HORIBA Scientific

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Raman Spectroscopy with Practical Applications

May 29, 2019

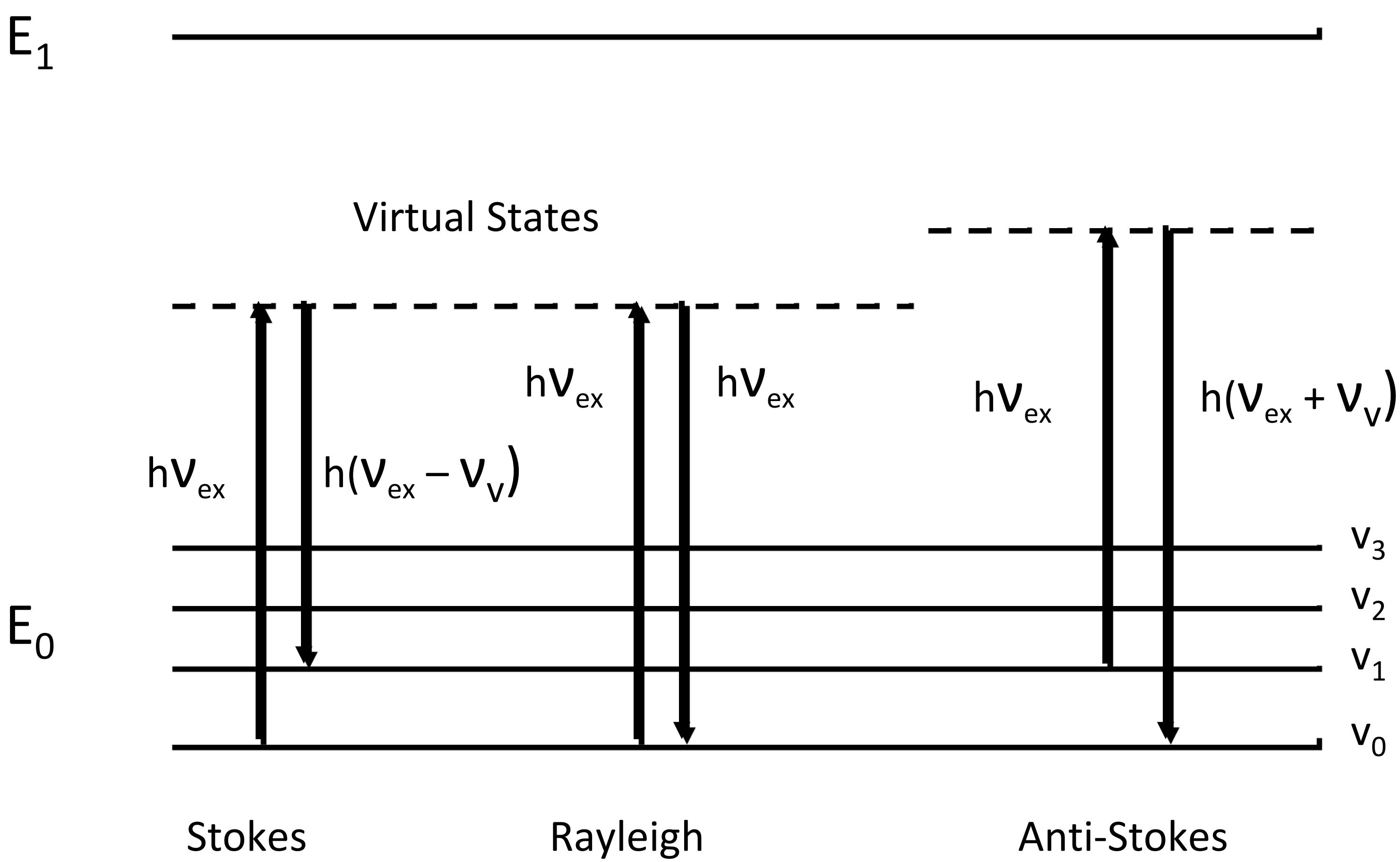
Presentation Topics

- Raman spectroscopy and photoluminescence
- Polymorphism
- Liquid and head space Raman spectroscopy
- Raman spectroscopy of polymers
- Particle size characterization with chemical identification

Vibrational Spectroscopy

- Vibrational spectroscopy studies vibrations in a system using light.
- IR and Raman spectroscopy are the most common and complementary to each other.
  - IR spectroscopy is absorption (or reflection) spectroscopy
  - Raman spectroscopy is scattering spectroscopy
- Applications of vibrational spectroscopy
  - Molecular spectroscopy
    - Vibrations of atoms within molecules
    - Gas, liquid and solid
  - Solid state and material science
    - Vibrations of atoms within molecules (e.g. molecular crystals, amorphous materials)
    - Vibrations between atoms and molecules (e.g. amorphous materials)
    - Vibrations of crystalline lattice
    - From liquid to solid (e.g. gel, crystal)

Raman Scattering



Raman Spectra of Polystyrene at 532, 638 and 785 nm Excitation

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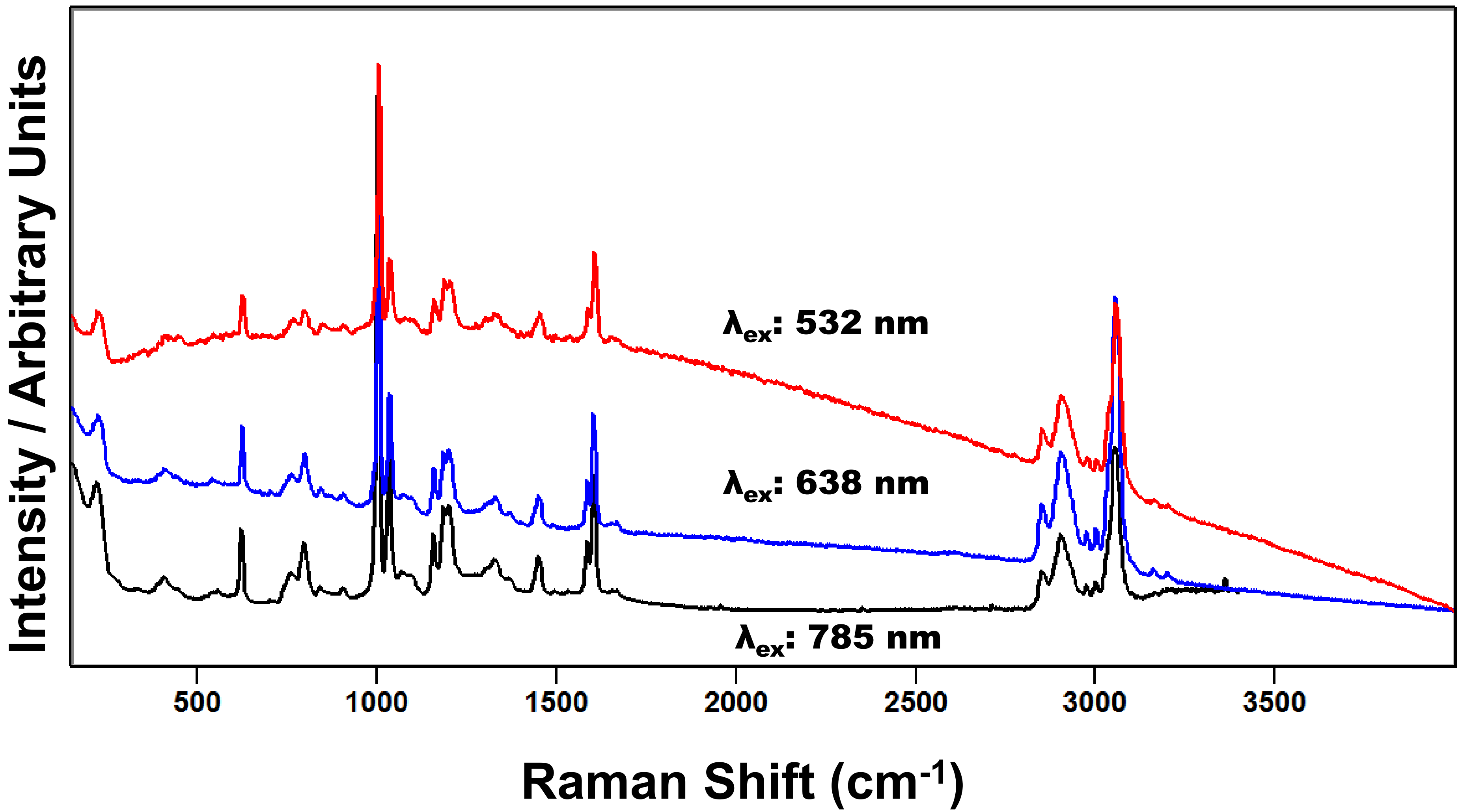

Raman Spectra of Polystyrene at 532, 638 and 785 nm Excitation

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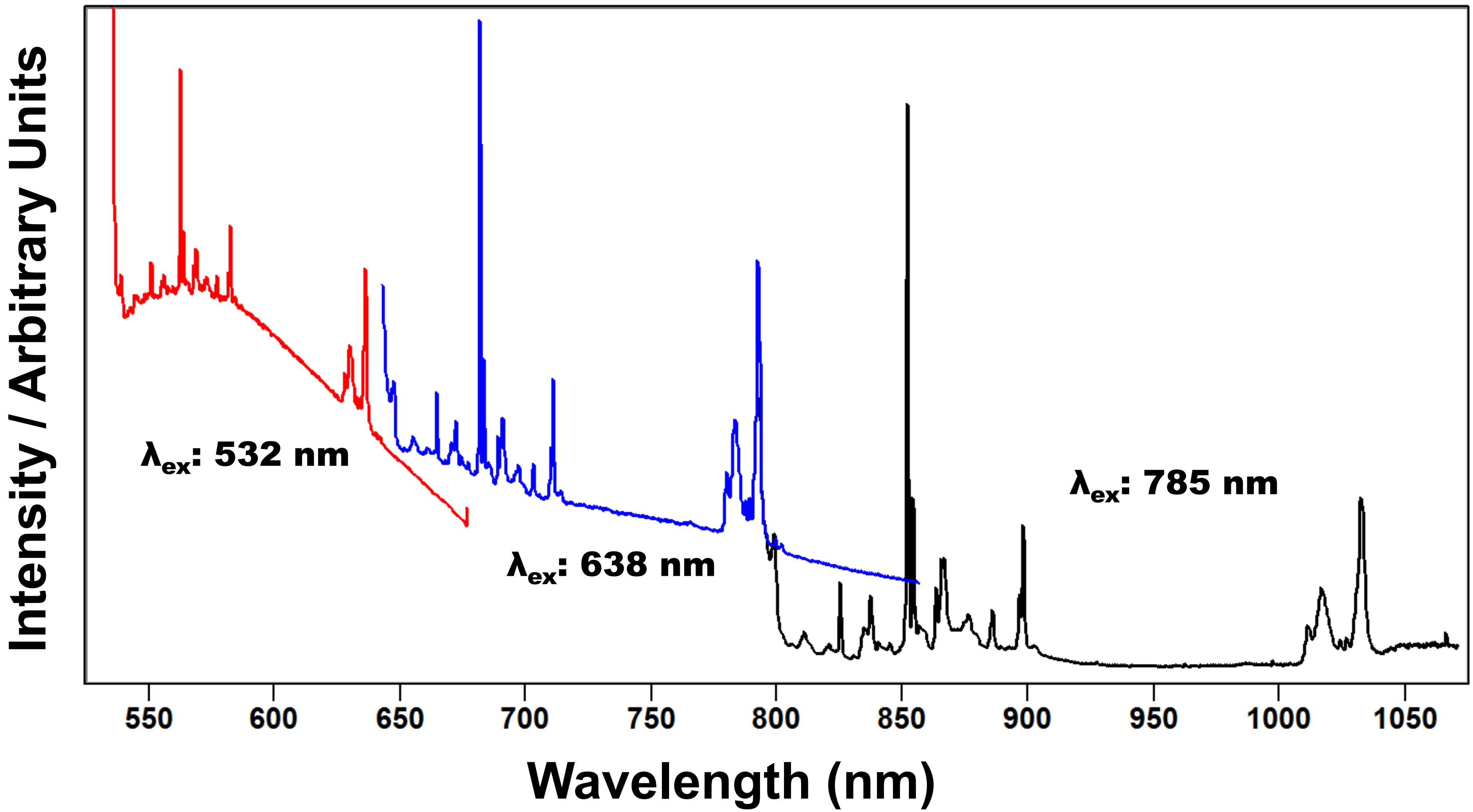

Raman Spectra of Glass Microscope Slide at 532, 638 and 785 nm Excitation

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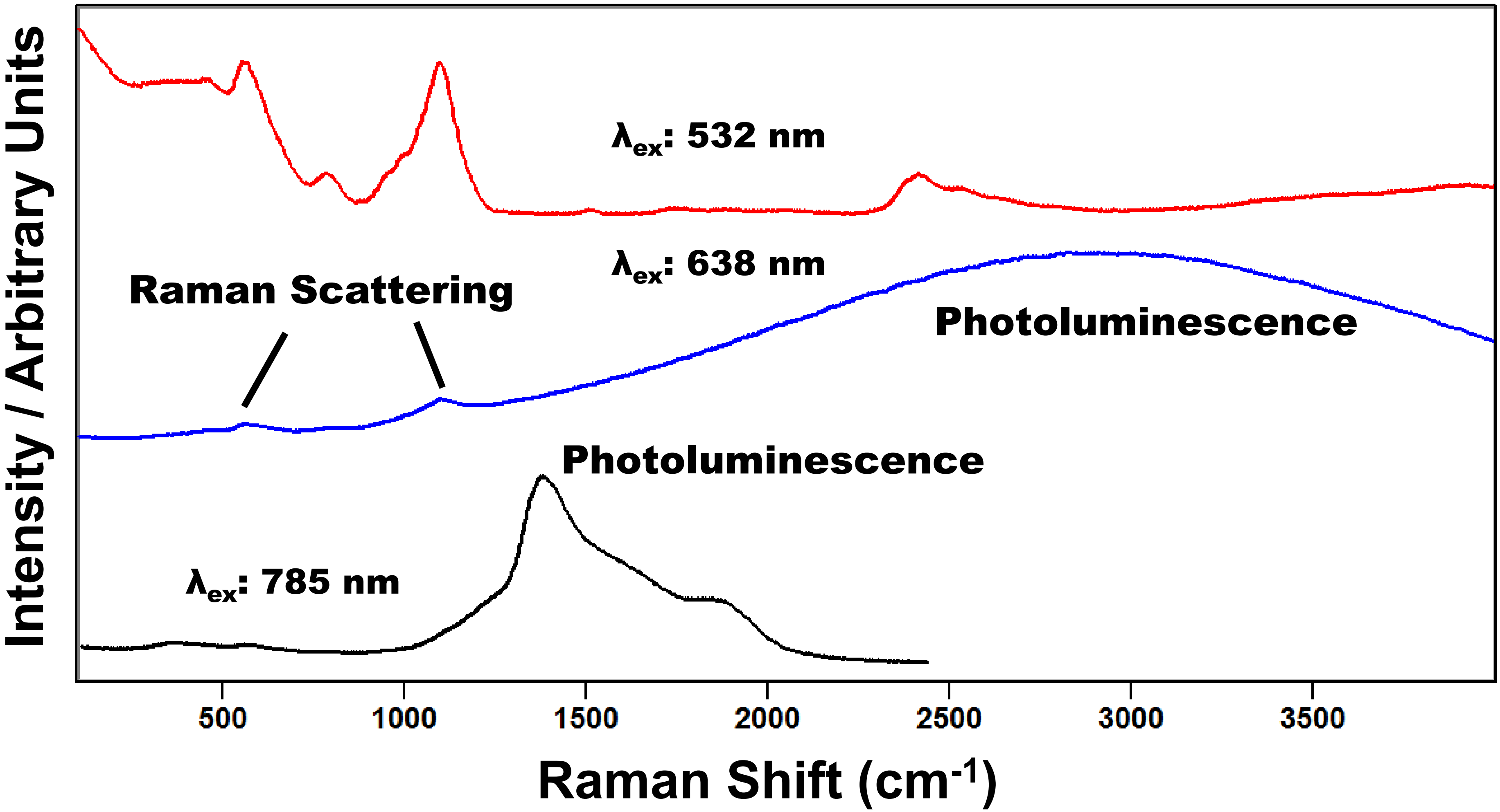
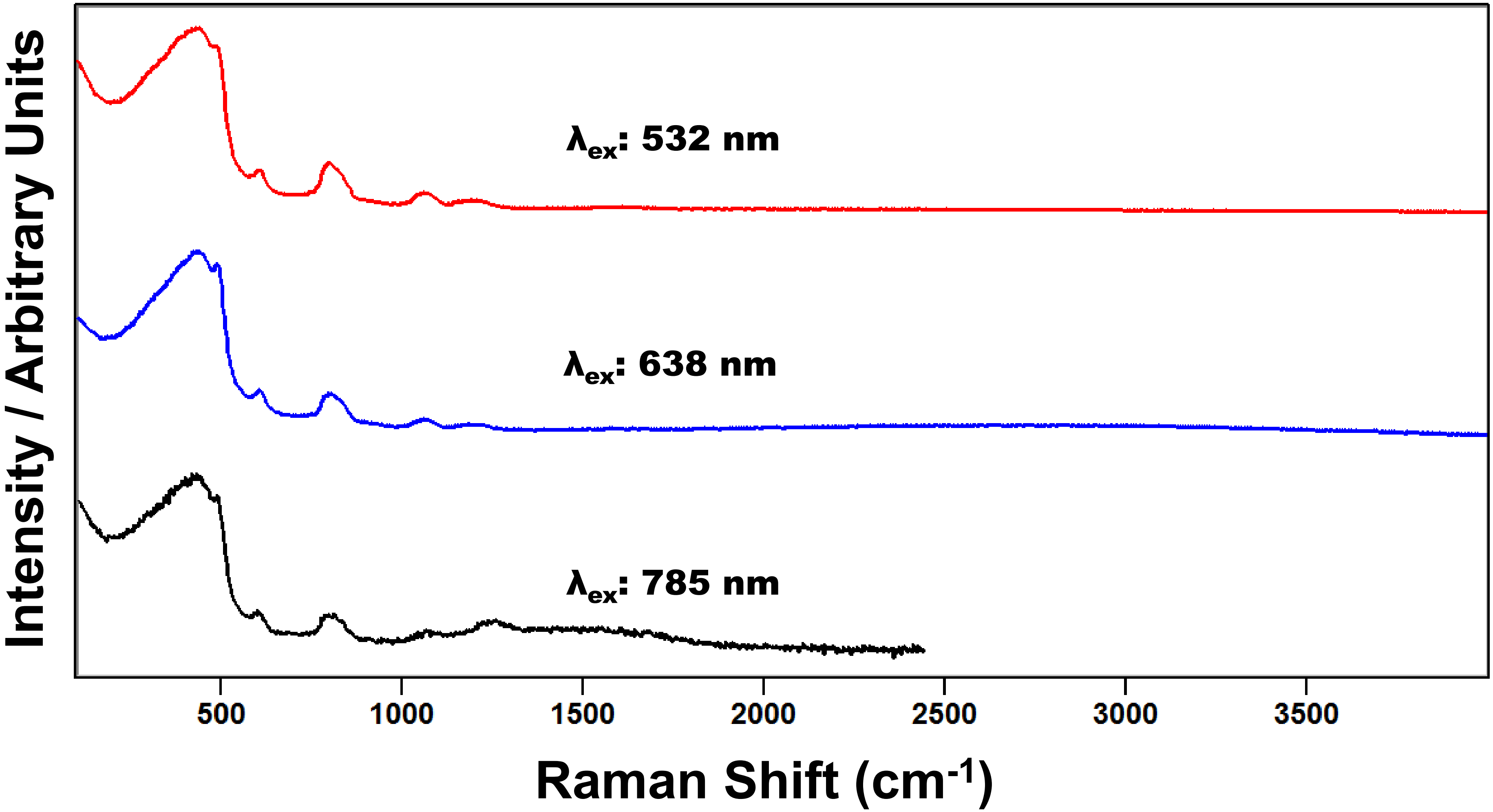
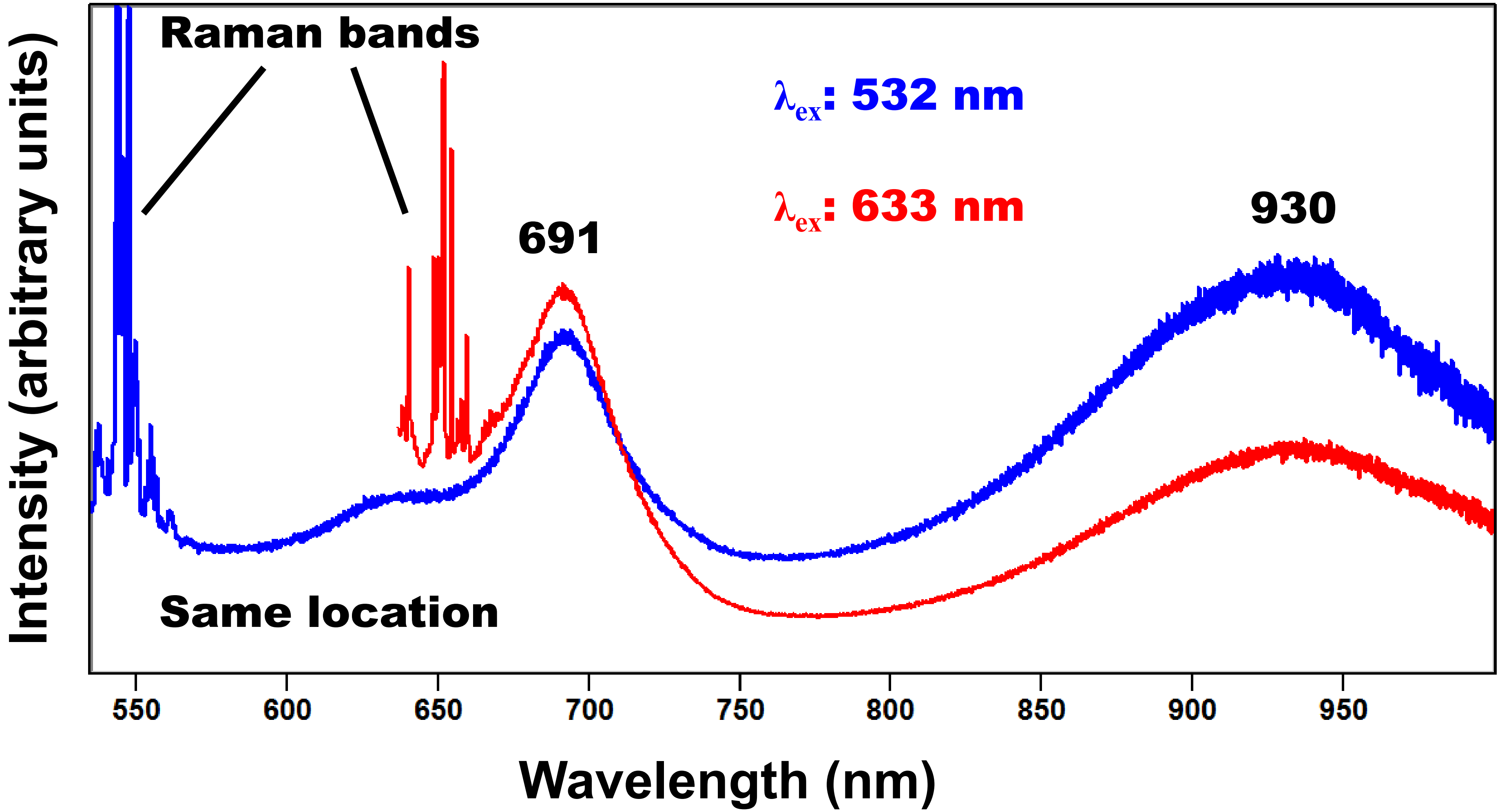


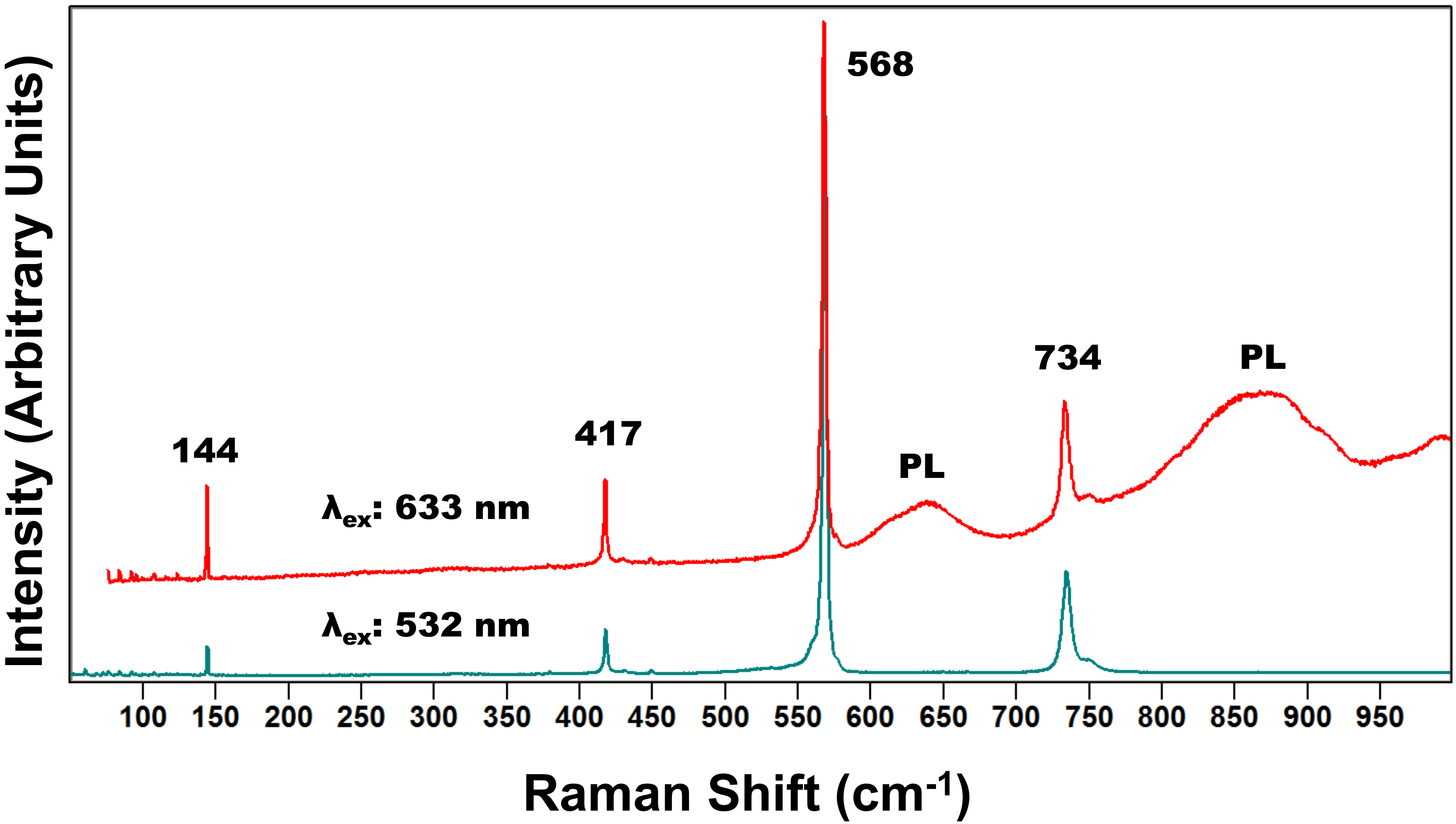
Raman Spectra of Fused Quartz at 532, 638 and 785 nm Excitation



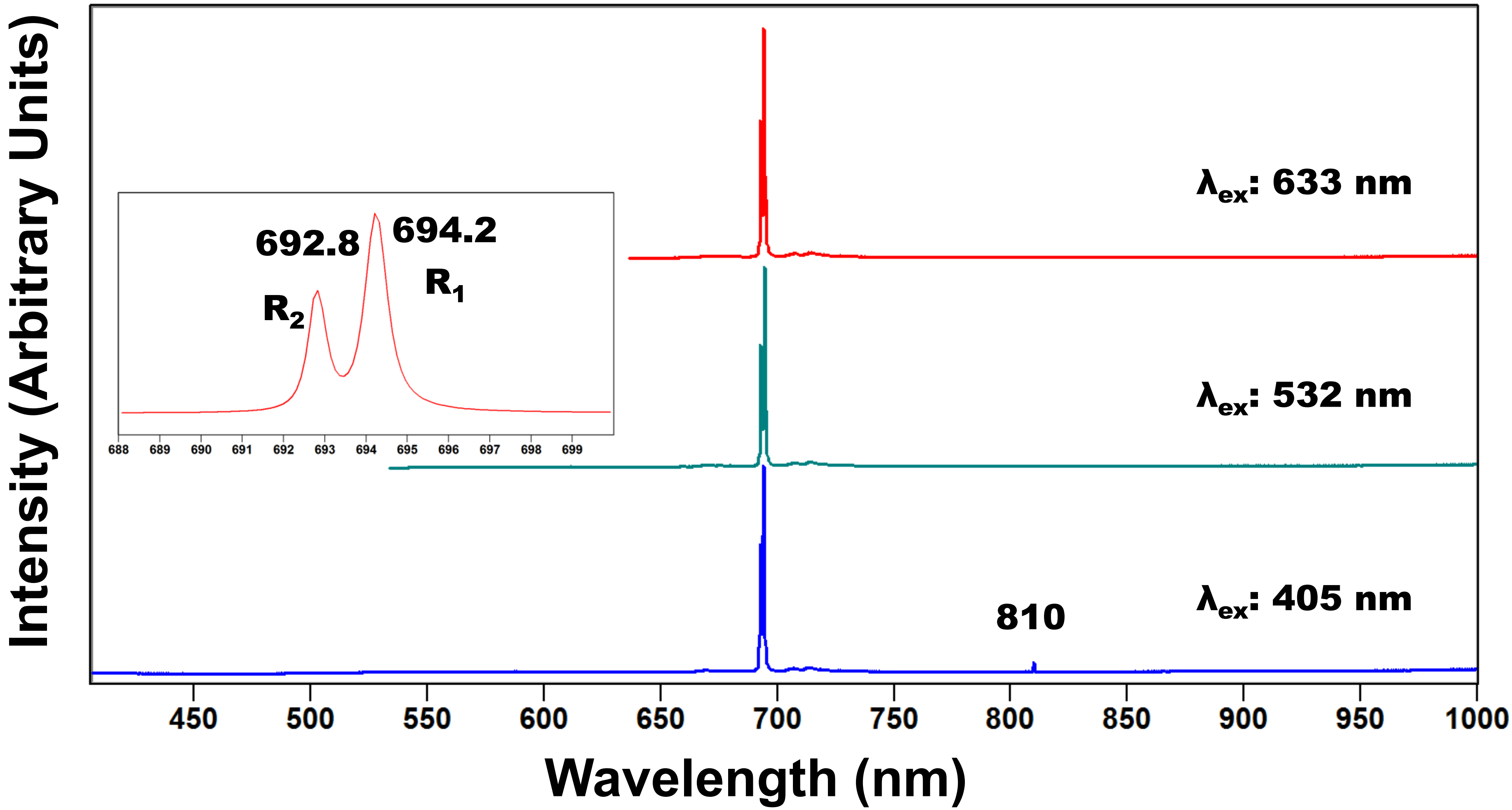
Photoluminescence of Few-Layer MoS_2



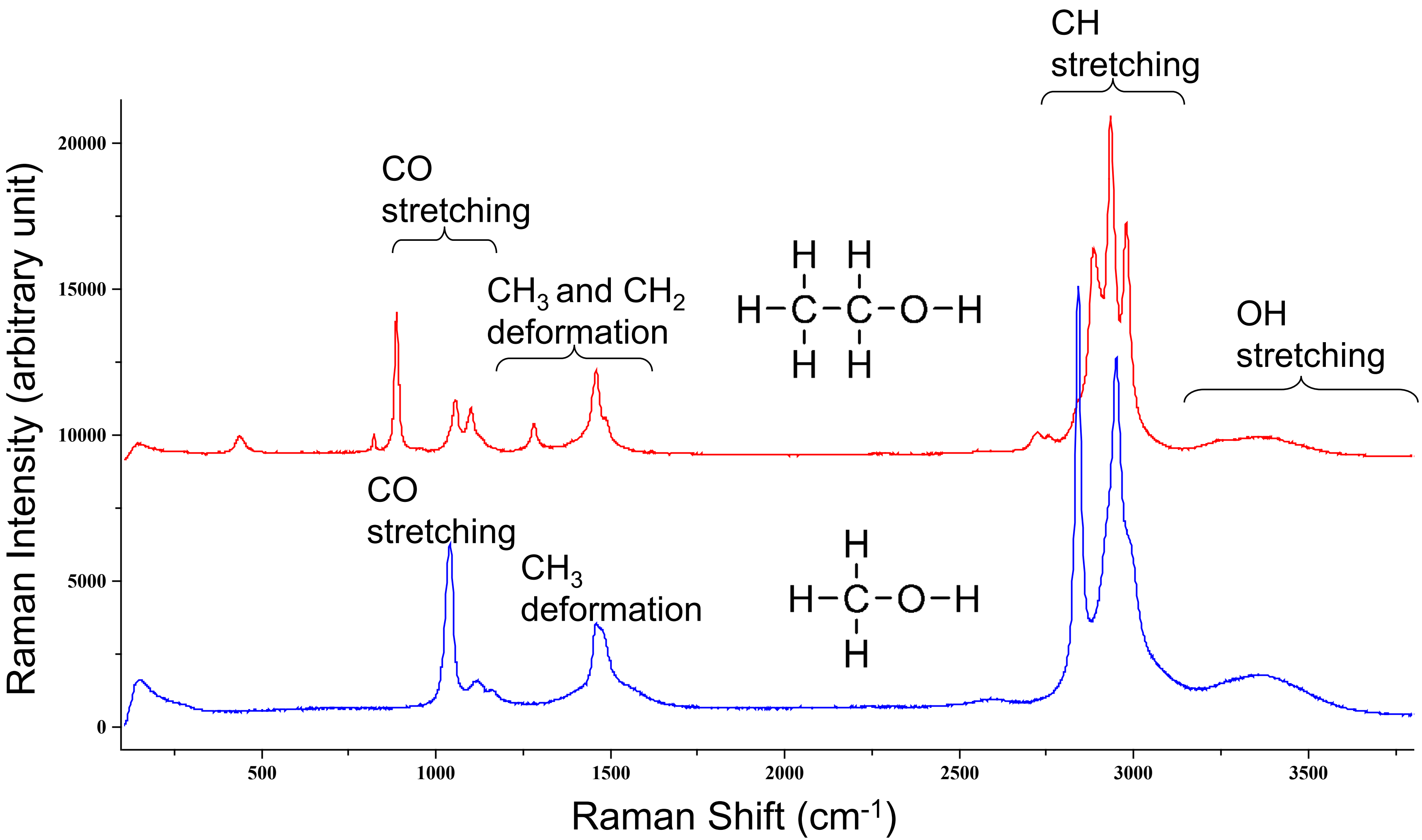
Raman Spectra of Al_2O_3:Cr at 532 and 633 nm Excitation



Photoluminescence Spectra of Al_2O_3:Cr at 405, 532 and 633 nm Excitation

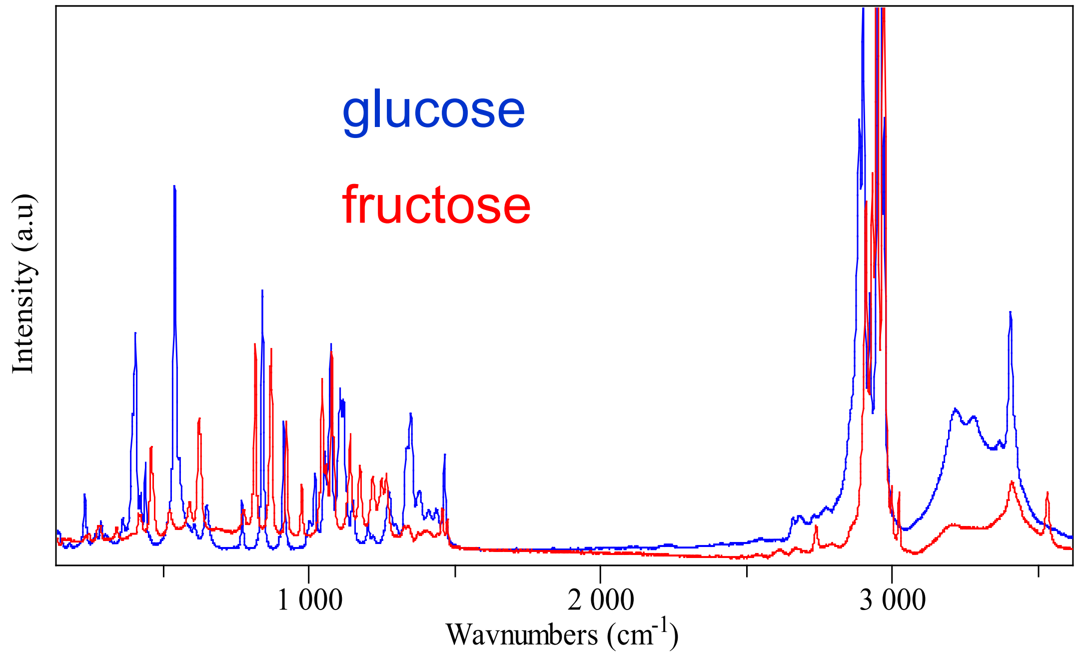


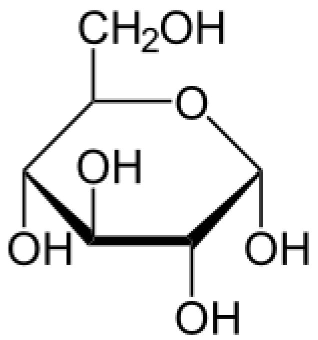
Raman Spectra of Methanol and Ethanol

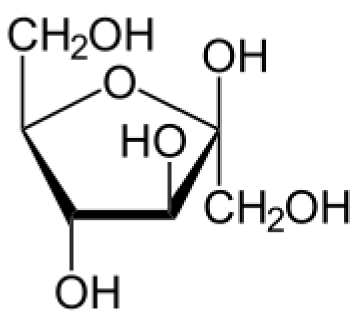


13

Spectral Analysis: Comparison



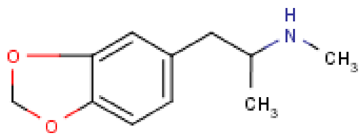




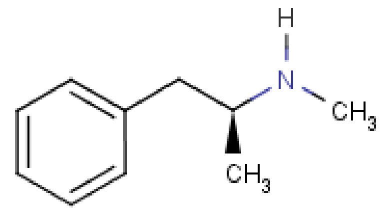
The same chemical composition $C_6H_{12}O_6$
but different molecular structures

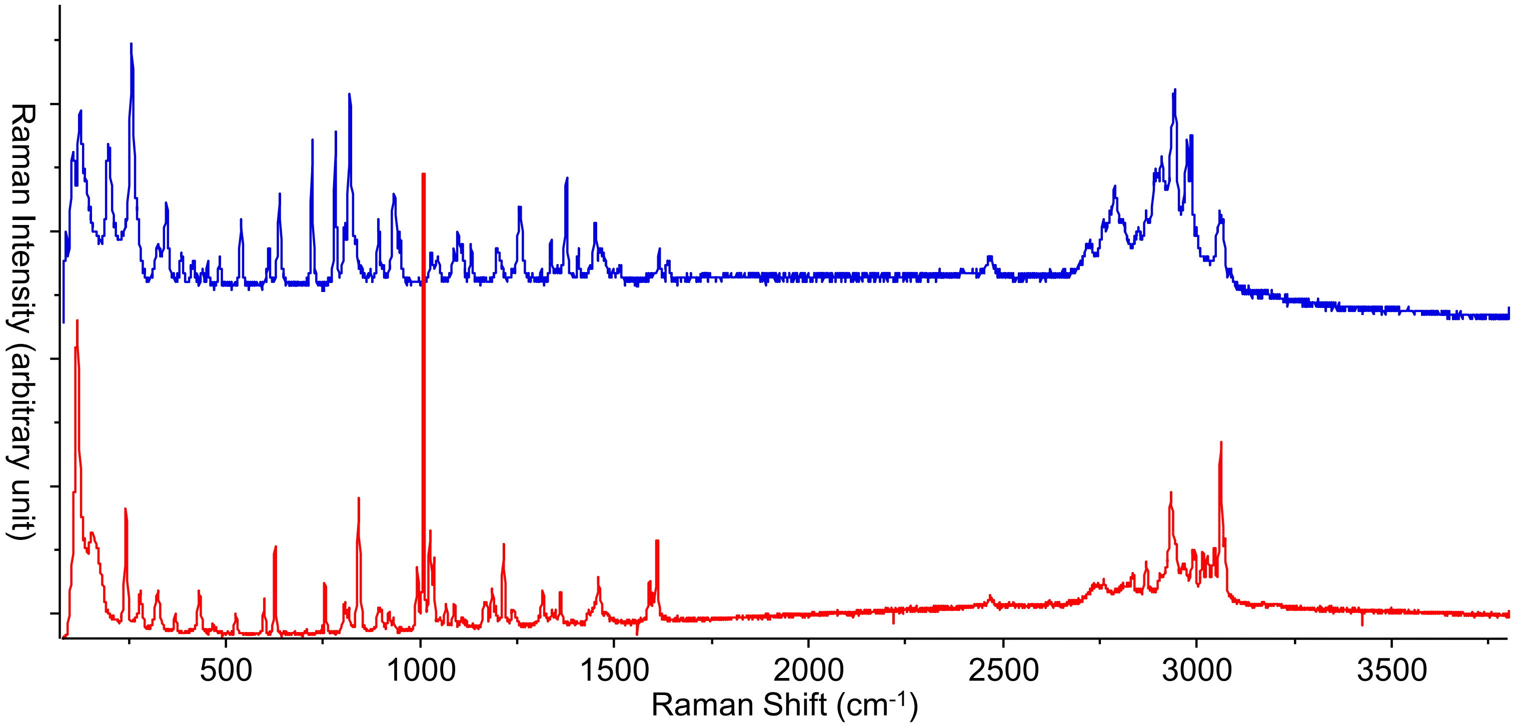
Similar Molecular Structures

3,4-Methylenedioxymethamphetamine (MDMA)



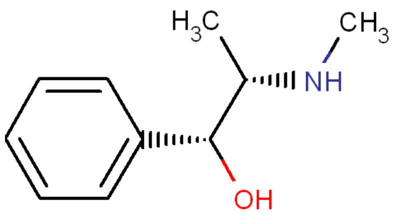
Methamphetamine



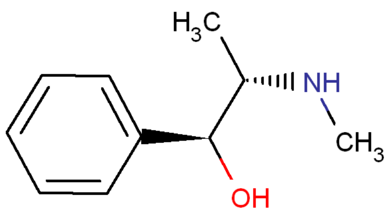


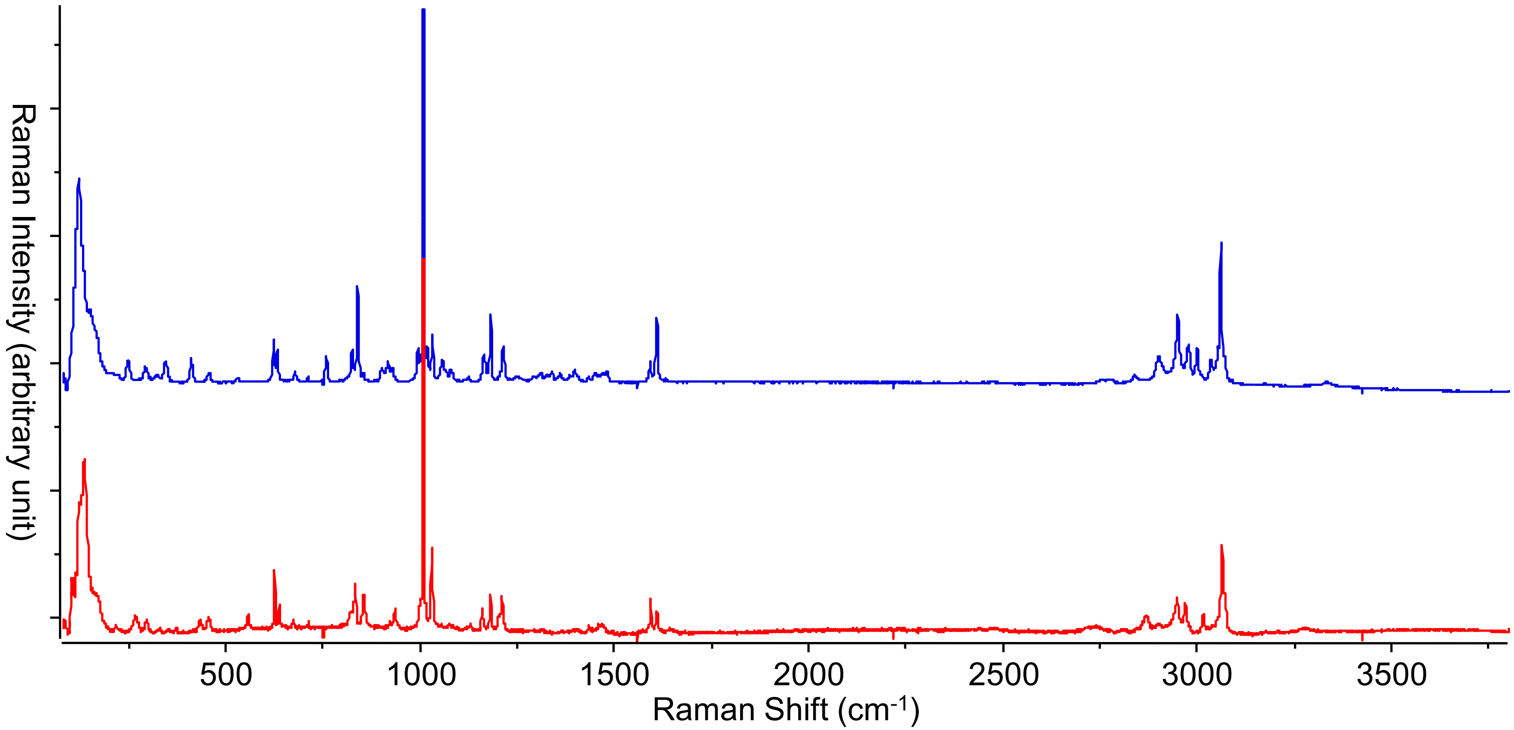
Diastereomers

Ephedrine

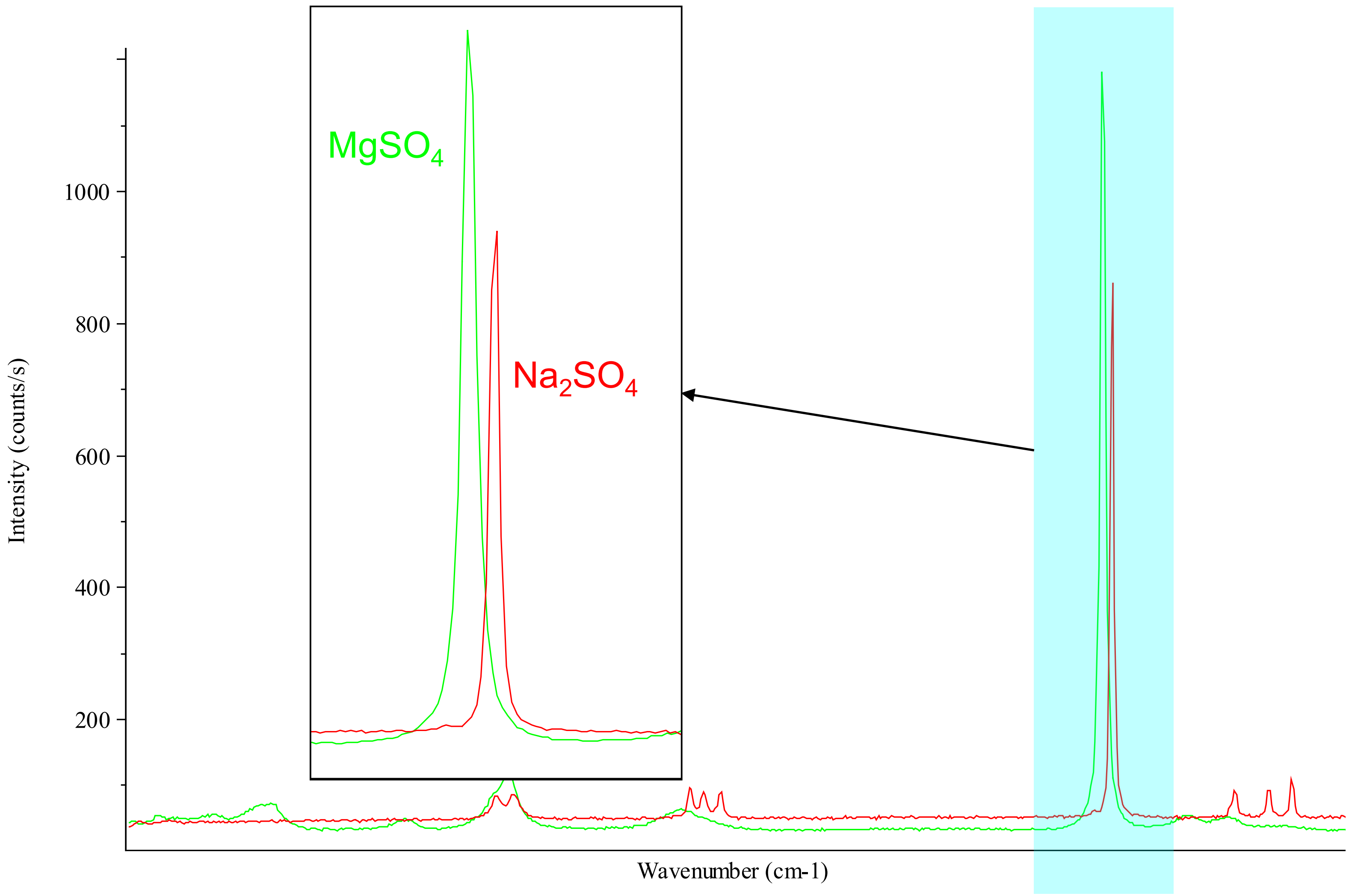


Pseudoephedrine

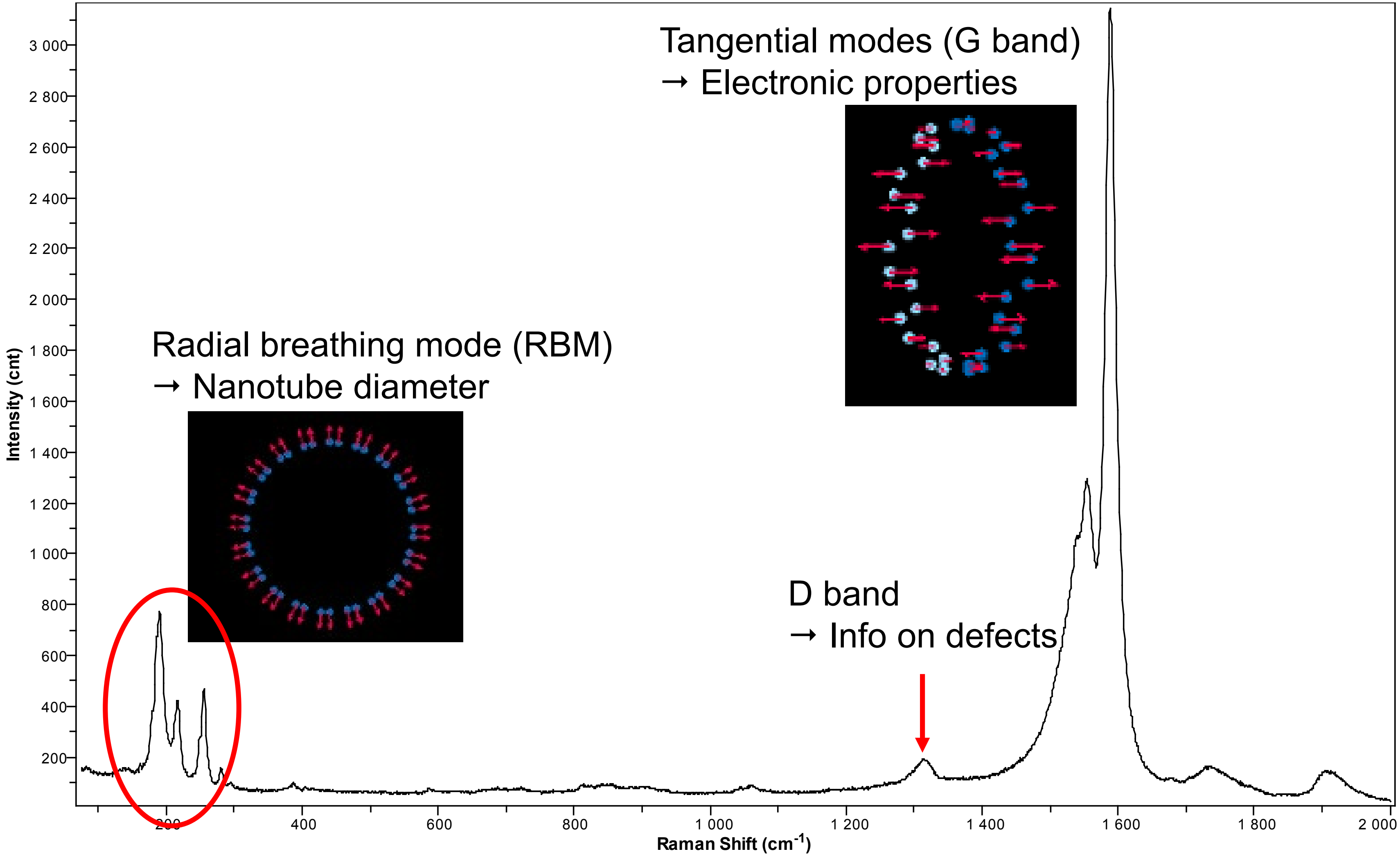




Substitution



Carbon Nanotubes



Raman Spectroscopy and Polymorphism

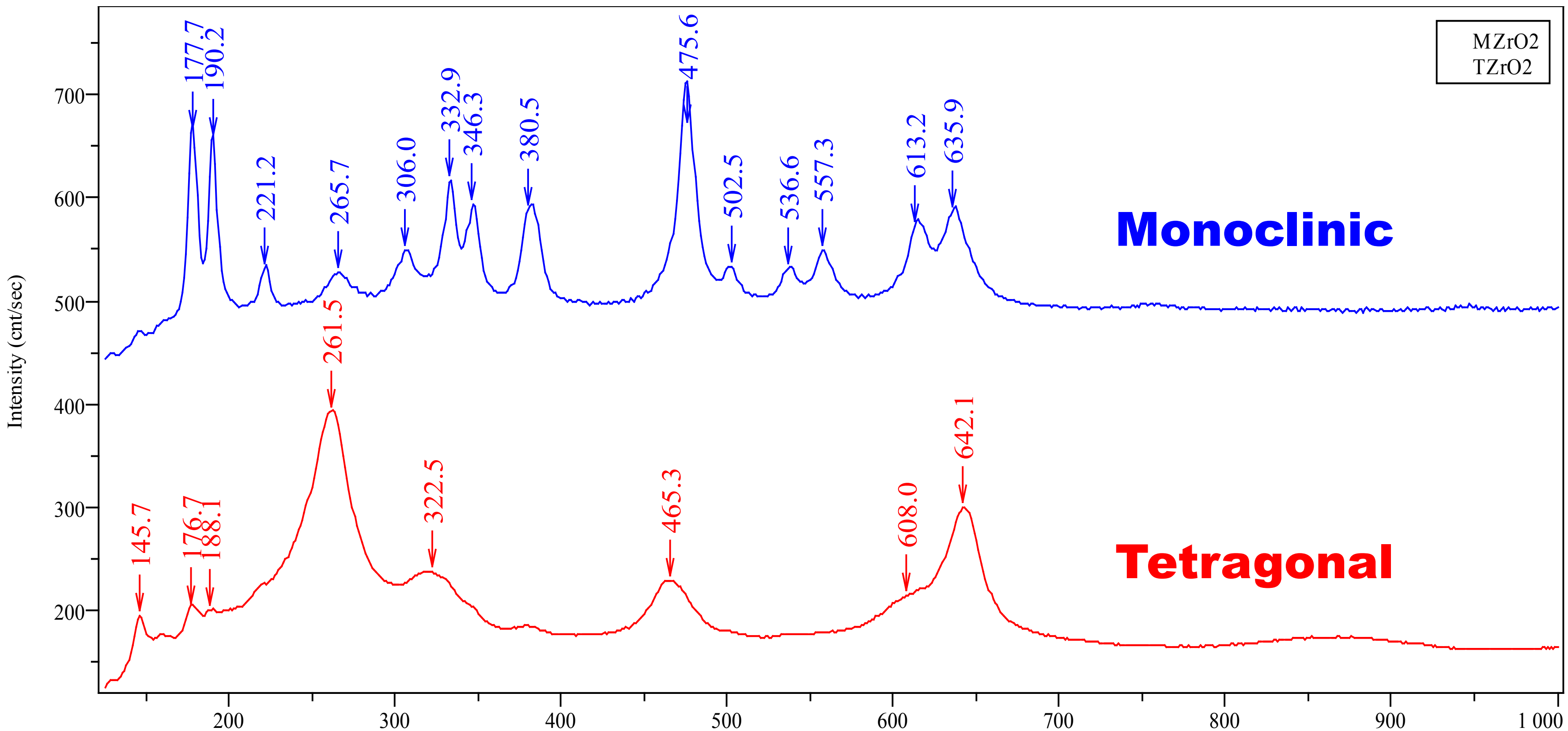
Monoclinic and Tetragonal ZrO_2

Anatase and Rutile TiO_2

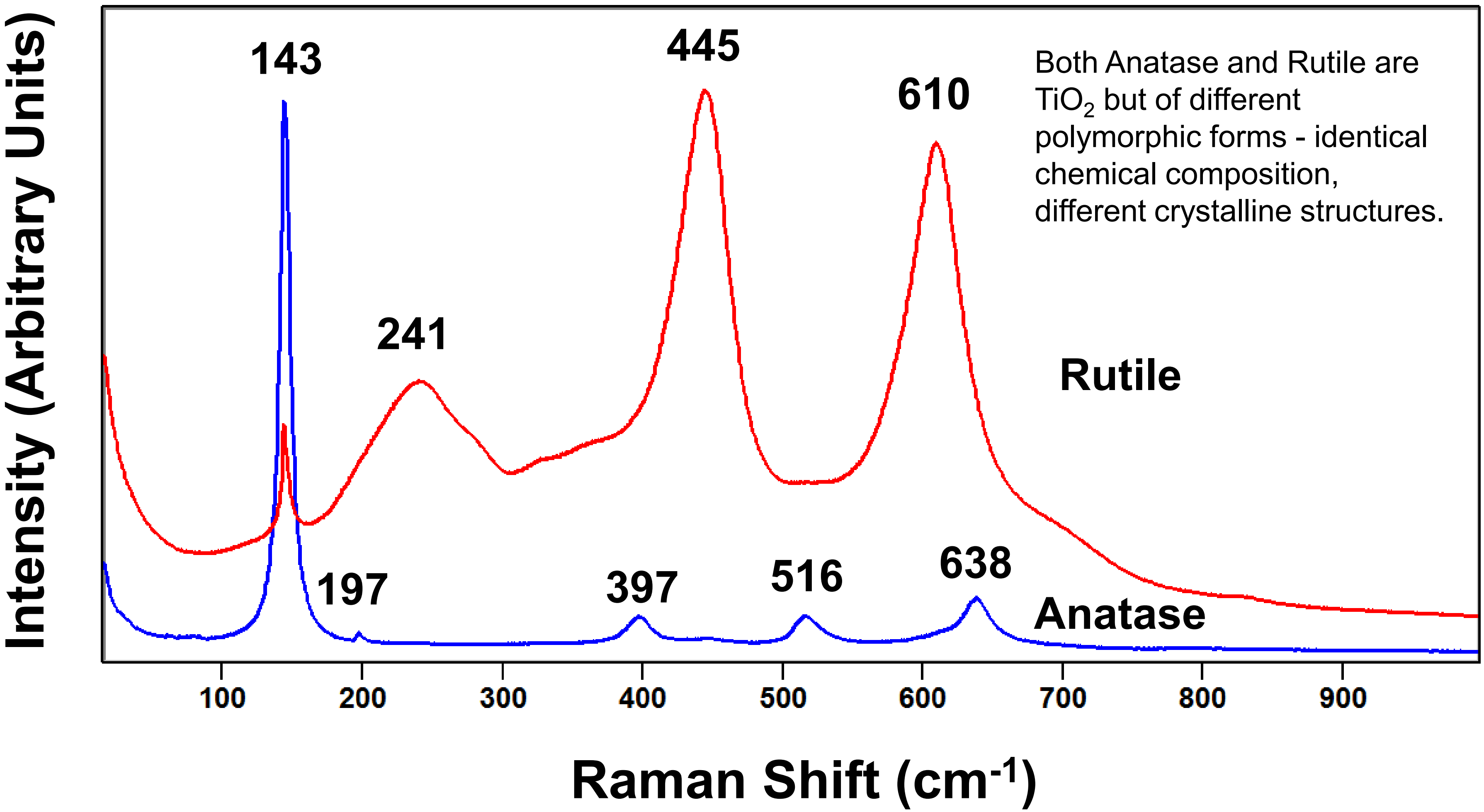
Acetaminophen Forms I and II

ZrO_2 : Monoclinic and Tetragonal

At ambient conditions the monoclinic phase is stable. The high T tetragonal phase can be stabilized by alloying with oxides such as Y_2O_3, Al_2O_3, CaO. There is a third phase which is cubic, and stable at even higher temperatures.

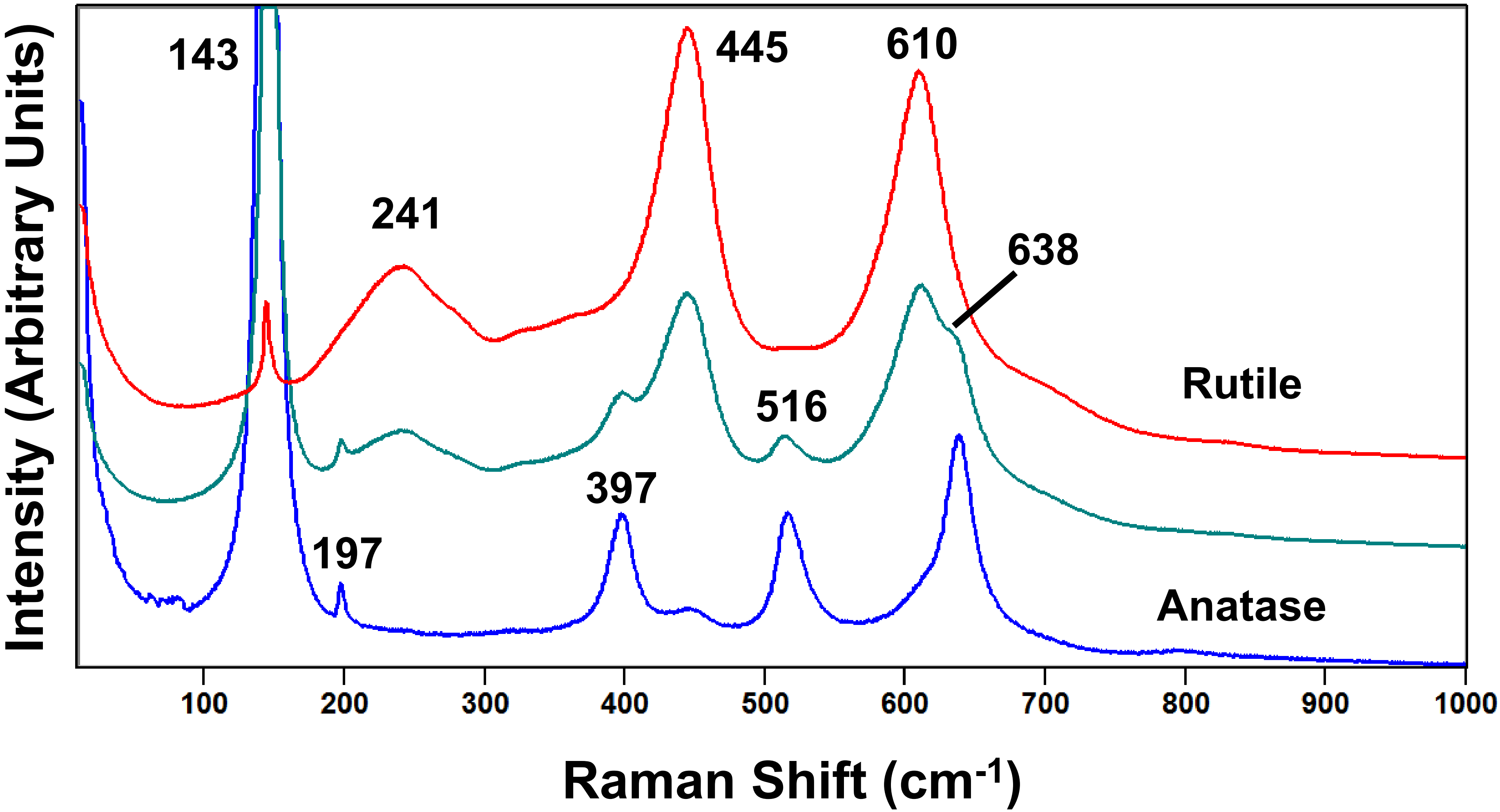


Anatase and Rutile TiO_2 with 532 nm Excitation

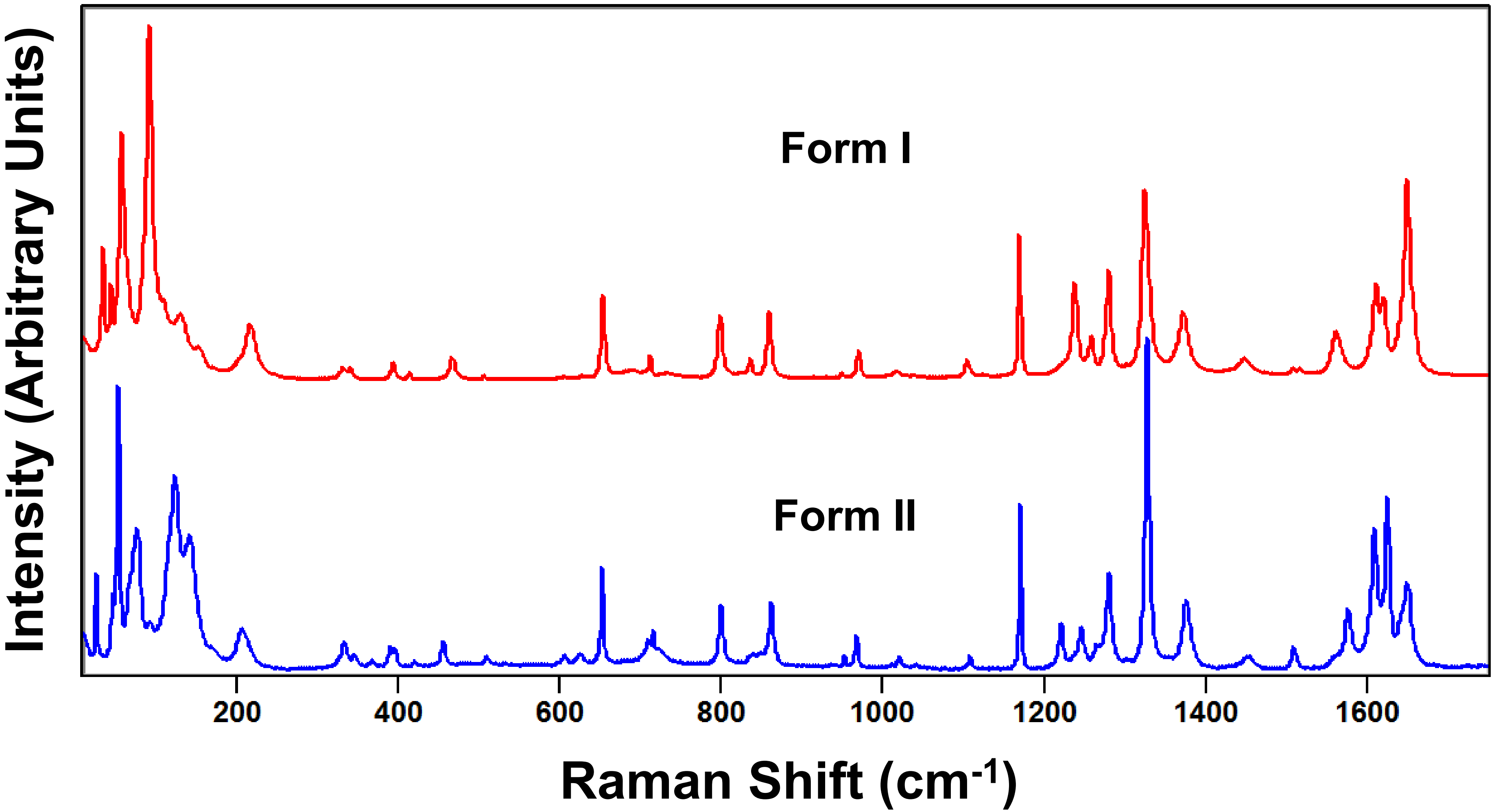


Both Anatase and Rutile are TiO_2 but of different polymorphic forms - identical chemical composition, different crystalline structures.

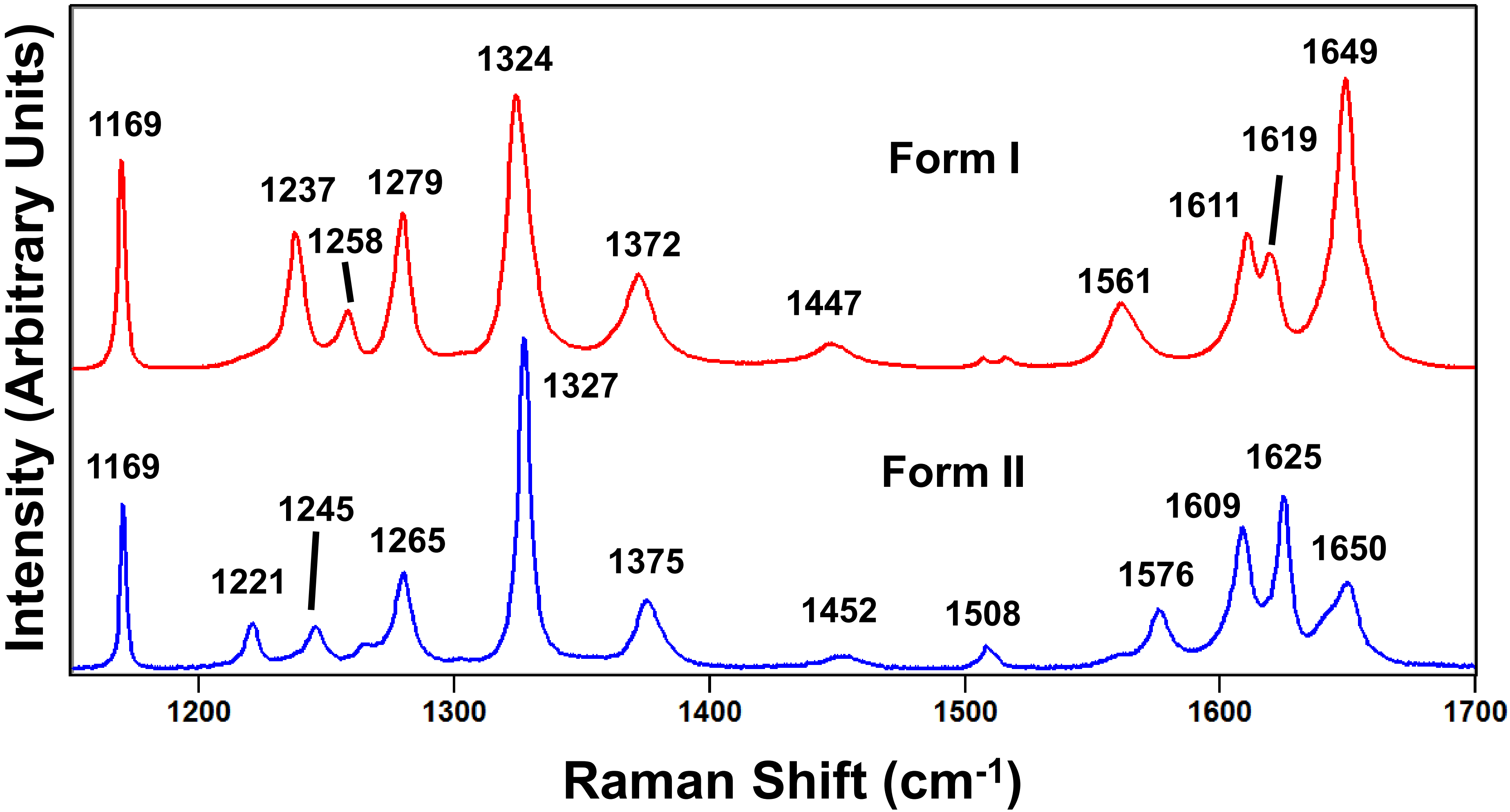
Rutile with Anatase TiO_2 Impurity, Green Spectrum



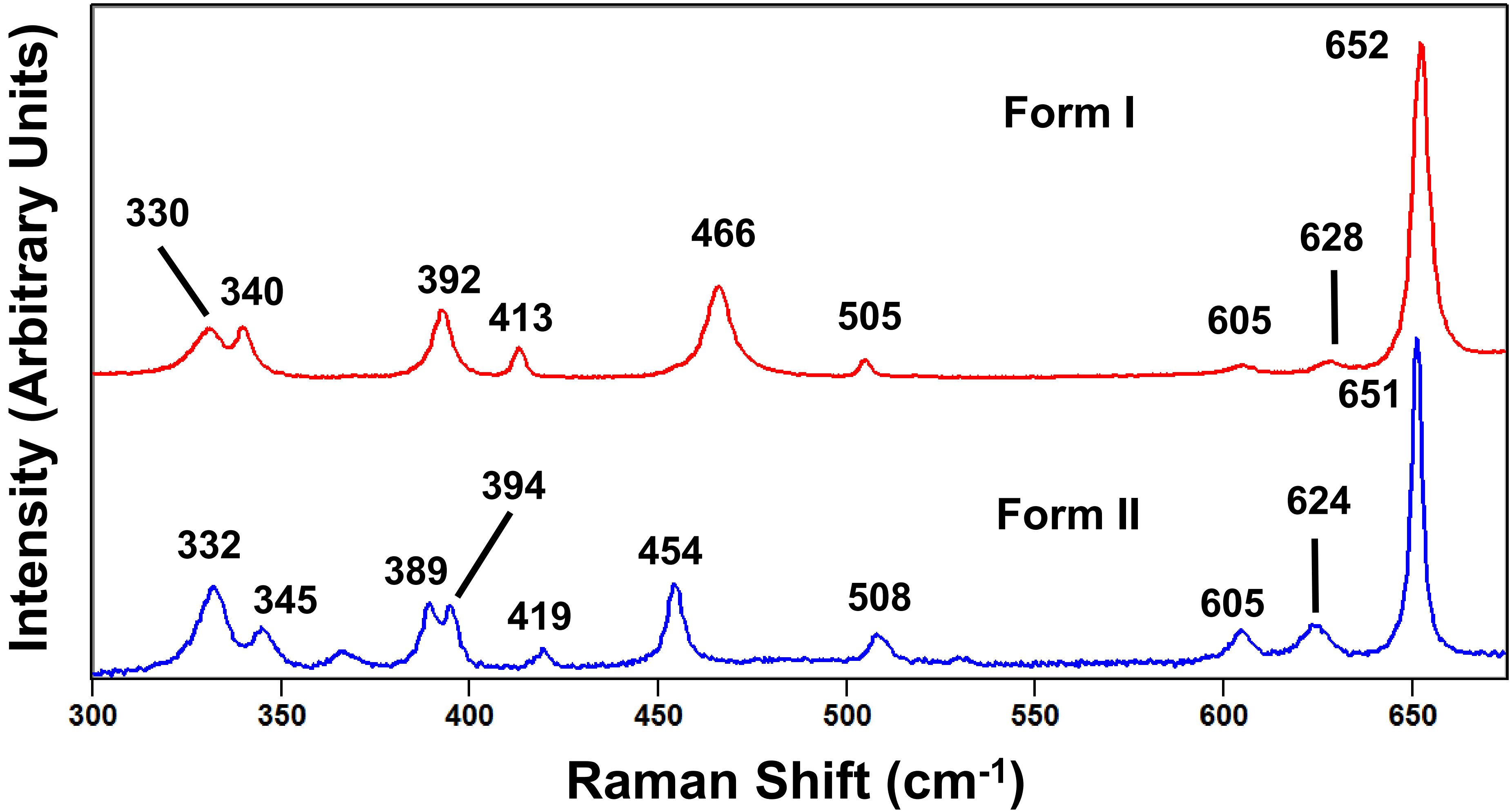
Acetaminophen Form I (Red) and Form II (Blue)



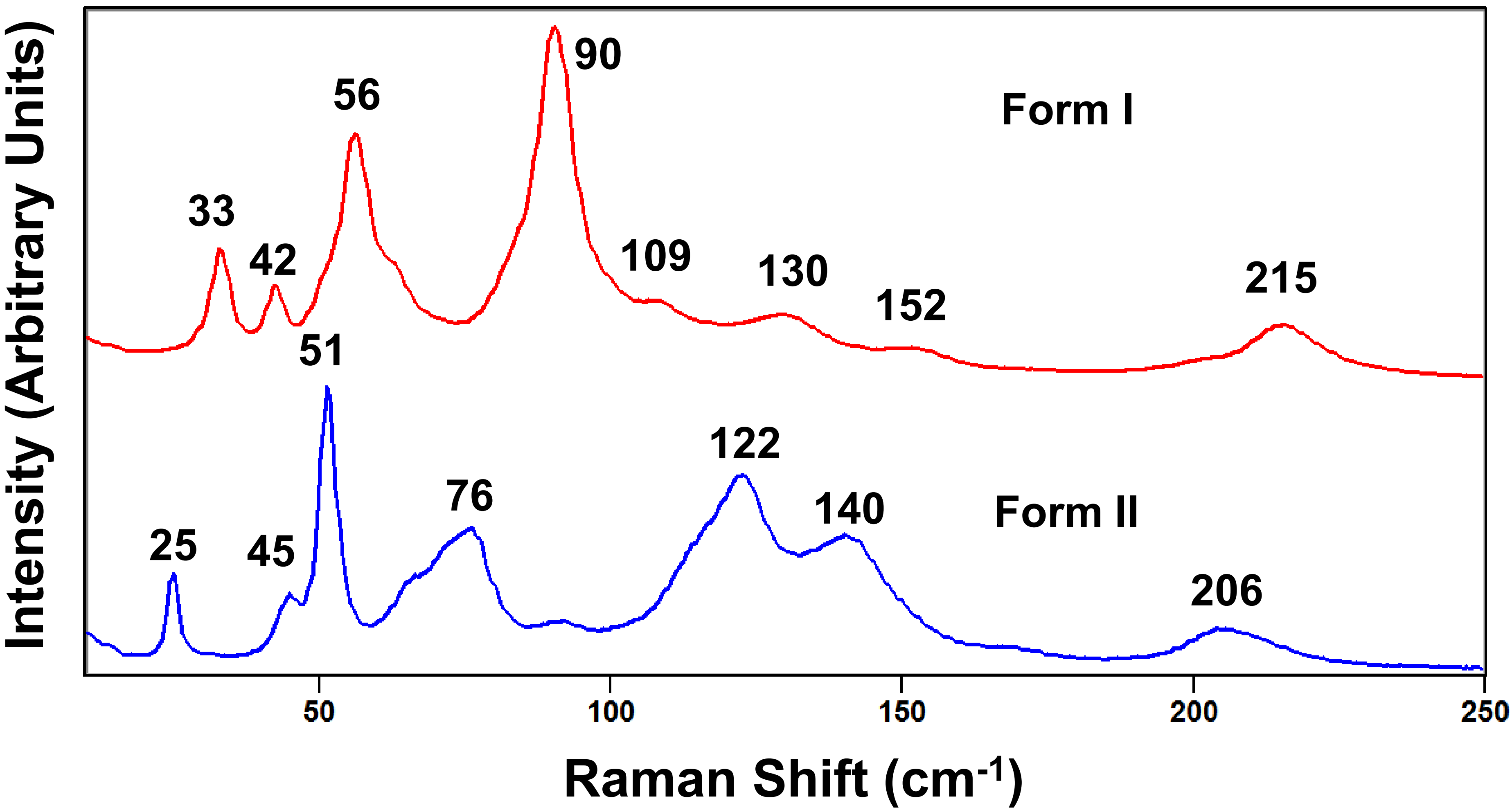
Acetaminophen Form I (Red) and Form II (Blue)



Acetaminophen Form I (Red) and Form II (Blue)



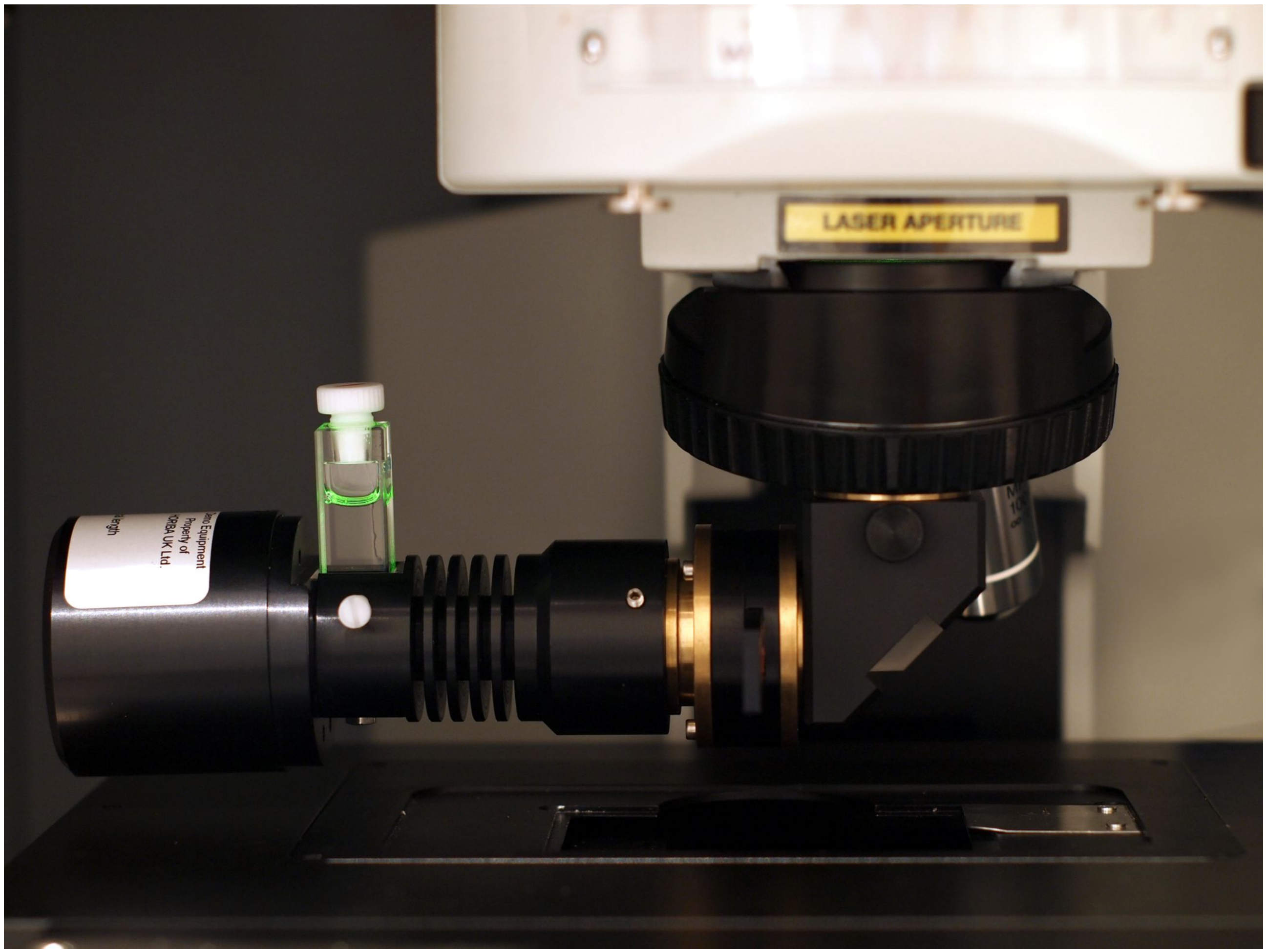
Acetaminophen Form I (Red) and Form II (Blue)



Liquid and Head Space Raman Spectroscopy

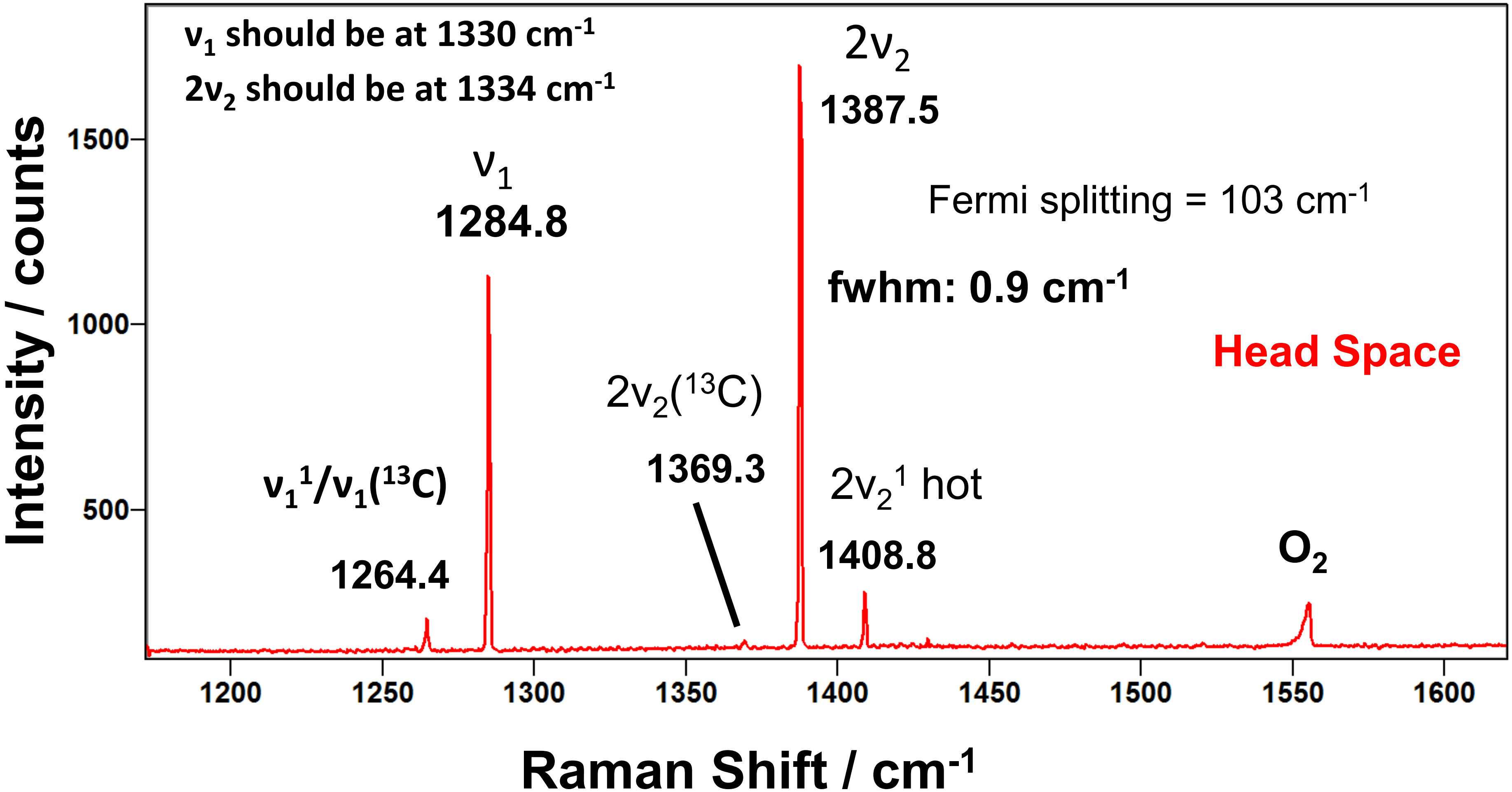
Hydrogen Bonding and Molecular Interactions

Macro-Raman Sampling from a Cuvette

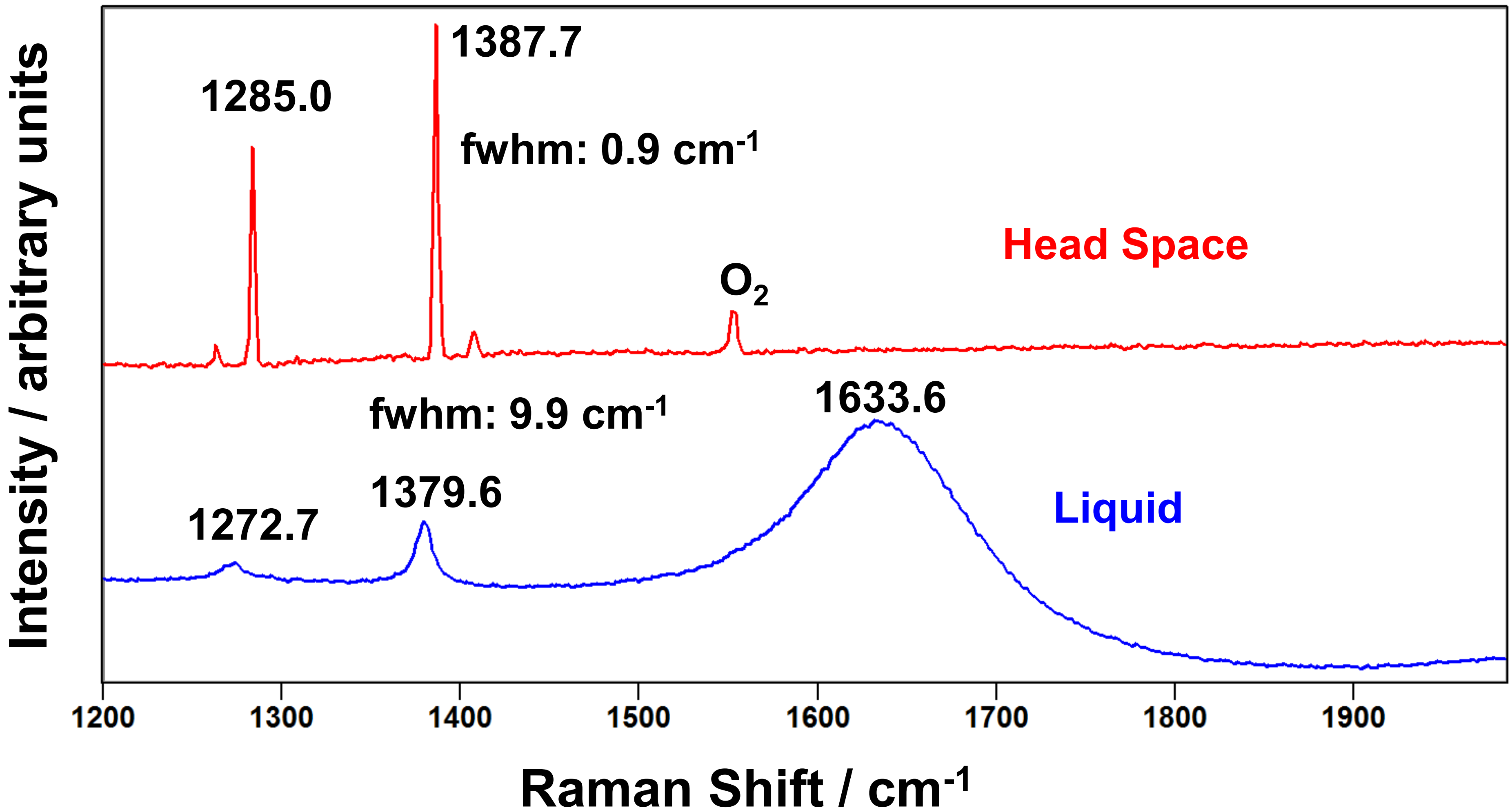


Macro-Raman Sampling from a Bottle

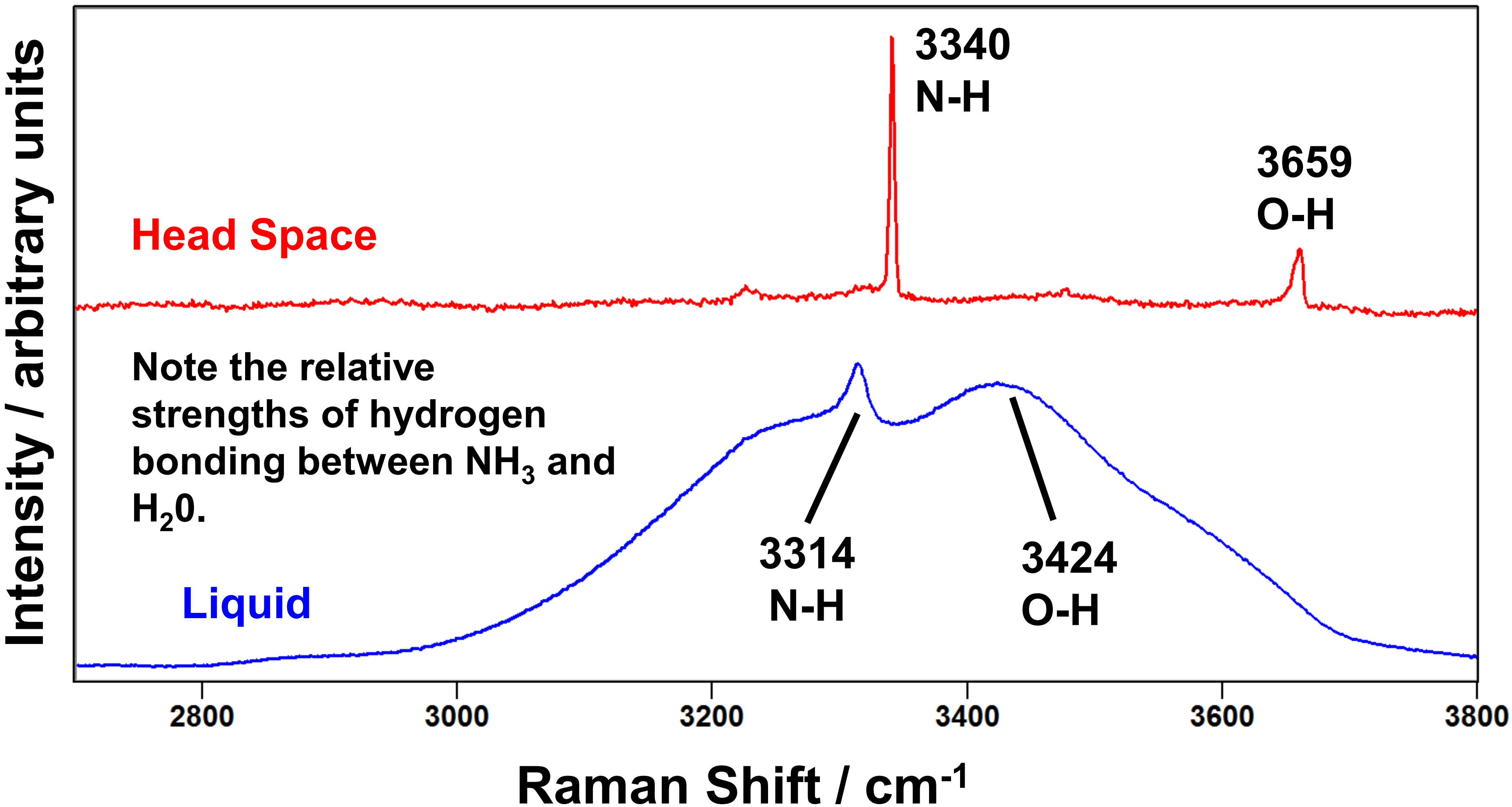
Head Space of Beer – CO_2



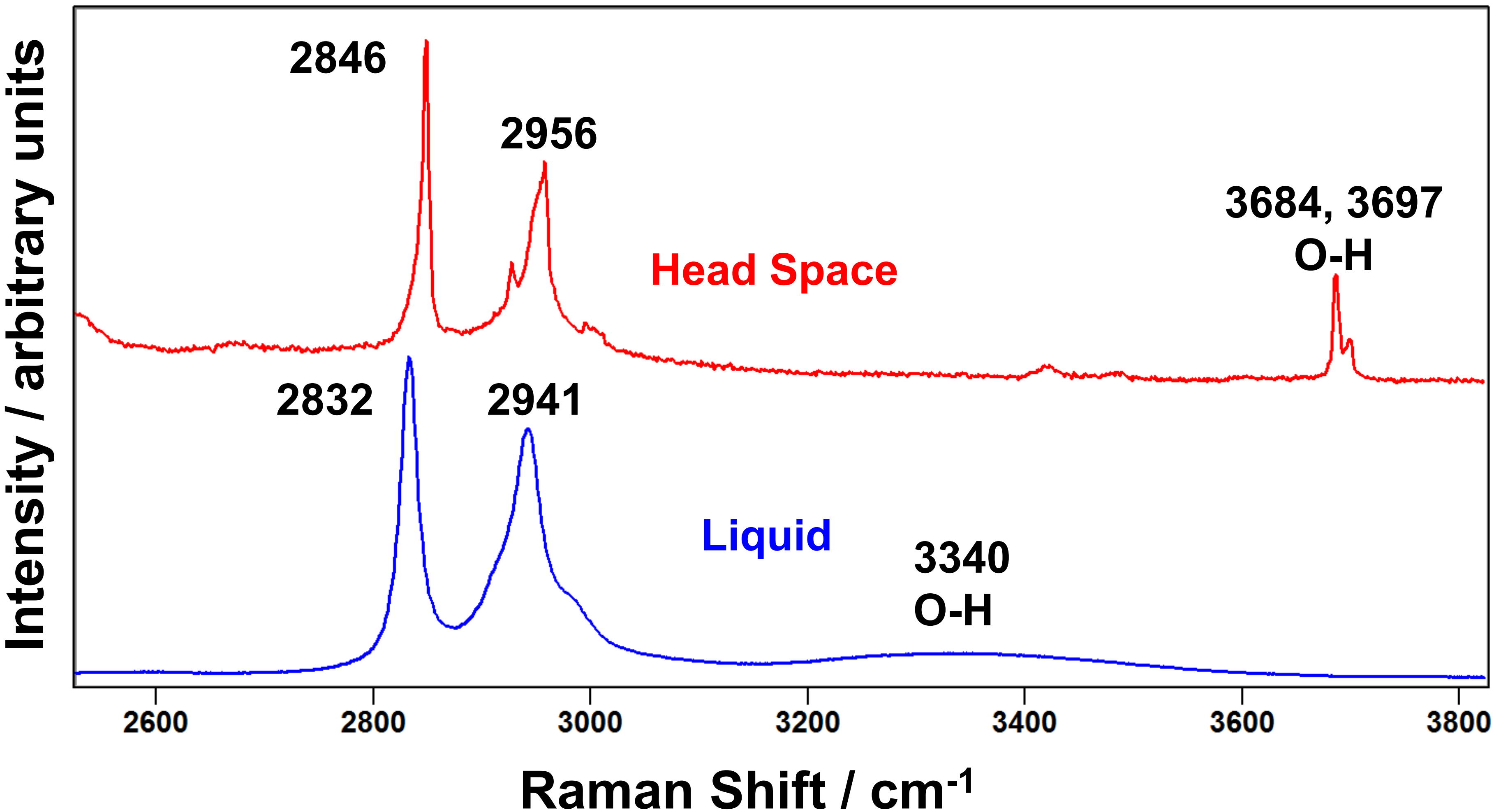
Sparkling Water – CO_2



Ammonia – Hydrogen Bonding



Methanol – Hydrogen Bonding



Raman Spectroscopy of Polymers

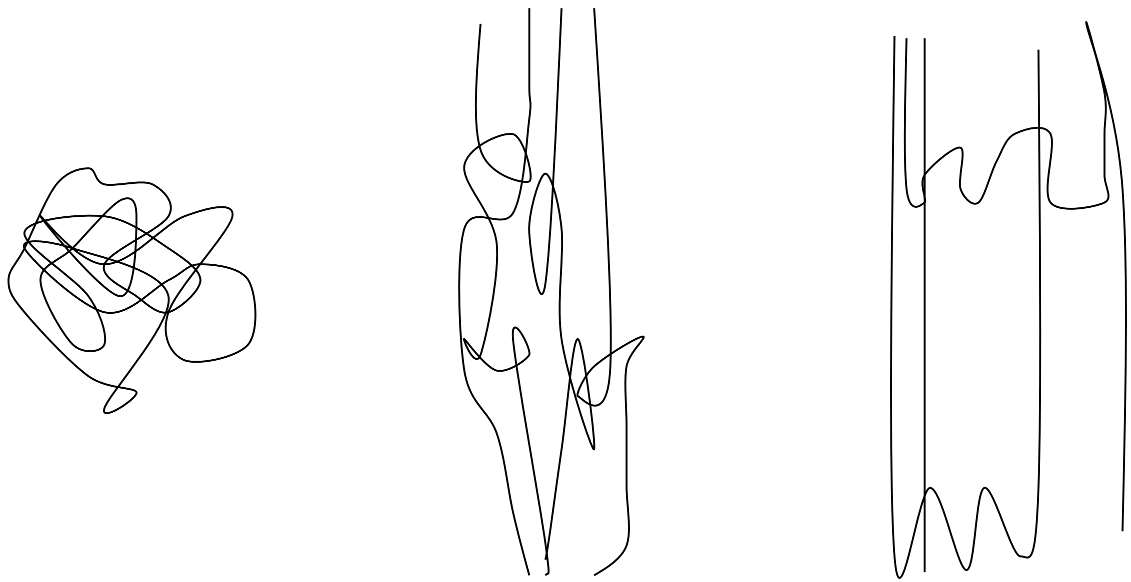
Aromatic Polymers

PET

Stretched Polypropylene

Polymers

- Very long chain of (usually) organic repeating unit. Extensive flexibility is possible:
  - Non-oriented “spaghetti” form (amorphous), or oriented chains, as a result of extrusion, which can be amorphous or crystalline
  - Orientation is a requirement for crystallinity (but not visa versa)
  - Often there are lamellae, regions where the chains fold back and forth over each other

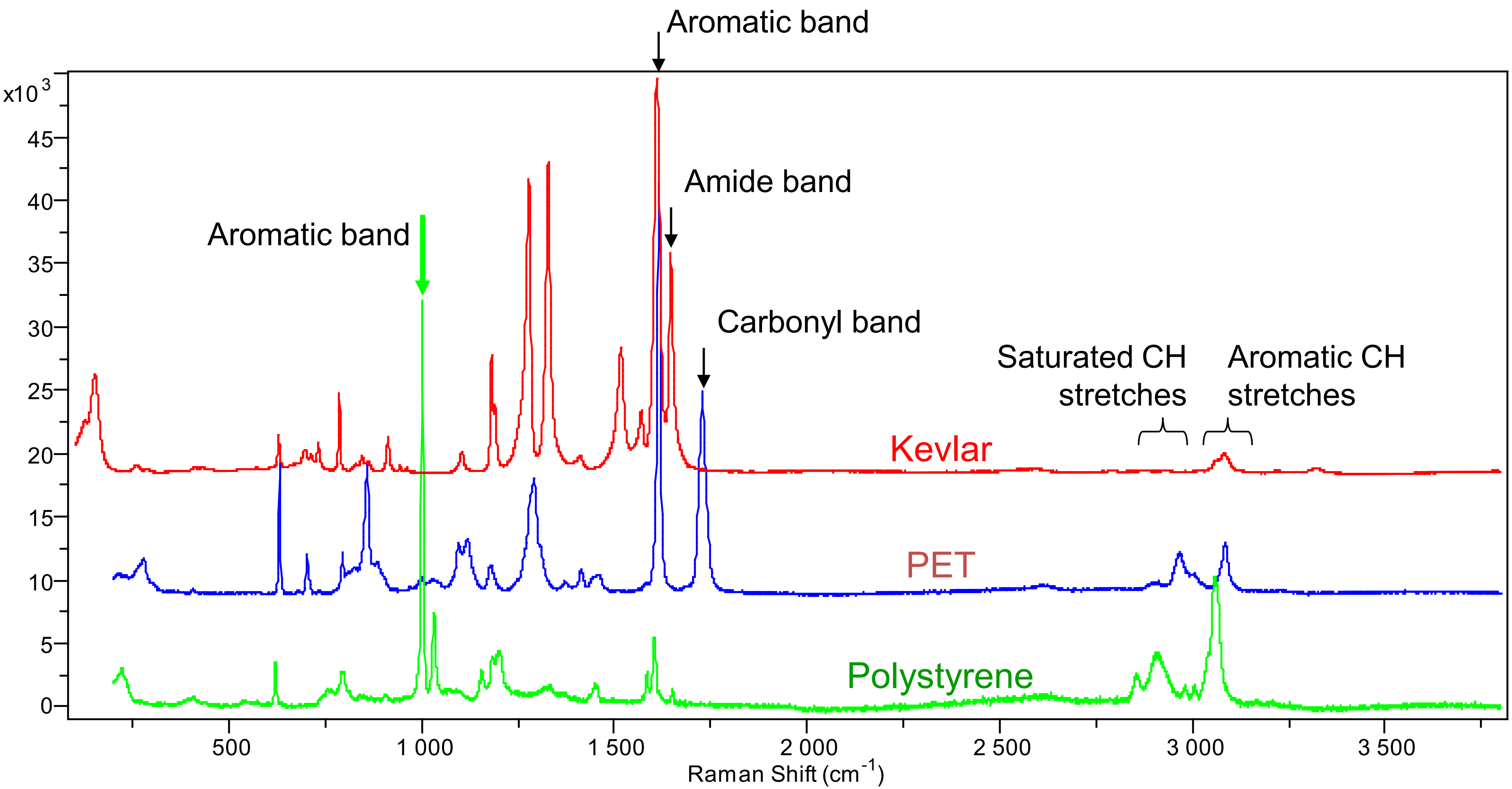


Raman Characterization of Polymers

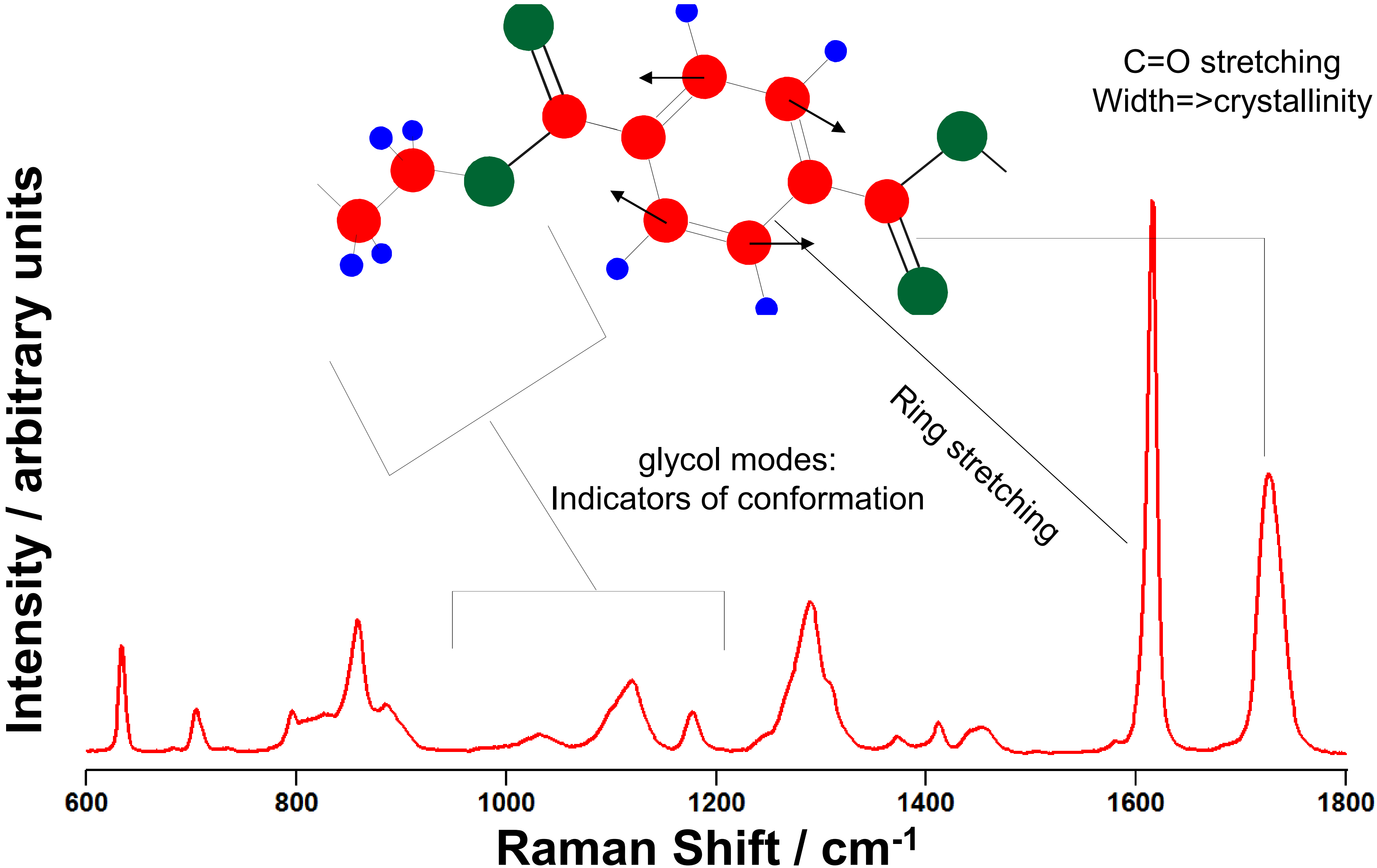
- Types of Information
  - Chemical Identification
  - Tacticity (side group positioning)
  - Morphology
    - Orientation
    - Crystallinity
- Applications
  - Contaminant ID
  - Composition of copolymer or blend
  - Engineering strength, elasticity, dyeability, etc.
  - Drug delivery (API solvent)
  - Barrier films (food, biomedical, etc.)

Raman Spectra of Aromatic Polymers

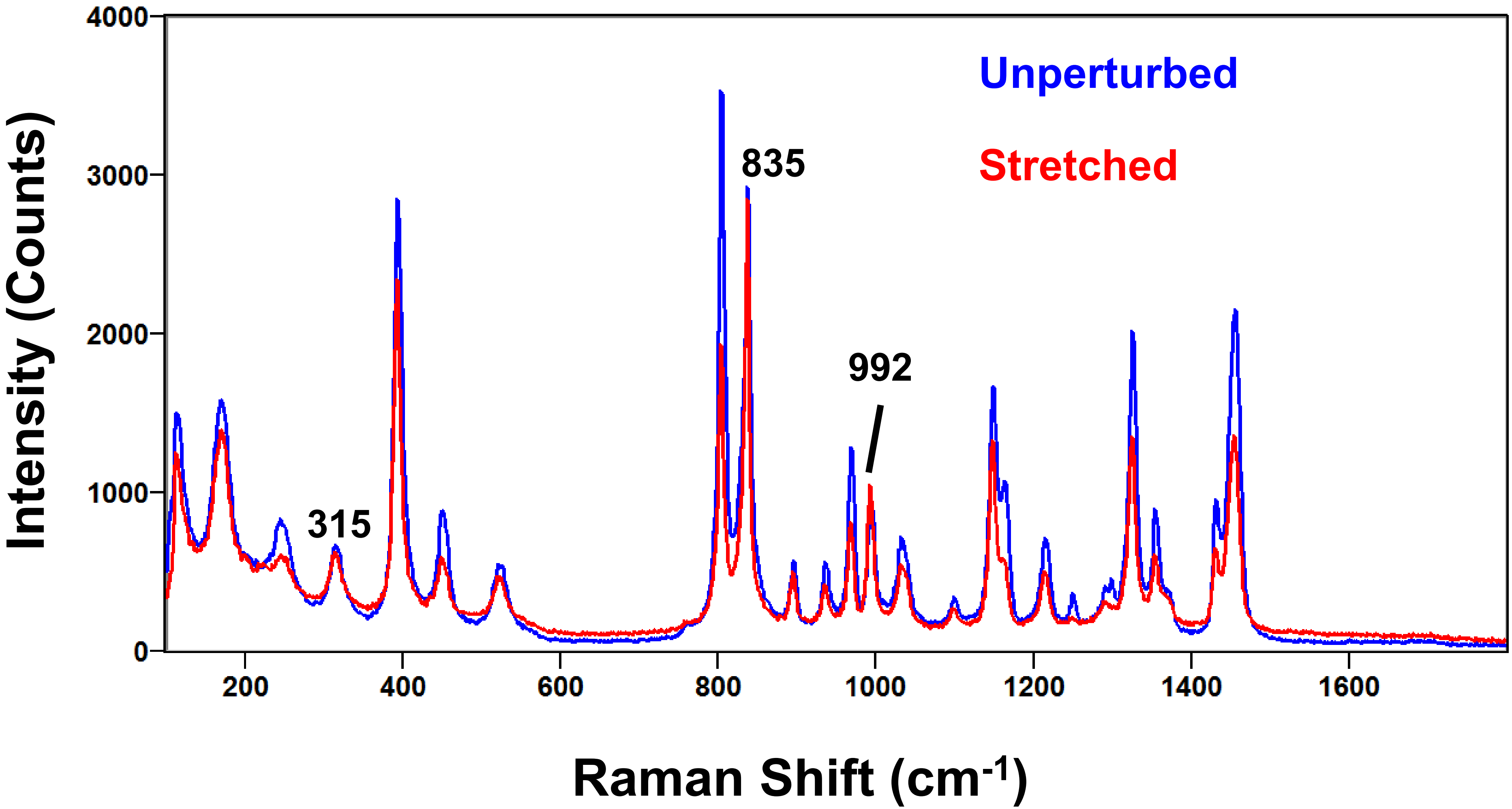
The strong band near **1000 cm^{-1}** that is characteristic of a ring mode in PS is never observed in any aromatic with 1,4 substitutions on the ring, as in Kevlar and PET.



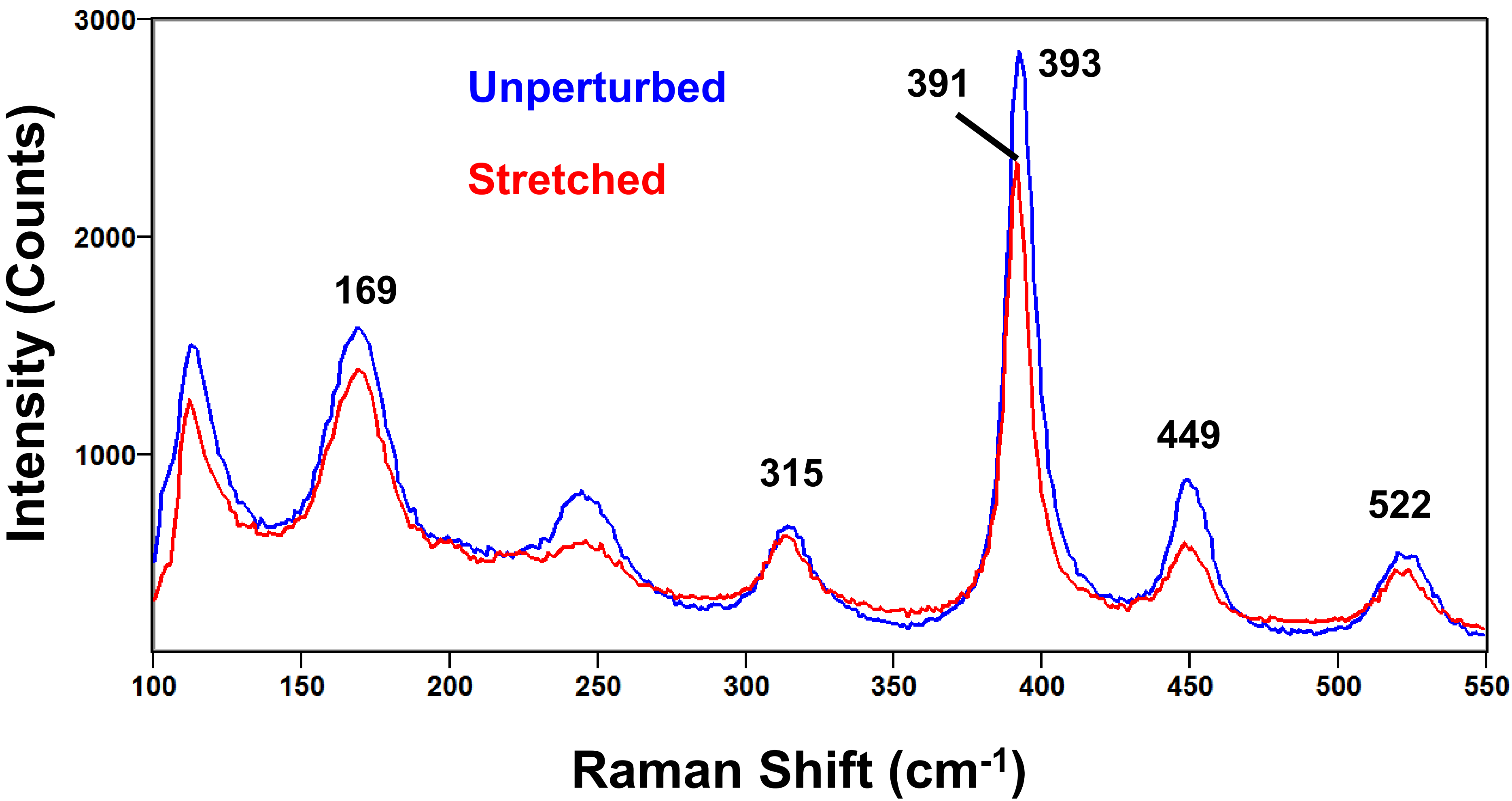
Raman Studies of PET: Polarization and Crystallinity



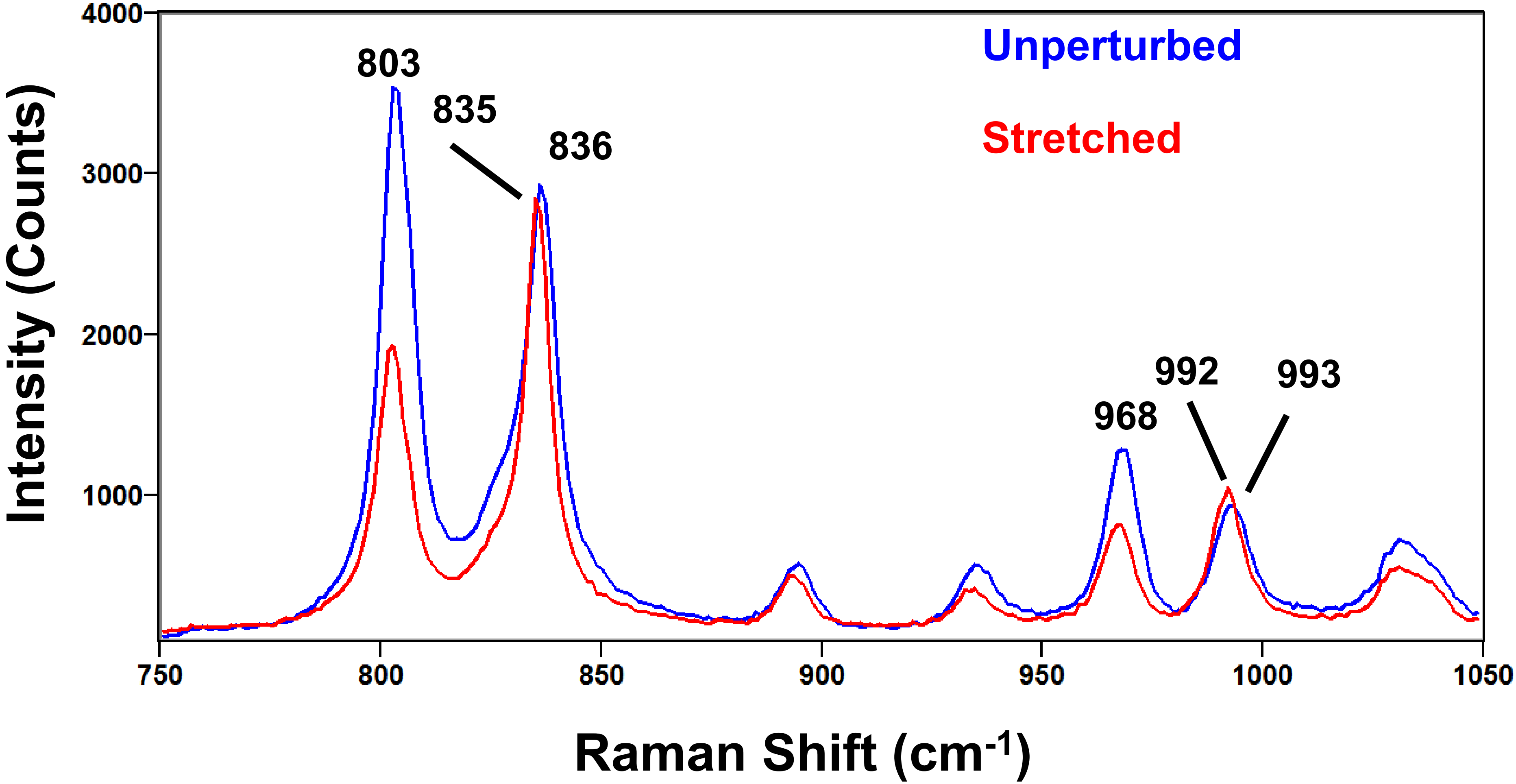
Stretched and Unperturbed Polypropylene



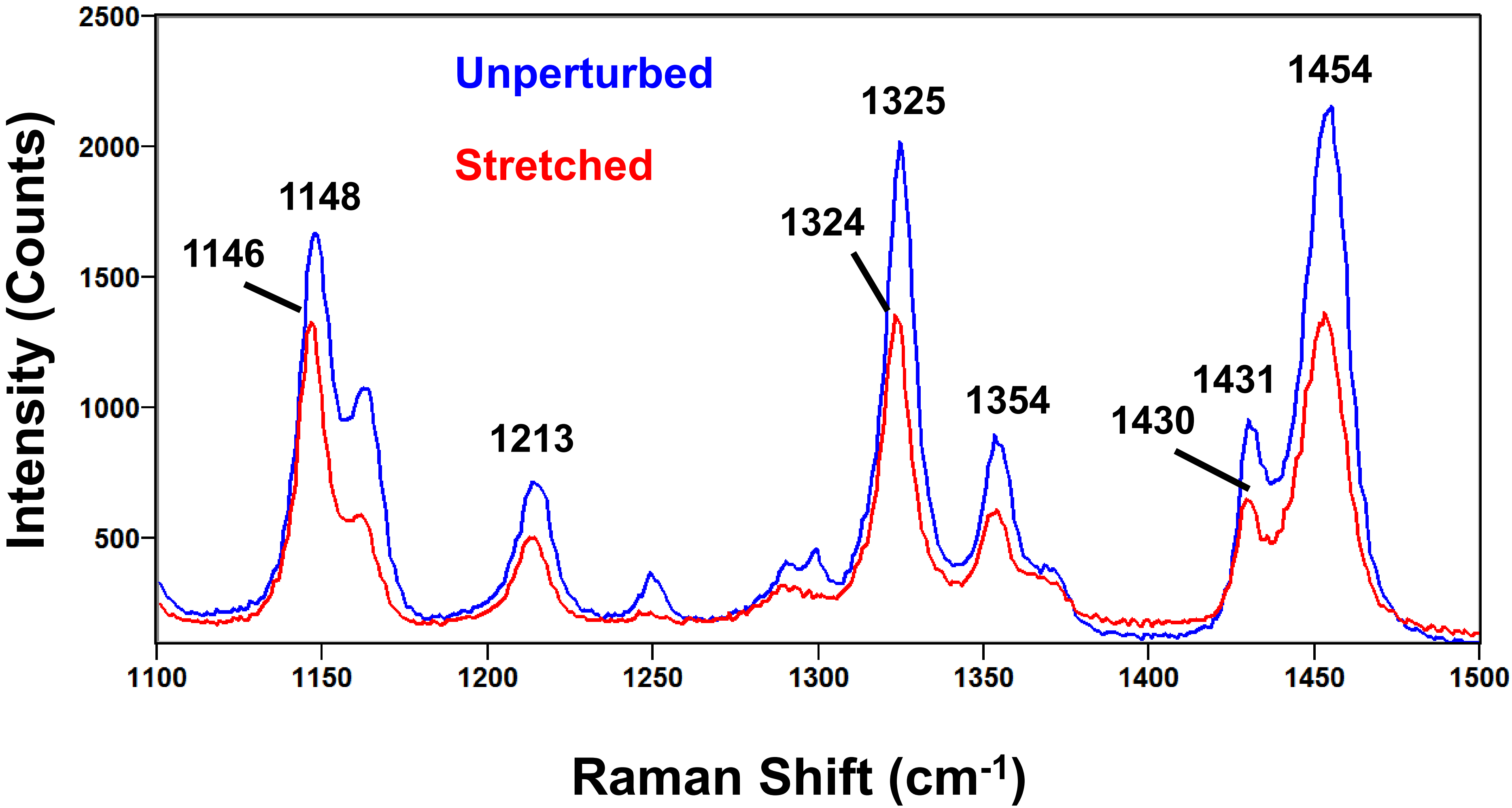
Stretched and Unperturbed Polypropylene



Stretched and Unperturbed Polypropylene



Stretched and Unperturbed Polypropylene

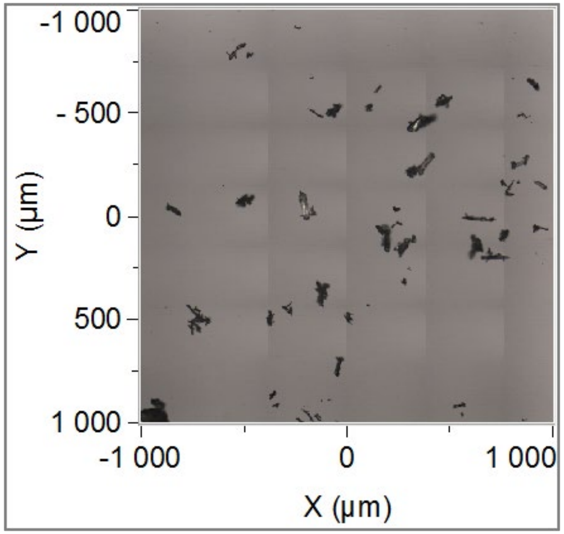


Introducing ParticleFinder

- ParticleFinder offers automated
  - Particle location on optical images
  - Particle size/shape characterization
  - Particle analysis using Raman spectroscopy
  - Particle chemical identification

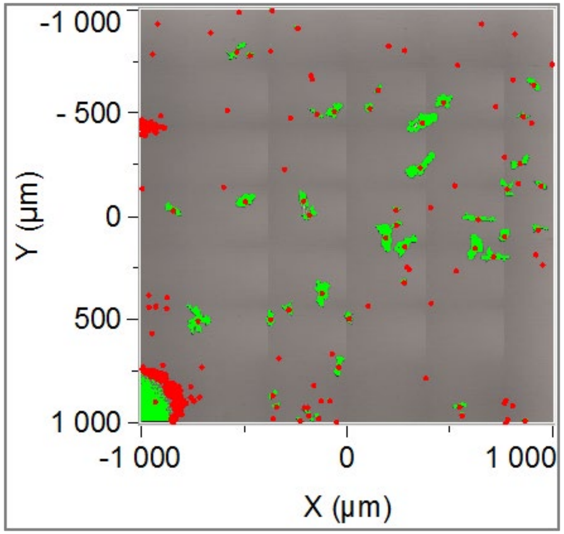
- ParticleFinder includes:
  - Morphological analysis
    - Thresholding
    - Morphological filtering
    - Size and shape parameters
  - Chemical analysis
    - Automated Raman acquisition
    - Fast analysis with high throughput systems
    - Flexible capabilities* for different sample types
      - Multiple laser wavelengths (UV, visible, NIR)
      - High spectral resolution
      - Ultra-low frequency

Step-by-Step



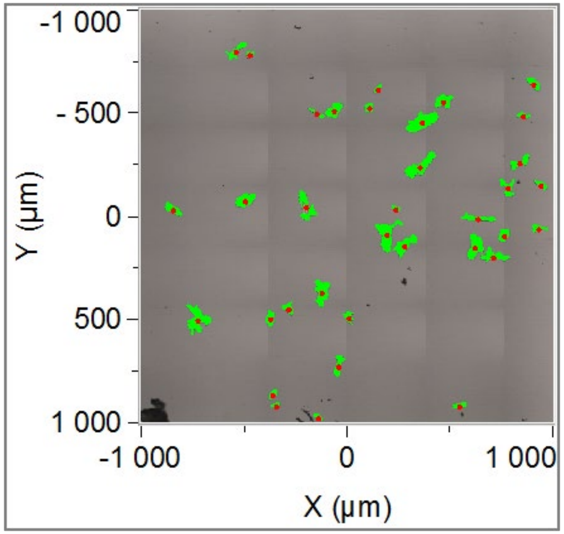
Acquire video

Single image, or montaged wide field of view image



Threshold

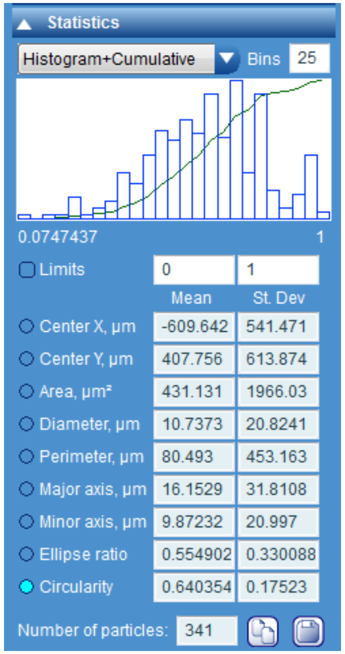
Locate dark particles on bright background, or bright particles on dark background



Process

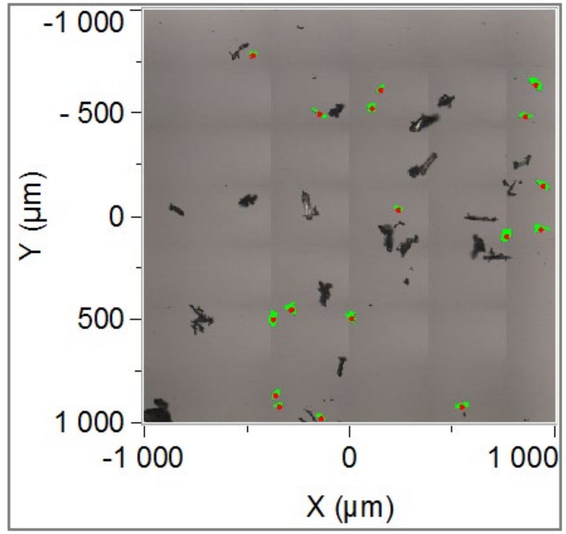
Erode/dilate/open/close/majority, fill holes, remove edge particles

Step-by-Step



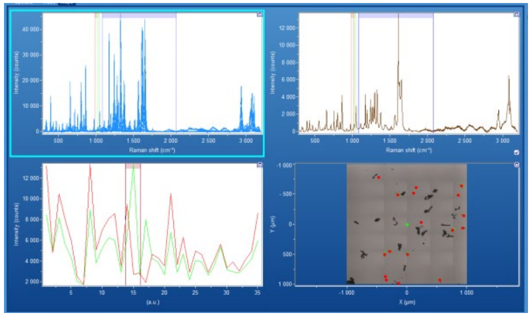
Characterize

Position, size, shape



Select

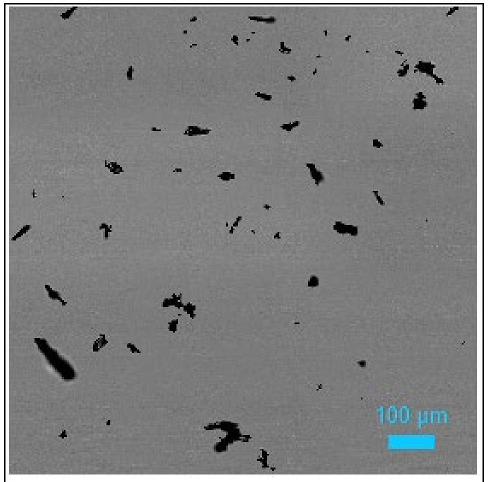
Screen particles based on position, size or shape



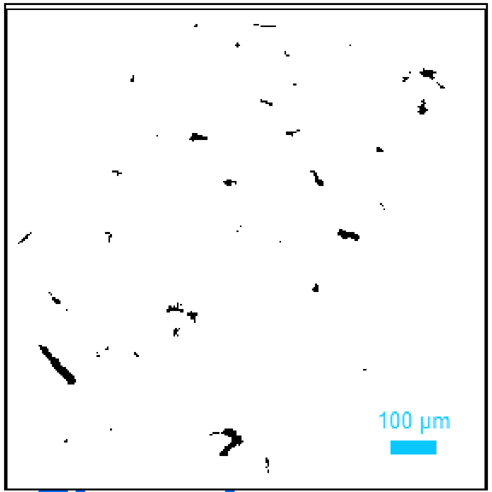
Acquire Raman

Automatically analyze each particle

Application Example



Video image

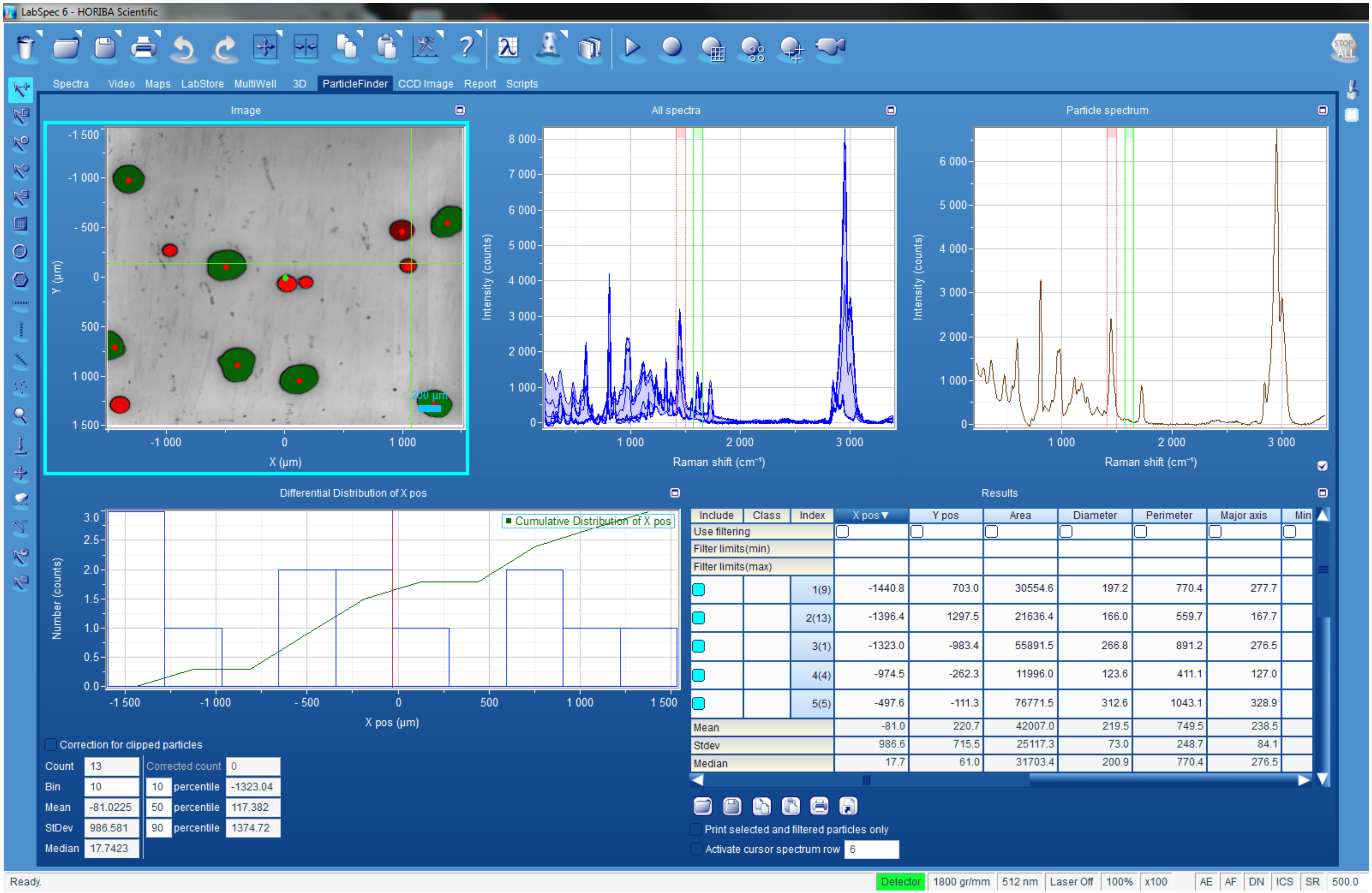


Binary image

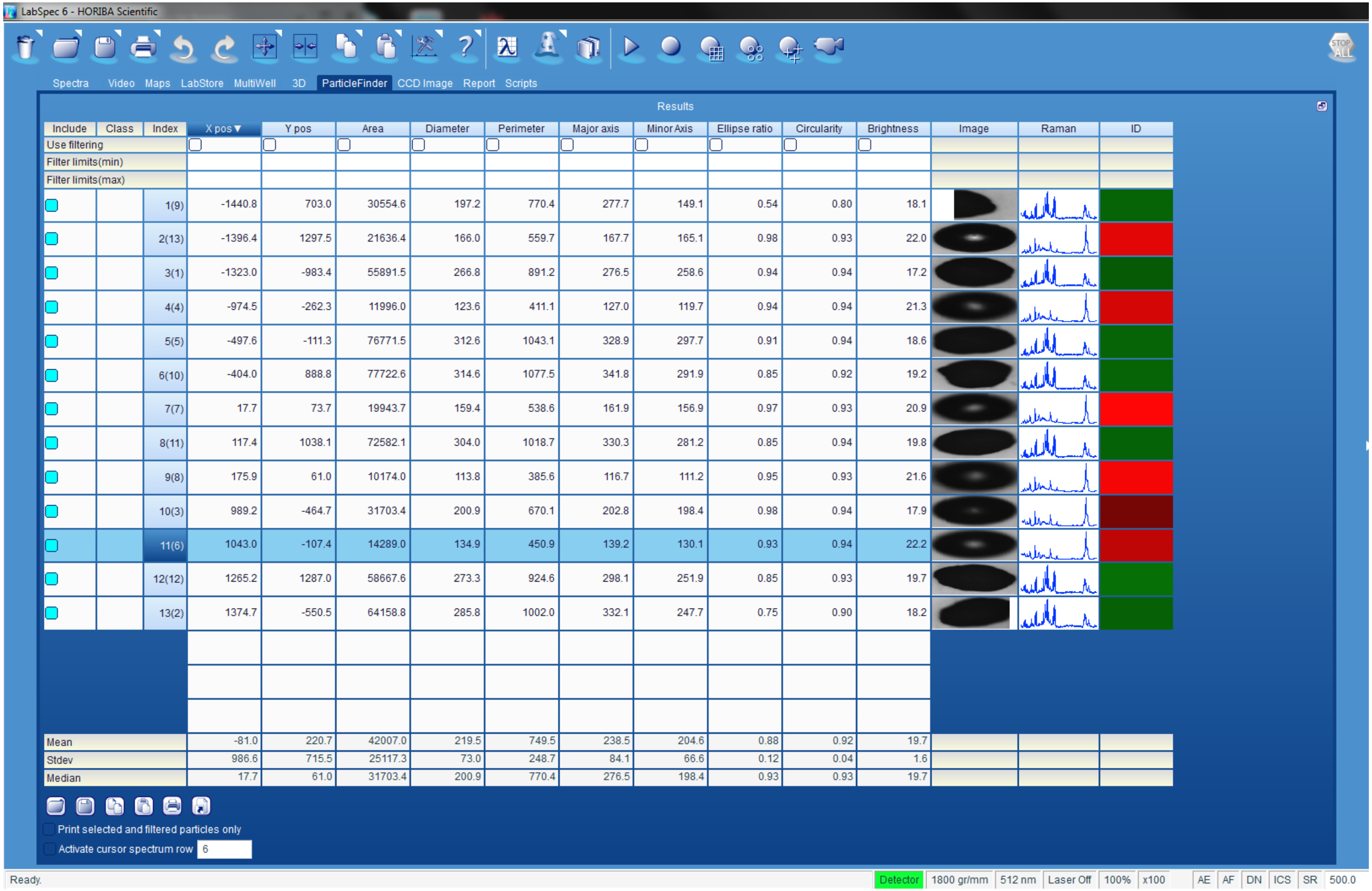
- Pharmaceutical crystals on glass slide
- 1×1 mm^2 area imaged with video montage (12 images)
- Image thresholds locate 44 particles
  - Exclude edge particles
  - Exclude particles with area < 50 µm^2

STATISTICS	(mean)	
DIAMETER	19.7	µm
PERIMETER	109.7	µm
AREA	386.0	µm^2
MAJOR AXIS	33.6	µm
MINOR AXIS	14.8	µm
ELLIPSE RATIO	0.50	
CIRCULARITY	0.64	

ParticleFinder Workspace – Paracetamol and PMMA



ParticleFinder Tabulated Results



Include	Class	Index	X pos ▼	Y pos	Area	Diameter	Perimeter	Major axis	Minor Axis	Ellipse ratio	Circularity	Brightness	Image	Raman	ID
Use filtering															
Filter limits(min)															
Filter limits(max)															
		1(9)	-1440.8	703.0	30554.6	197.2	770.4	277.7	149.1	0.54	0.80	18.1			
		2(13)	-1396.4	1297.5	21636.4	166.0	559.7	167.7	165.1	0.98	0.93	22.0			
		3(1)	-1323.0	-983.4	55891.5	266.8	891.2	276.5	258.6	0.94	0.94	17.2			
		4(4)	-974.5	-262.3	11996.0	123.6	411.1	127.0	119.7	0.94	0.94	21.3			
		5(5)	-497.6	-111.3	76771.5	312.6	1043.1	328.9	297.7	0.91	0.94	18.6			
		6(10)	-404.0	888.8	77722.6	314.6	1077.5	341.8	291.9	0.85	0.92	19.2			
		7(7)	17.7	73.7	19943.7	159.4	538.6	161.9	156.9	0.97	0.93	20.9			
		8(11)	117.4	1038.1	72582.1	304.0	1018.7	330.3	281.2	0.85	0.94	19.8			
		9(8)	175.9	61.0	10174.0	113.8	385.6	116.7	111.2	0.95	0.93	21.6			
		10(3)	989.2	-464.7	31703.4	200.9	670.1	202.8	198.4	0.98	0.94	17.9			
		11(6)	1043.0	-107.4	14289.0	134.9	450.9	139.2	130.1	0.93	0.94	22.2			
		12(12)	1265.2	1287.0	58667.6	273.3	924.6	298.1	251.9	0.85	0.93	19.7			
		13(2)	1374.7	-550.5	64158.8	285.8	1002.0	332.1	247.7	0.75	0.90	18.2			
Mean			-81.0	220.7	42007.0	219.5	749.5	238.5	204.6	0.88	0.92	19.7			
Stdev			986.6	715.5	25117.3	73.0	248.7	84.1	66.6	0.12	0.04	1.6			
Median			17.7	61.0	31703.4	200.9	770.4	276.5	198.4	0.93	0.93	19.7			

Conclusions

- Raman spectroscopy and laser excited photoluminescence can be performed using the same instrument.
- Raman spectroscopy can be used to differentiate polymorphs and characterize polymers.
- Vapor phase and liquid molecular interactions are manifest in Raman spectra.
- Particle size characterization with chemical specificity

Thank you