





# CHEM\*3440

## Chemical Instrumentation

Topic 11

Raman Spectroscopy

# Raman Spectroscopy

Another spectroscopic technique which probes the rovibrational structure of molecules.

C.V. Raman discovered in 1928; received Nobel Prize in 1931.

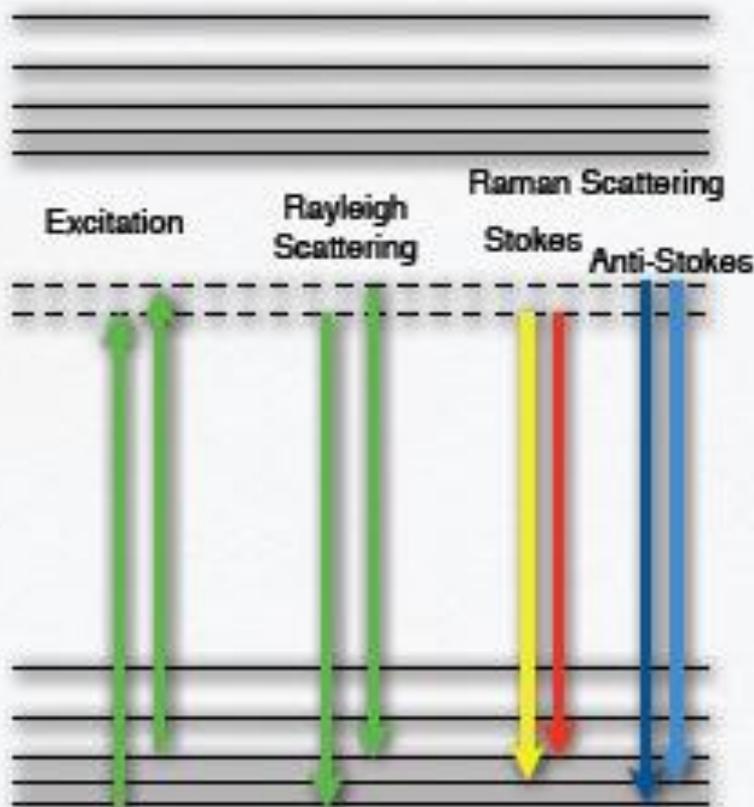
Can probe gases, liquids, and solids.

Must use a laser source for excitation.

Resurgence in recent years due to the development of new detectors with improved sensitivity.

Shift back away from FT-Raman to dispersive Raman with multichannel detector systems.

# How It Works - Virtual States



Excited Electronic State

Virtual Electronic State

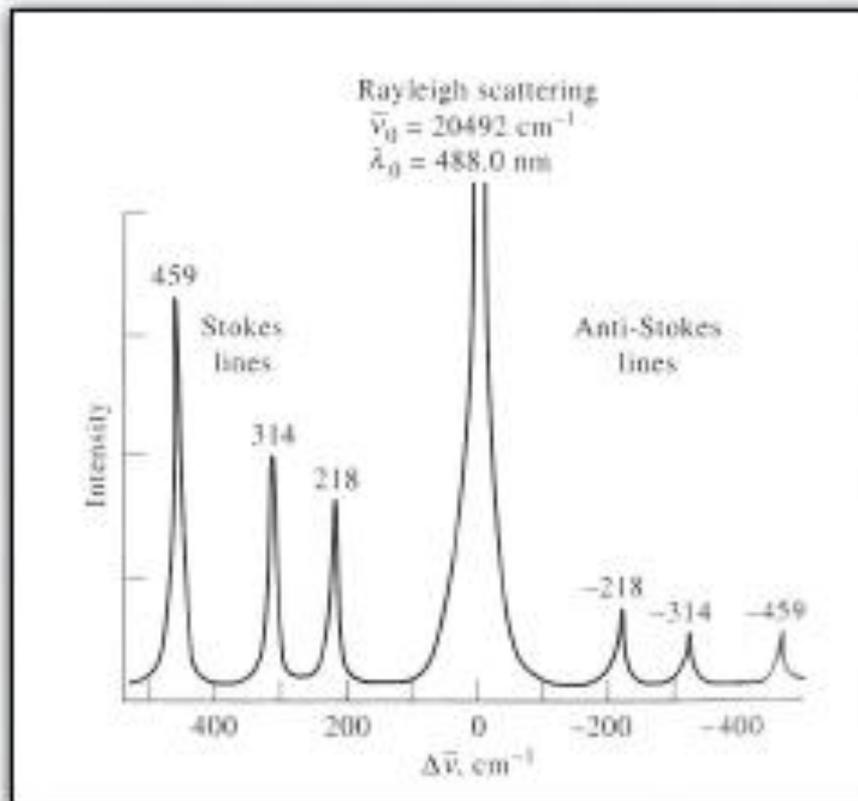
...it only exists while the electrical field of the photon is present.

Ground Electronic State

# The Spectrum

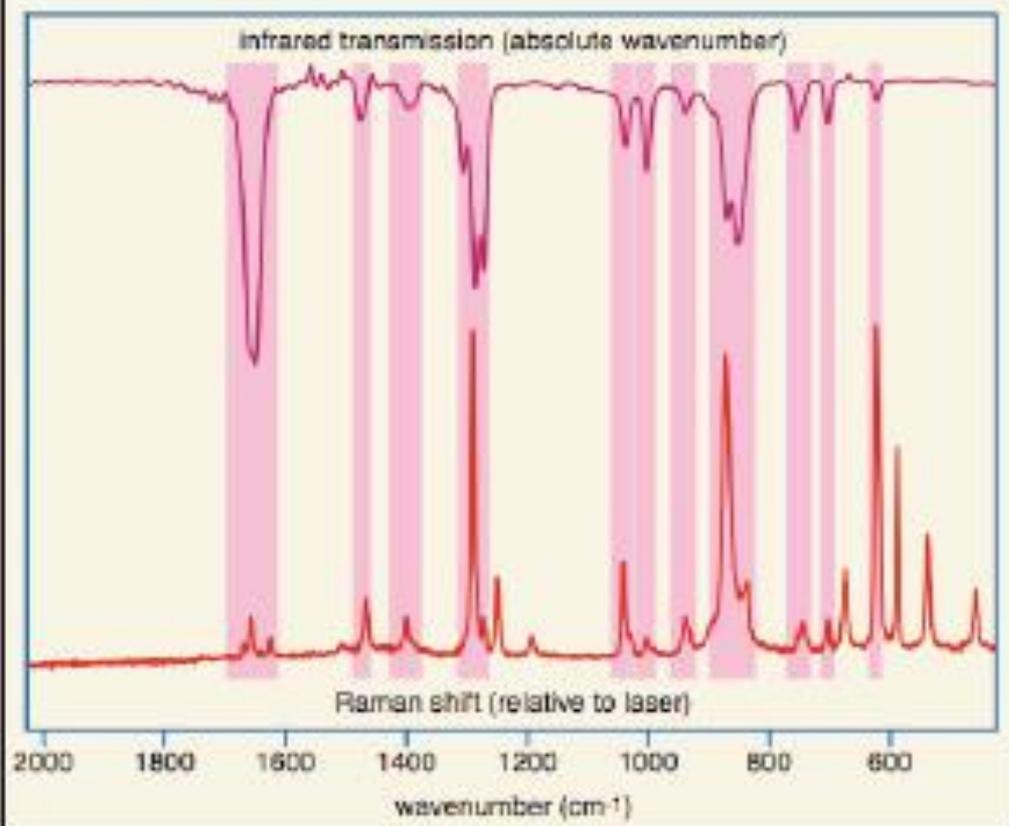
A complete Raman spectrum consists of:

- a Rayleigh scattered peak (high intensity, same wavelength as excitation)
- a series of Stokes-shifted peaks (low intensity, longer wavelength)
- a series of anti-Stokes shifted peaks (still lower intensity, shorter wavelength)
- spectrum independent of excitation wavelength (488, 632.8, or 1064 nm)



# Compare IR and Raman Spectra

## Raman and IR spectra



Spectra of PETN explosive.  
From D.N. Batchelder,  
Univ. of Leeds

# Some Raman Advantages

Here are some reasons why someone would prefer to use Raman Spectroscopy.

- Non-destructive to samples (minimal sample prep)
- Higher temperature studies possible (don't care about IR radiation)
- Easily examine low wavenumber region:  $100\text{ cm}^{-1}$  readily achieved.
- Better microscopy; using visible light so can focus more tightly.
- Easy sample prep: water is an excellent solvent for Raman. Can probe sample through transparent containers (glass or plastic bag).

# Origin of Raman Effect

$$E = E_0 \cos(\omega_{ex} t)$$

The oscillating electric field of the excitation light.

$$\mu_{\text{induced}} = \alpha E = \alpha E_0 \cos(\omega_{ex} t)$$

The induced dipole moment from this oscillating field.

$$\alpha = \alpha_0 + (r - r_{eq}) \frac{d\alpha}{dr}$$

The molecular polarizability changes with bond length.

$$r - r_{eq} = r_{\text{max}} \cos(\omega_{\text{vib}} t)$$

The bond length oscillates at vibrational frequency.

$$\alpha = \alpha_0 + \left( \frac{d\alpha}{dr} \right) r_{\text{max}} \cos(\omega_{\text{vib}} t)$$

Hence the polarizability oscillates at same frequency.

$$\mu_{\text{induced}} = \left( \alpha_0 + \left( \frac{d\alpha}{dr} \right) r_{\text{max}} \cos(\omega_{\text{vib}} t) \right) E_0 \cos(\omega_{ex} t) = \alpha_0 E_0 \cos(\omega_{ex} t) + E_0 r_{\text{max}} \left( \frac{d\alpha}{dr} \right) \cos(\omega_{ex} t) \cos(\omega_{\text{vib}} t)$$

Substitute.

$$\cos x \cos y = \frac{1}{2} [\cos(x+y) + \cos(x-y)] \quad \text{Remember trig identity.}$$

$$\therefore \mu_{\text{induced}} = \alpha_0 E_0 \cos(\omega_{ex} t) +$$

$$\frac{E_0 r_{\text{max}}}{2} \left( \frac{d\alpha}{dr} \right) [\cos((\omega_{ex} + \omega_{\text{vib}}) t) + \cos((\omega_{ex} - \omega_{\text{vib}}) t)]$$

Induced dipole has Rayleigh, Stokes, and anti-Stokes components.

# Watch Out For Fluorescence

Spectrum of anthracene.

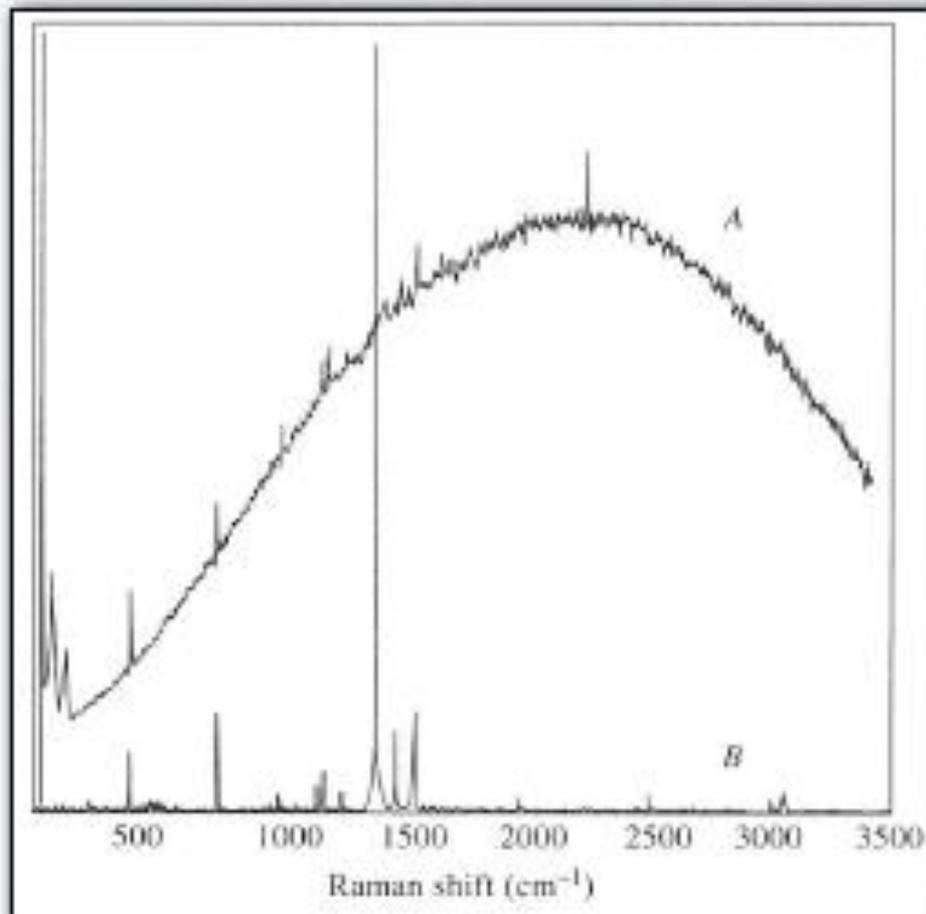
A: using Ar<sup>+</sup> laser at 514.5 nm.

B: using Nd:YAG laser at 1064 nm.

Want to use short wavelength because scattering depends on 4th power of frequency.

...BUT...

Want to use long wavelength to minimize chance of inducing fluorescence.



# Sources

Raman intensity is weak and the excitation source must be strong to generate sufficient signal.

Source must be monochromatic so that spectrum is sufficiently uncomplicated.

Intense lamps can work, but when monochromatized, have very little power. Scattering efficiency increases as  $\nu^4$ : the bluer the light, the more the scattering.

The bluer the light, the greater the chance of producing fluorescence. Lasers are used almost exclusively.

Ar<sup>+</sup> Ion: 488.0 and 514.5 nm

Kr<sup>+</sup> Ion: 530.9 and 647.1 nm

He:Ne: 632.8 nm

Diode Lasers: 782 and 830 nm

Nd:YAG: 1064 (532 when doubled) nm



I just checked. Here is a 500 mW Ar ion laser for sale on eBay for \$1000.

# Sources con't

Experiment used to require considerable excitation power

- Ion lasers, 40 W cw
- He:Ne, 10 W cw
- YAG, 1 J/10 ns pulse (100 MW average pulse)

But detectors have improved so much, the source power requirements have been decreased.

- Diode laser, 25 mW
- other lasers can be made correspondingly smaller.

# Detectors

Scattered light is low intensity, so high gain PMT's have been used in the past. This was used for scanned and FT-Raman instrumentation for many years.

Now cooled CCD arrays are used; experiment is now multichannel.



Cooled NIR detector, 1024 x 256 pixel array, 26  $\mu\text{m}$  square pixels. From Jobin Yvon.

# Resonance Raman Effect

The Raman effect is quite weak; Rayleigh emission is  $10^5$  to  $10^6$  times more intense.

If virtual state is close to a real molecular state, the transition probability is greatly enhanced. Resonance Raman is enhanced  $10^2$  to  $10^6$ .

Can detect concentrations as low as  $10^{-6}$  M.

Resonance Raman spectra much simpler because enhancements only occur with transitions associated to the chromophore.

All Raman processes are **coherent**; the excited state exists only during the time that the photon is there. It is not an absorption-reemission process as with fluorescence. Lifetime on order of  $10^{-14}$  sec.

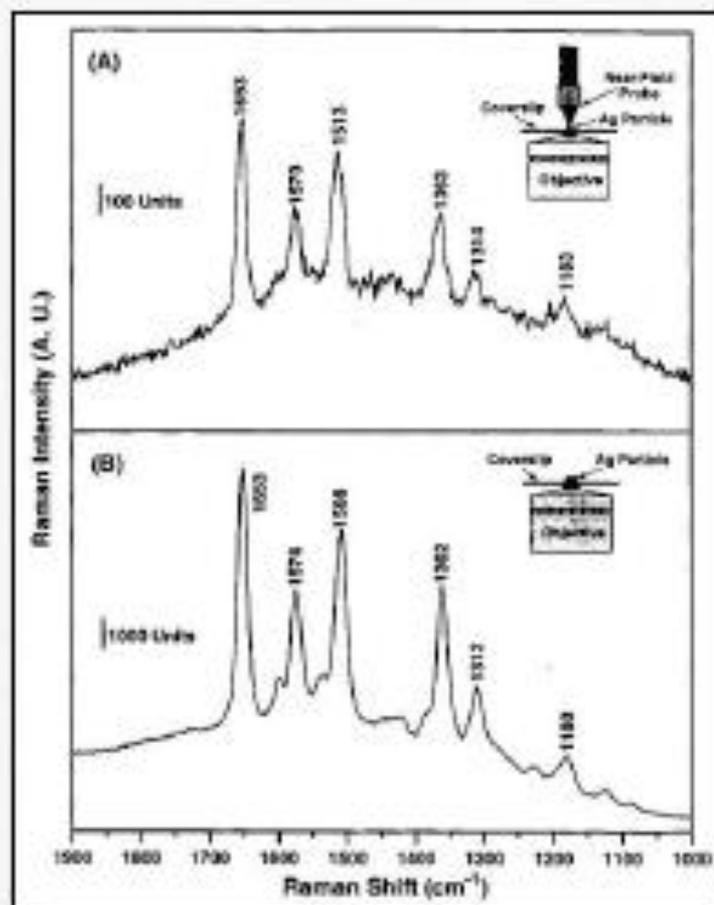
# Surface Enhanced Raman Effect

When molecules are absorbed on very small particles of Au, Ag, Cu or on nano-roughened surfaces of the same, the Raman signal is increased  $10^4$  to  $10^7$ .

Some debate around origin of the effect. Attributed to enhanced electric fields at particles with small curvature.

Couple SERS with Resonance Raman, to achieve intensity amplifications of as much as  $10^{12}$ . Can detect extremely low concentrations – in nM to pM range.

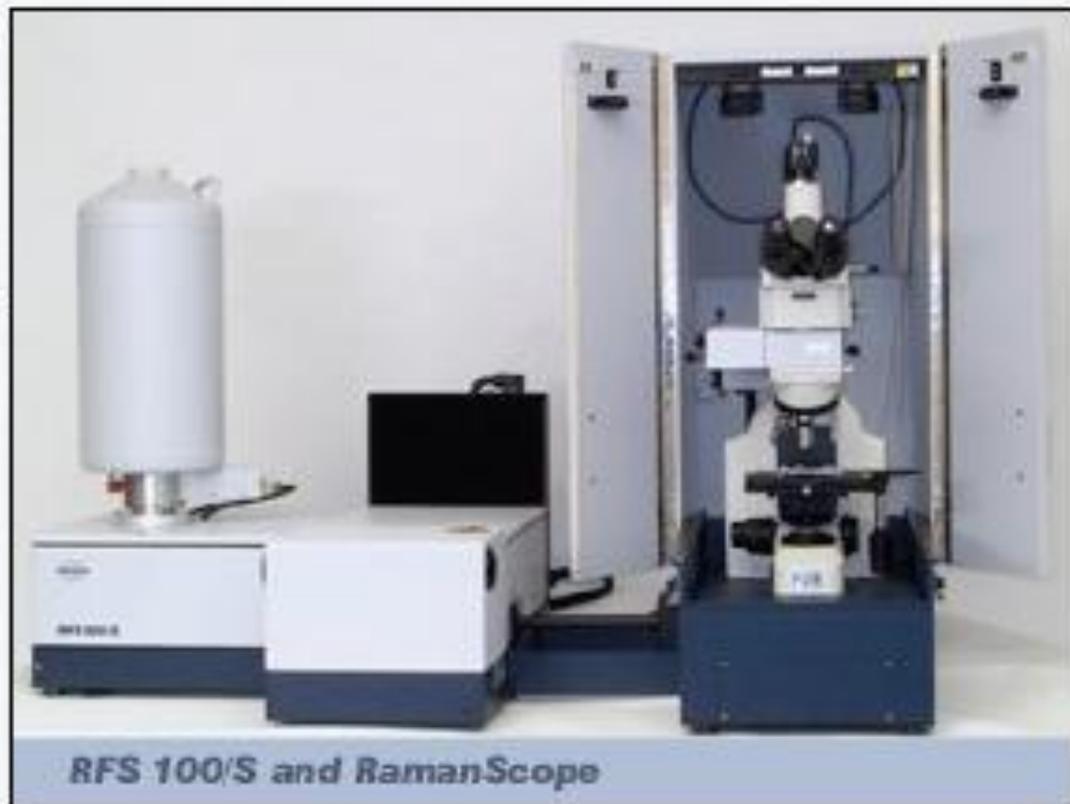
Spectrum is of Rhodamine 6G on Ag nanoparticles showing enhancement.



# FT- Raman

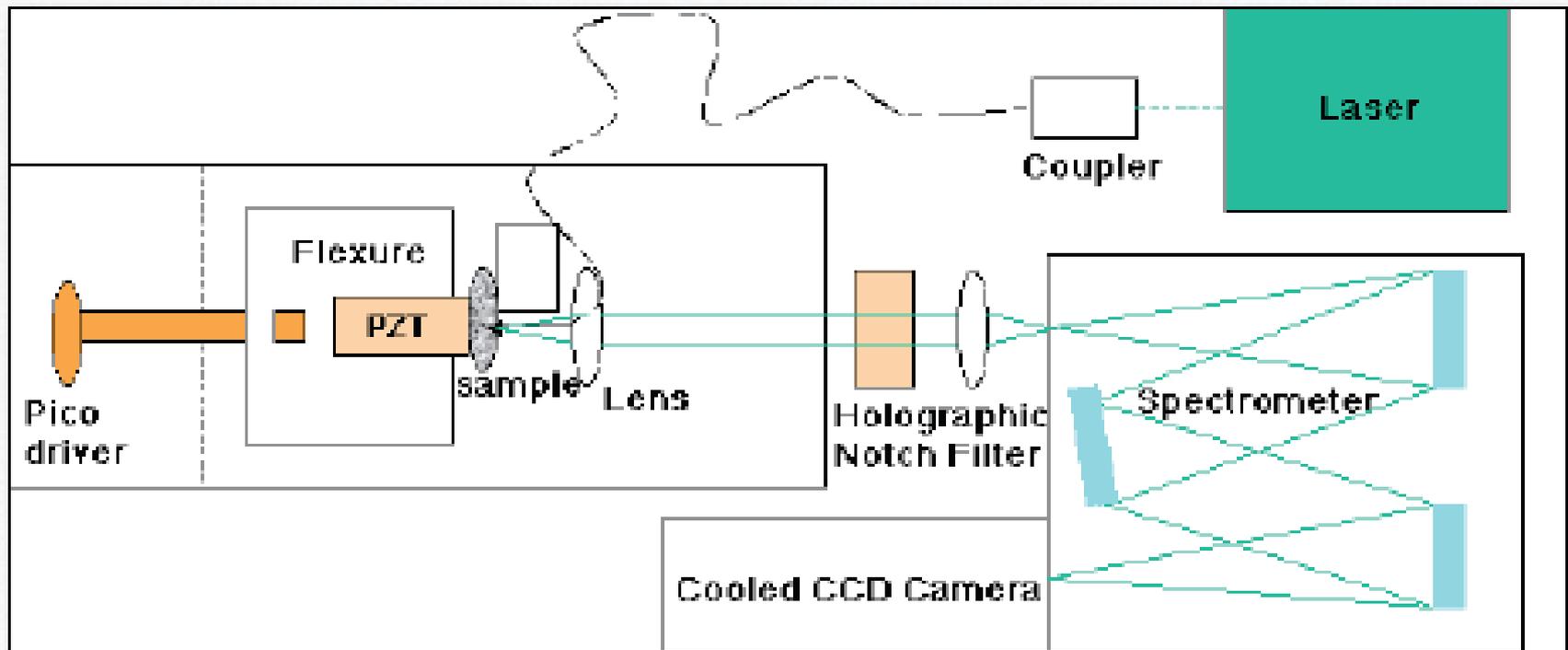
Use a laser source in NIR or Visible, coupled with interferometer. Can perform FT-Raman studies.

Advent of highly sensitive array detectors has cut into the FT-Raman territory. Most manufacturers going back to dispersive instruments.



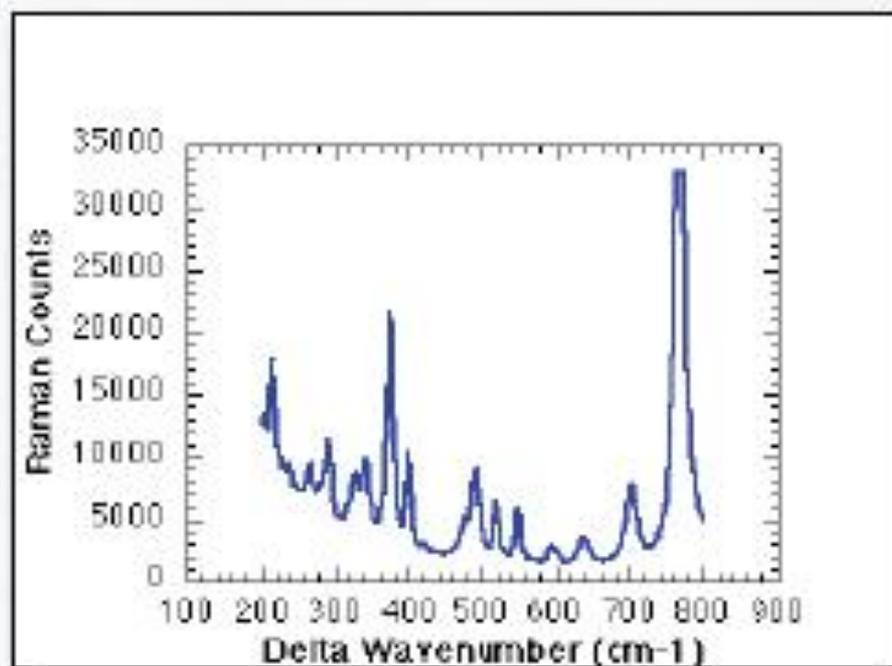
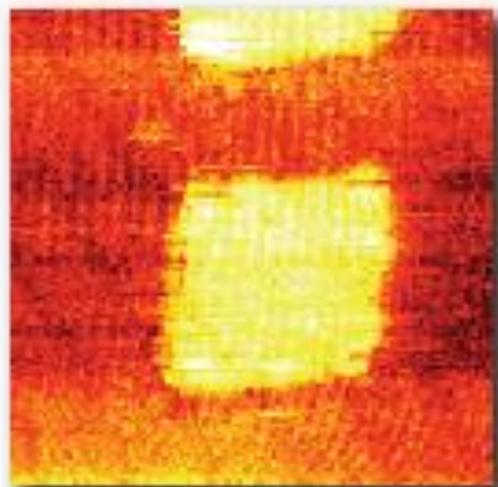
# Multichannel Raman Spectroscopy

Instrument of Hans Hallen in Physics Dept. at North Carolina State.



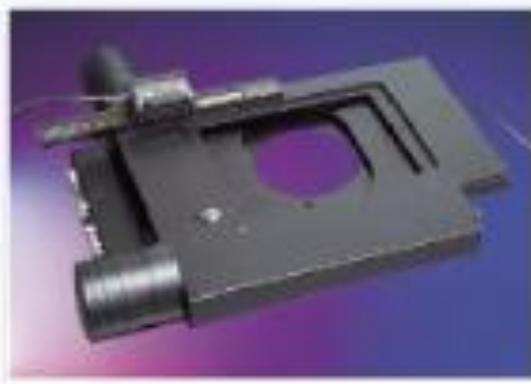
# NSOM Raman Imaging

Spectrum of potassium titanyl phosphate. From Hans Hallen at NCSU. Squares are  $5 \times 5 \mu\text{m}$  square of this material doped with Rb. A near-field scanning microscope was used and the Raman signal was used to key the substrate response.



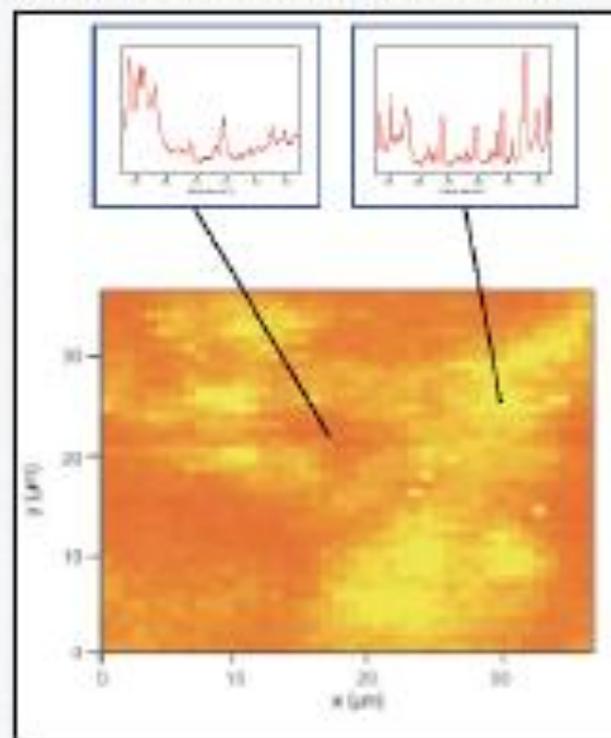
# Chemical Mapping

Focus laser to small spot. Tune spectrometer to particular Raman transition peak. Raster scan the sample under the laser beam, record intensity changes. Resultant map correlates with substance. Acquire an entire spectrum at every point, then choose the feature with which to key the image.



Motorized stage from Renishaw for chemical mapping.

This is a drug tablet. The yellow corresponds to the active ingredient. Particles are in the 10's of  $\mu\text{m}$  range.

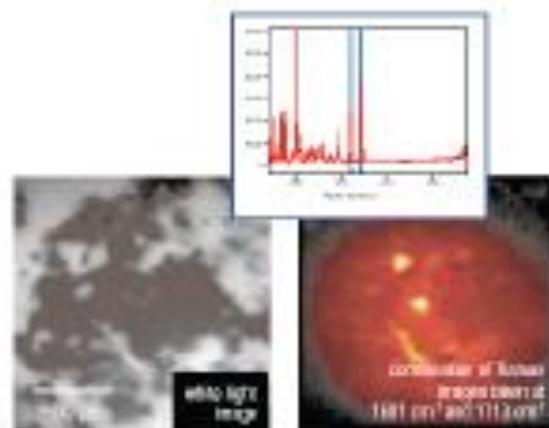


# Chemical Imaging

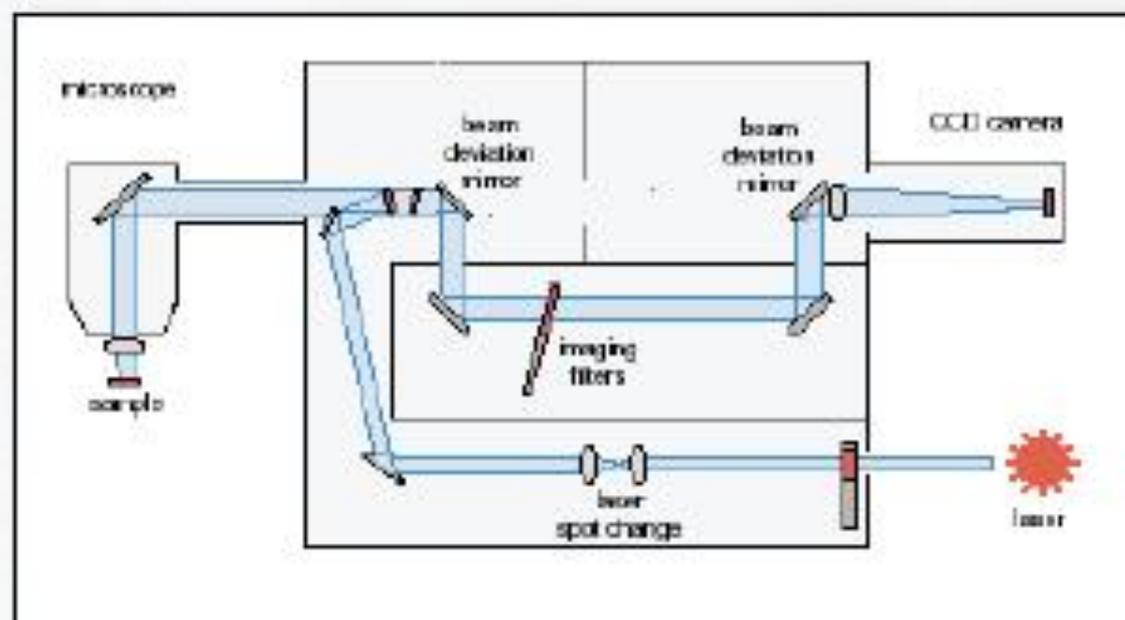
Now defocus the laser (not a small spot but rather "baths" the sample in laser radiation).

Pass the emitted radiation through a narrow bandpass filter, adjusted to a particular wavelength, chosen to be a certain Raman band.

Focus this light on the CCD camera. Bright regions correspond to locations of substance giving rise to Raman signal.



Mixture of cocaine and sugar.  
Bright spots are cocaine.

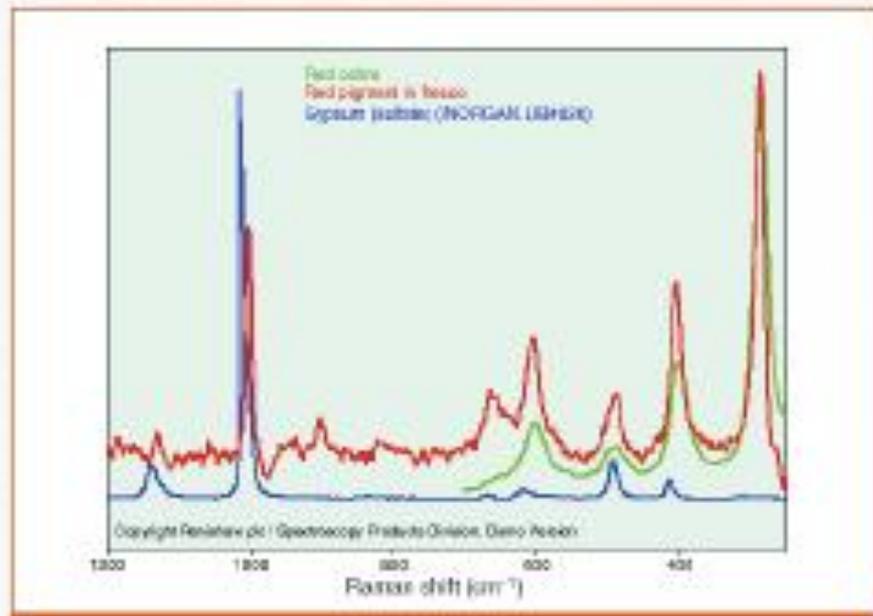


# Applications - Art Restoration



This 12<sup>th</sup> century fresco on a church wall in Italy needed to be restored. What paints to use?

Raman analysis clearly identified the paints and pigments that were originally present, permitting a correct choice of cleaning materials and subsequent repainting to restore its original condition.

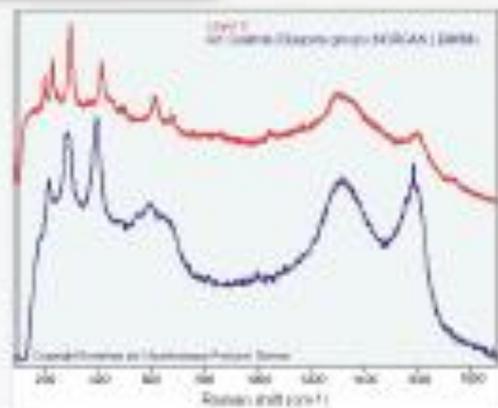
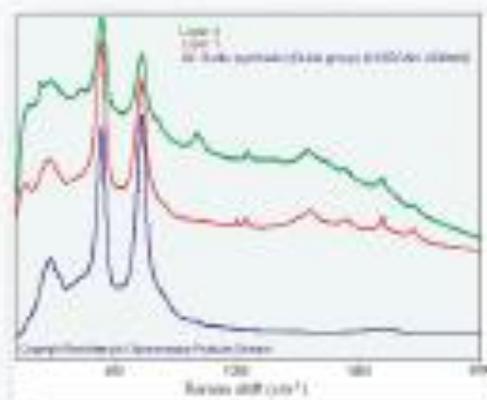


# Applications - Paint Chips

Forensic analysis of paint chips in vehicle accidents. Often multiple layers. Can analyze with IR by stripping successive layers. Image edge with microRaman.



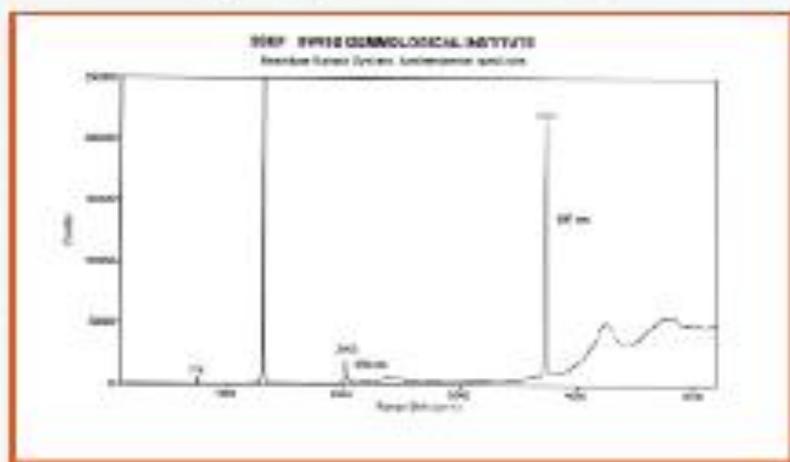
Layers 1 and 3 turned out to be rutile phase  $\text{TiO}_2$  - a white paint. Layer 2 was a Goethite, a red pigment and corrosion inhibitor. Layer 4 was molybdate orange, a common red paint in the 70's in North America and still used in the U.K. today. Layer 5 was a silicate based paint. Data arising from a case investigated by LAPD.



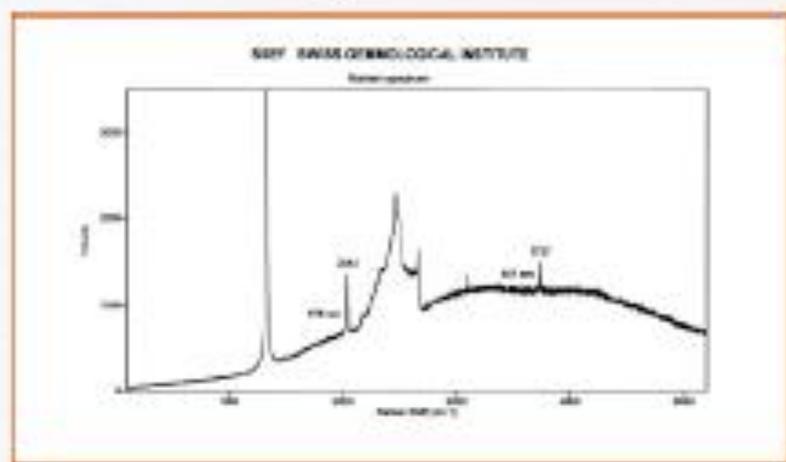
# Applications - Gem Forgery

In 1999 a new process was developed – called GE POL – whereby brown type IIa diamonds could be treated to become indistinguishable from naturally clear diamonds. Raman presented way to distinguish them.

Originally brown diamond

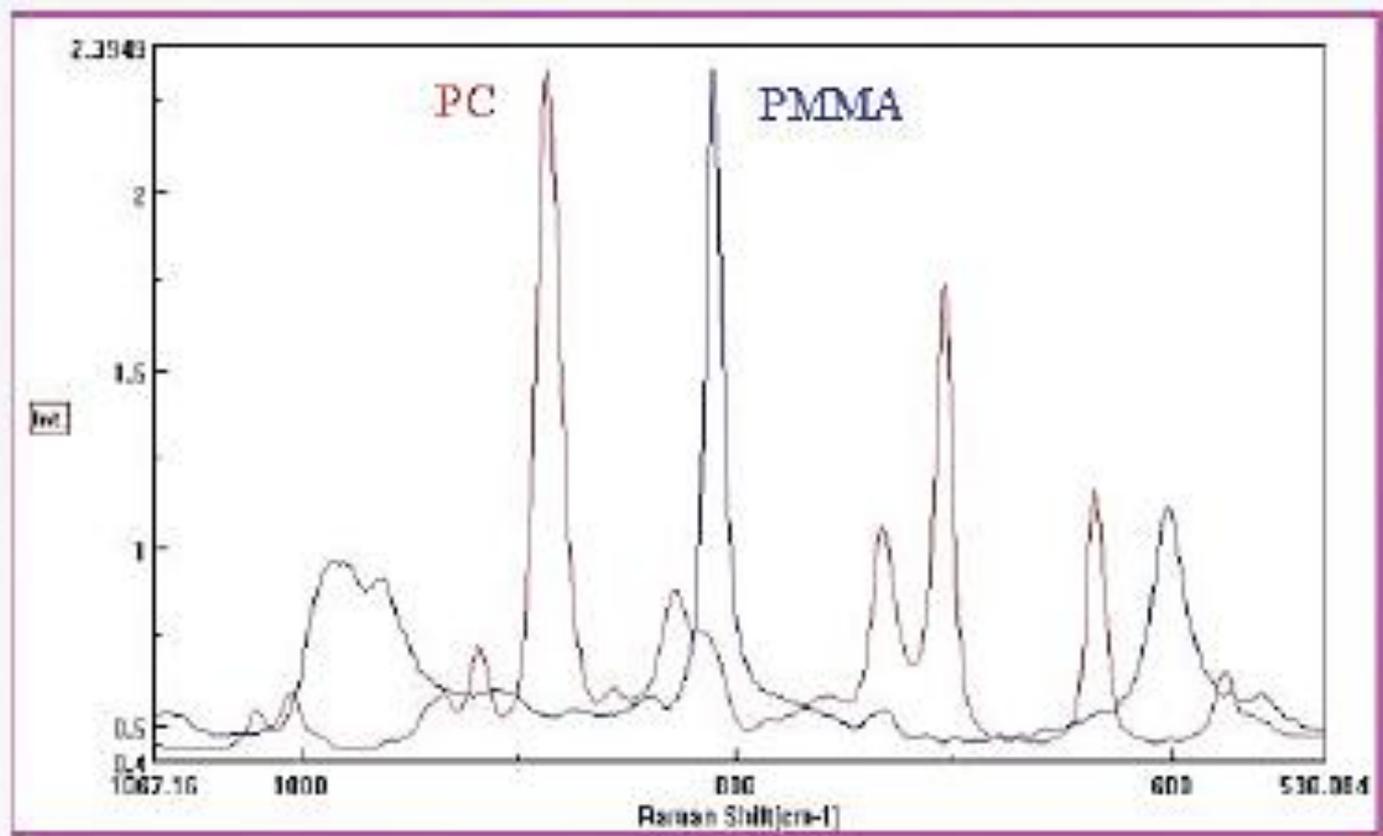


Naturally clear diamond



# Applications - Bullet Proof Glass

Identify poly(carbonate) from poly(methylmethacrylate).  
Both used for shatter-proof glass



# Applications - Sunscreen Formulations

Here are the spectra of 5 common sunscreen ingredients. Raman is able to determine from a spectrum on the arm the nature of the sunscreen being used.

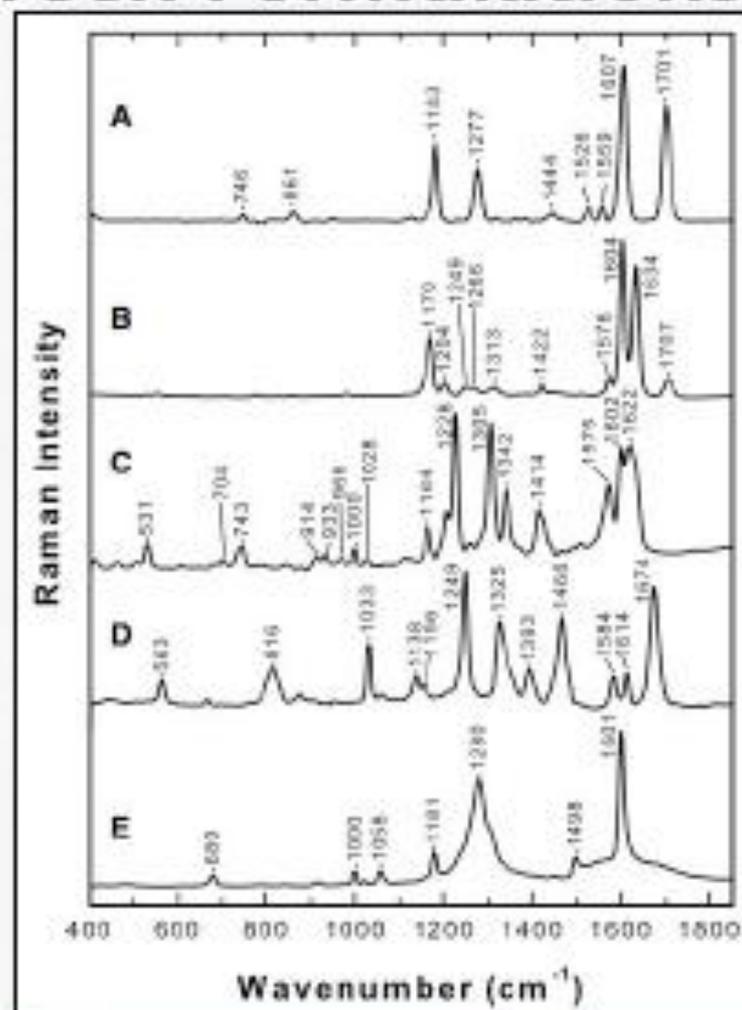
A: ODPABA (octyl N,N-dimethyl-p-aminobenzoic acid)

B: OMC (octyl p-methoxycinnamate)

C: BZ3 (oxybenzone)

D: OCS (octyl salicylate)

E: DBM (dibenzoylmethane)



G.R. Luppnow et al., J. Raman. Spec. 34, 743 (2003).