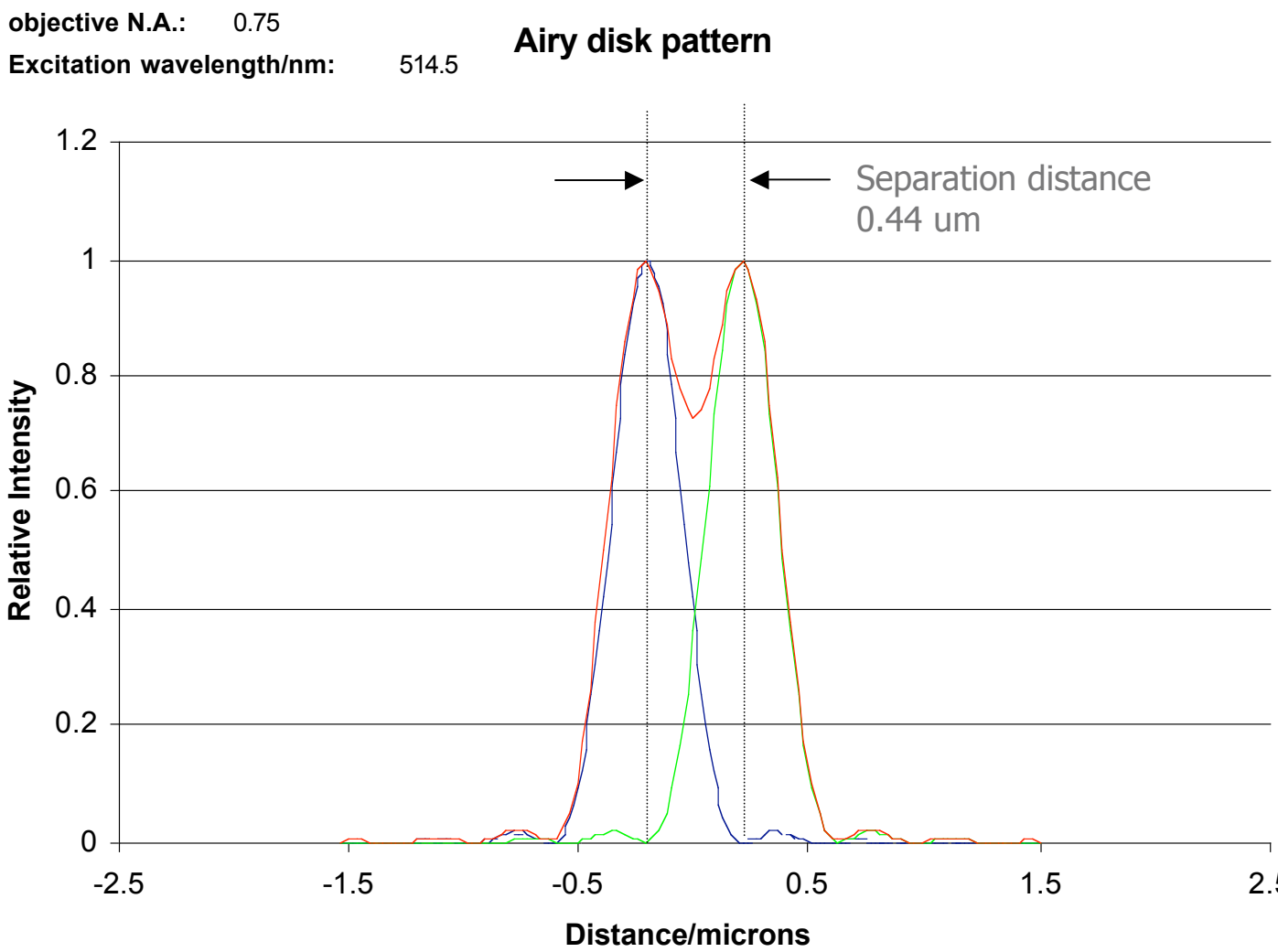
1) Excitation wavelength: λ

2) effective numerical aperture : N.A.

3) d_l is determined by twice the Rayleigh criteria of the adjacent distance required to spatially resolve the presence of an identical size spots

Laser focused spot size

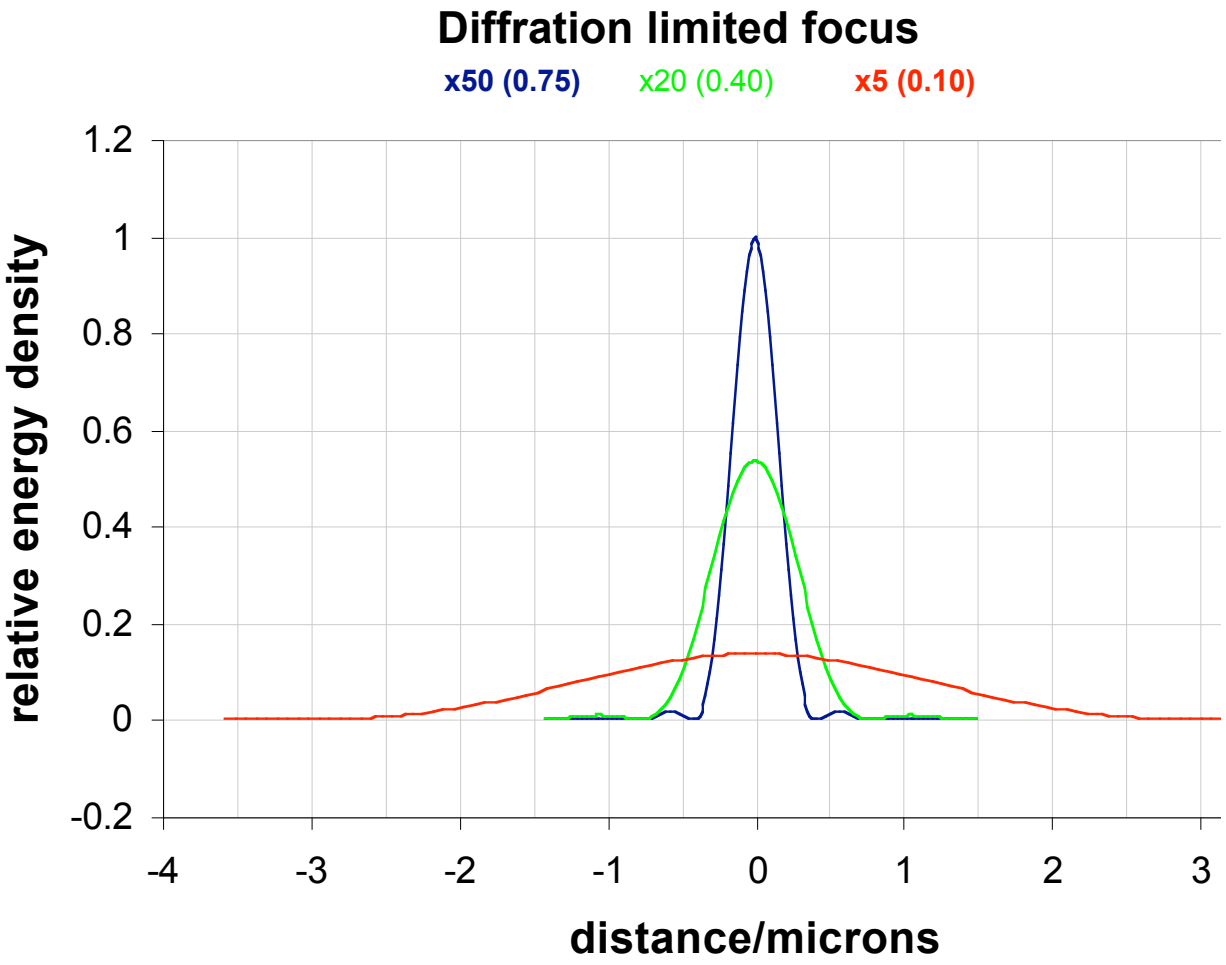
The laser focused spot size does not necessarily define the lateral spatial resolution of the Raman system. The lateral spatial resolution, is often discussed in terms of the Rayleigh criteria for the collected Raman light. The Rayleigh criteria requires that the distance between two points sources of light of equal intensity be greater than the distance from the peak to the first airy disk minimum. Complete discrimination of two adjacent materials occurs at twice the Rayleigh criteria



It's important to remember that the objective used to deliver the laser light affects the laser energy density.

The relative energy density and peak power for the X5, X20 and X50 objectives are shown relative to the X50 objective.

The peak energy density decreases by ~50% for the X20 and 87% for the X5 objective



Airy disk calculation for X5, X20 and X50 objective calculated for 514.5 nm l

Laser focus and depth of field

The system laser focus depth (h_l) is determined by:

1) Excitation wavelength: λ

2) Microscope objective focal length : f

3) Effective laser beam diameter at the the objective back aperture: D_l

$$h_l = 2.53 * \lambda \left(\frac{f}{D_l} \right)^2$$

DO NOT CONFUSE LASER FOCUS DEPTH WITH CONFOCAL COLLECTION DEPTH

Laser focus and illuminated volume

The system laser focus volume (τ_l) is determined by:

1) Excitation wavelength: λ

2) Microscope objective focal length : f

3) Effective laser beam diameter at the the objective back aperture: D_l

$$\tau_l = 3.21 * \lambda^3 \left(\frac{f}{D_l} \right)^4$$

DO NOT CONFUSE LASER FOCUS VOLUME WITH CONFOCAL COLLECTION VOLUME

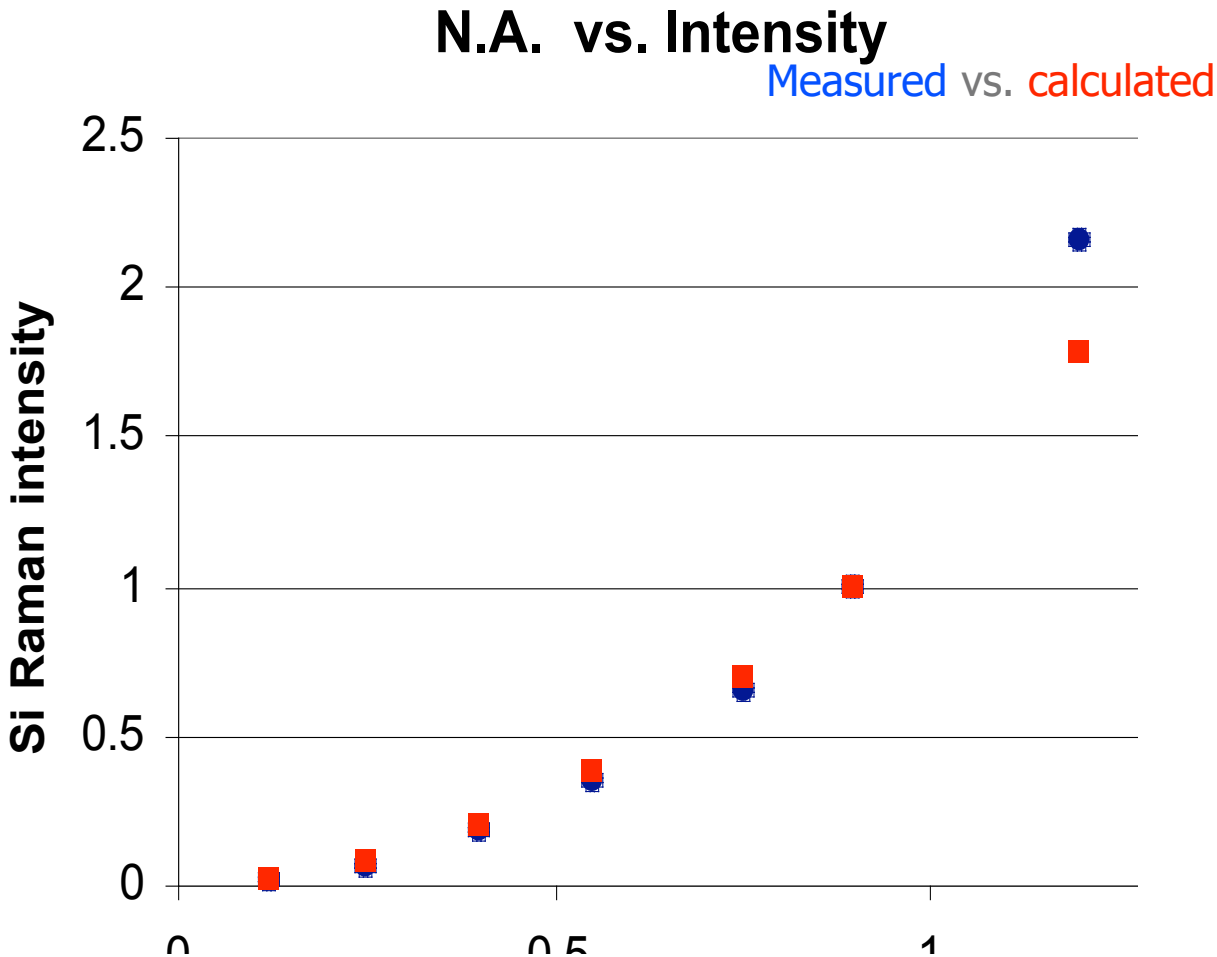
Collecting the light

$$\sigma = 4/\pi * (N.A.)^2$$

Opaque sample

Objective	N.A	rel σ
5x	0.12	0.02
10X	0.25	0.08
20X	0.4	0.2
50Xulwd	0.55	0.37
50X	0.75	0.69
100X	0.9	1
100X oil	1.2	1.78

Oil immersion objective increase is likely due to reduced reflection losses



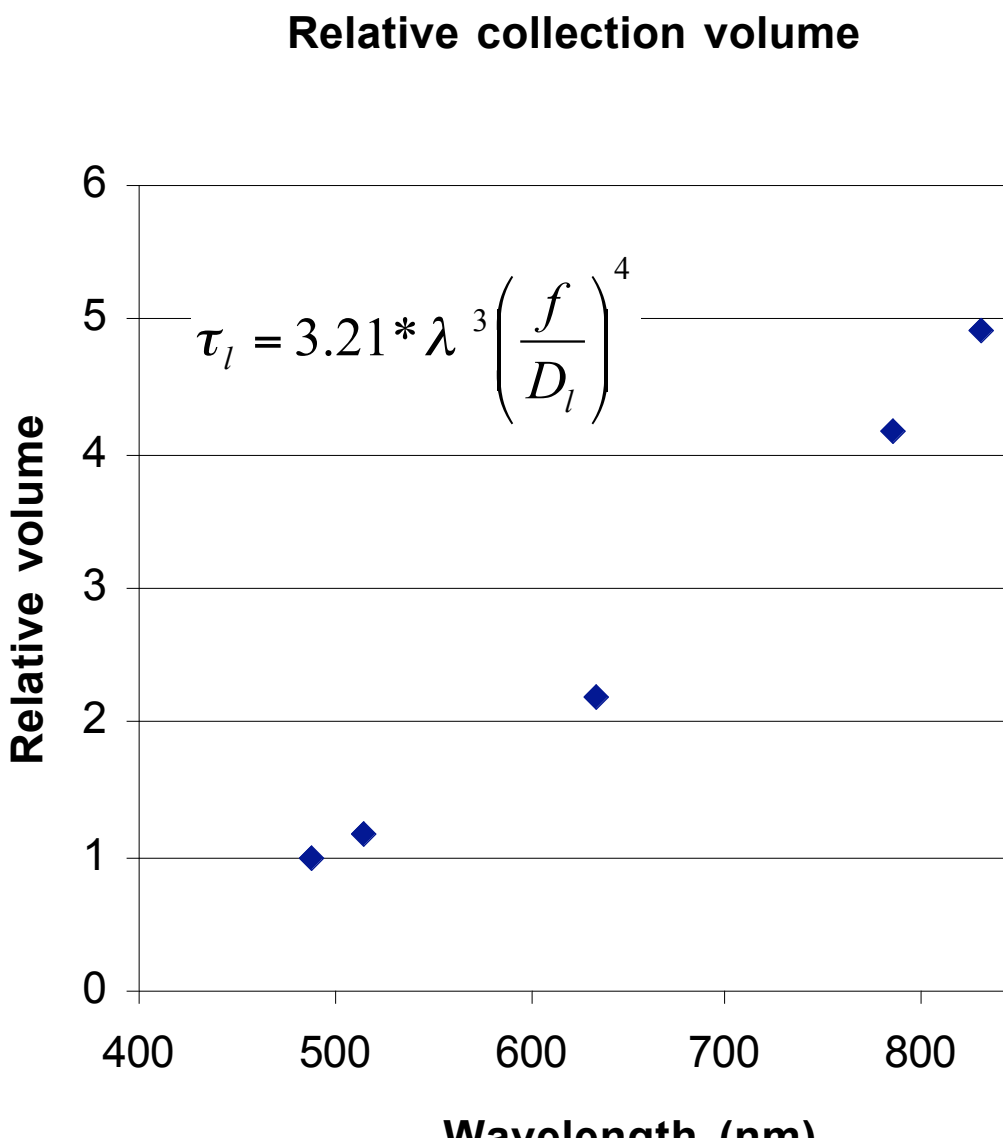
Solid collection angle is proportional to $(N.A.)^2$ not $1/(f/\#)^2$

Collecting the light

The system laser focus volume (τ_l)

$$\tau_l = 3.21 * \lambda^3 \left(\frac{f}{D_l} \right)^4$$

Macro-sampling is improved with longer wavelength excitation



Extended scanning

(Renishaw patent EP 0638788)

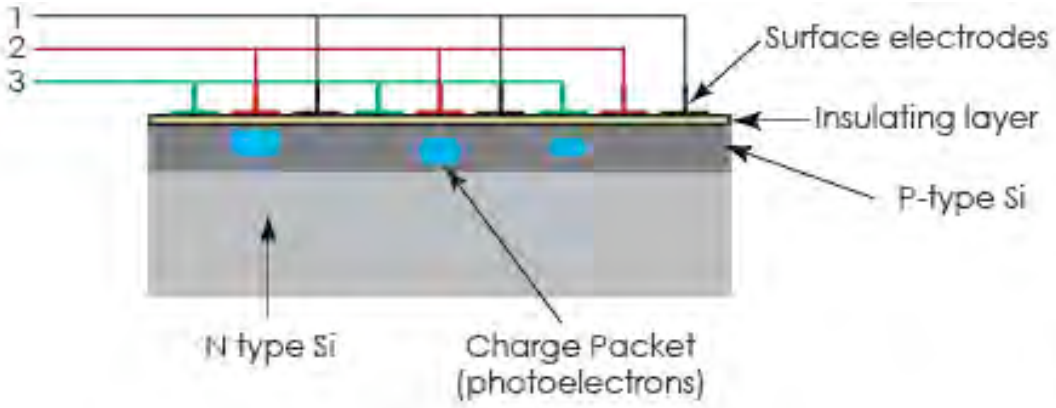
From the Renishaw Raman software the user can select:

- a fixed grating measurement with a spectrum 'window' of 400 cm^{-1} to 1000 cm^{-1} (configuration dependent)
- a unique 'extended scanning' facility allowing the user to choose any Raman shift range up to about 10000 cm^{-1} (configuration dependent). Essential for extended range scanning for Raman and photoluminescence

Extended scanning is implemented by moving the grating and the charge generated on the CCD camera synchronously.

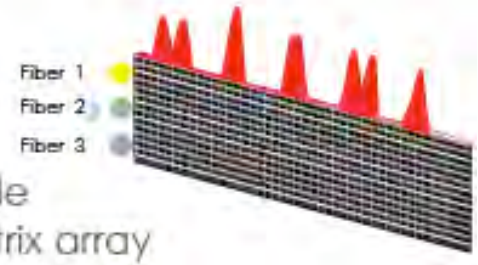
This feature is NOT available on any other instrument and is KEY to system performance

CCD Basics

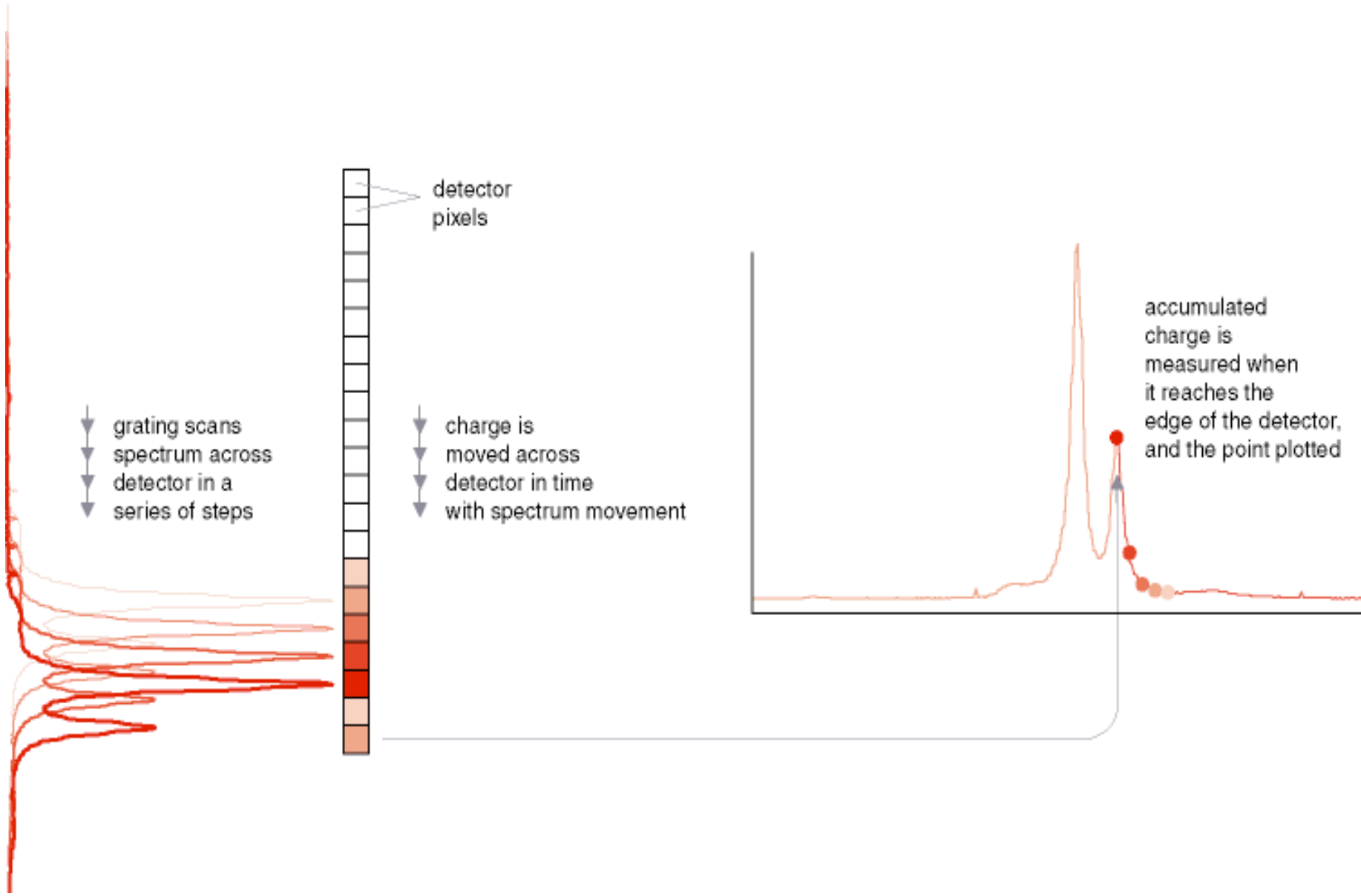


CCD (Linear and Matrix)

Only one read out circuit for all pixels
Extremely quiet
Extremely efficient
Smaller full well capacity
Higher QE's possible
Lower dark signals possible
Multiple spectra with matrix array



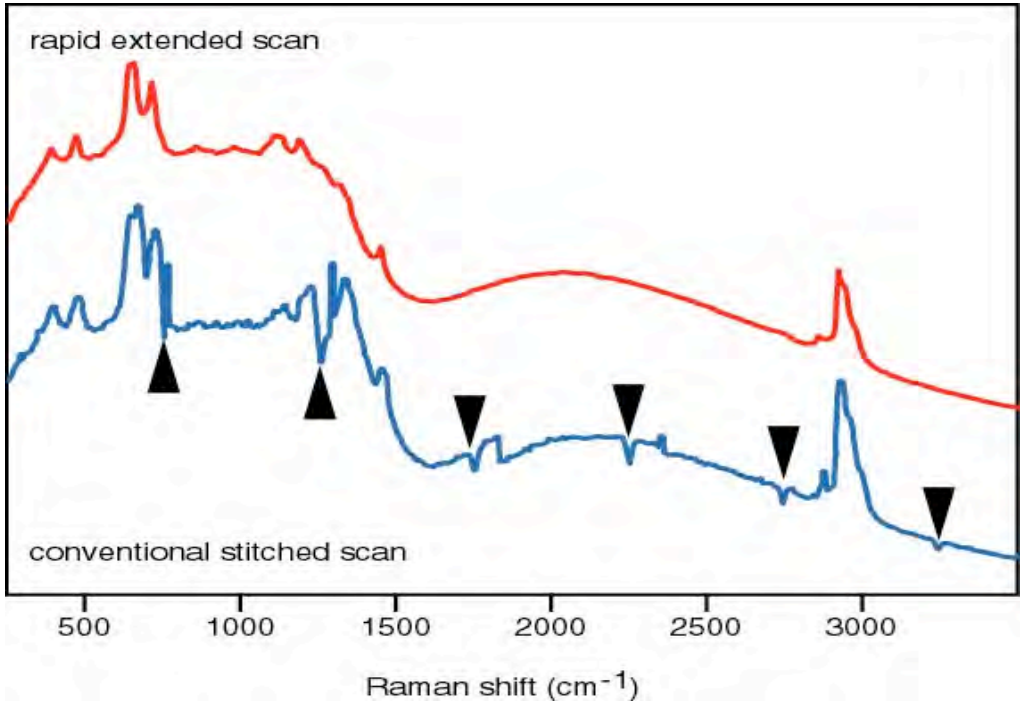
Extended scanning: how it works



Extended scanning vs stitched scanning

Advantages of extended scanning

- use a single grating
- no stitching required and no “discontinuities” at joins
- flexible wavenumber coverage (up to 10000 cm^{-1})
- pixel-to-pixel variation is averaged out - enhancing noise reduction
- no compromise on resolution across the scanned range
- simple to use



To acquire useful Raman spectra all you need is:

Sufficient spectral and spatial resolution and coverage

The ability to separate spectral peaks narrower than the narrowest anticipated spectral features of your sample

The ability to collect all of the spectral data required for the analysis

The ability to optically restrict the data collection to an area / volume small enough to eliminate acquisition of unwanted spectral data of nearby substances

Adequate S/N

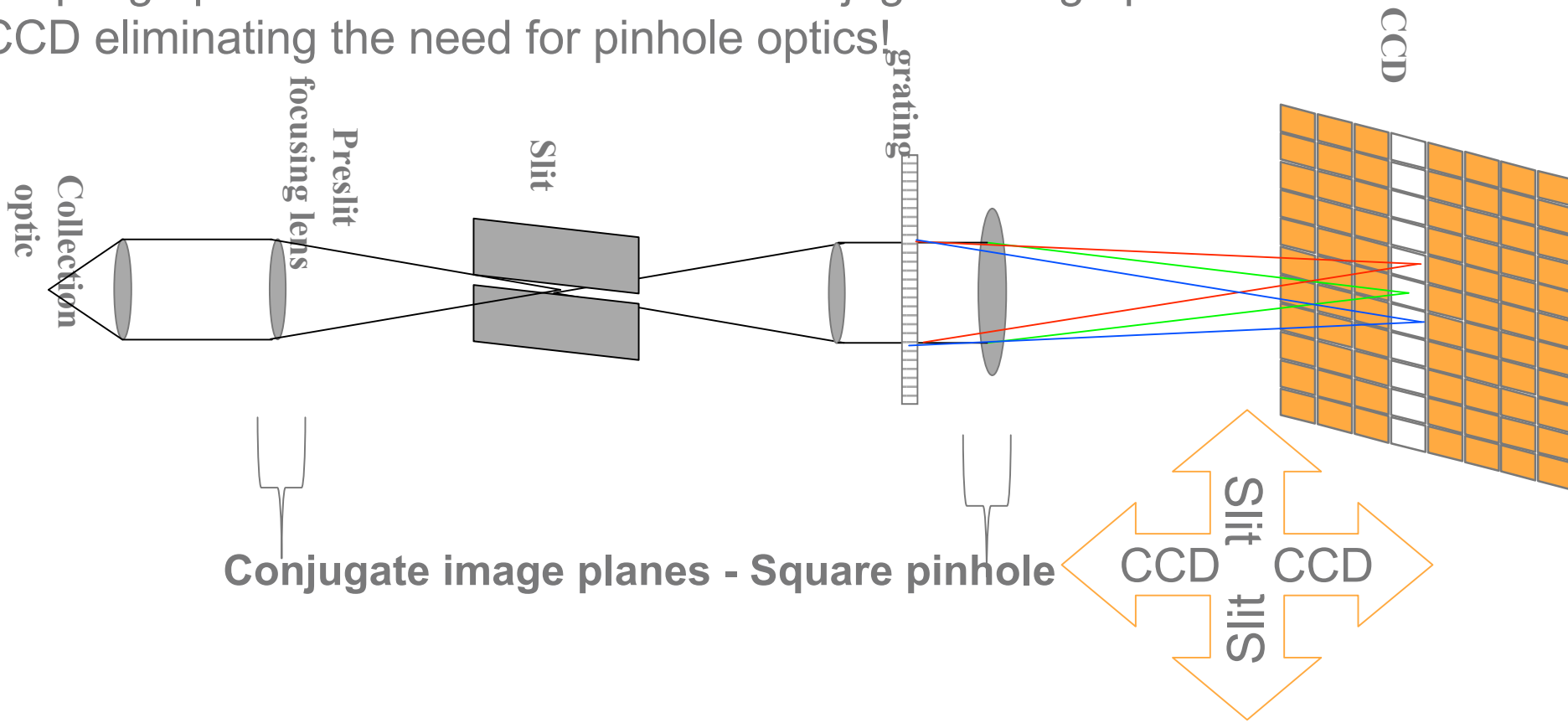
The ability to collect and detect enough photons to distinguish their electronic signal above system generated noise before the sample changes or dies.

Repeatability

The ability to consistently get the same right or wrong values

Confocal Raman microscopy without pinhole optics

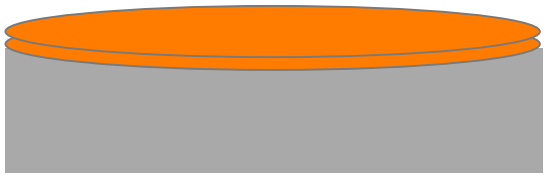
The use of a stigmatic spectrograph and stigmatic microscope-spectrometer coupling optics creates two additional conjugate image planes at the slit and CCD eliminating the need for pinhole optics!



Confocal Raman collection

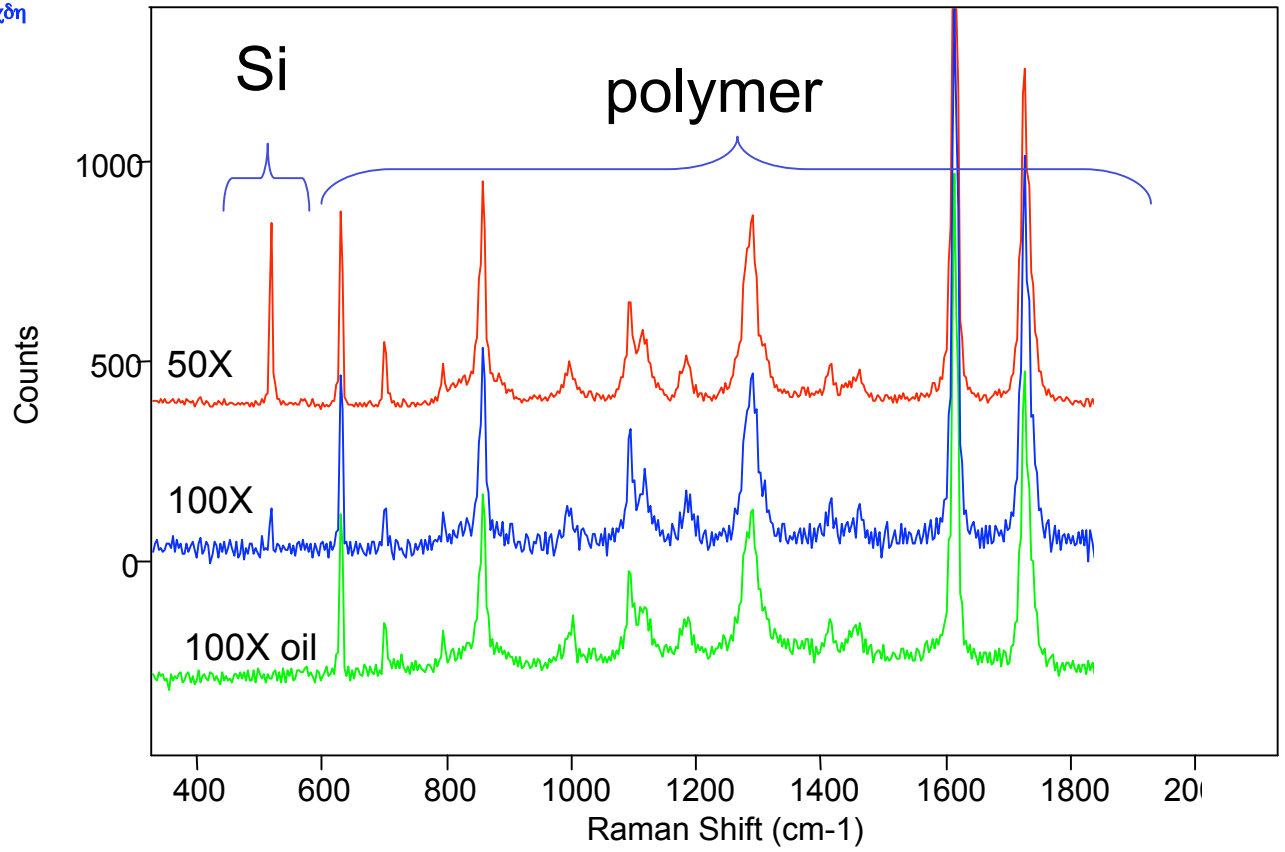
2 um polymer film

αβχδη



Silicon Wafer

Higher numerical aperture objectives effectively eliminate the Raman spectrum of underlying layers!



3: CONFO~15

Confocal 100X

Laser: 15802.78cm-1

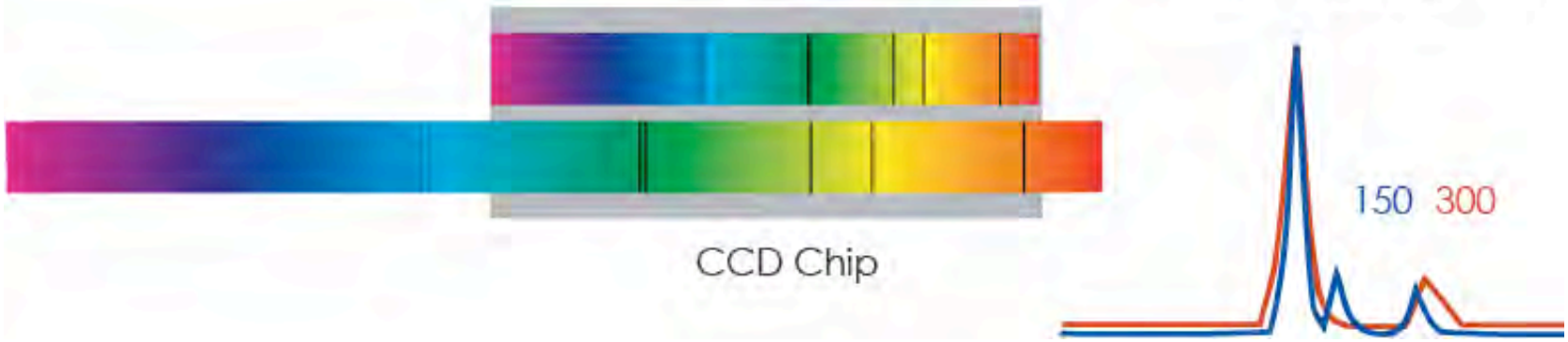
White Light Correction:

Spectral resolution and coverage are controlled by focal length and groove density

Dispersion, expressed in nm/mm describes the spreading of a spectrum over a wider area. A difracti
spreads the spectrum horizontally. Given a grating with X grooves/mm, doubling the grooves to 2X v
the spectrum twice as much.

DISPERSION IS DIRECTLY PROPORTIONAL TO GROOVE DENSITY
DISPERSION IS DIRECTLY PROPORTIONAL TO FOCAL LENGTH

A 150mm focal length spectrograph with a 2400g/mm grating has the theoretical resolution of a 300mm focal length spectrograph with a 1200g/mm grating



Spectrometer issues associated with different excitations

Shorter wavelength excitation requires higher dispersion spectrometers and produce higher levels of stray light in the system.

1 nm is equivalent to:

160 cm-1 @ 250 nm excitation
94 cm-1 @ 325 nm excitation
38 cm-1 @ 514 nm excitation
16 cm-1 @ 785 nm excitation

Lines show fingerprint region
Stars represent excitation lines

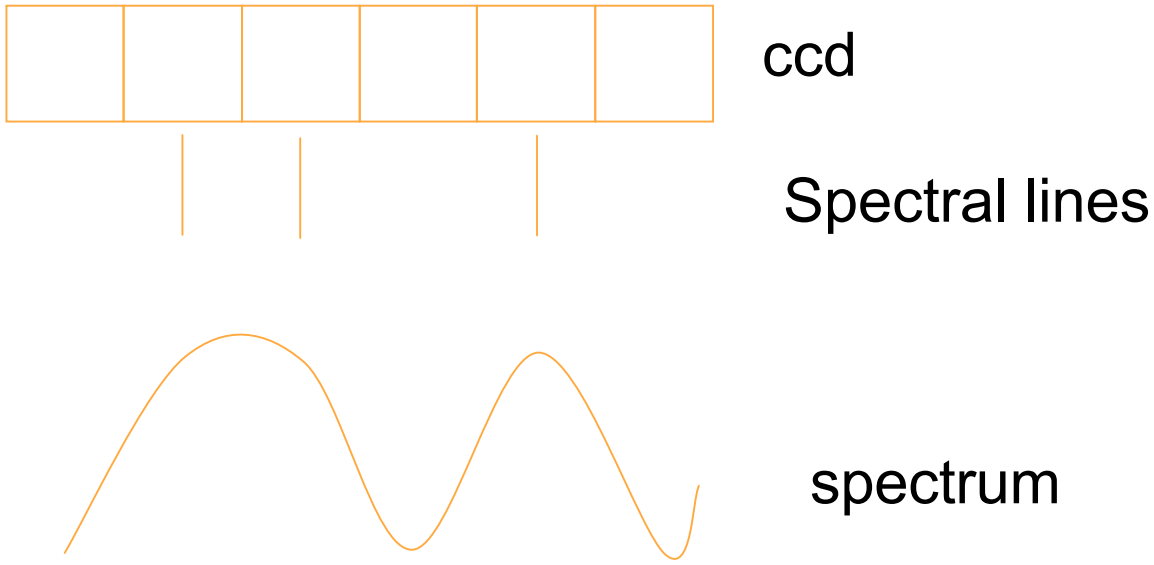
System parameters that affect spectral resolution and coverage

- The dispersion of the spectrometer
  - Focal length
  - Grating groove density
    - Multiple gratings
      - for resolution/coverage trade-off
      - For using multiple excitation wavelength
  - Grating rotation
  - Optical aberrations in the spectrometer
  - Mutichannel Detector
    - Pixel size
    - Width (under certain circumstances)
  - Laser
    - Wavelength stability
    - Wavelength choice

Raman microscopy: spectral resolution

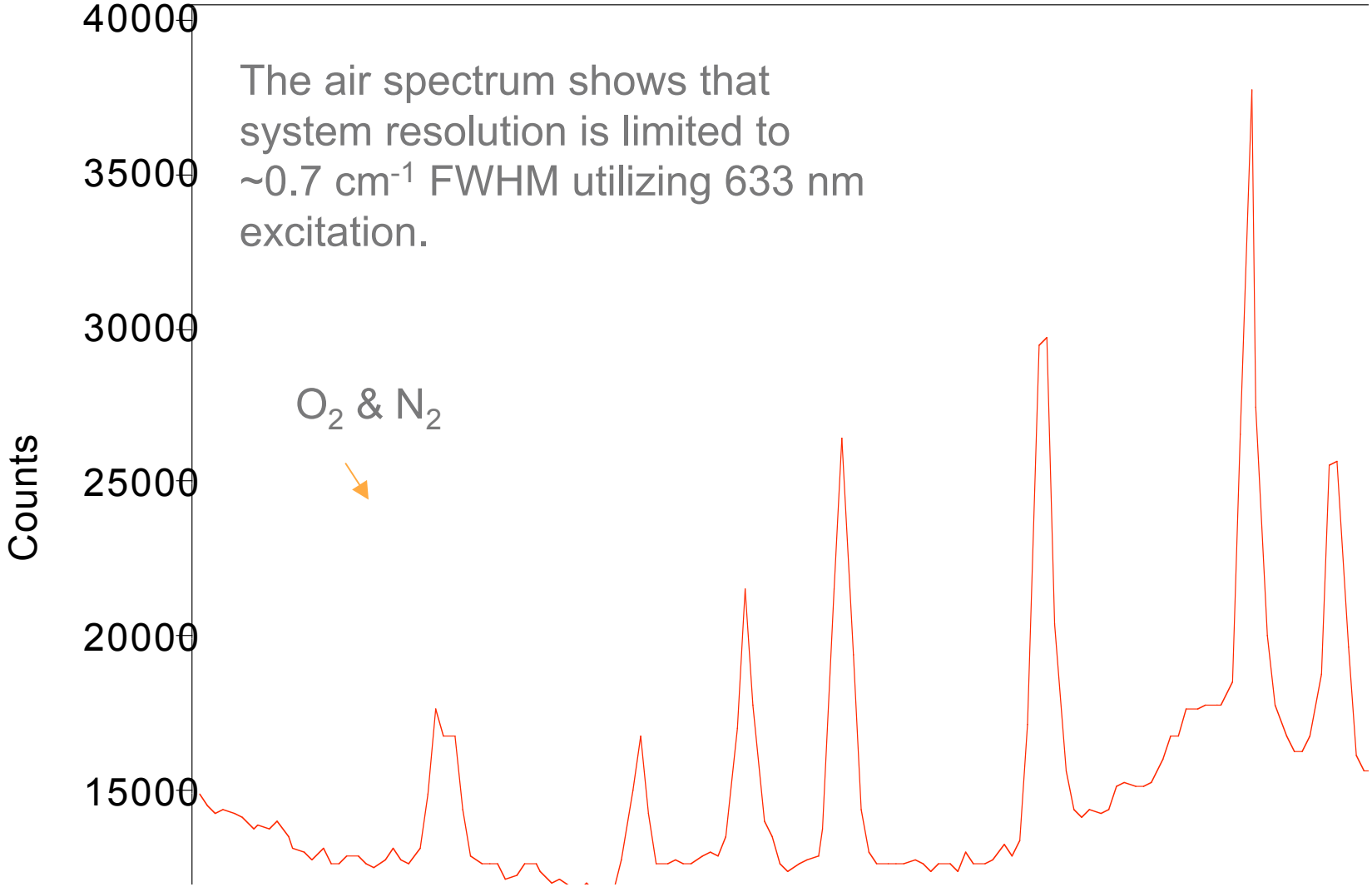
Spectrometer resolution

The slit-width determined resolution of the spectrometer is determined by the convolution of the entrance slit with the CCD pixel.



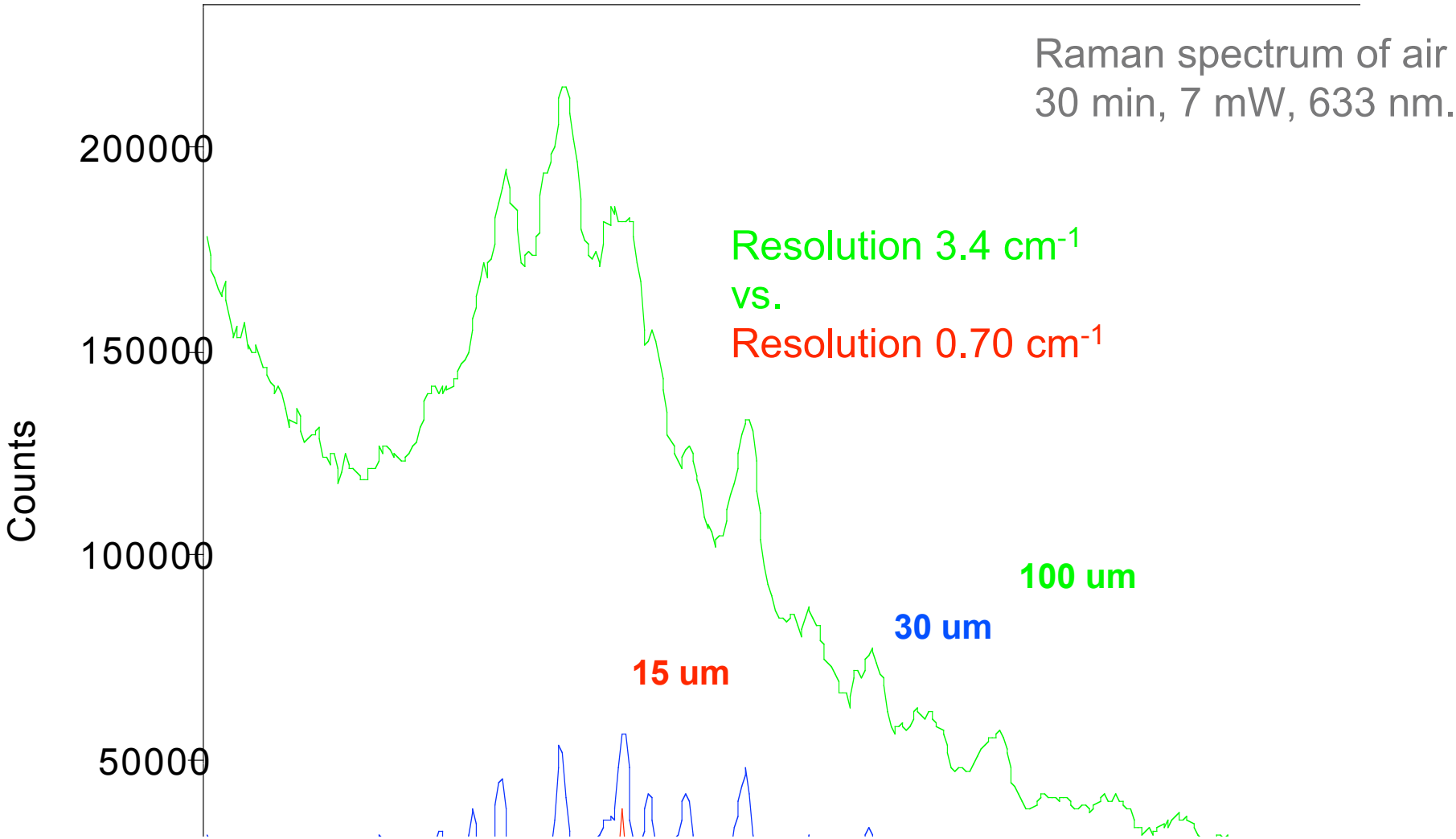
Raman microscopy: spectral resolution

Spectrometer resolution is best determined by measuring the air spectrum



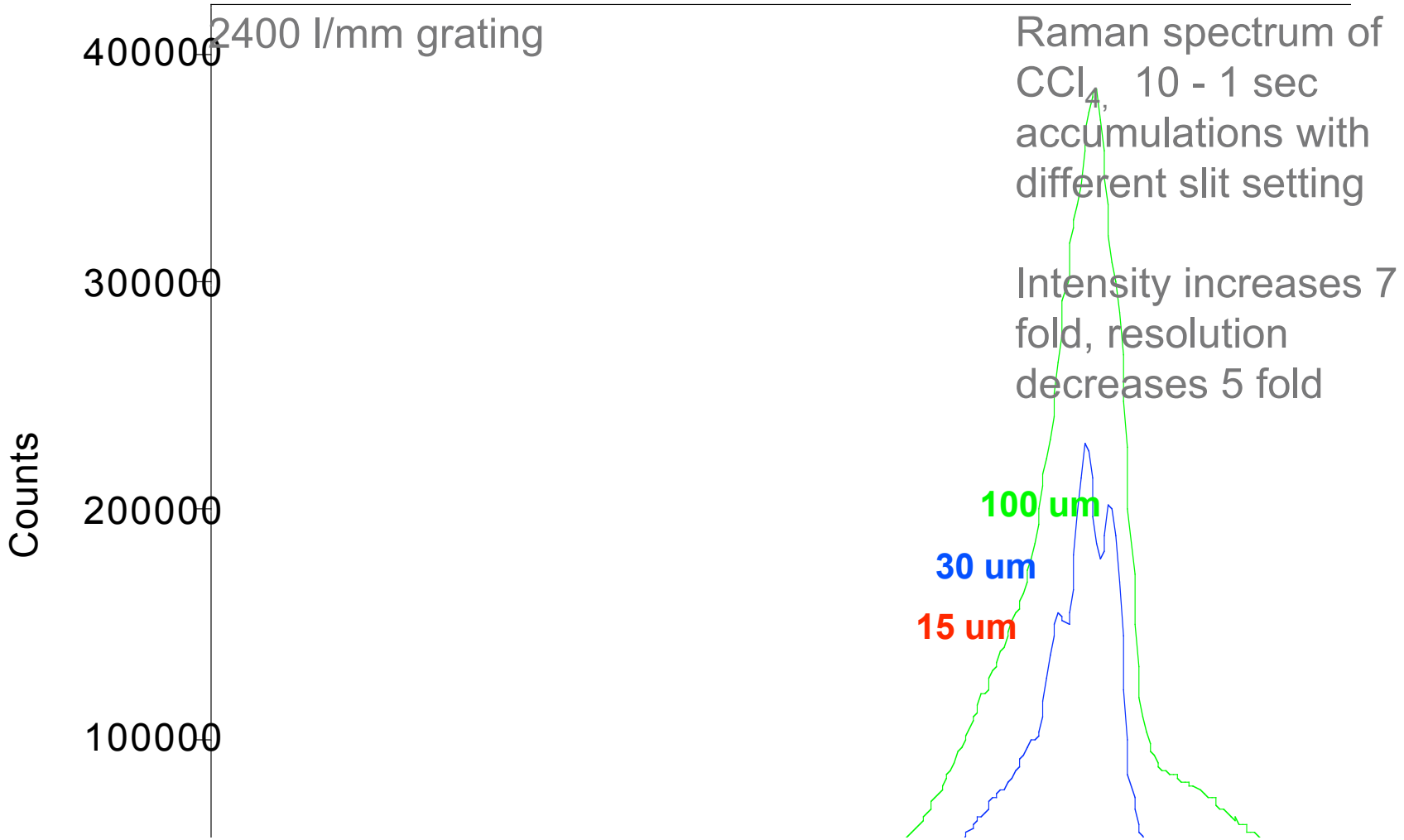
When the spectrometer determines measured spectral linewidth

Increasing the entrance slit increases light throughput but decreases resolution



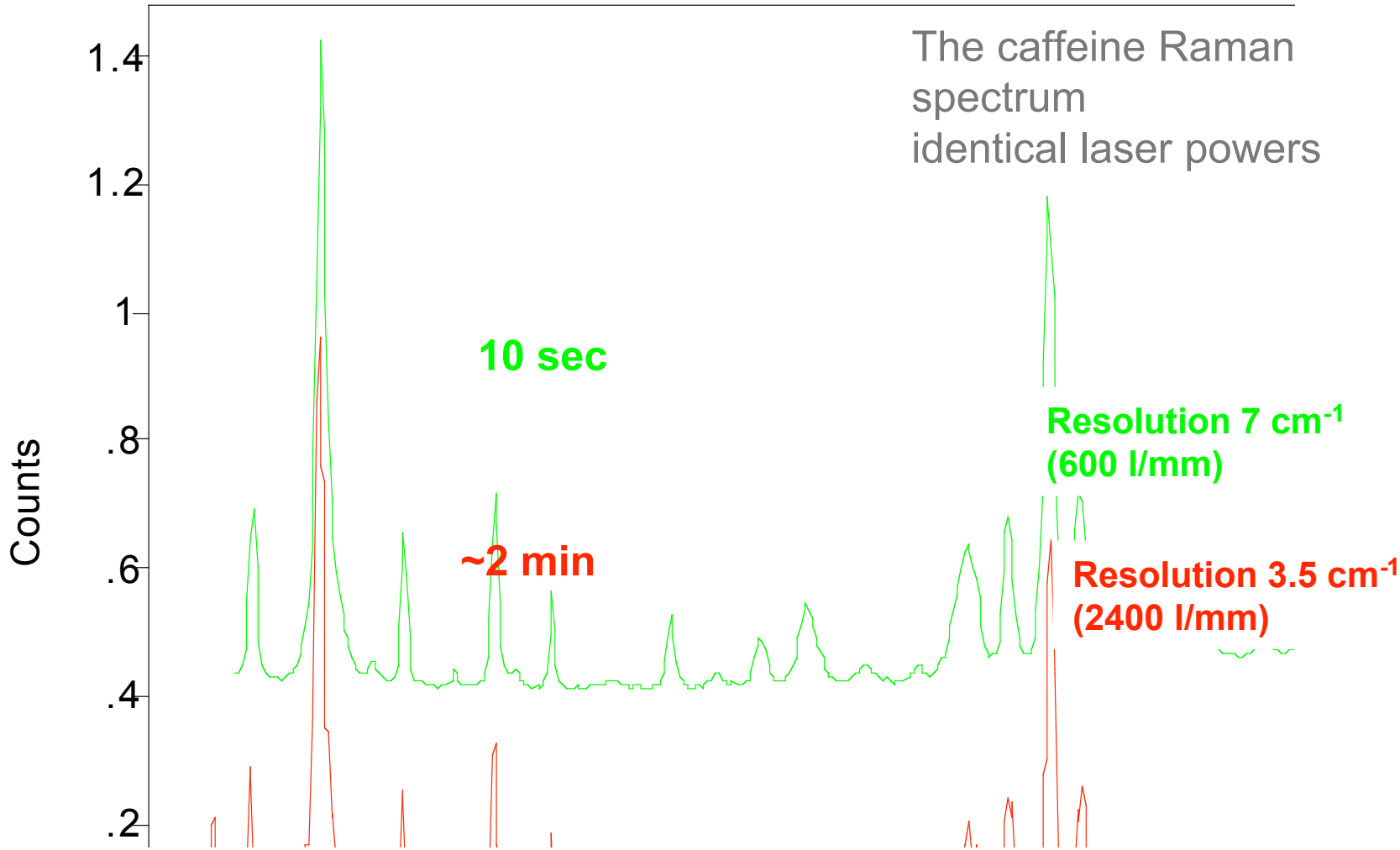
Trading spectral resolution for throughput

Increasing the entrance slit increases throughput but decreases resolution



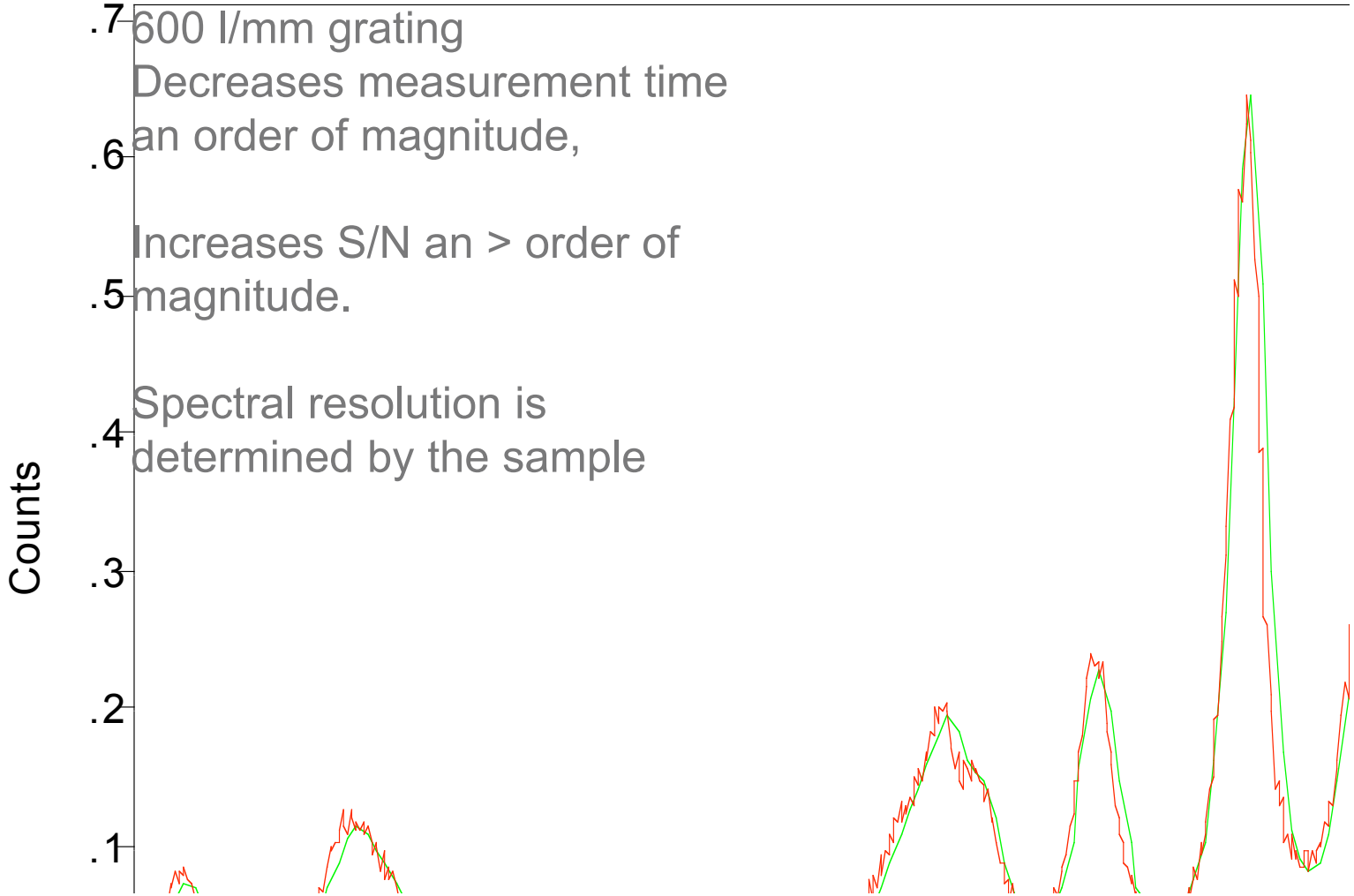
Sample determines measured spectral linewidths

Single static scan with 600 l/mm, **10 stitched static scans with 2400 l/m**



Sample determines measured spectral linewidths

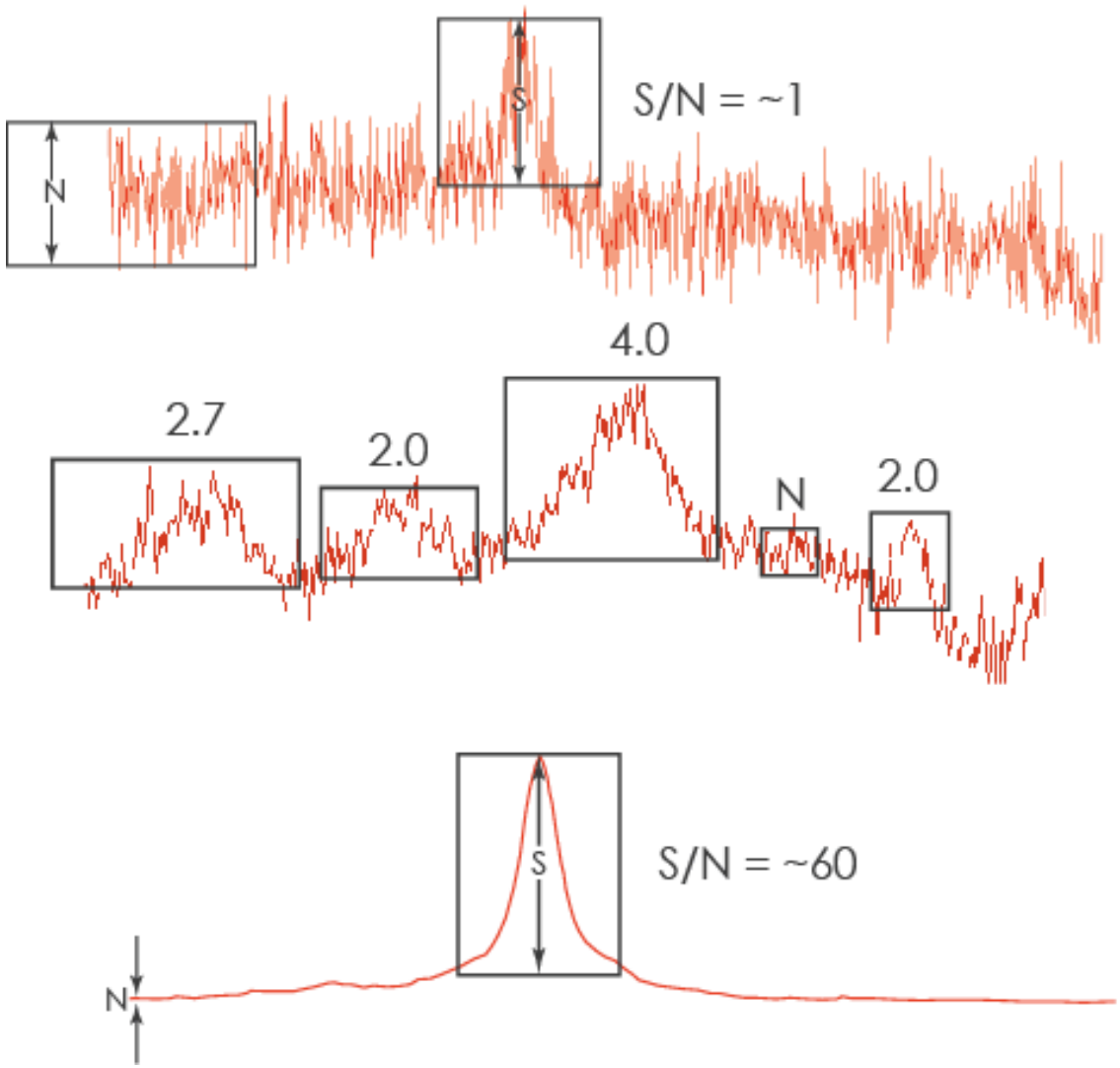
Matching the spectrometer resolution and the and CCD pixel resolution to the natural linewidths of the sample optimizes S/N



System parameters that affect S/N

- **Laser**
  - Power
  - Wavelength
  - Modality
  - Stability
  - Delivery optics
- **Collection Optics**
  - Aperture
  - Focus
    - Diffraction limited spot size
  - Transmission
  - Robustness

Factors affecting S/N



Sources of

Shot Noise = Sqrt #
Dark Noise = Sqrt c
Read Out Noise
Stray Light

Factors aff
signal stre

Detector Responsi
Input Optics
Spectrograph Ape
Relative Detector
Grating Efficiency

Select a CCD for best Raman performance

What limits the CCD performance?

1. Read noise: How many photon generated electrons are required to achiev a signal level greater than the read noise?

    Raman systems that require off chip binning increase read noise to the square root of the number of pixels binned.

2. Dark Charge rate: How long can you integrate before the binned CCD pixels generate a charge equivalent to the read noise?

At the integration time that the dark charge signal contributes to the noise either through shot noise or uniformity of response, it must be subtracted.

3. Uniformity of response: How many photon generated electrons can be measured before the shot noise is exceeded by the non-uniformity of response?

At the point uniformity of response noise exceeds shot noise the pixels must be read out individually (without binning) for response correction.

Optimal CCD operating temperature

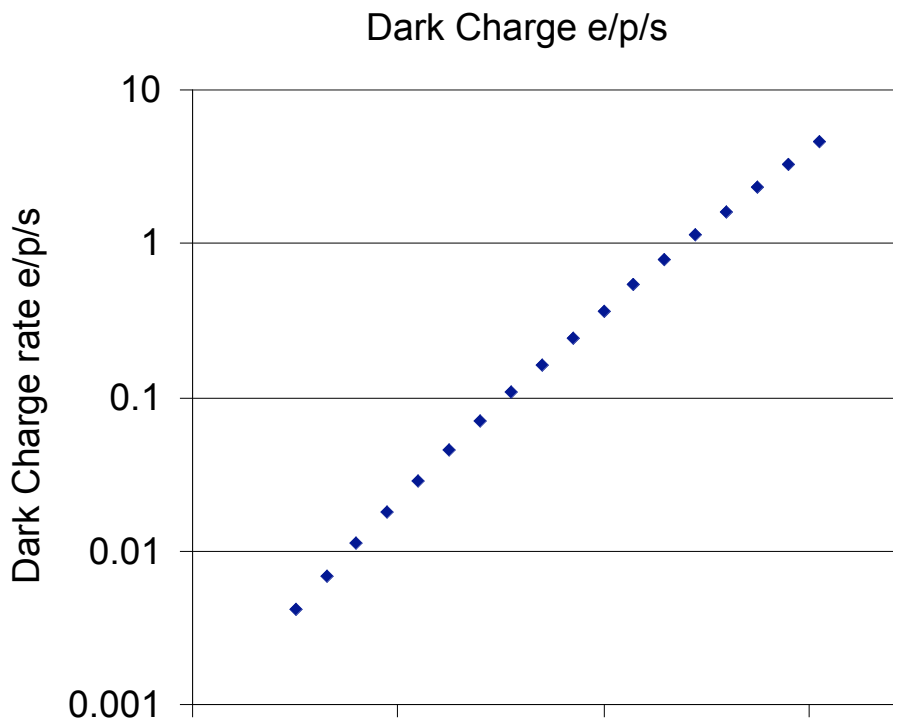
The best CCD temperature operation is determined by the CCD dark charge rate and the requirements for operation near the detector limit of ~1050 nm

- Low temperatures decrease the CCD dark charge rate. The CCD dark charge rate decreases ~50% for each 6-9 degree decrease in operating temperature.

$$\frac{Qd}{Qd_0} = 122 * T^3 * e^{\frac{-6400}{T}}$$

Qd dark charge rate (e/p/s) at operating temperature T

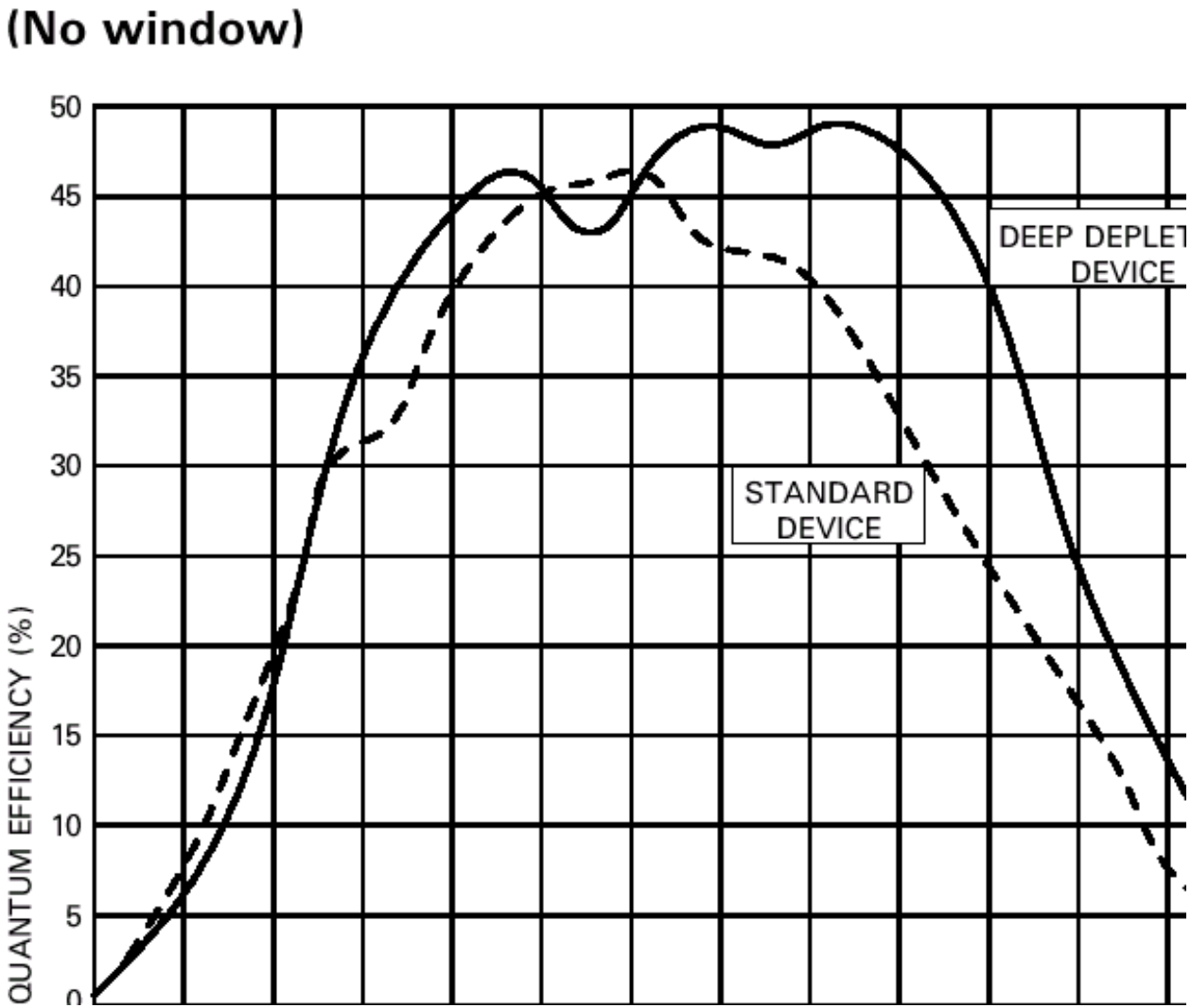
Qd_o - dark charge rate at reference temperature (typically 23-25 ^oC)



Select a CCD for best Raman performance

Select response uniformity rather than QE

Renishaw CCD typical response curve. The peak QE is ~50%, but the response uniformity is an order of magnitude better than with higher QE CCD chips

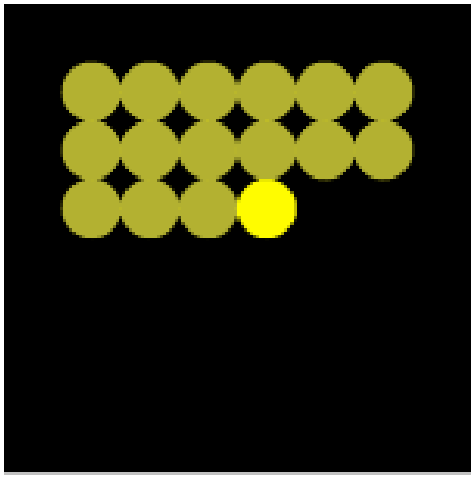


StreamLine™

- StreamLine™ technology
  - Unique Renishaw technology (patent pending)
  - Combination of hardware and software
  - Enables very fast Raman imaging of samples
- Application areas
  - Pharmaceuticals
  - Materials science
  - Semiconductors
  - Polymers
  - Biosciences
  - etc.

Spectral imaging

- Acquire data from different points on the sample.
- Generate maps based on parameters of resulting spectra. Examples:
  - Univariate: intensity of band
  - Multivariate: chemometrics:
    - Component analysis based on reference samples
    - Principal component analysis (no references)



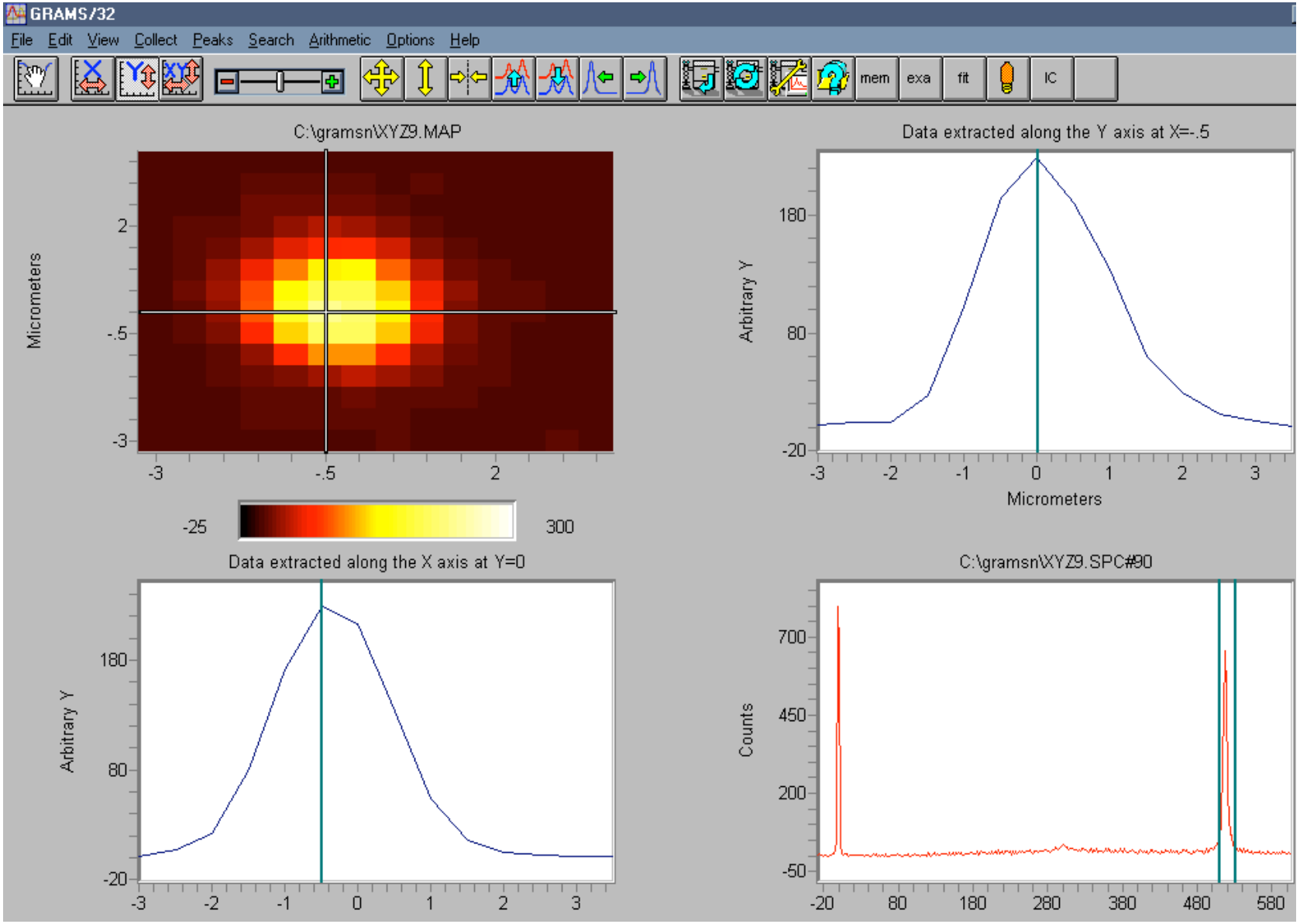
Point mapping

Mapping stage repeatability

- Measure the Raman spectrum of ~1 μm Si particle with 1 μm laser spot (backlash of 10 μm enabled)
- Move away from then return to the particle to repeat the Raman measurement (32 times each direction)
- Compare performance of the motorized mapping stage with the 0.1 μm encoders on to the performance with the encoders off

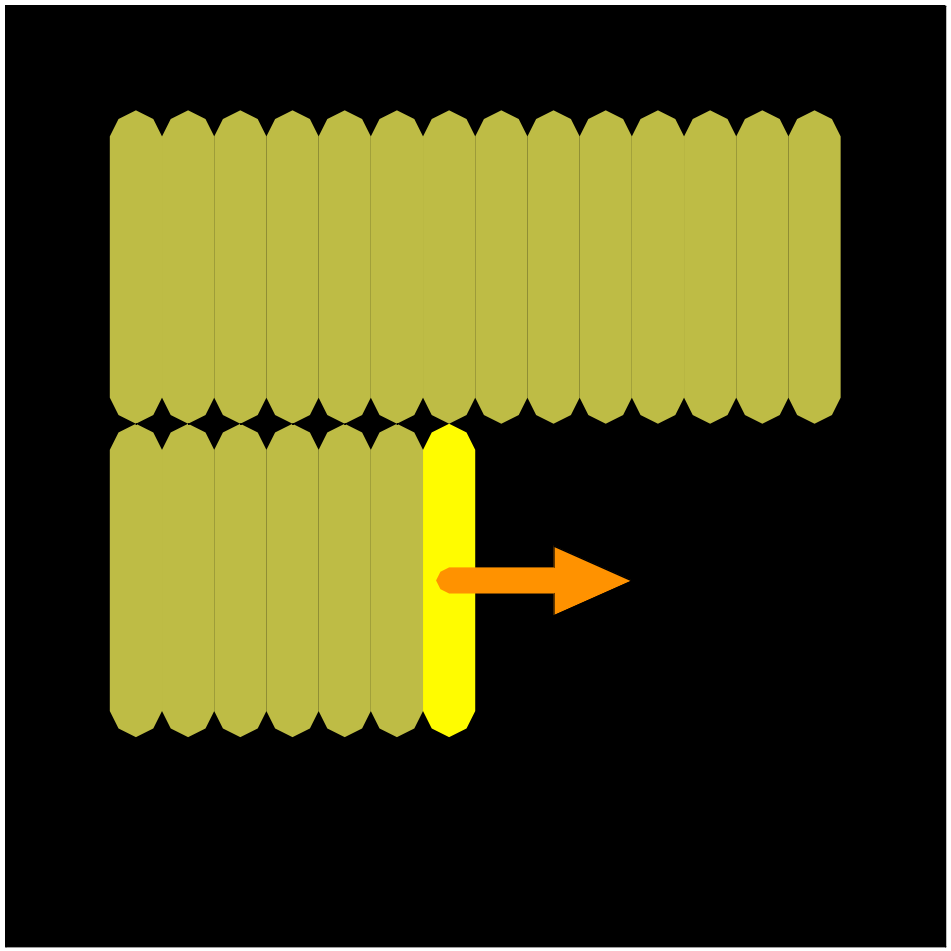
Specification:	
unencoded	2 μm
encoded	0.3 μm

The Si particle



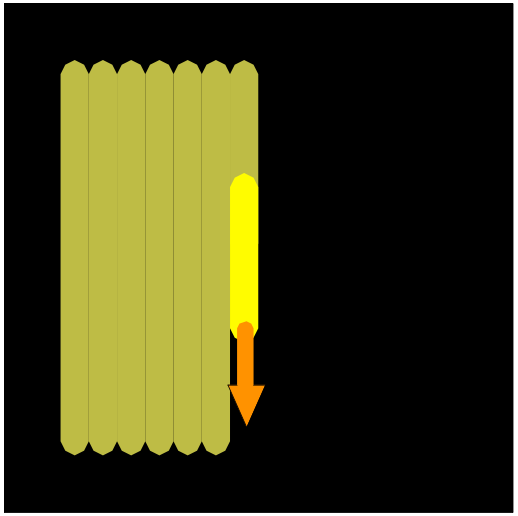
Raman line mapping

- Method
  - Generate laser line on sample
  - Simultaneously acquire spectra from positions along the line
  - Move line over sample, perpendicular to its length
- Advantages
  - Larger area illuminated by line
- Disadvantages
  - Stop/start movement overhead
  - Artefacts…line uniformity



StreamLine™

- Move line the other way!
- Synchronise the stage and the detector
- Advantages
  - Smooth fast continuous movement
  - Artefacts eliminated
  - Large area illuminated by line



Features of StreamLine™ imaging

- StreamLine™ offers:
  - Power density up to 100x less than point laser configurations
  - No joining or uniformity artefacts
  - Macro (whole tablet) and micro (<1 µm) sampling capabilities
  - Zero dead time between sequential spectral acquisitions
  - Confocal information maintained
  - High spectral resolution options available
  - Multi-wavelength capabilities from the UV to NIR
  - High speed with unparalleled data quality

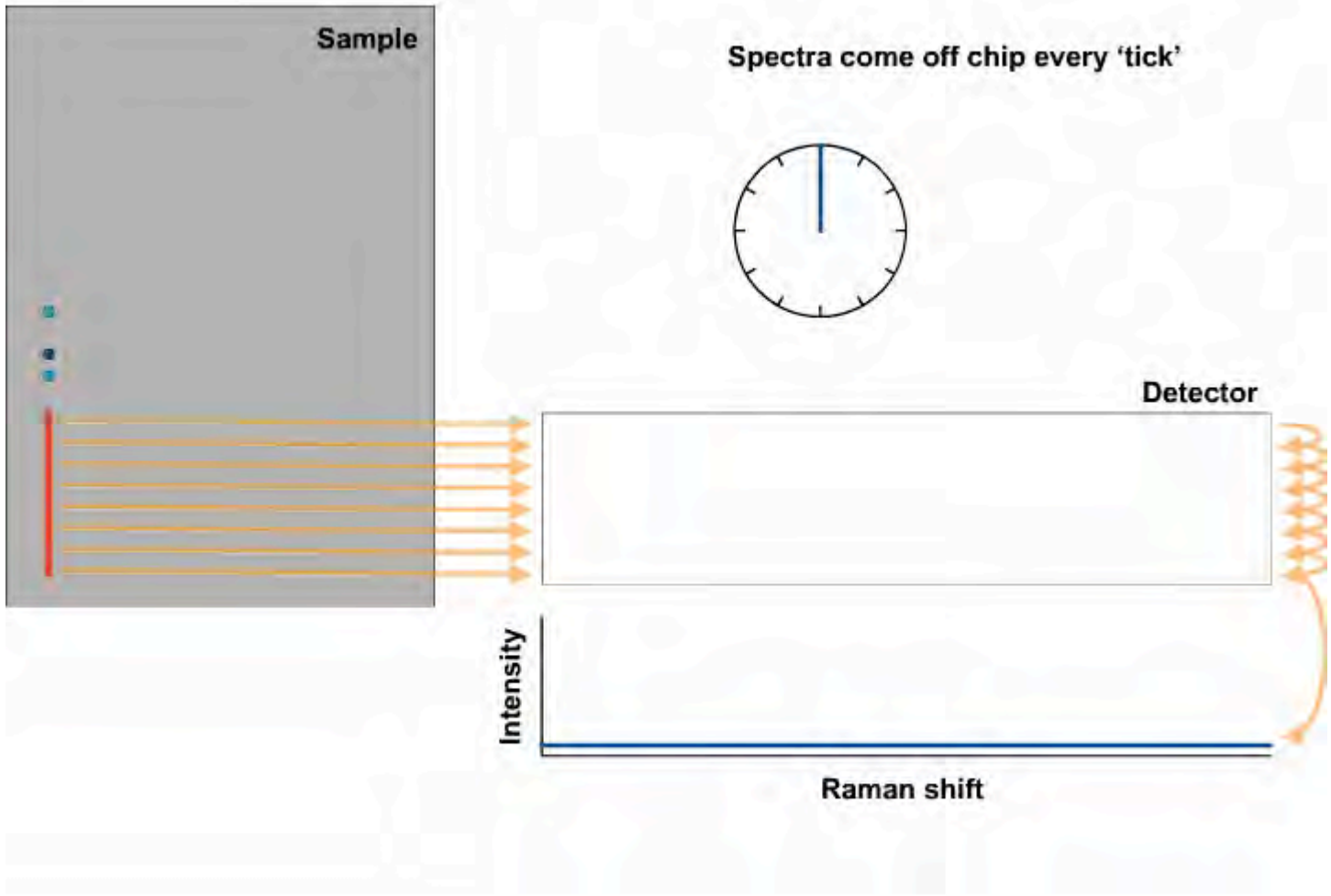
StreamLine™

- Technology for very fast Raman imaging
- Unique Renishaw technology (patent pending)
- Innovative hardware, unique software
- Collect excellent quality data where point by point would damage sample
- Parallel data readout, synchronised with sample movement

100µm

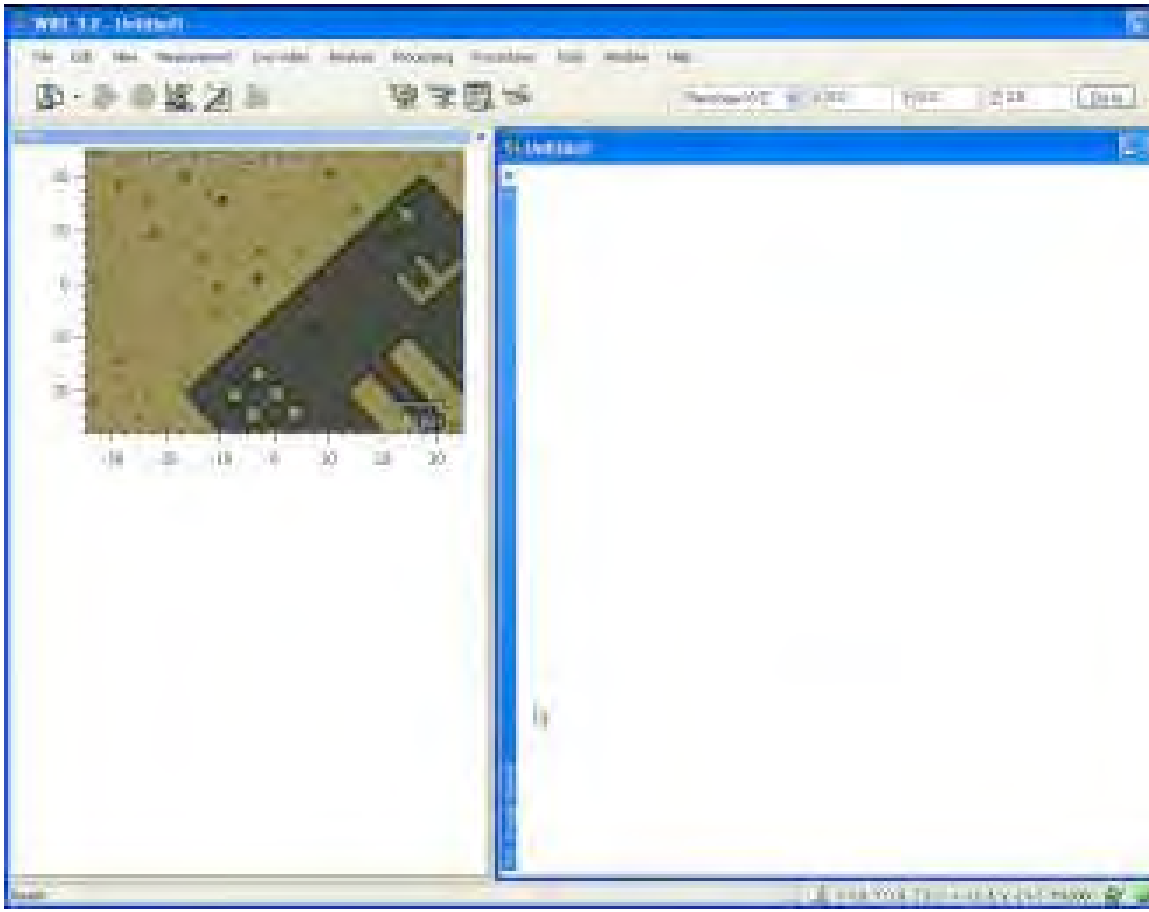
StreamLine™ imaging: how it works?

– Each sample point passes beneath each part of the laser line
– The charge is stepped synchronously with the stage movement
– Parallel data readout



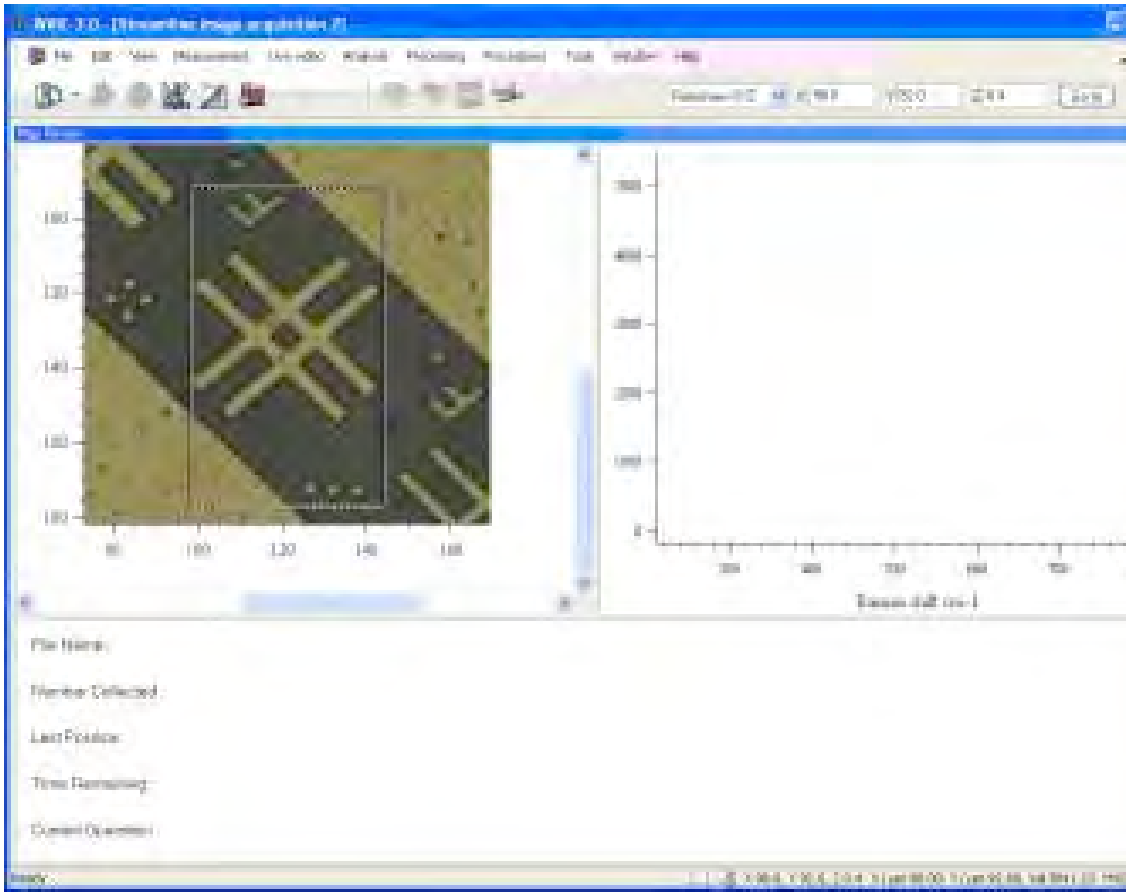
White-light montage

- Used for detailed sample survey
- 4_4 white-light montage generated with 50_ objective
- Montage can then be used to define multiple imaging experiments
- Multiple experiments may be queued
- White-light image saved with spectral data



StreamLine™ in action

- Example StreamLine™ video
- Silicon target with metallised structure, imaged with 532nm laser
- 4 x 4 montage white-light image used to define experimental area
- Imaged area bigger than 50x objective field of view
- Live imaging of Si 520cm^{-1} band
- Bicubic interpolation applied to image during acquisition



Metallised Si target analysis

- Line profile along the Y axis
- Feature size approximately 5 µm

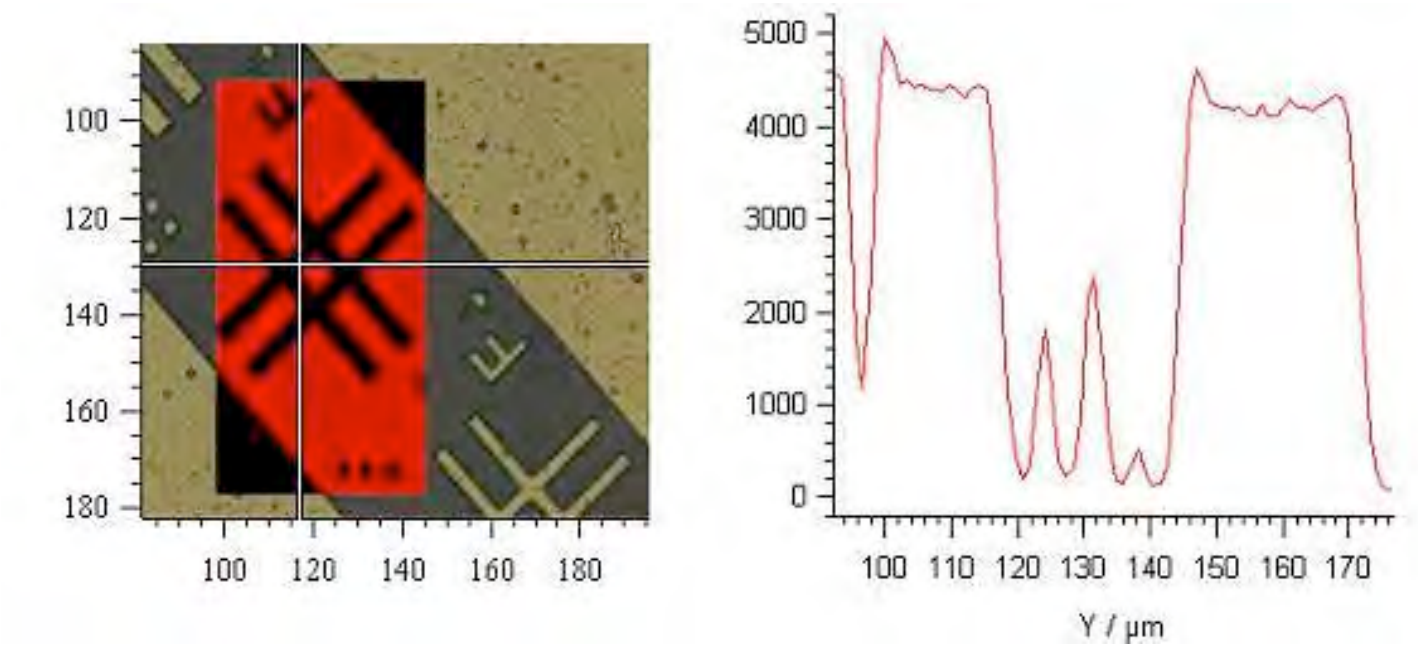
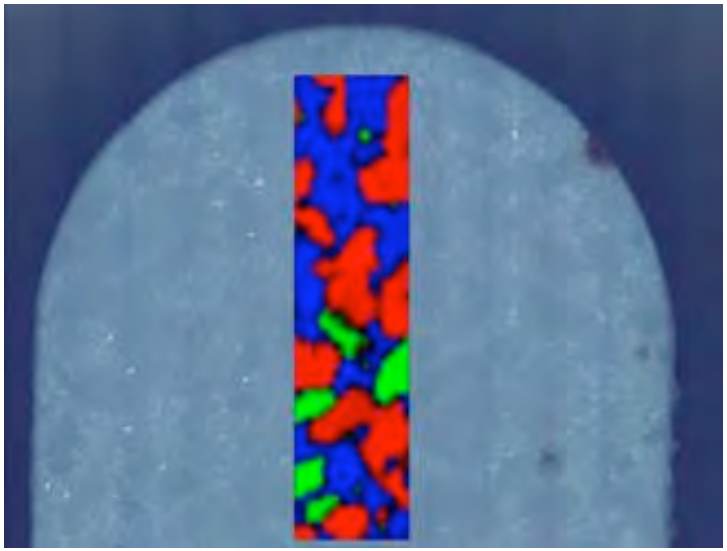
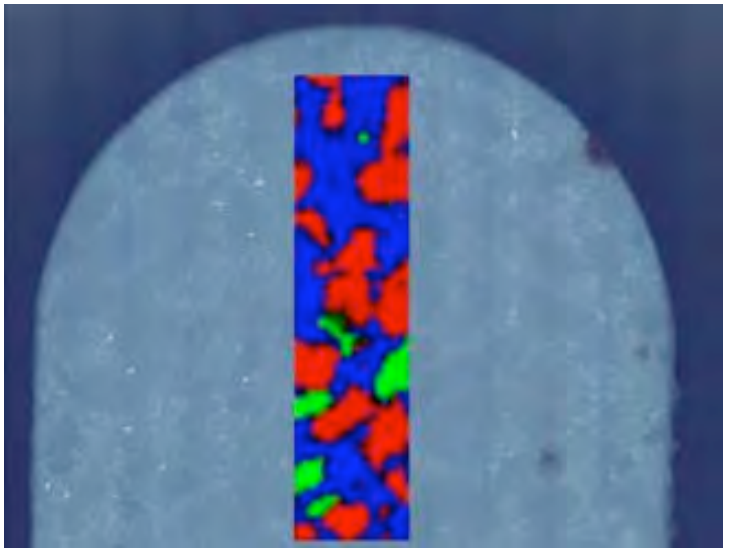


Image quality comparison



StreamLine™ 1 minute, 40 seconds



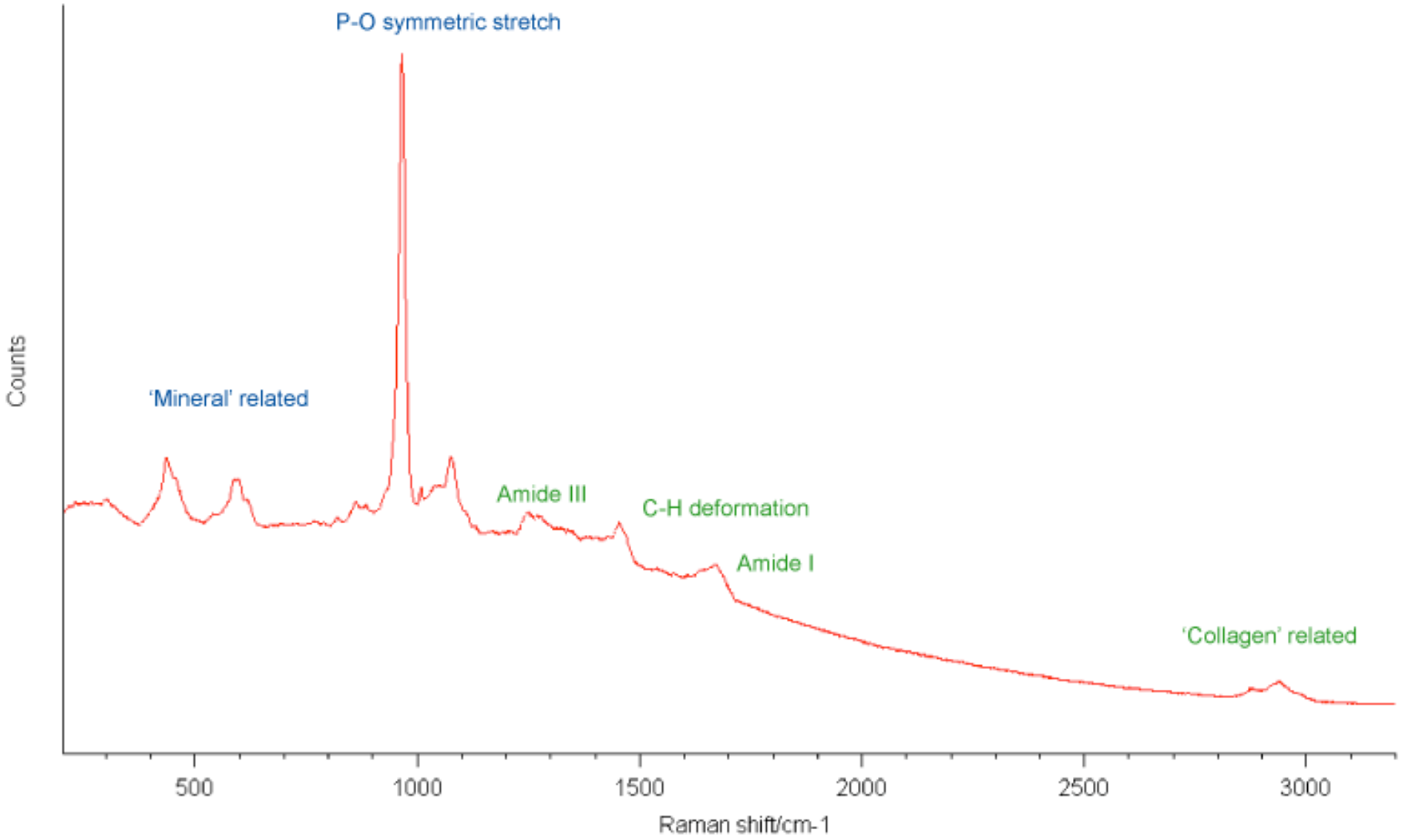
Point by point 1hour, 6 minutes

- Same area on tablet analysed using point by point and StreamLine™ techniques
- Image generated using direct classical least square (DCLS) multivariate method
- Image shows distribution of Aspirin, Paracetamol and Caffeine components
- Identical data quality

Image of complete tooth section

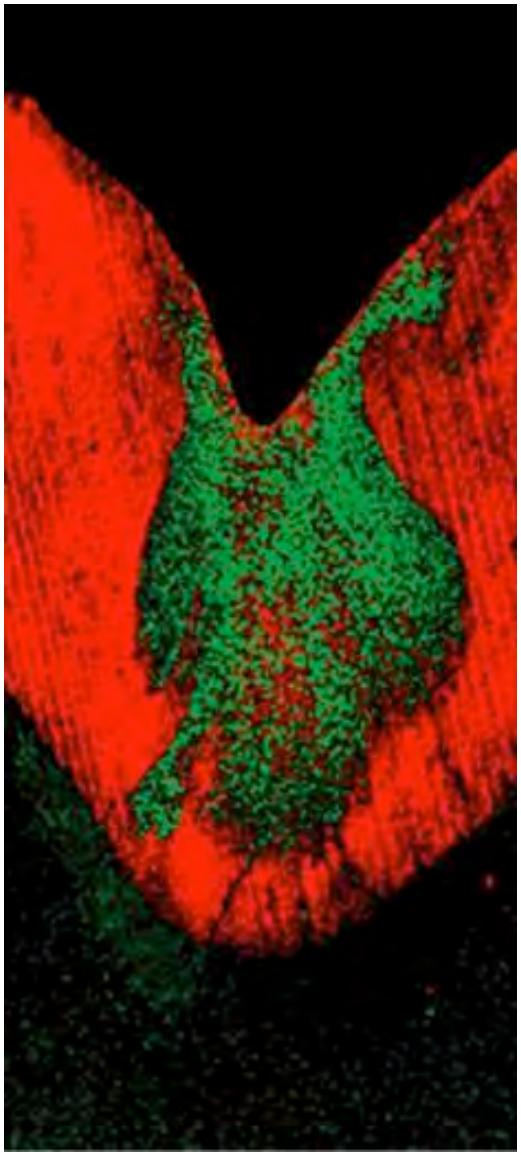
- First ever whole tooth Raman image
- Different regions clearly indentified
- Color coding:
  - Yellow: enamel
  - Green: dentine
  - Red: fluorescent areas
- Details
  - 9 mm x 16 mm area
  - 84,024 spectra
  - 20 minutes
  - 785 nm excitation

Spectrum from dentine region of tooth



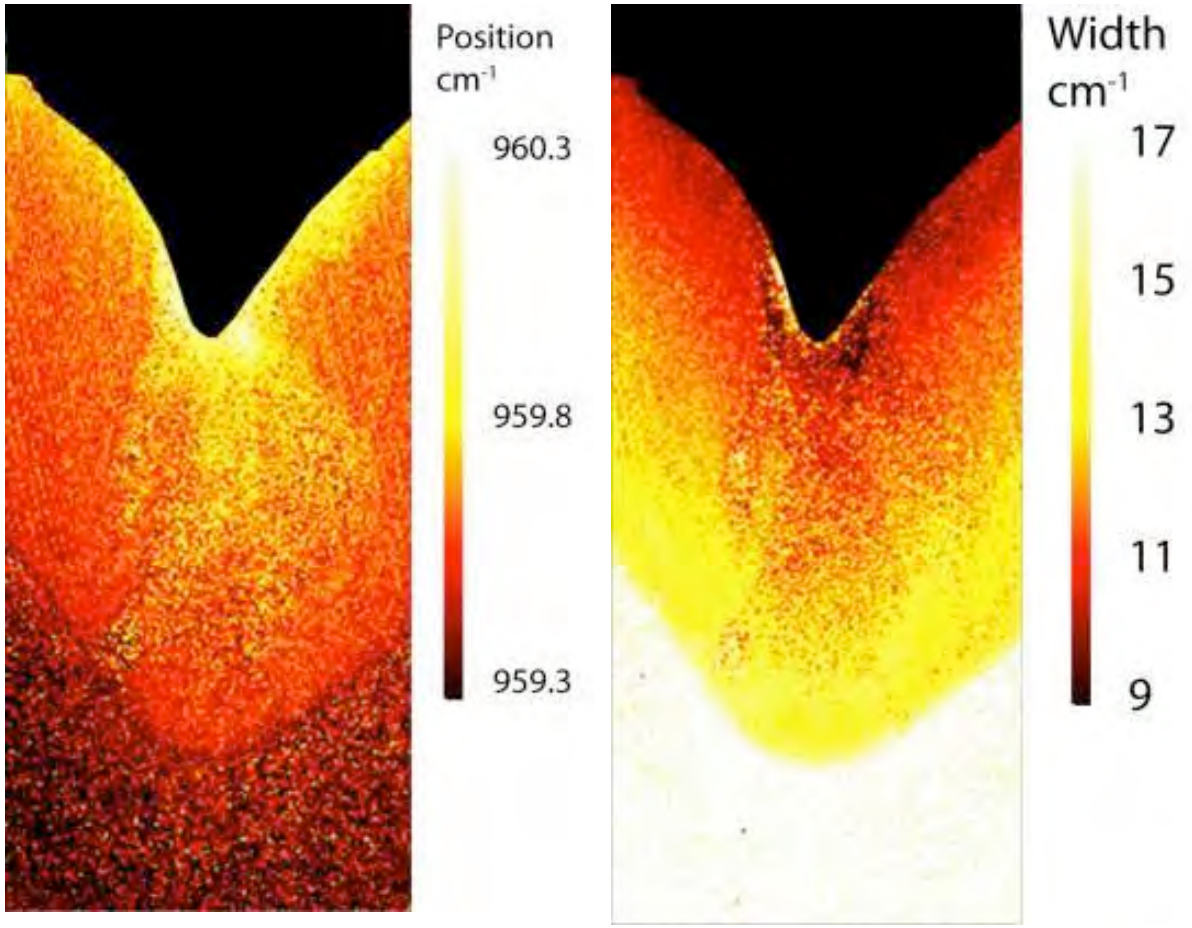
Dental caries polarisation images

- Image is a ratio of two data sets:
  - Parallel-polarisation
  - Crossed-polarisation
- Color coding:
  - Red: strong polarisation dependence - Sound enamel
  - Green: weak polarisation dependence - Carious region
- Details
  - 1.5 mm x 3.4 mm area
  - 42,642 spectra
  - 27 minutes
  - 785 nm excitation
- StreamLine is compatible with the full range of spectral options available for the inVia Raman microscope



Dental caries curve-fit analysis image

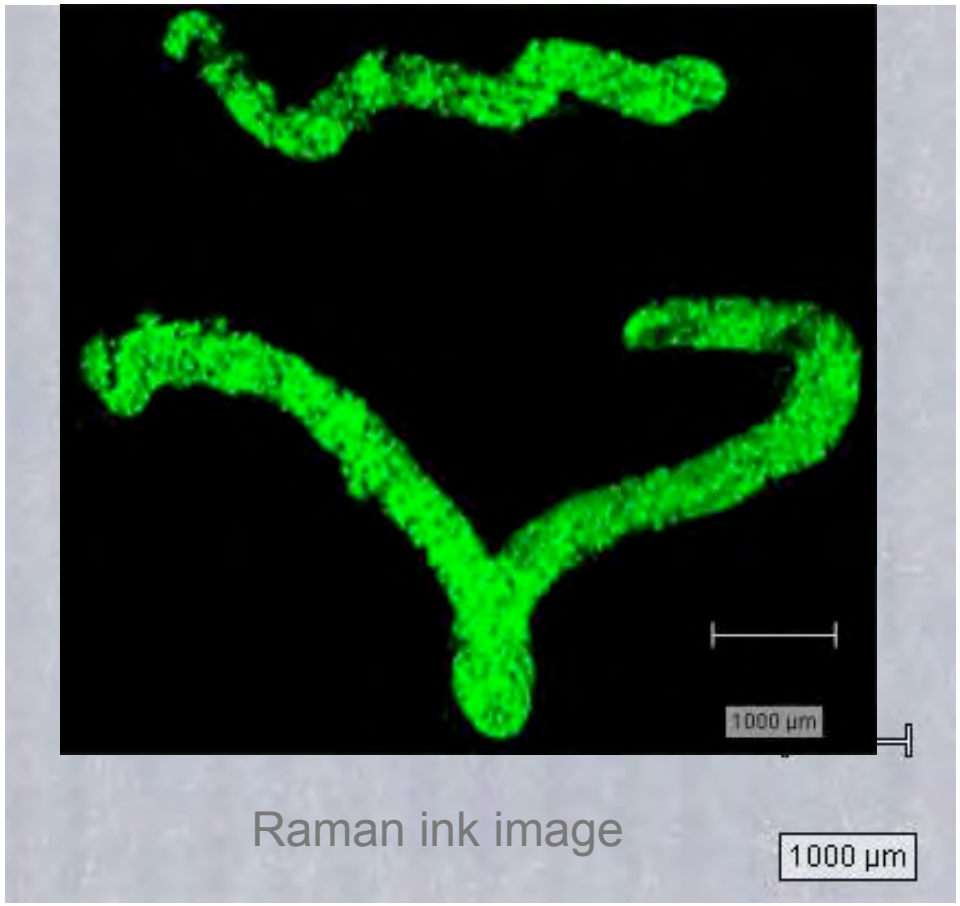
- Curve fit data analysis on P-O symmetric stretch band
  - Peak width
  - Peak position
- Details
  - 1.5 mm x 3.4 mm area
  - 42,642 spectra
  - 27 minutes
  - 785 nm excitation



Whole ink character imaging

First ever whole ink character Raman image

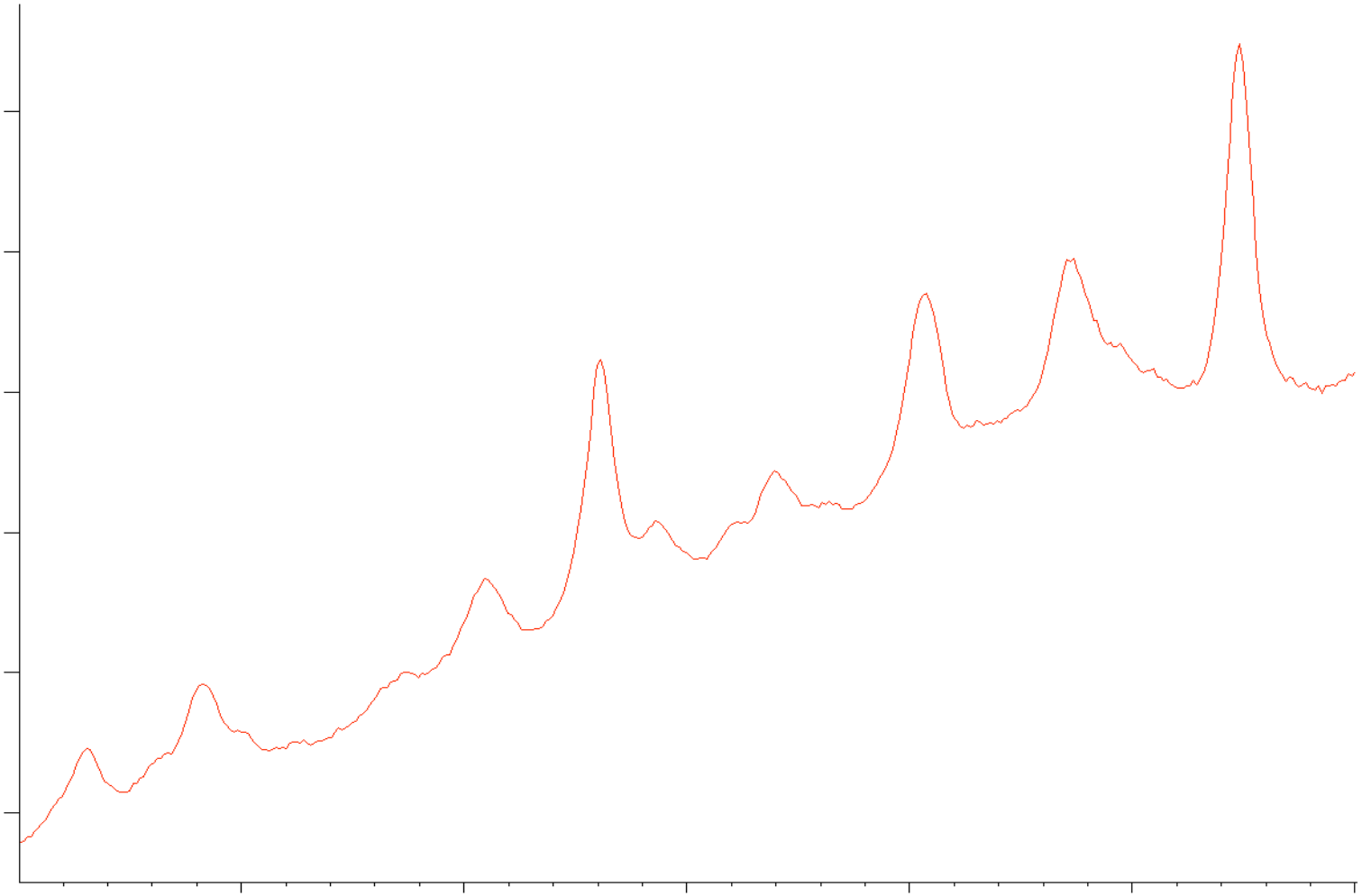
- 43,400 spectra
- 29 minutes
- 514 nm
- 20x objective
- 30 µm spatial resolution
- Image created using component method



White light montage

Whole ink character imaging

High quality ink spectrum from image (noise filtered)



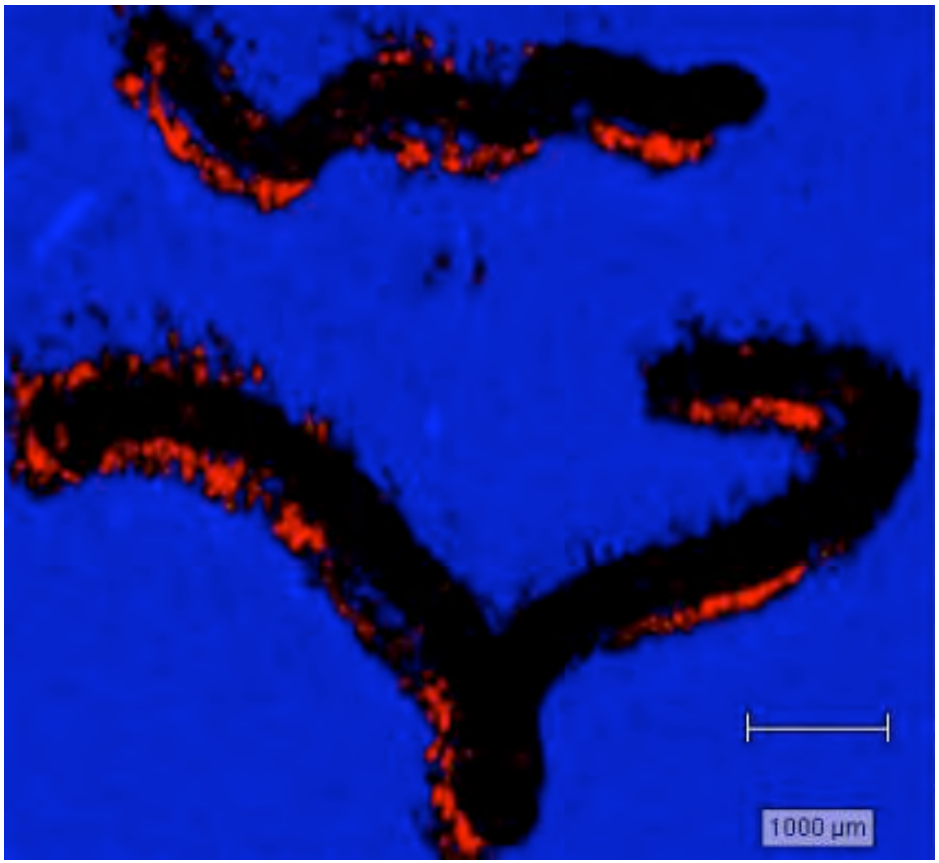
Whole ink character imaging

Image can also reveal pen contact on paper

Blue – paper

Red – paper with pen contact away from ink

Useful information provided on pen angle during stroke



Crossed ink example 1: dual crossed ink lines

First ever Raman crossed line image

Double crossed line example using two black ball point pens

Image collected of all lines and paper in one experiment

- Details
  - 1040 µm (X) by 2607 µm (Y)
  - 90,440 spectra
  - 90 minutes total time
  - 514 nm excitation
  - 20x objective

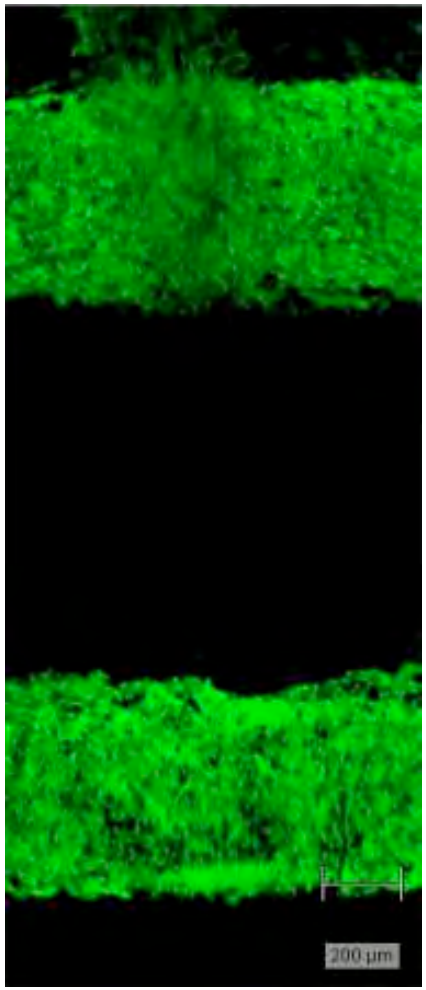
Crossed ink example 1: dual crossed ink lines

Component Raman image of ink 1 (green)

Shows smearing of top horizontal line

Also the image provides information on the direction of the crossing

This suggests that the top ink 1 line is beneath a further line crossing it.



Direction of smearing

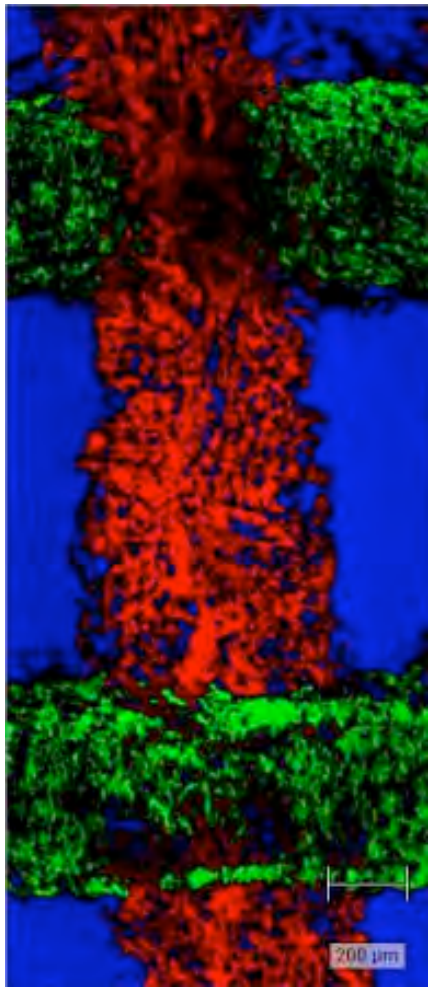
Crossed ink example 1: dual crossed ink lines

Component Raman image overlay from WiRE 3 – confirms order of deposition

Top cross – Ink 1 (green) under ink 2

Bottom cross – Ink 2 (red) under ink 1

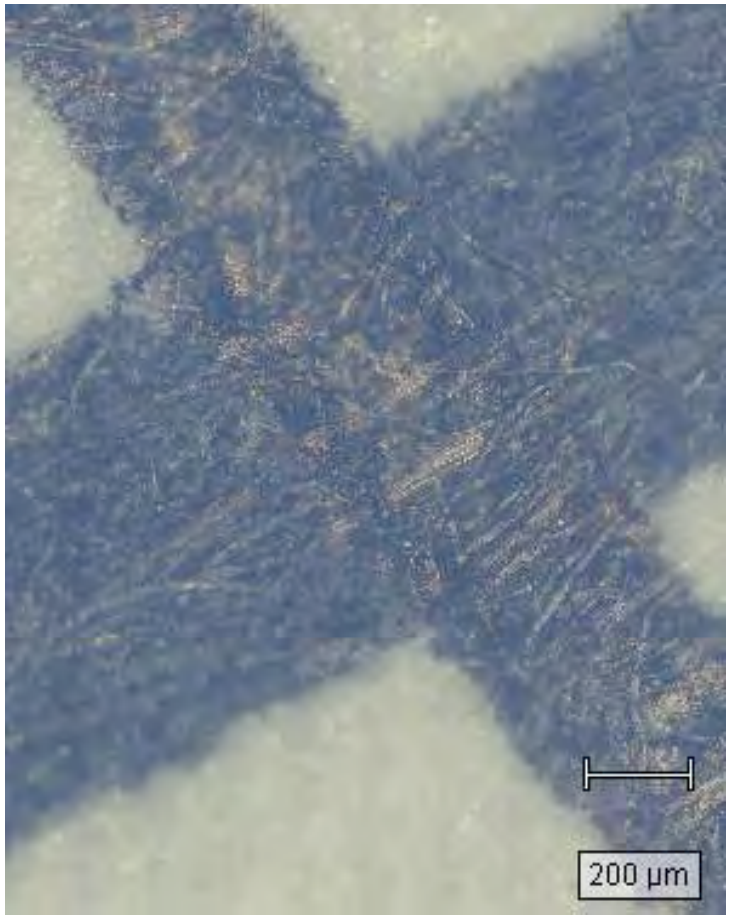
Ink 1 (green)
Ink 2 (red)
Paper (blue)



Crossed ink example 2: single crossed ink lines

Single crossed line example using **two black** ball point pens

- Details
  - 990 µm (X) by 1430 µm (Y)
  - 47,422 spectra
  - 33 minutes total time
  - 514 nm laser wavelength
  - 20x objective

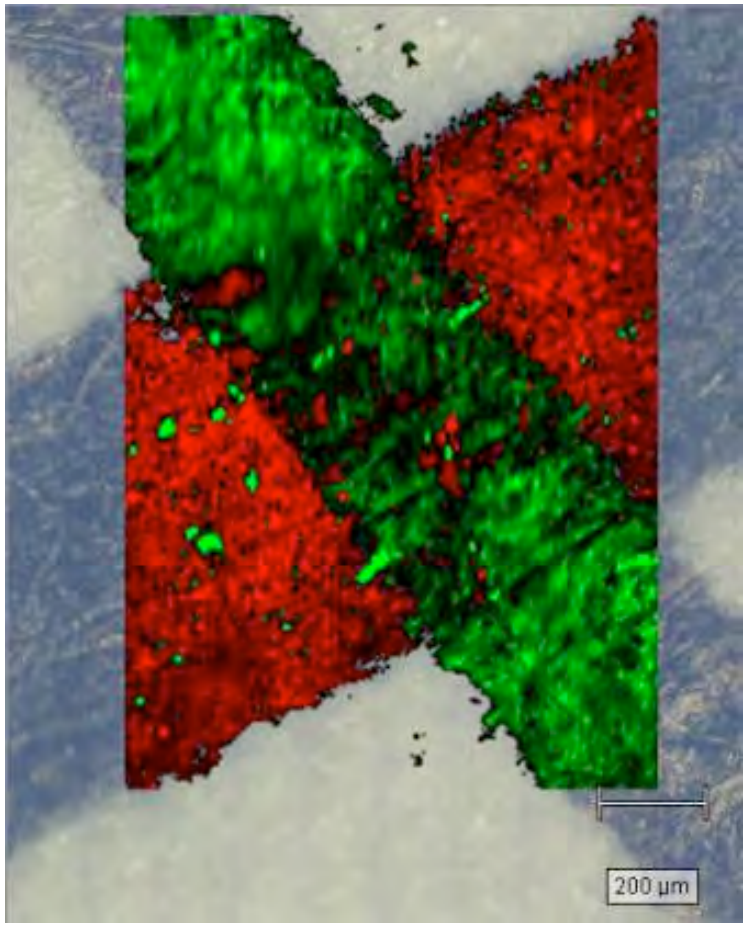


Crossed ink example 2: single crossed ink lines

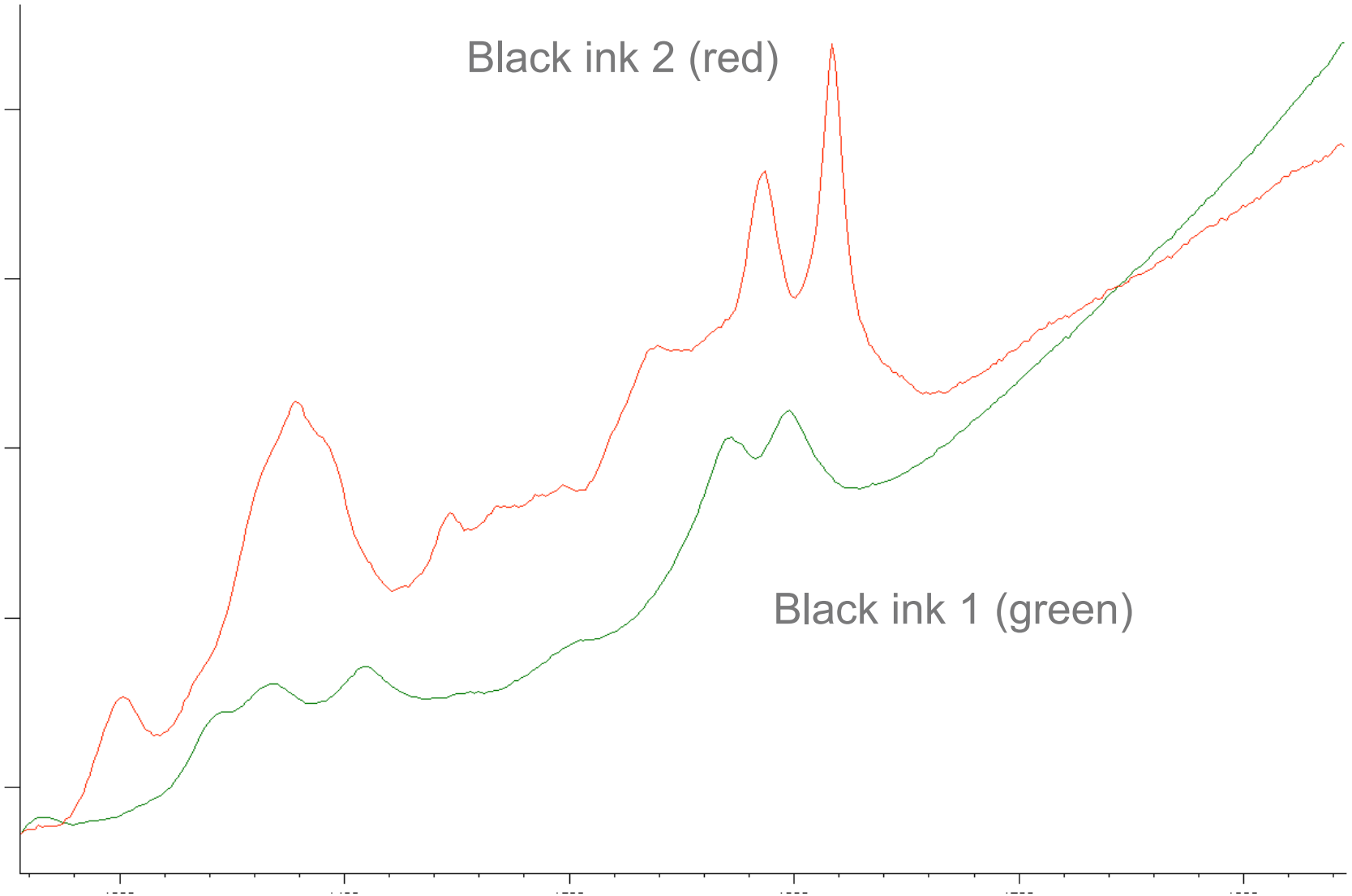
Component Raman image overlay from WiRE 3 superimposed on white light image

Cross – Black ink 1 (green) over black ink 2 (red)

Black ink 1 (green)
Black ink 2 (red)



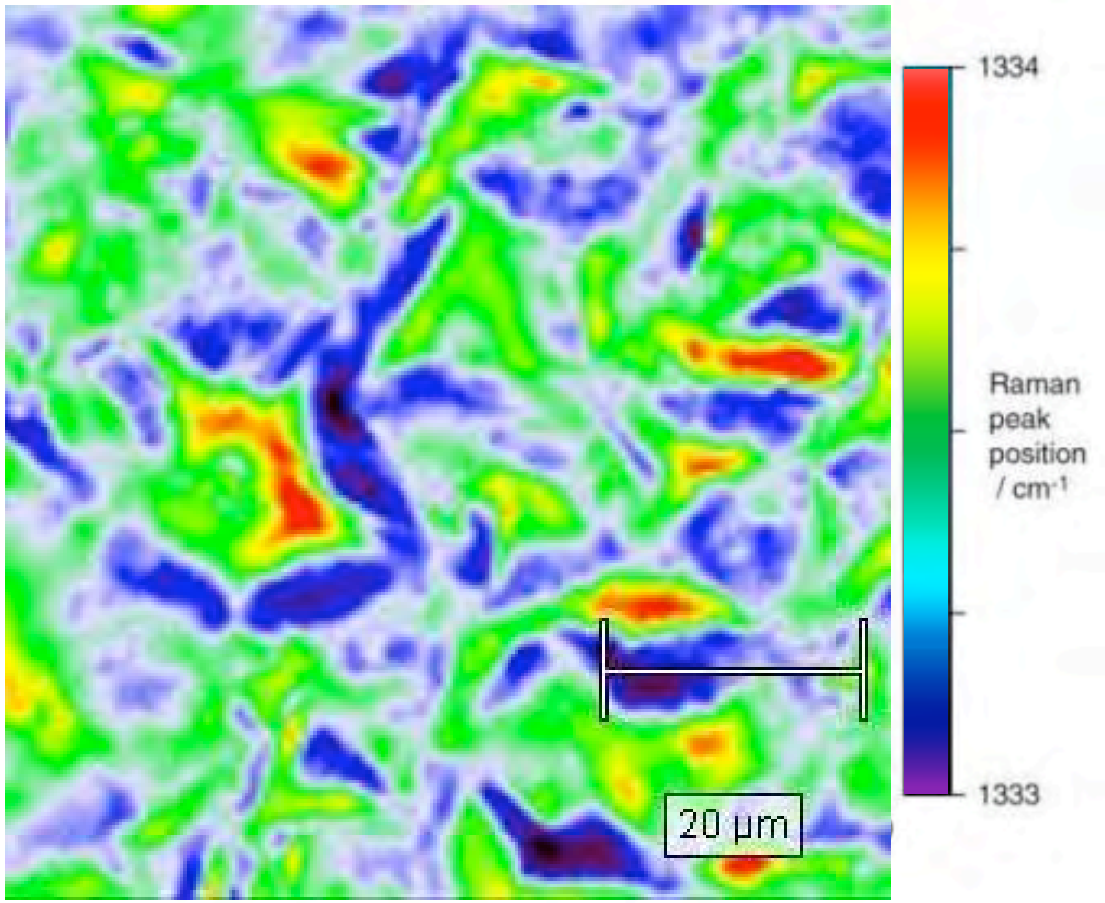
Crossed ink example 2: spectra from image



Raman and PL imaging of polycrystalline CVD diamond fil

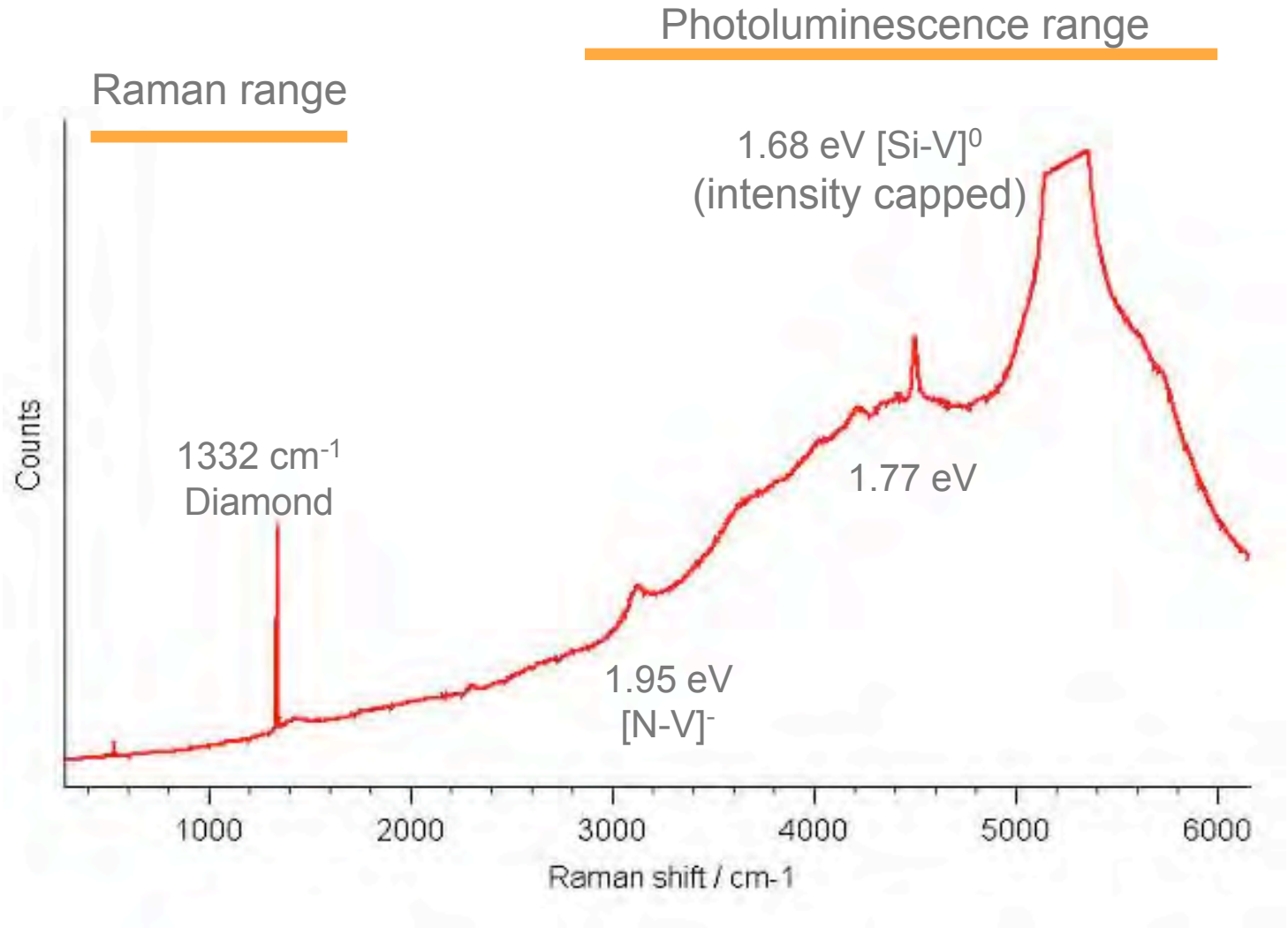
- CVD diamond sample grown onto silicon substrate using chemical vapour deposition (CVD) method
- Rough growth surface is subsequently polished optically flat
- Raman and photoluminescence measured in sequential experiments
- Curve-fit analysis used for image generation
- 18,000 spectra collected in 6 minutes

Diamond peak position



Raman and PL imaging of polycrystalline CVD diamond fil

Details of spectral analysis

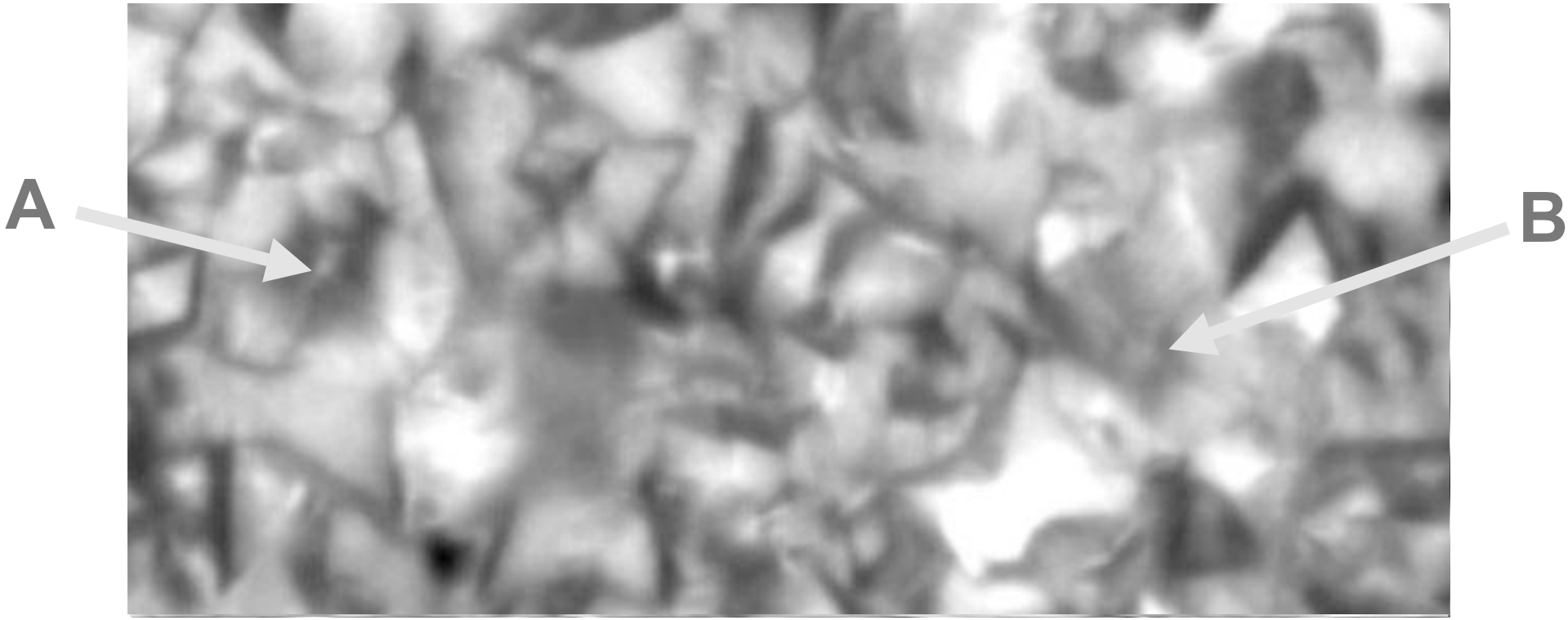


- Standard spectral resolution configuration used for Raman bands, lower resolution used for photoluminescence features

Raman and PL imaging of polycrystalline CVD diamond fil

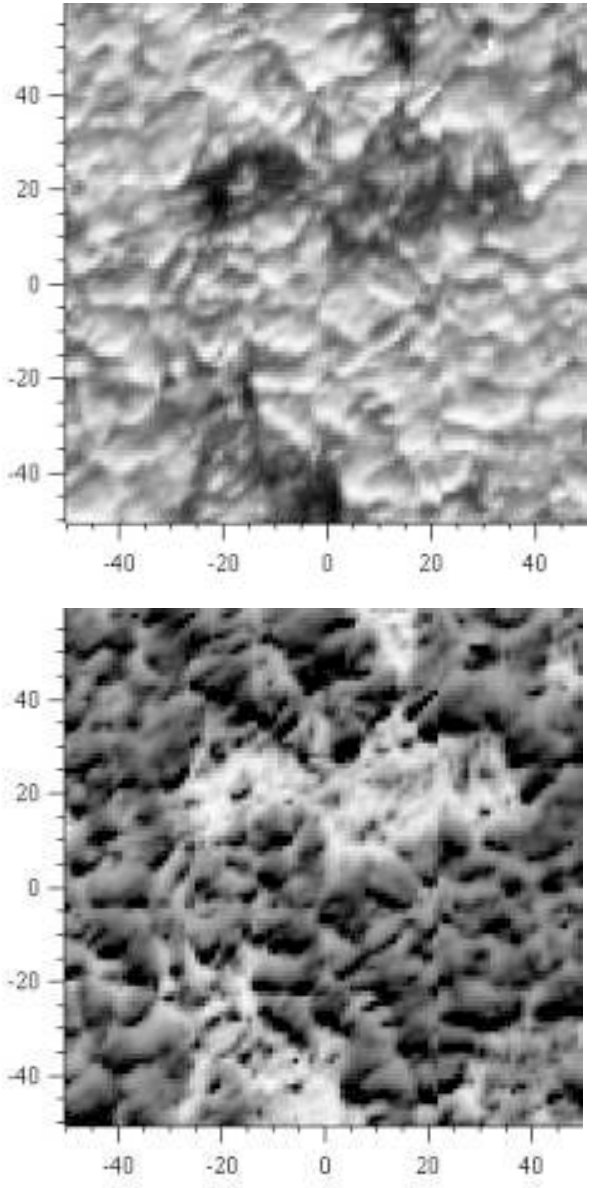
- 50,000 spectra collected in 15 minutes with 0.5 micrometer resolution
- Sequence derived from 2 imaging experiments (Raman and Photoluminescence)
- A and B highlight two areas of highly twinned crystal facets exhibiting five-fold symmetry

Intensity of 1.68 eV $[Si\text{-}V]^0$ PL band



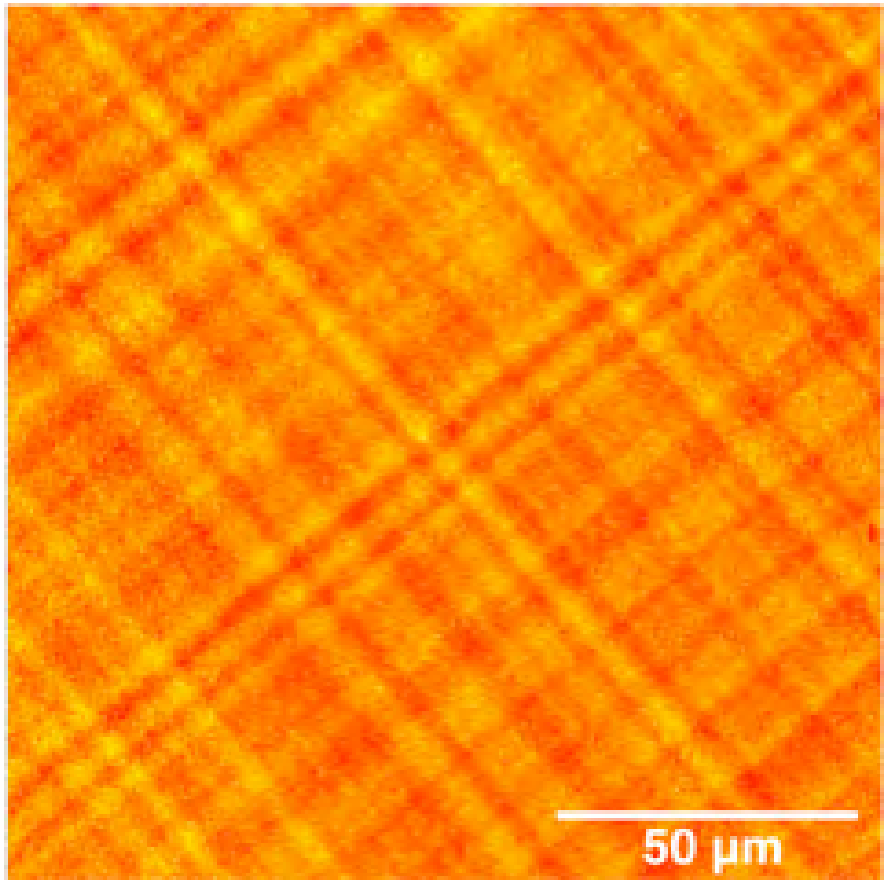
Diamond nucleation region

- Diamond film
  - nucleation side of a free-standing diamond film
- Map shows:
  - Top image: Diamond-rich area
    - 1332cm^{-1} diamond band component
  - Bottom image: Graphitic-rich region
    - G and D bands graphite components
- Details
  - 110 µm _ 110 µm area
  - 10,000 spectra
  - 10 minutes

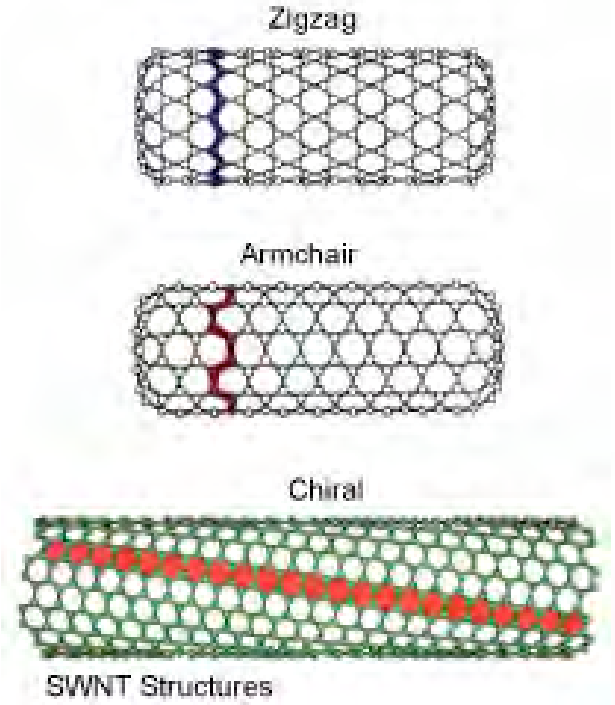


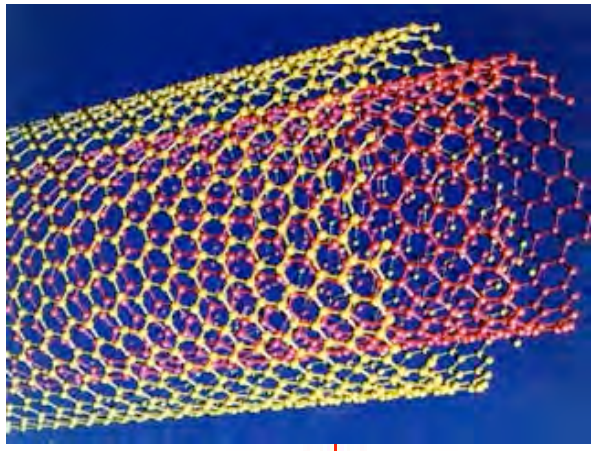
Si-Ge cross hatch

- Semiconductor sample
  - SiGe layer deposited onto substrate
  - Graded layer with increasing germanium content towards layer surface
  - Crosshatch structure is not engineered
  - Pattern is generated a mechanism for strain relief
- Map shows:
  - Variation in Si-Si 510 cm^{-1} band position (~ 0.2 cm^{-1} positional band shift)
- Details
  - 55,000 spectra
  - 13 minutes
  - 0.5 micrometer resolution
  - 532 nm excitation

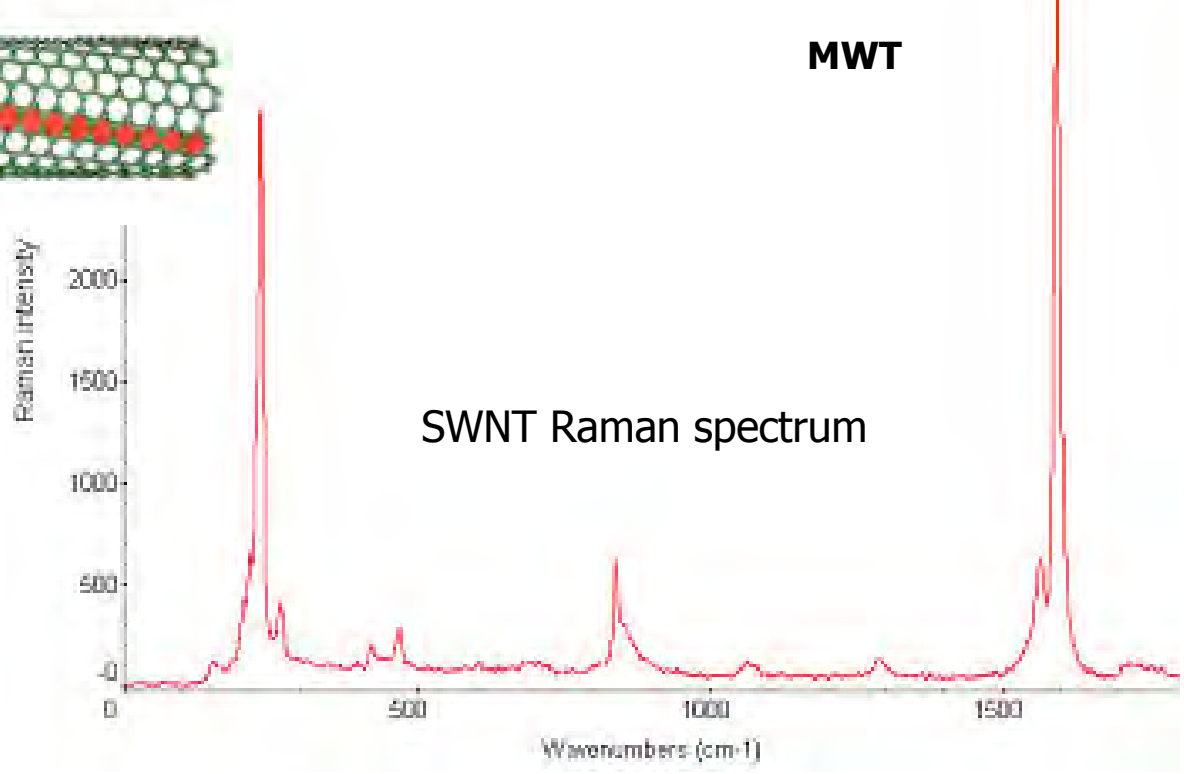


Carbon nanotube lattice structures





MWT



SWNT Raman spectrum

Resonance Raman

If the wavelength of the laser is close to an excited electronic state of a bond in molecule, i.e. where it is strongly absorbed or fluoresces, the signal enhancement can be increased by a factor between 100 and 10,000.

Advantage: You can select a wavelength to enhance the sensitivity to a particular type of bond or vibrations.

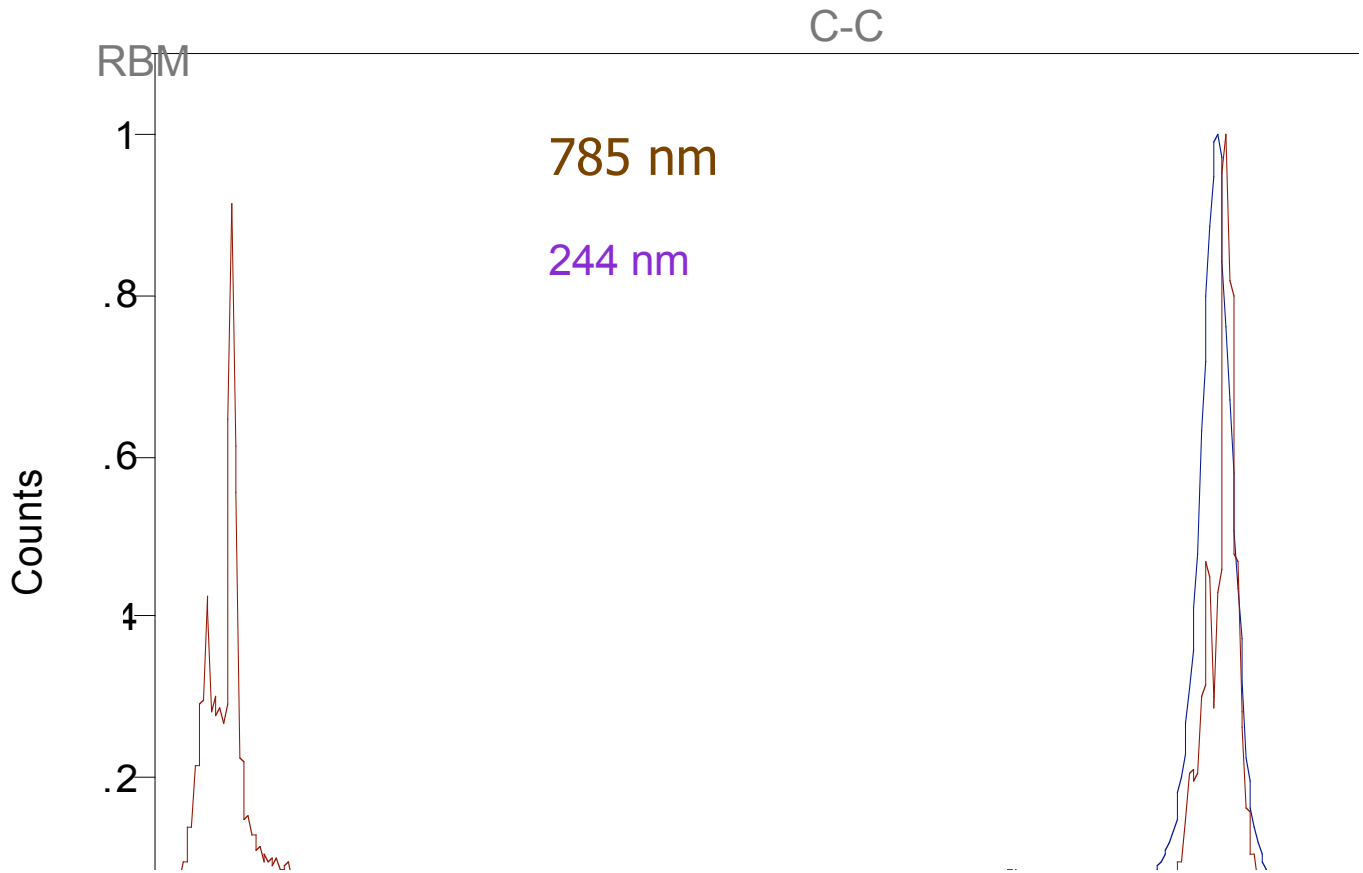
Potential disadvantages:

- increased fluorescence
- increase absorption/heating

In the study of carbon nanotubes multiple laser wavelengths are used to increase sensitivity to specific vibrational modes within a molecule.

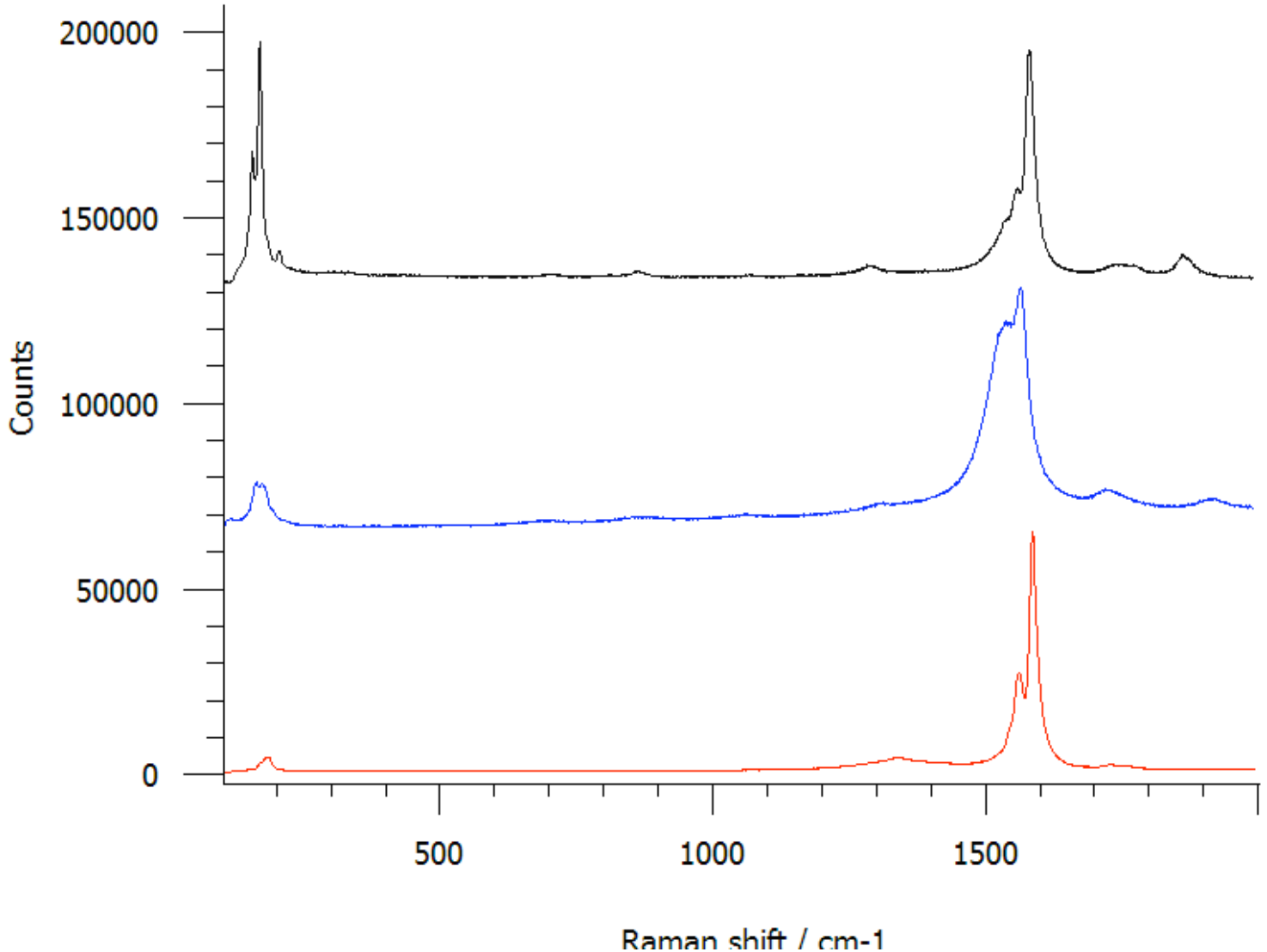
Resonance Raman spectroscopy of SWNT

Since the Raman spectral measurment for nano-tubes is typically a resonance Raman measurement the excitation wavelength can dramatically affect the spectral feature intensity and shift.

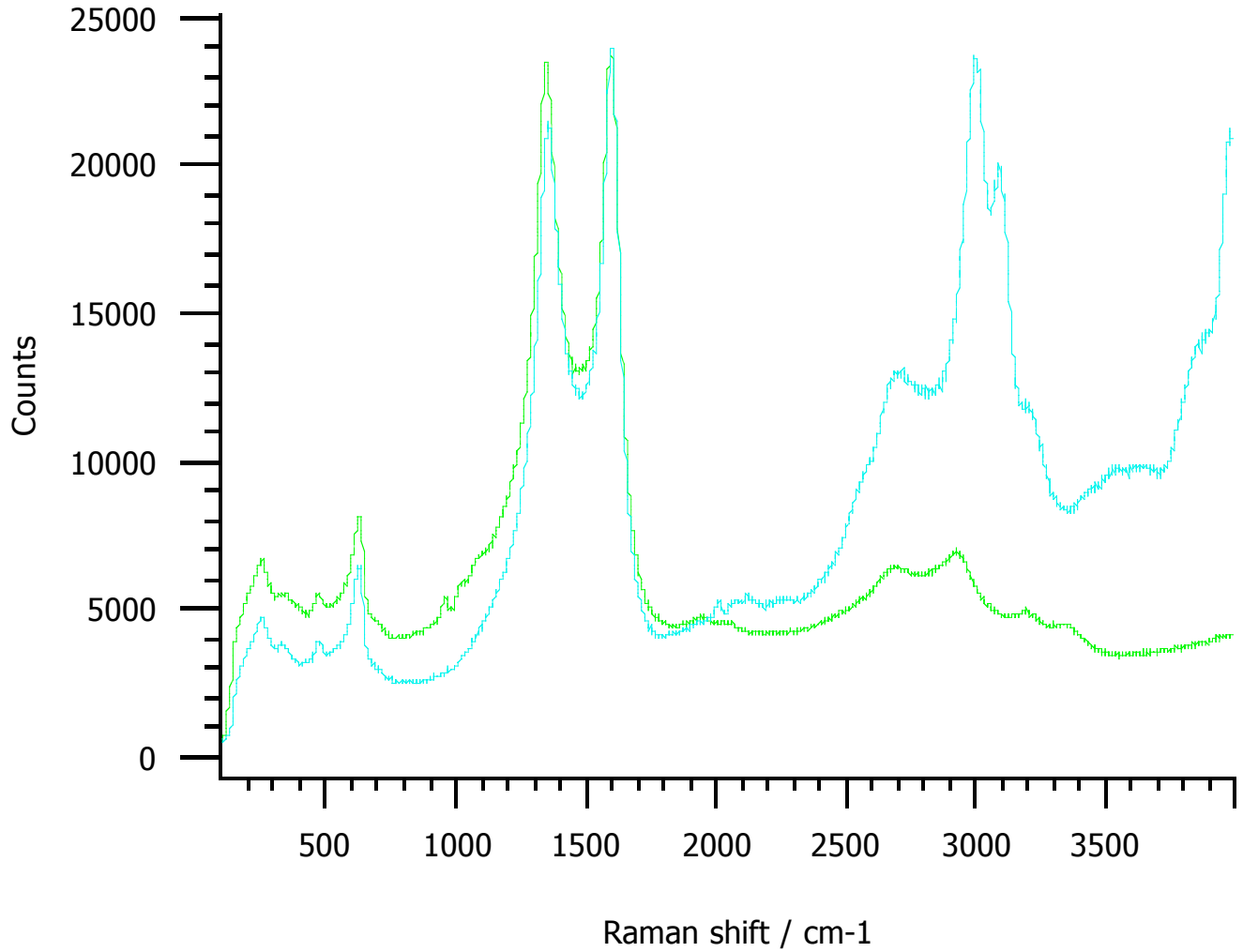


244 nm and 780 nm excited Raman spectra of nanotubes

Resonance Raman of SWINTs



Raman spectroscopy of MWNT



514 nm excited and 488 nm excited Raman spectra MWNT material

Raman and Fraud

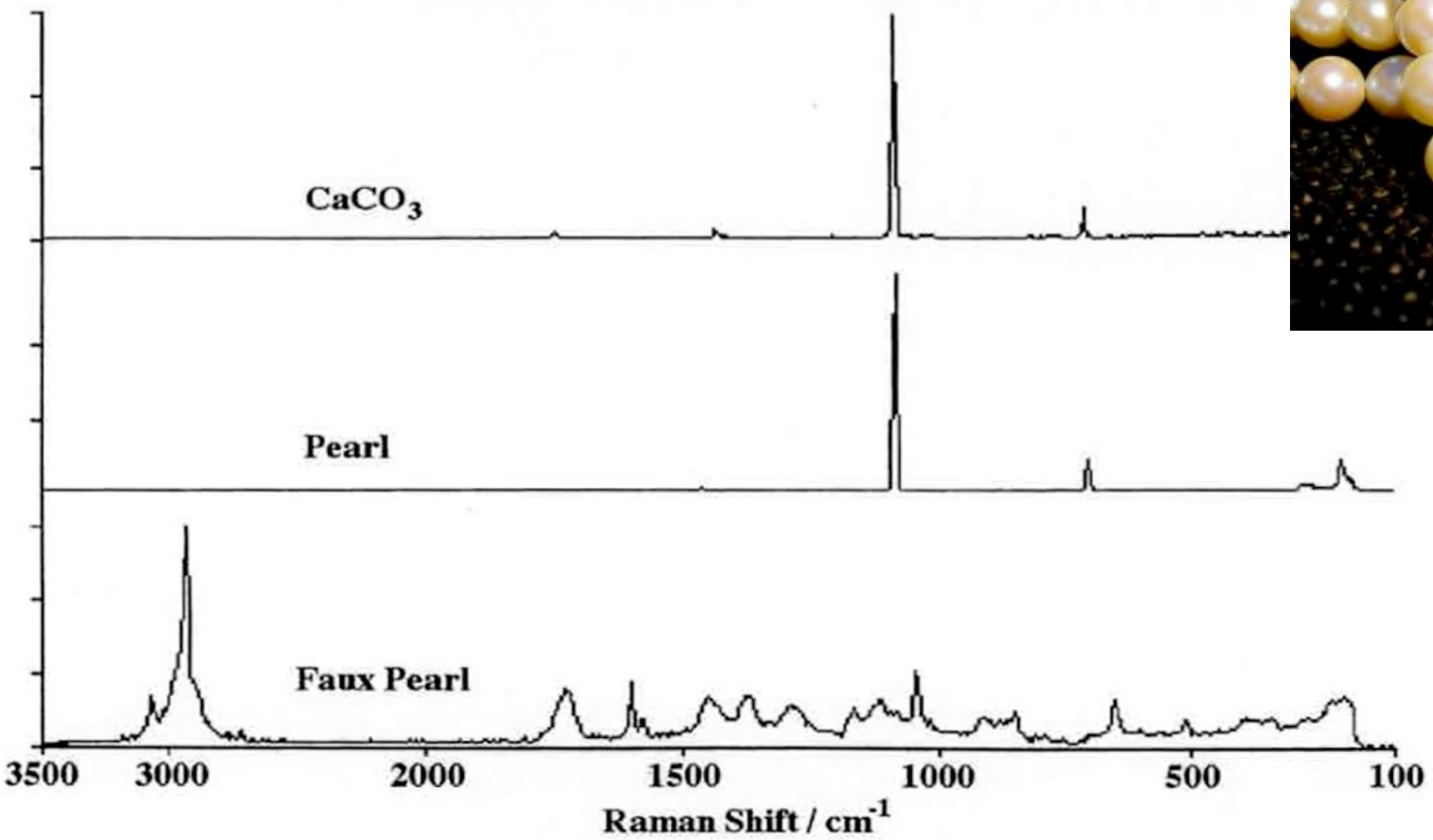


Figure 3 The Raman spectra of calcium carbonate (top), natural pearl (middle), and faux pearl (bottom). (Adapted with permission from Ref. 9.)

Lewis, I. R.; Edwards, H. G. M., *Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line*, Marcel Dekker, New York; 2001.0

vory or Plastic?

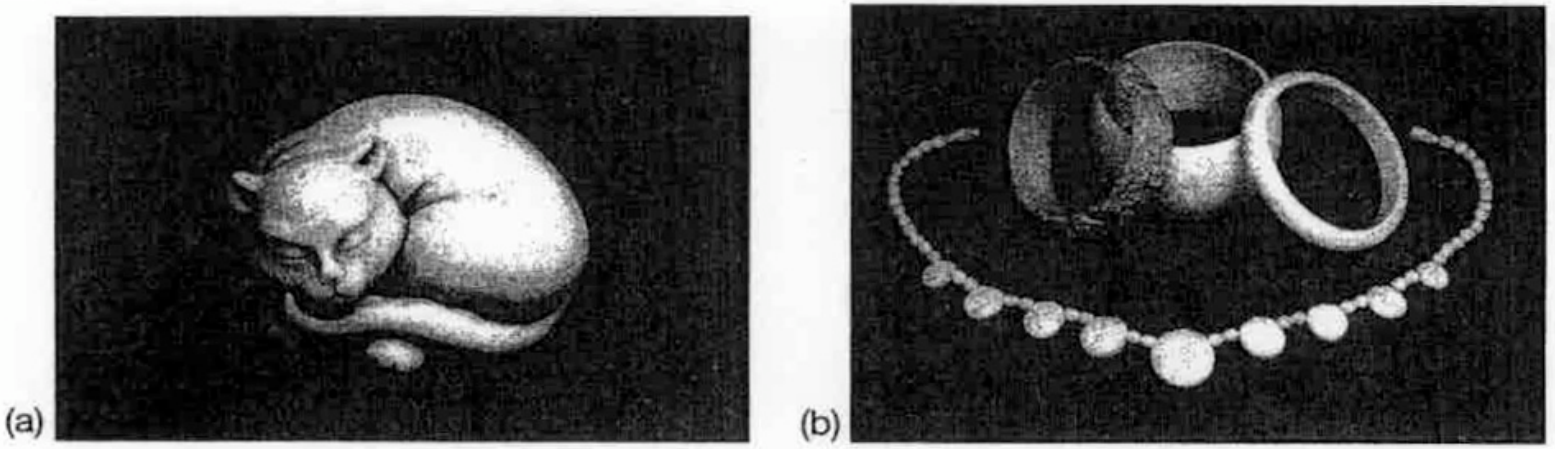


Figure 14 Specimen of (a) carved cat and (b) bangles, believed to be of ivory; 16th to 19th centuries.

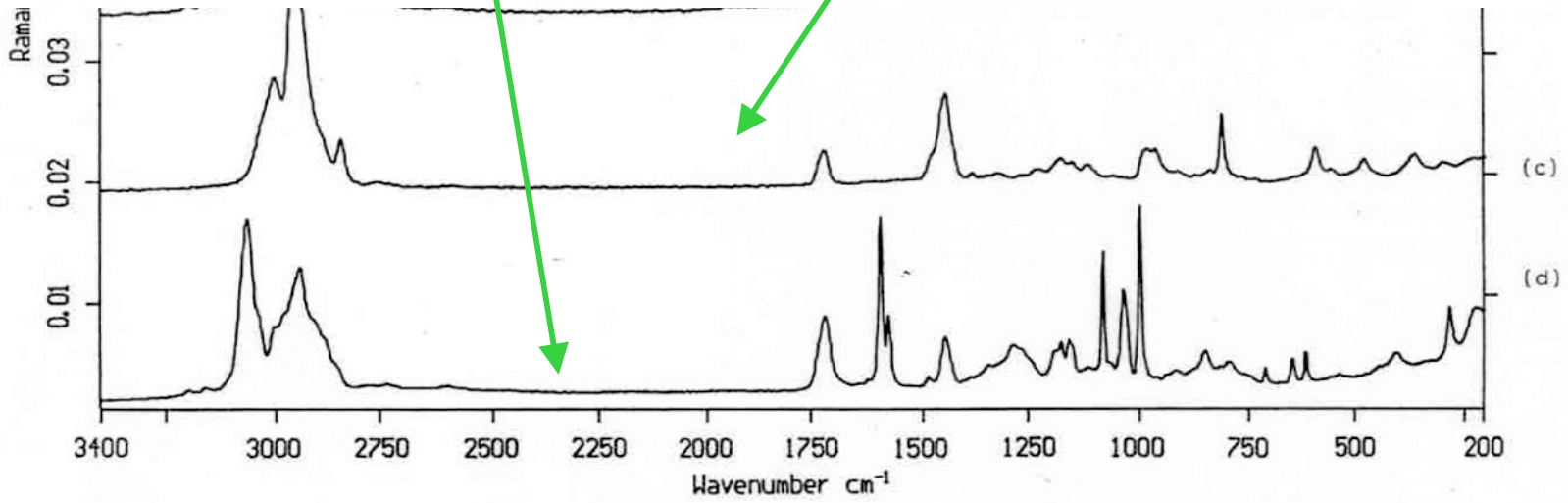
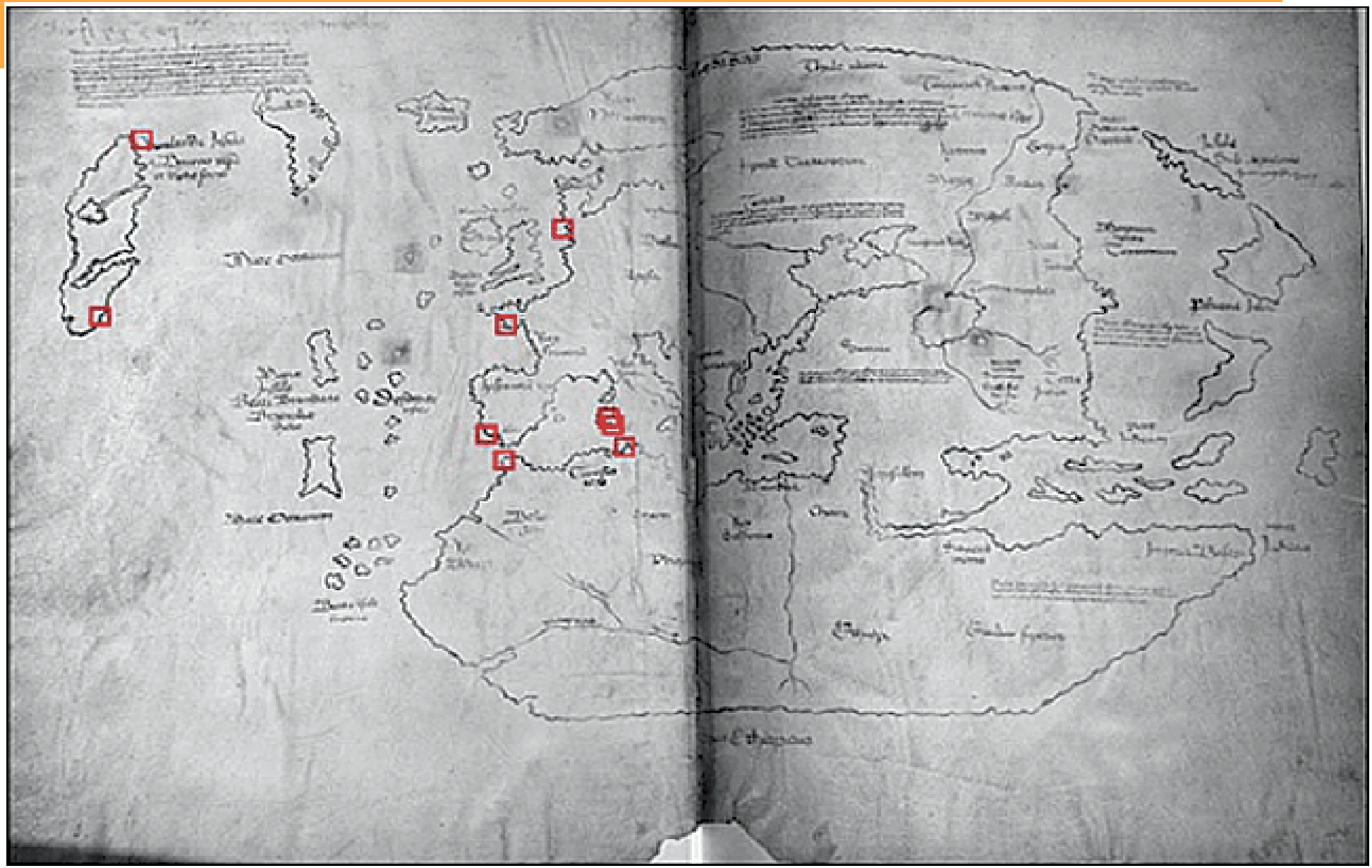


Figure 15 FT-Raman spectra of fake ivory specimens: (a) carved Victorian bangle, (b) large bangle, (c) small bangle, (d) cat. The absence of the characteristic proteinaceous features in true ivory near 1650 and 1450 cm^{-1} and the strong phosphate mode near 960 cm^{-1} should be noted. Also, the presence of the aromatic ring bands at 3060, 1600, and 1000 cm^{-1} in (b) and (d) indicate a polystyrene resin content, whereas the carbonyl stretching band at 1725 cm^{-1} in all fake specimens indicates the presence of poly(methyl methacrylate). In the cat specimen, the band at 1086 cm^{-1} uniquely identifies a calcite additive in the specimens of imitation ivory studied. (Reproduced with permission from HGM Edwards, DW Farwell. Ivory and simulated ivory artifacts: Fourier-transform Raman diagnostic study. Spectrochimica Acta, Part A, 51:2073–2081. © 1995, Elsevier Science B.V.)

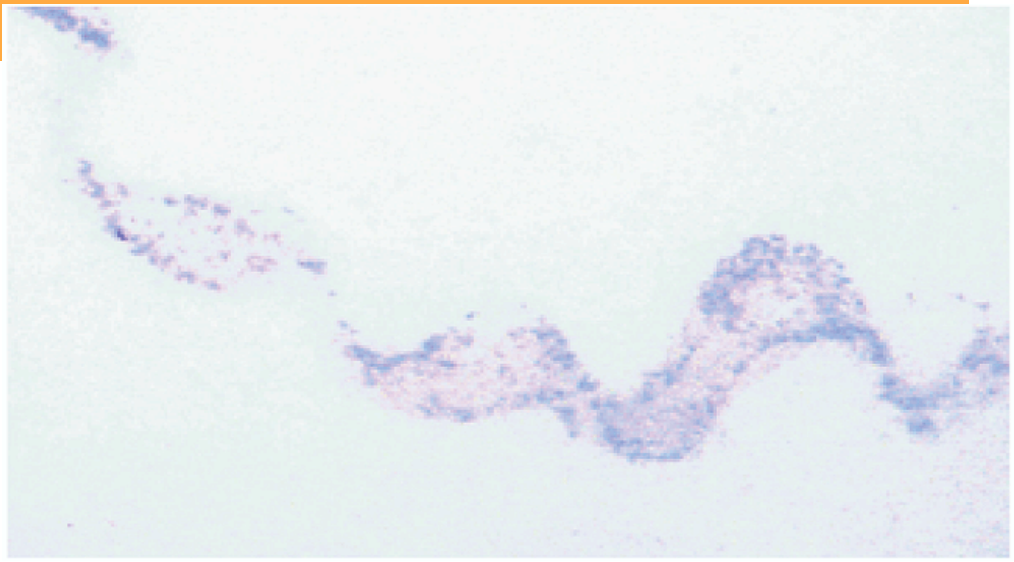
Lewis, I. R.; Edwards, H. G. M., *Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line*, Marcel Dekker, New York: 2001

The Vinland Map: Genuine or Forged?



Brown, K. L.; Clark, J. H. R., *Anal. Chem.* **2002**, *74*,3658.

The Vinland Map: Forged!



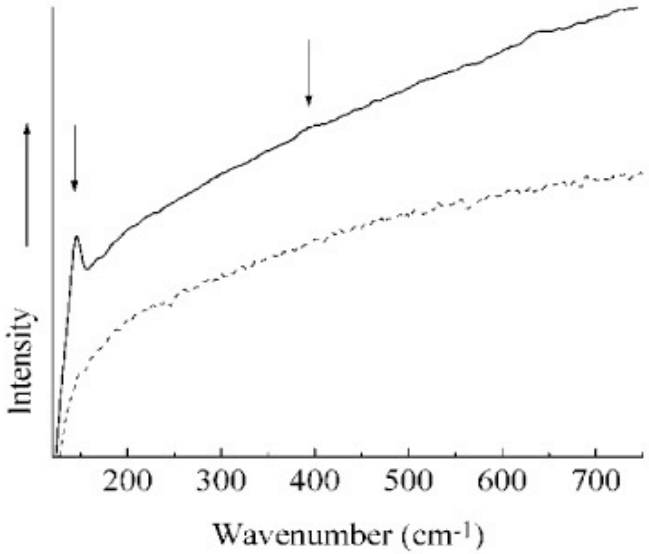


Figure 5. Anatase and plain parchment from the Vinland Map; solid line, anatase in yellow line; dotted line, plain parchment.

CONCLUSIONS

The use of Raman microprobe spectrometry has conclusively identified the materials used in the construction of two significant historical documents, the Vinland Map and the Tartar Relation. Although the inks used for the Tartar Relation are entirely appropriate for the period of its construction, one of those used to draw the Vinland Map is not. The presence of a yellow line containing anatase, closely associated with a stable carbon ink, indicates that the VM is a modern forgery.

Brown, K. L.; Clark, J. H. R., *Anal. Chem.* **2002**, *74*,3658.

Surface-Enhanced Raman Scattering (SERS)

SERS: Surface Enhanced Raman Scattering

Discovered in 1977, Jeanmire et al. & Albrecht et al.

--Strongly increased Raman signals from molecules attached to metal nanostructures

--**SERS active substrates**: metallic structures with size about 10--100 nm (e.g. colloidal Ag, Au, roughened surfaces)

General contributions:

1)Electromagnetic field enhancement

2) Chemical 'first layer' effect

SERS Enhancement Mechanisms

Chemical Mechanism:

Laser excites (a) new electronic states arising from chemisorption or (b) shifted or broadened adsorbate electronic states yielding a resonance condition.

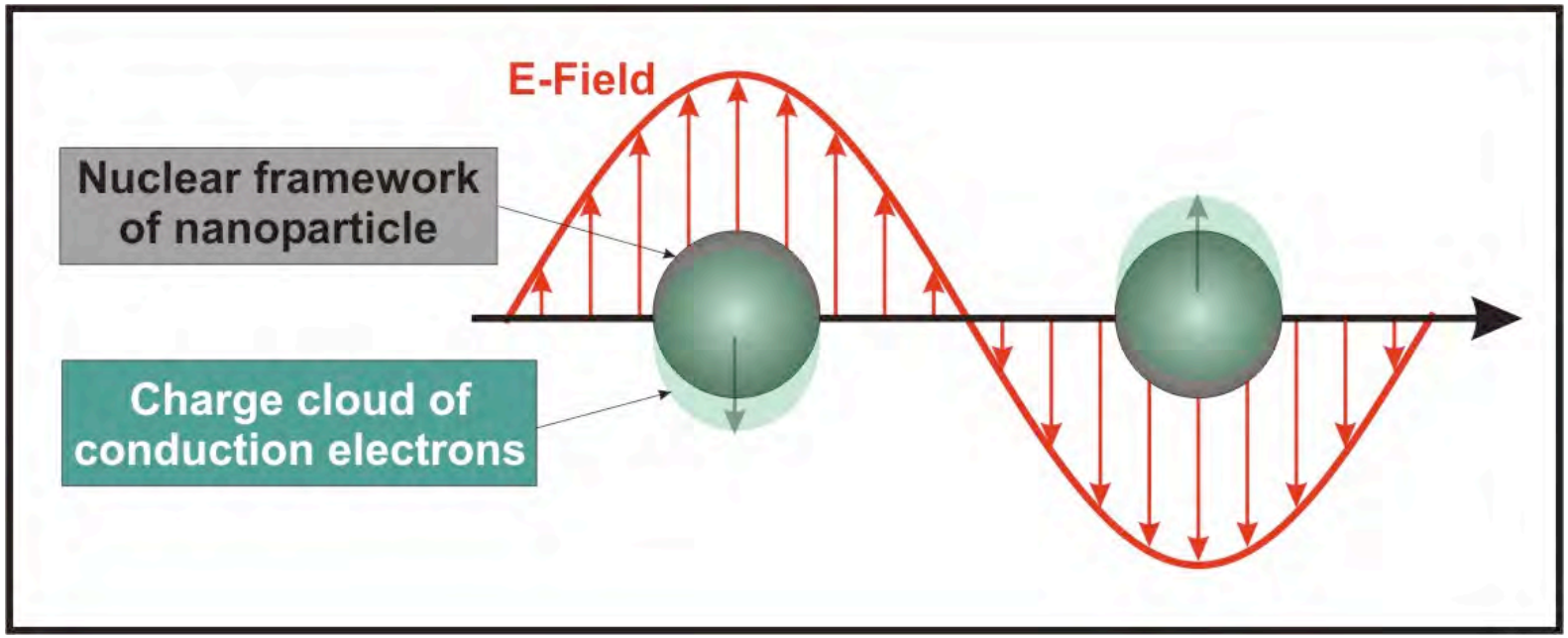
- Short range (1-5 Å)
- No roughness requirement
- Contributes EF ~ 10^2 – 10^4

Electromagnetic Mechanism:

LSPR induces large electromagnetic fields at roughened metal surface where molecules are adsorbed.

- Long range (2-4 nm)
- Affected by all factors determining LSPR
- Contributes EF > 10^4

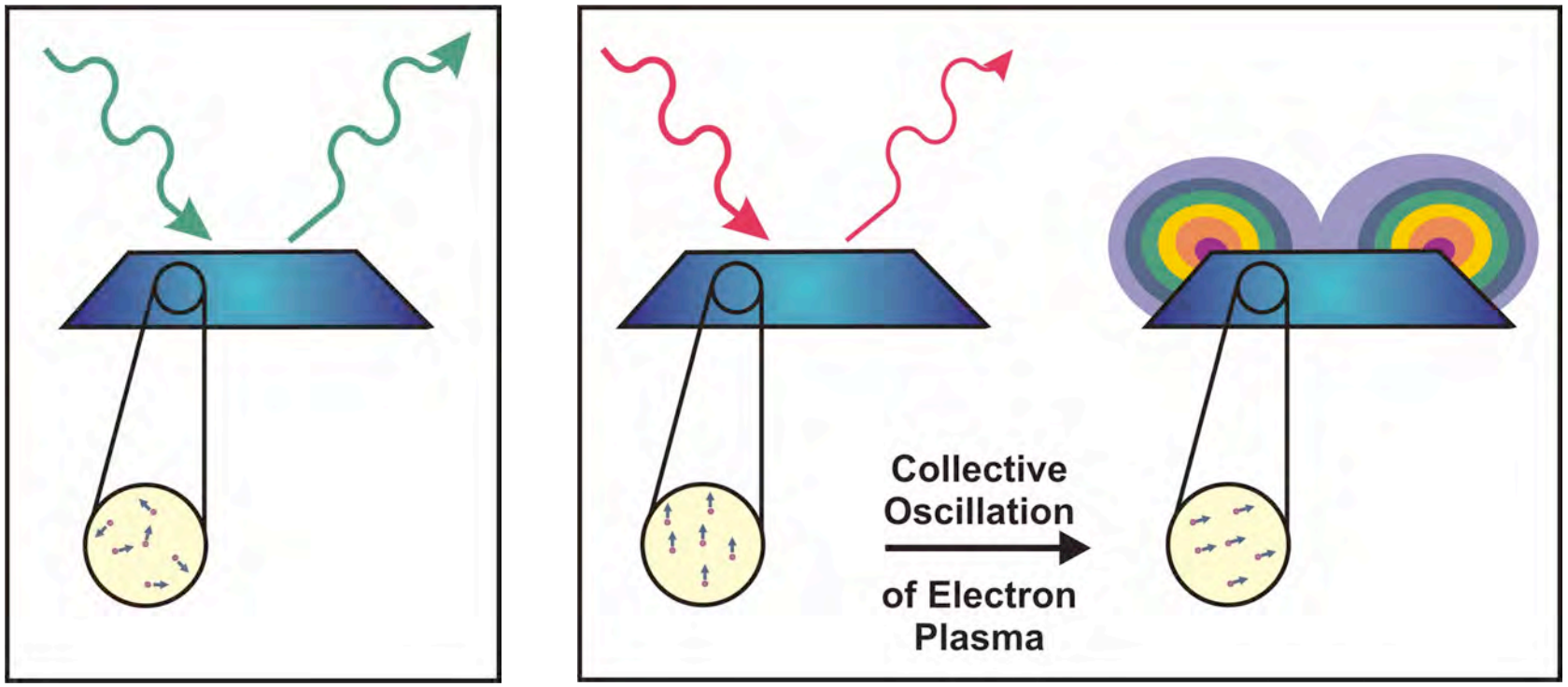
ocalized Surface Plasmon Resonance



The resonance results in (1) wavelength-selective extinction and (2) enhanced EM fields at the surface.

Spectral location of the LSPR is dependent upon particle size, shape, composition, and dielectric environment.

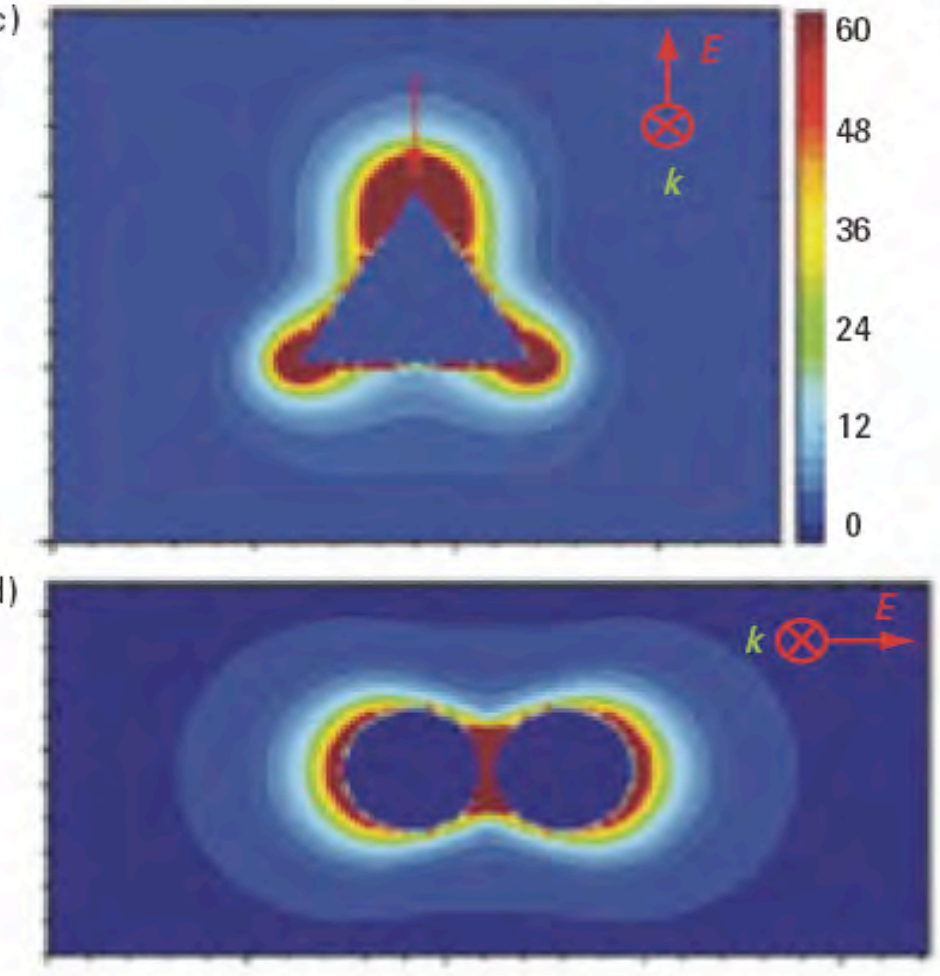
Localized Surface Plasmon Resonance



Non-resonant Resonant

1) Resonant λ is absorbed
2) EM fields localized at nanoparticle surface

Nanostructured Substrates



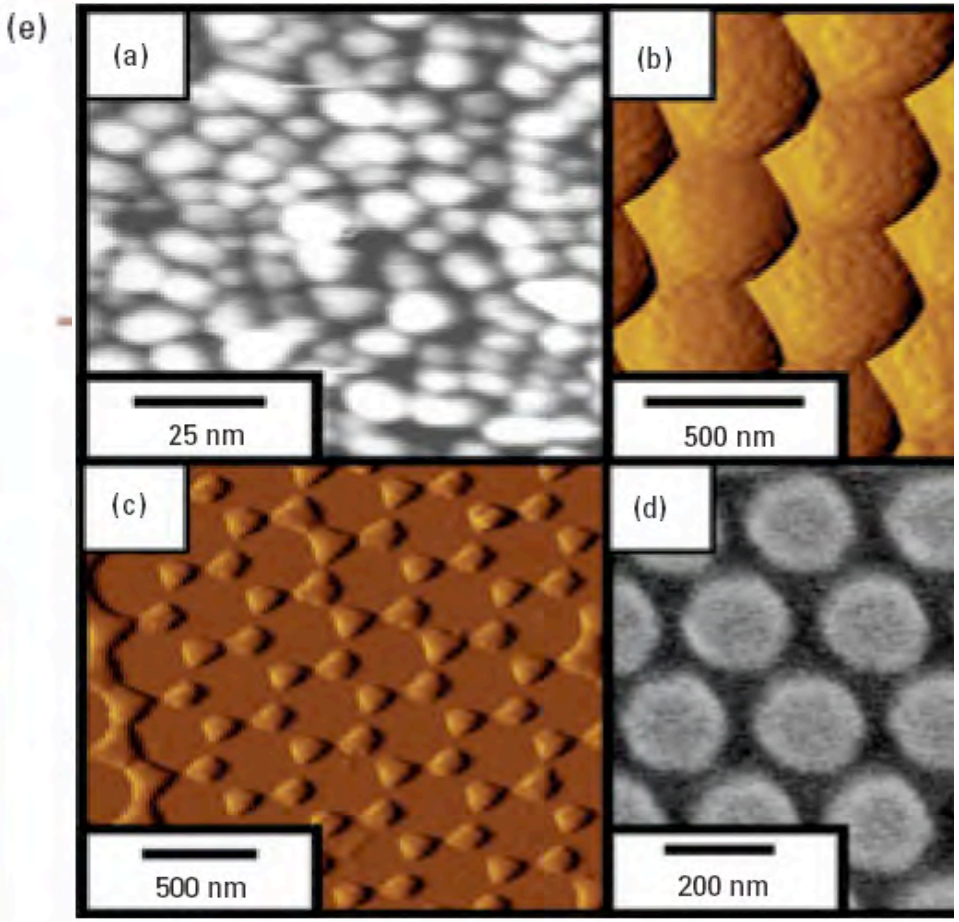


FIGURE 2. Sample substrates.

(a) Metal island film, (b) metal film over nanospheres, (c) triangular nanopart cated with nanosphere lithography, and (d) cylindrical nanoparticle array fabr electron-beam lithography.

http://pubs.acs.org/cgi-bin/article.cgi/ancham-a/0000/77/i17/pdf/905feature_vanduyne.pdf

Commercial SERS Substrates

D3 produces the Klarite range of substrates for Surface Enhanced Raman Spectroscopy. Klarite substrates enable faster, higher accuracy detection of biological and chemical samples at lower detection limits for a wide range of applications in homeland security, forensics, medical diagnostics and pharmaceutical drug discovery. Manufactured using techniques from semiconductor processing Klarite substrates offer high levels of enhancement and reliability.

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Raman Websites and On-Line Databases

www.spectroscopynow.com/coi/cda/landing.cda?chId=6&type=Education
(many links including,
An Introduction to Raman Spectroscopy: Introduction and Basic Principles, by J. Javier Laserna,)

Database:
http://wwwobs.univ-bpclermont.fr/sfmc/ramandb2/index.html

Vendors:
http://www.renishaw.com
http://www.optics.bruker.com/
http://www.nicolet.com/
http://www.jobinyvon.com