Improved sensing using simultaneous deep UV Raman and fluorescence detection-II

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Outline

- Background on improved sensing
- Raman & fluorescence as orthogonal detection modes
- Combining Raman & fluorescence for improved sensing
- Deep UV instruments: standoff to macro to micro
- Raman & fluorescence spectra with miniature laser/detector

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Background on Improved Sensing

- Goal is to use deep UV methods to increase the probability of detection and reduce the probability of false detection for specific, targeted, chemical, biological, and explosives (CBE) materials

- This paper is an extension of work presented at the 2012 SPIE DSS Conference: *Bhartia, R., W. F. Hug, and R.D. Reid, "Improved sensing using simultaneous deep UV Raman and fluorescence detection", SPIE Security & Defense, Vol. 8358, No. 46, April 26, 2012*

- We will focus on advancements since this prior paper

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Background on Improved Sensing

- We are developing hand-held sensors for in situ detection and classification of trace concentrations of CBE materials on surfaces at short range standoff distances.
- The sensors are light weight, including deep UV laser, Raman and fluorescence spectrometers, computer, display, and batteries.
- The sensors employ excitation of targets by a low energy deep UV laser to excite targeted samples.

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Raman & Fluorescence as Independent & Orthogonal Modes of Detection

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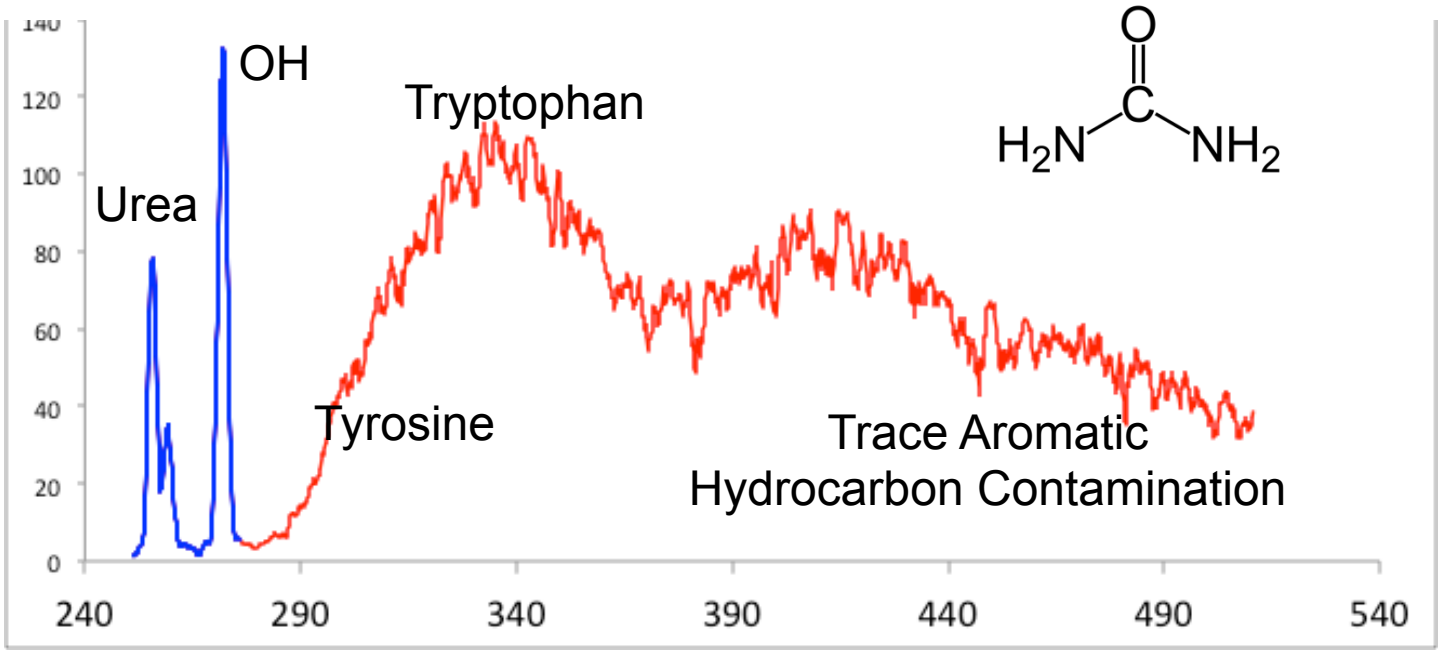
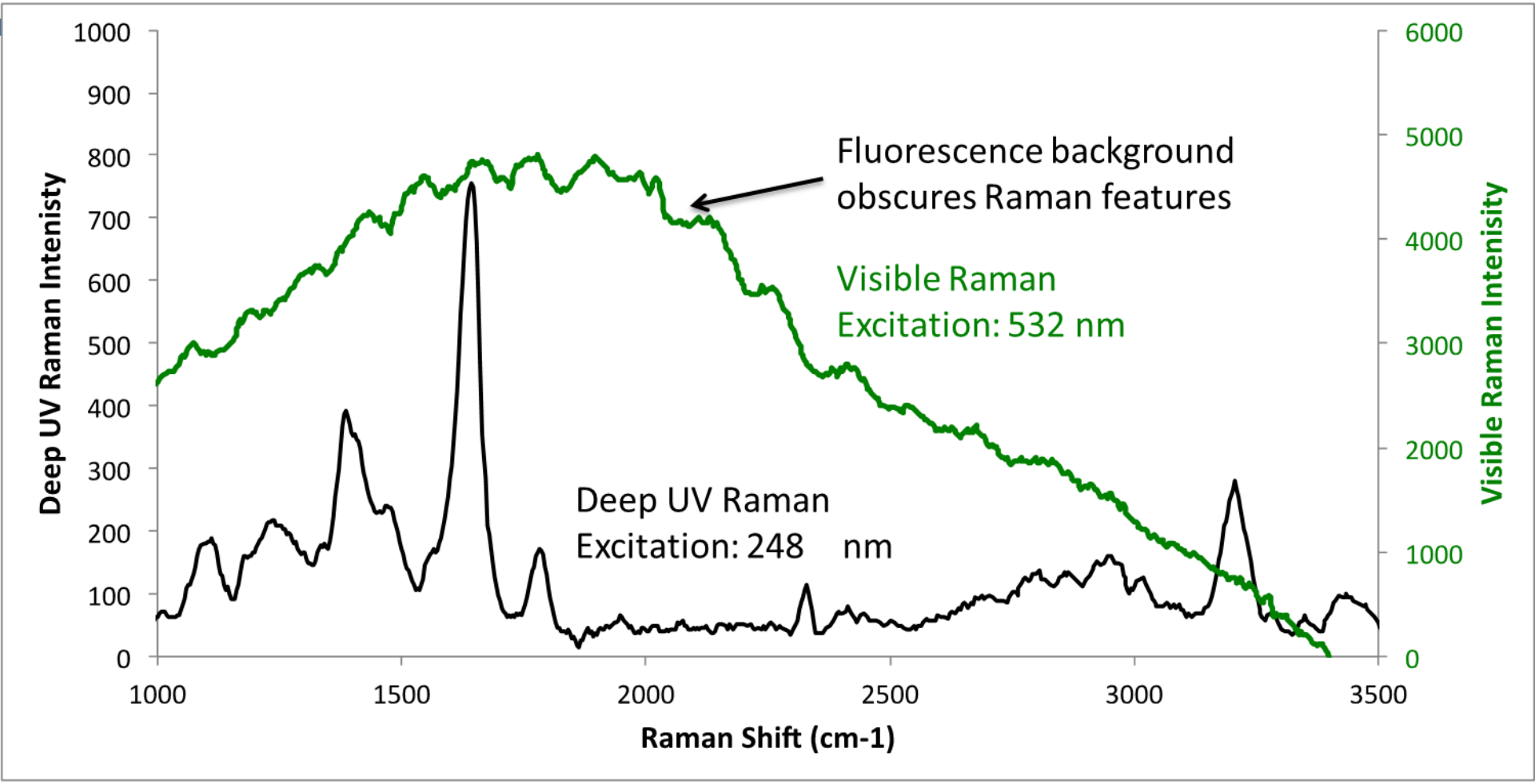
Why the Deep UV?

- **Canonical reason**: Fluorescence-free Raman, higher sensitivity, solar blind
- In deep UV both Raman & fluorescence can be collected simultaneously
- Fluorescence sensitivity is higher than even strong deep UV enhanced Raman bands
- Raman provides information on chemical bonds
- Fluorescence provides information on overall electronic structure



Fluorescence Free Raman Spectra of Crude Oil

with Excitation at 532 nm and 248 nm



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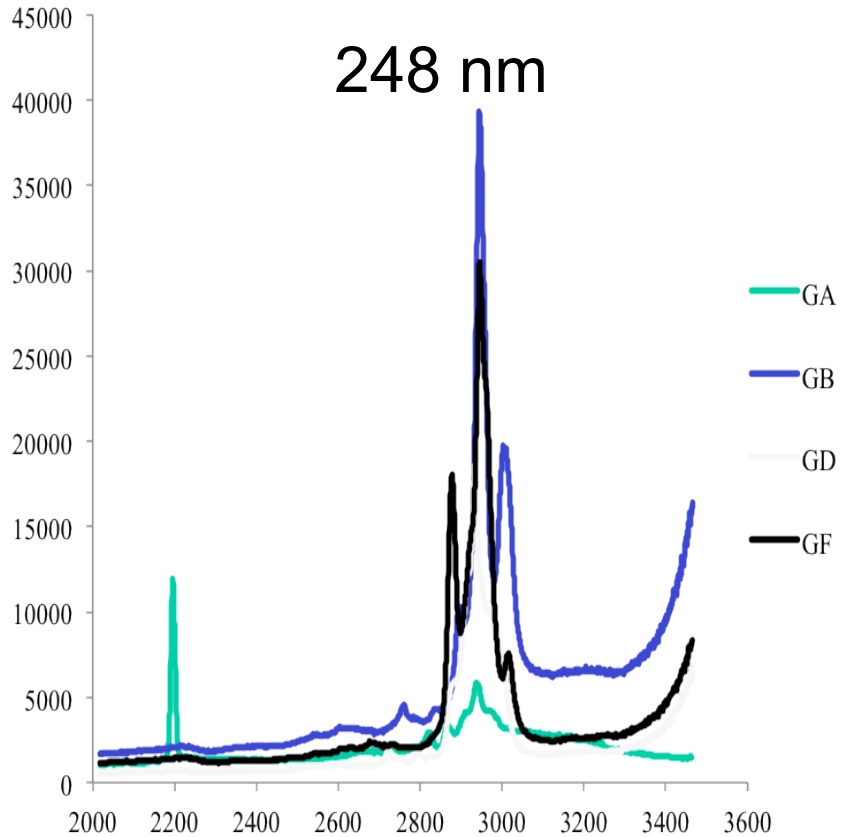
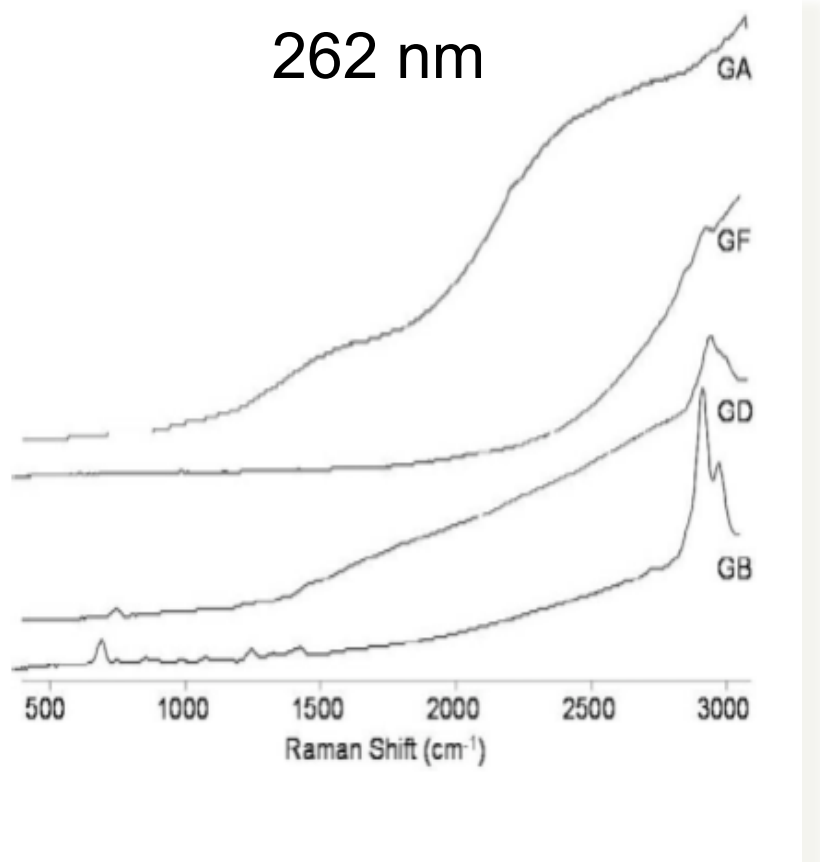
Sensitivity to Excitation Wavelength

Raman Spectra with Excitation at 248 nm versus 262 nm

(Example is G Agents)

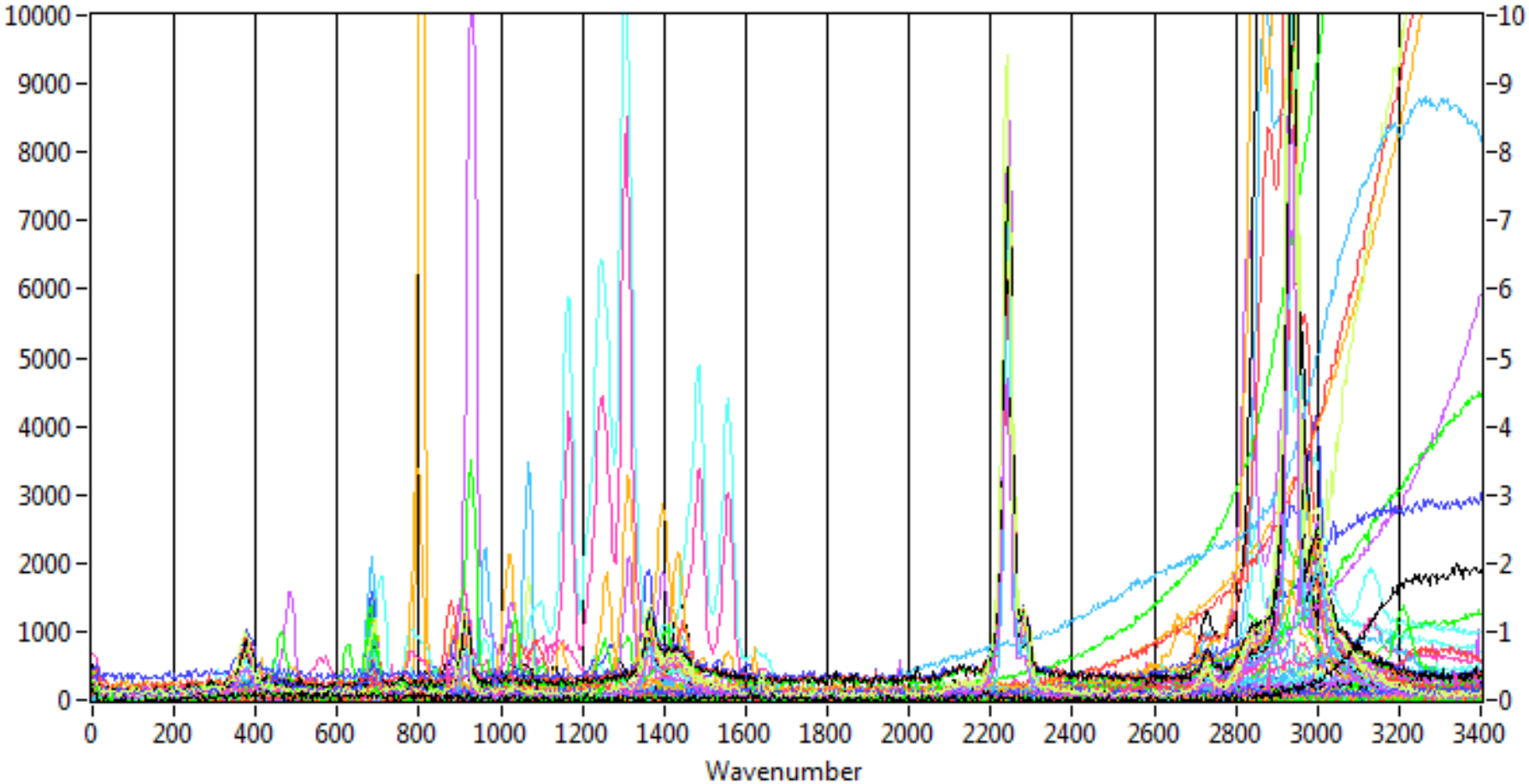




Adapted from Christesen, SD et al. Appl Spec. 2008 Oct; 62(10):1078-83

Raman Spectra of 52 Compounds

with no baseline subtraction or compensation, Ex=248 nm



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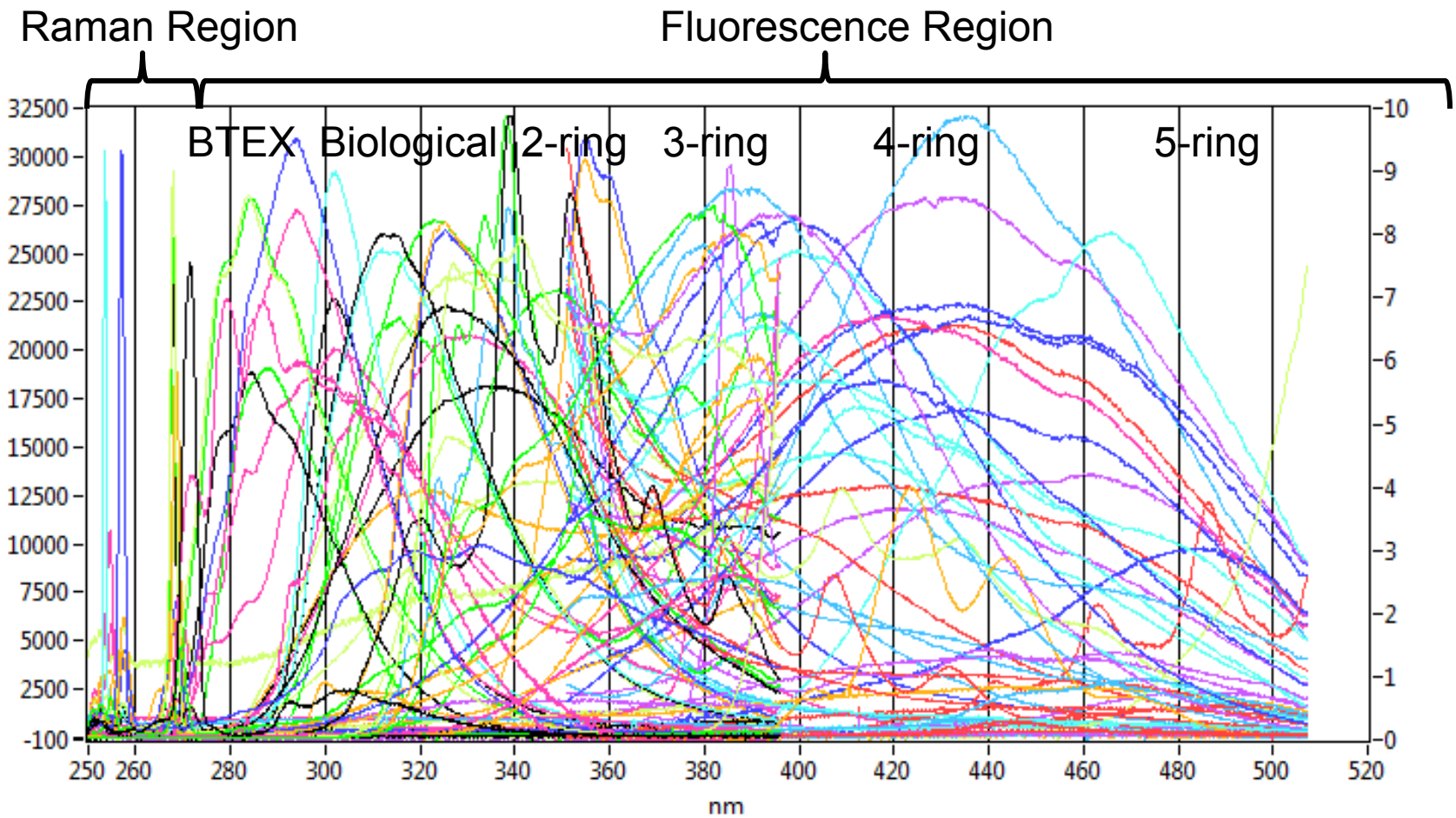
Fluorescence Spectra of 52 Compounds

with no baseline subtraction or compensation, Ex=248 nm



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Combining Raman & Fluorescence

Raman Active		Weak Fluorescence	Strong Fluorescence	
Water	HMX	TDG DMMP	C4	Microbes
Amino Acids	PETN	DIMP TEPO	Semtex	Toxins/Proteins
Alcohols	RDX	Ammonia Nitrate	ANFOs	Narcotics
Aliphatics		Urea Nitrate		
DNA/RNA	TNT	Nitroglycerin	Aromatic Amino Acids	
Lipids	Perchlorates	Ketones/Aldehydes		

- Raman provides information about chemical bonds and functional groups, including those that do not fluoresce (aliphatics and simple compounds)

- Fluorescence data provides information about the electronic structure of target & substrate ingredients (aromatics, ketones, aldehydes)

- Fluorescence is over 10^4 to 10^7 times more sensitive than Raman, providing longer standoff distances or detection at lower concentrations

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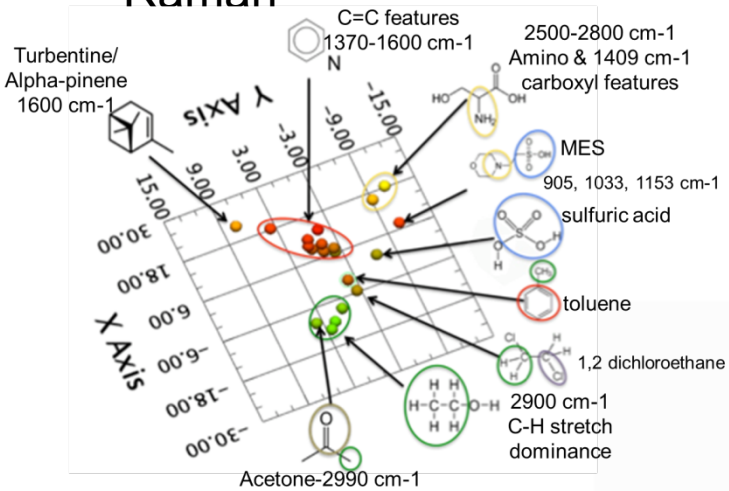
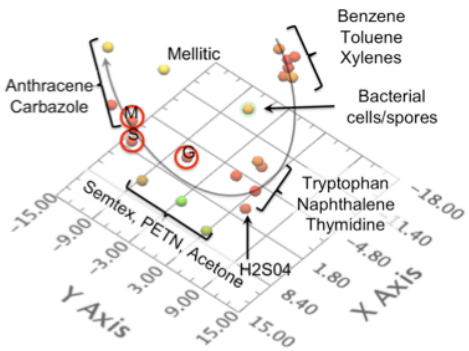
Fluorescence/Raman Fusion

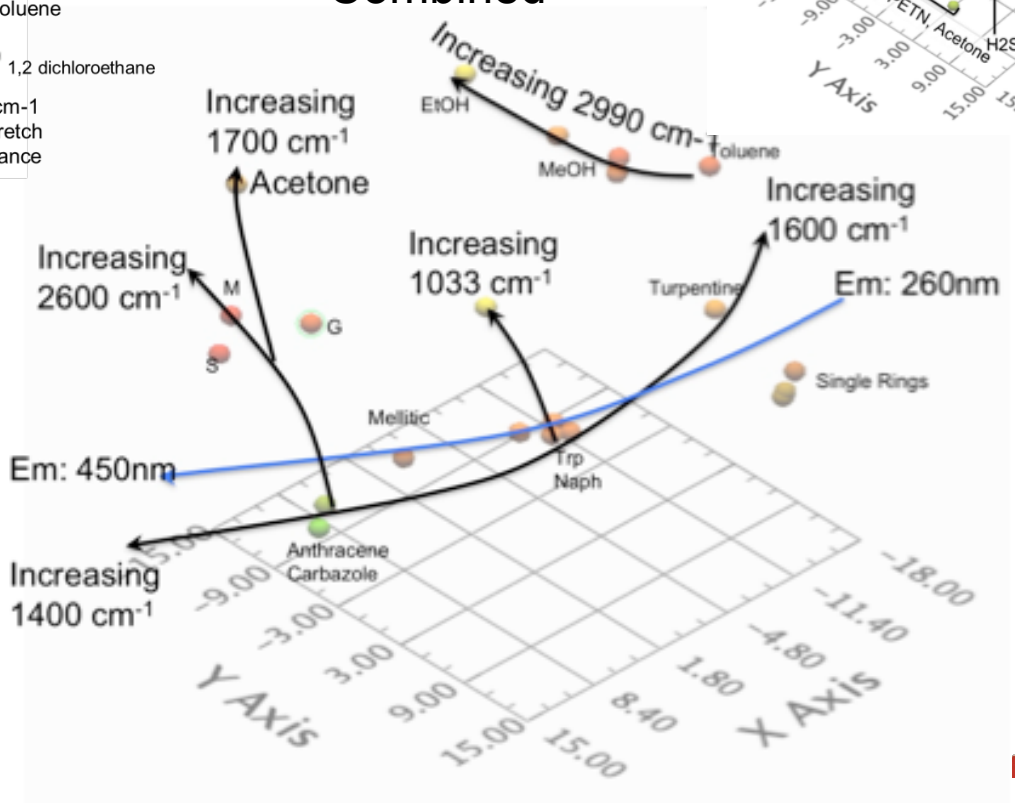
Raman



Fluorescence



Raman & Fluorescence Combined



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Deep UV Instruments

- The advantages of deep UV Raman methods have been demonstrated in many laboratory environments using high power laser and large instruments.
- Our focus is developing miniature hand-held sensors for in situ detection in field applications.
- The sensors are light weight, including deep UV laser, Raman and fluorescence spectrometers, computer, display, and batteries.
- The sensors employ excitation of targets by a low energy deep UV laser to excite targeted samples.

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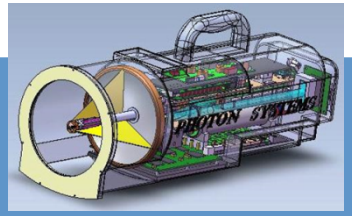
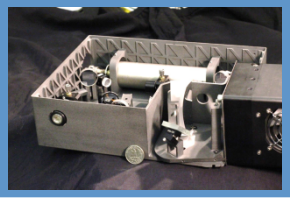
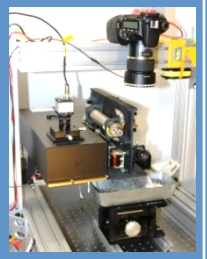
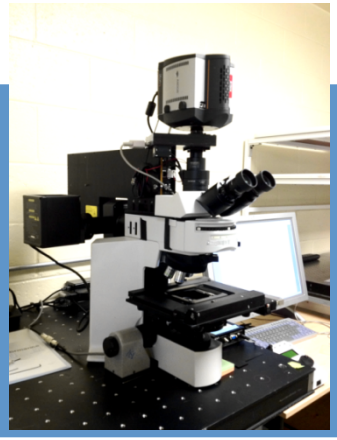
Surface Raman & Fluor Instruments

Over wide spatial scales



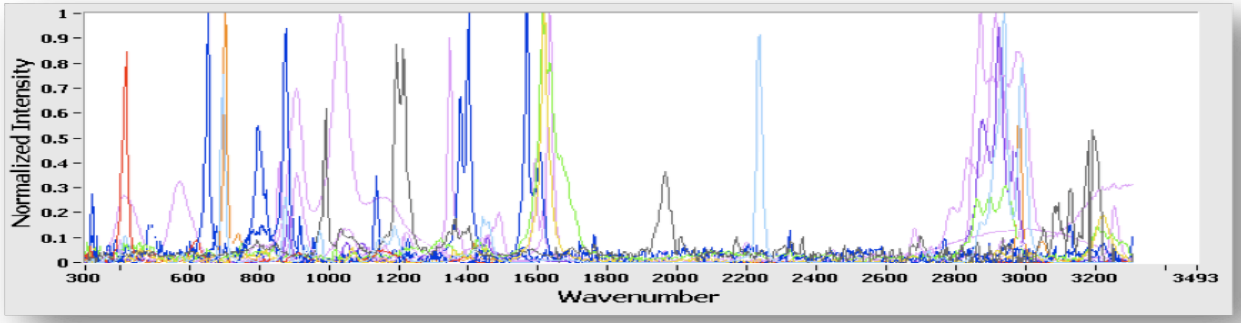






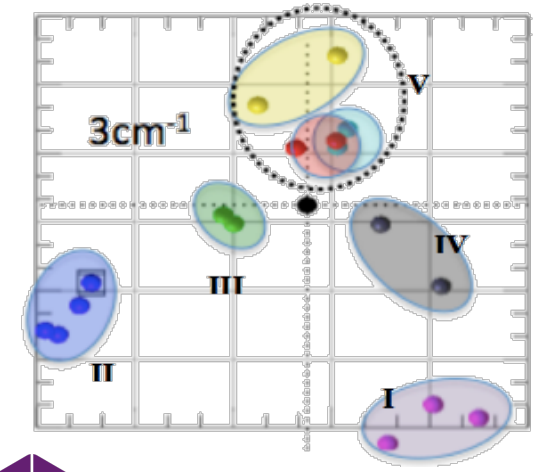
	Standoff (TUCBE)	Macroscopic (MOSAIC)	Microscopic (μMOSAIC)
Working distance	1-25 m	2-20 cm	1-10 mm
Spatial resolution	1-10 mm	50 to 500 μm	150 – 200 nm
LOD	60 spores or low μg per cm^2 at 5 m	Single spore or ng/ cm^2 at 5 cm	Small fraction of single live spore

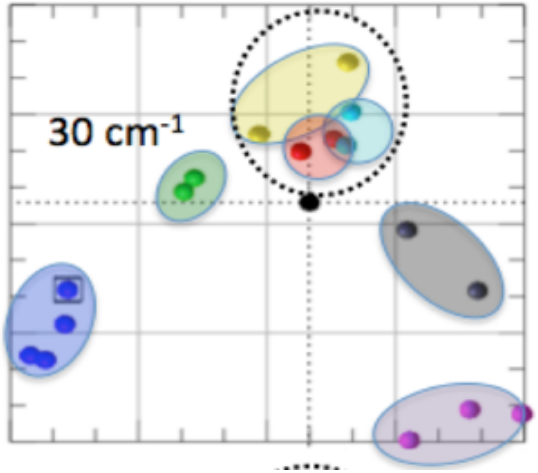
Raman Resolution effect on Chemometrics

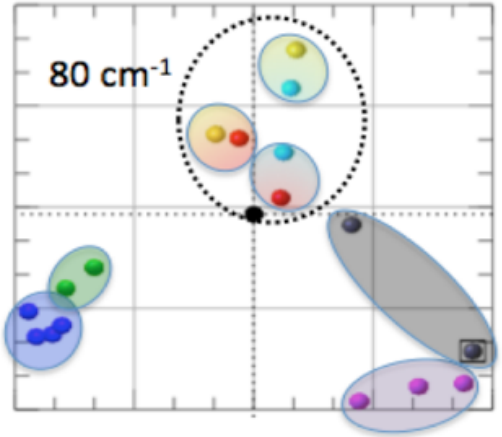


acetone cyanohydrin
Allyl isothiocyanate
Arsenic trichloride
benzene
carbon disulfide
chloroacetone
chloroacetonitrile
chlorosulfonic acid
cyclohexanone
dichloromethane
ethanol
formaldehyde
hexachloro cyclopentadiene
hydroden peroxide
nitromethane
parathion
pentane
sulfuric acid
turpentine

Group 1 compounds containing a *ketone or terpene structures*.
Group 2 carbon-based compounds with *methyl or hydroxyl groups*.
Group 3 consist of linear *carbon-chloride* compounds.
Group 4 consist of *single ring aromatic* compounds.
Group 5 consists of 3 subgroups that can be best described as *explosive or highly reactive materials* and include sulfur compounds, H202, and nitromethane.







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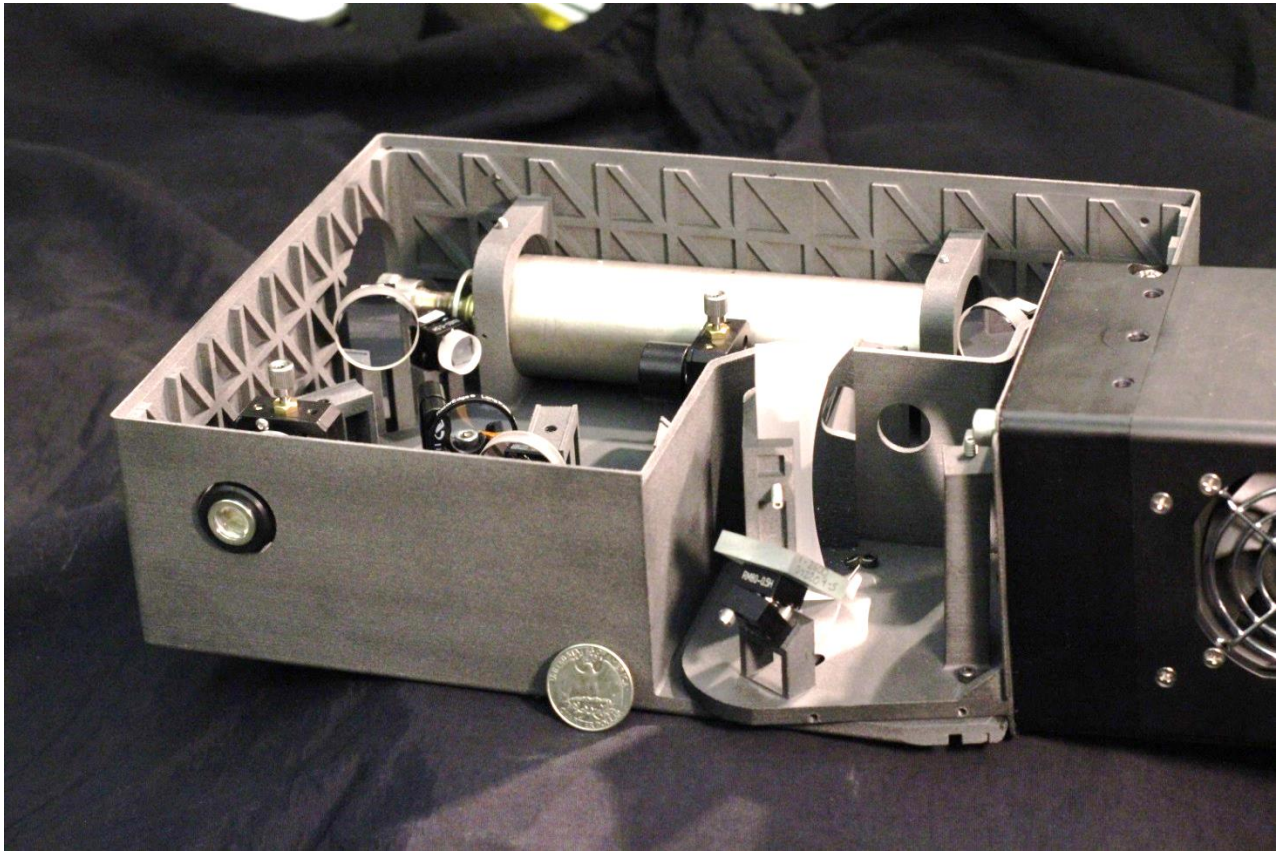
Next Gen DUV Raman & Fluorescence CBE Sensor

Employing miniature DUV laser and CCD detector used in following data



Custom miniature deep UV Raman/fluorescence 3D chemical imaging prototype for planetary science on Mars. 45th LPSC 2014. DUV laser is the silver cylinder.

6.3”x 7.9”x 2.4”, 8.8 lbs: including laser, spectrometer, detector, 1 cm^2 mapper, autofocus, all electronics

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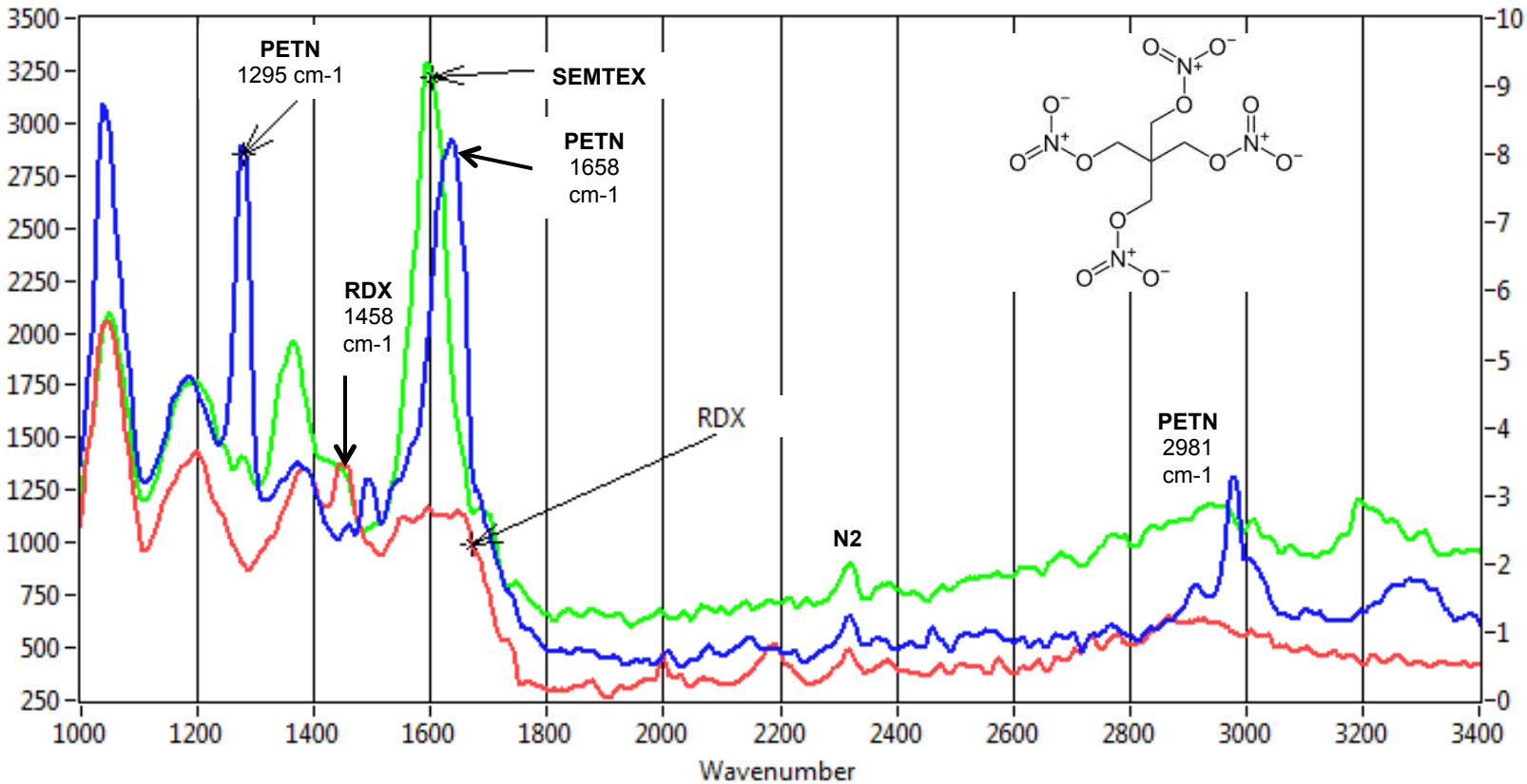
Raman Spectra of Bulk SEMTEX (PETN +RDX)

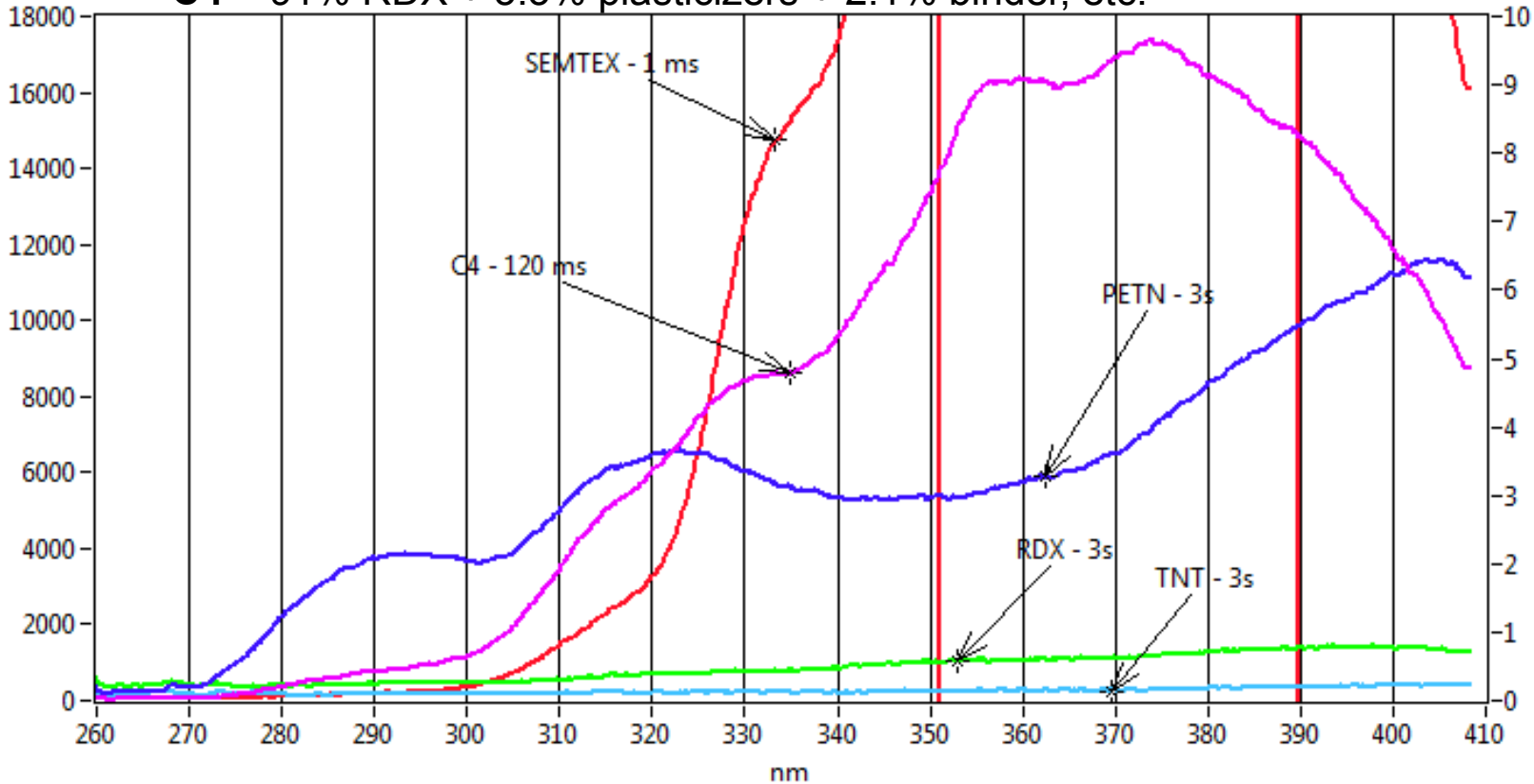
with no baseline subtraction or compensation, Ex=248 nm



Fluorescence Spectra of Bulk Explosives

with no baseline subtraction or compensation, Ex=248 nm

SEMTEX = 76% PETN + 4.6%RDX + 9.4% binders + 9% plasticizers, etc
C4 = 91% RDX + 5.3% plasticizers + 2.1% binder, etc.



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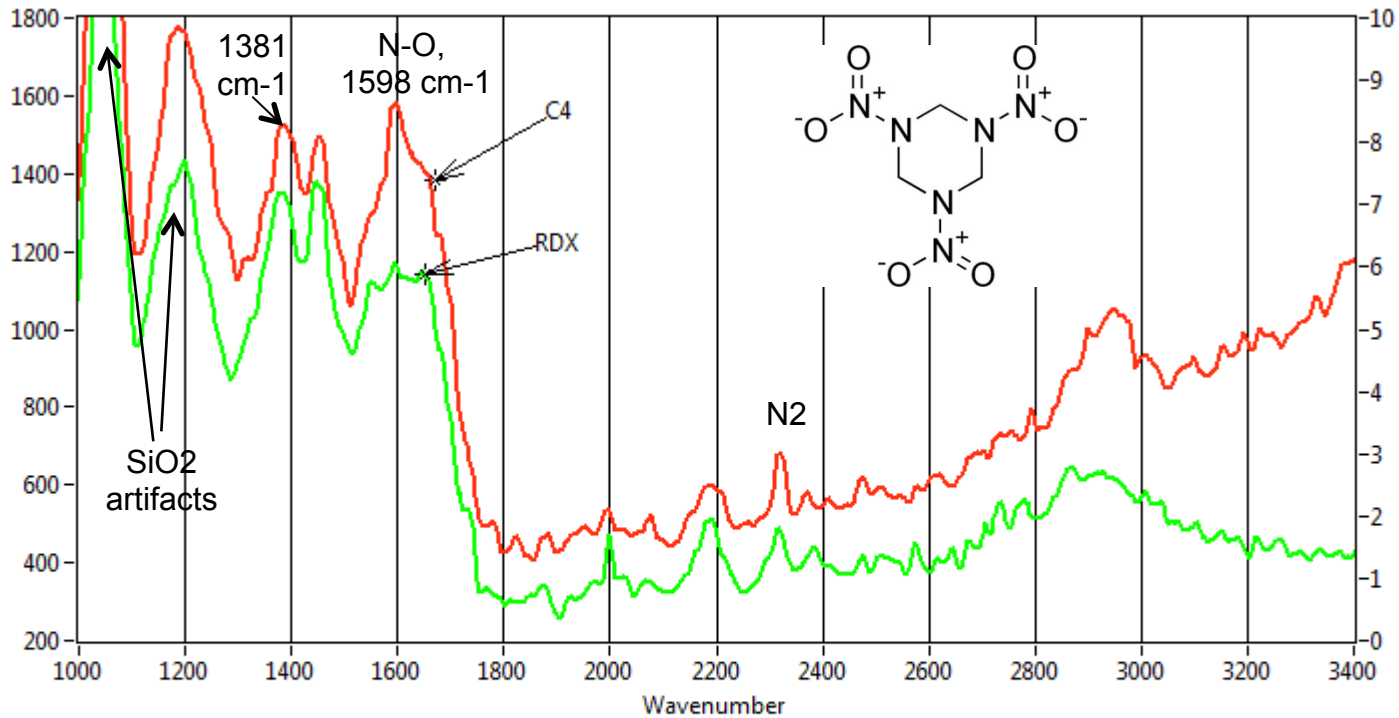
Raman Spectra of Bulk C4 (RDX)

with no baseline subtraction or compensation, Ex=248 nm



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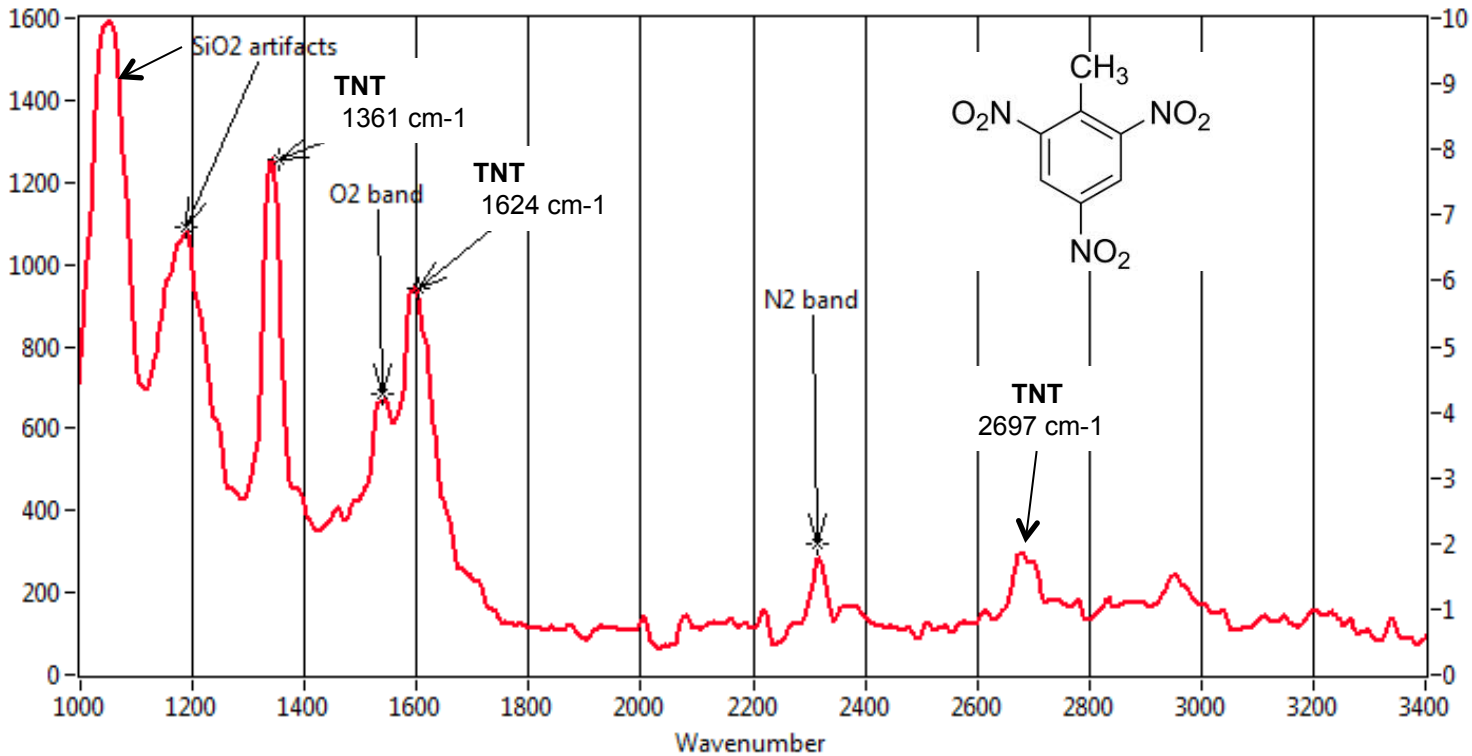
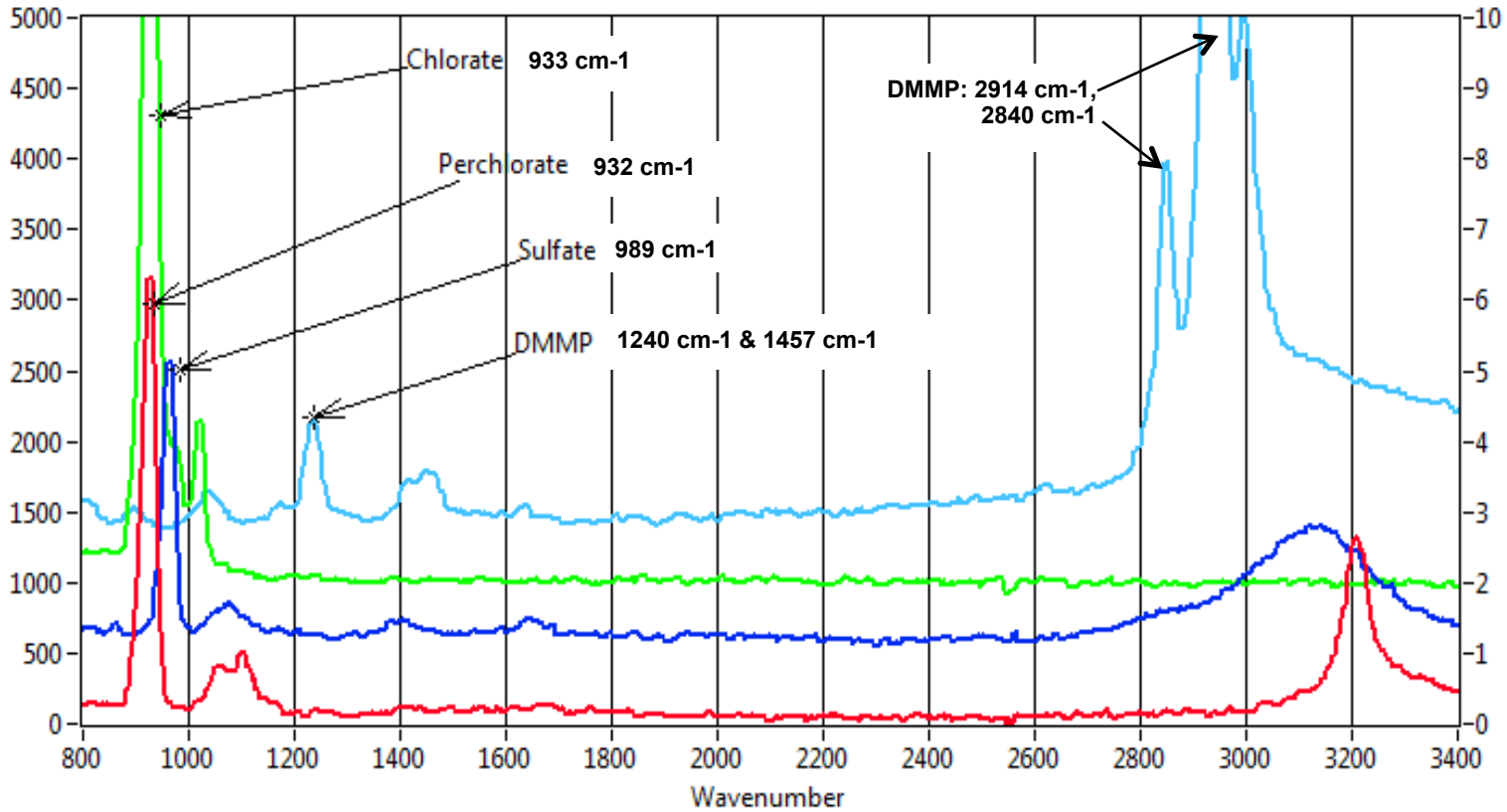
Raman Spectra of Bulk TNT

with no baseline subtraction or compensation, Ex=248 nm



Raman Spectra of Oxidizers & DMMP

with no baseline subtraction or compensation, Ex=248 nm baseline offset for clarity



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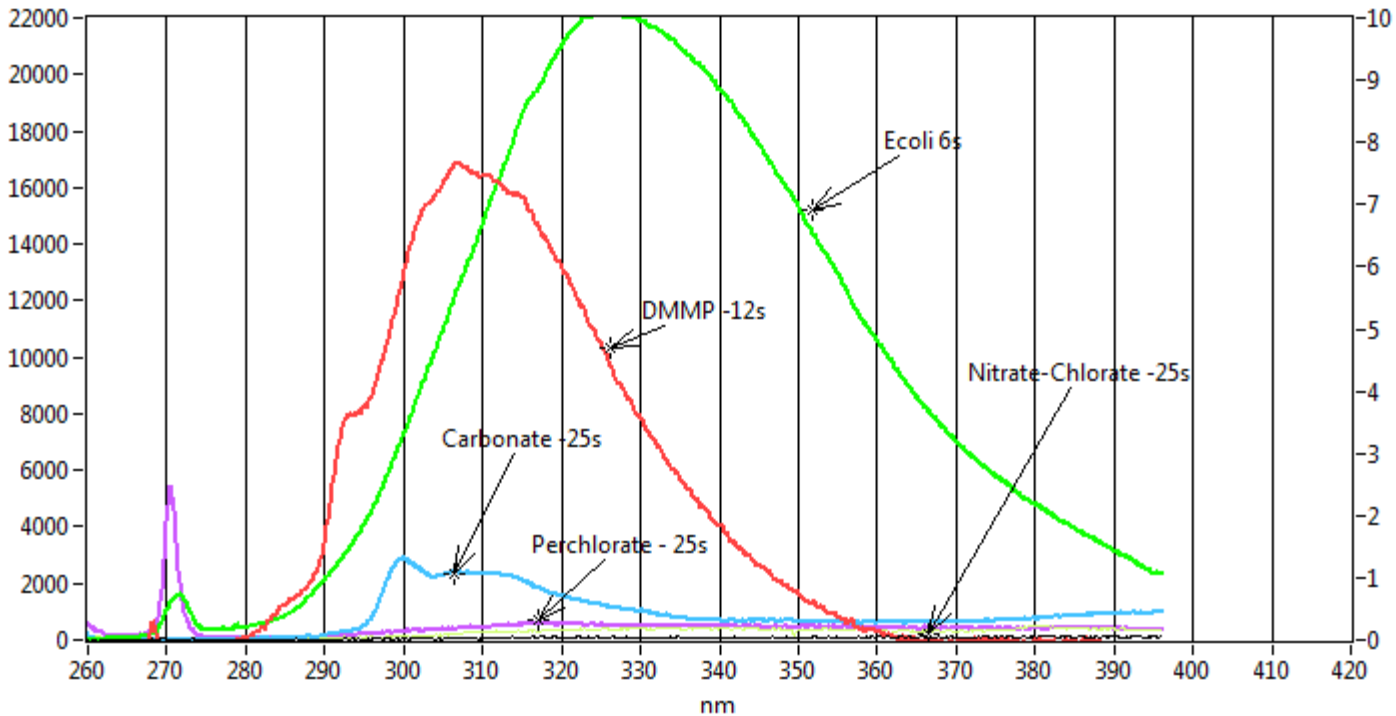
Fluorescence Spectra of CBE Materials

with no baseline subtraction or compensation, Ex=248 nm



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Summary

- Fluorescence-free Raman spectra can be obtained with excitation below 250 nm
- Combined Raman & fluorescence detection method enhance both sensitivity and specificity in identifying unknown targets
- Excitation below 250 nm provides separation between Raman & fluorescence and enables simultaneous detection of both.
- Detection of Raman & fluorescence in the deep UV can be accomplished using low energy lasers without major alteration or damage/ignition of targets

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Funding For This Work

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-Dr. Augustus Fountain & Dr. Steven Christesen

DTRA Contract No. HDTRA1-09-C-0010
-Dr. Timothy Leong

NASA/ASTID, Contract No. NNH10ZDA001N

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Questions ?

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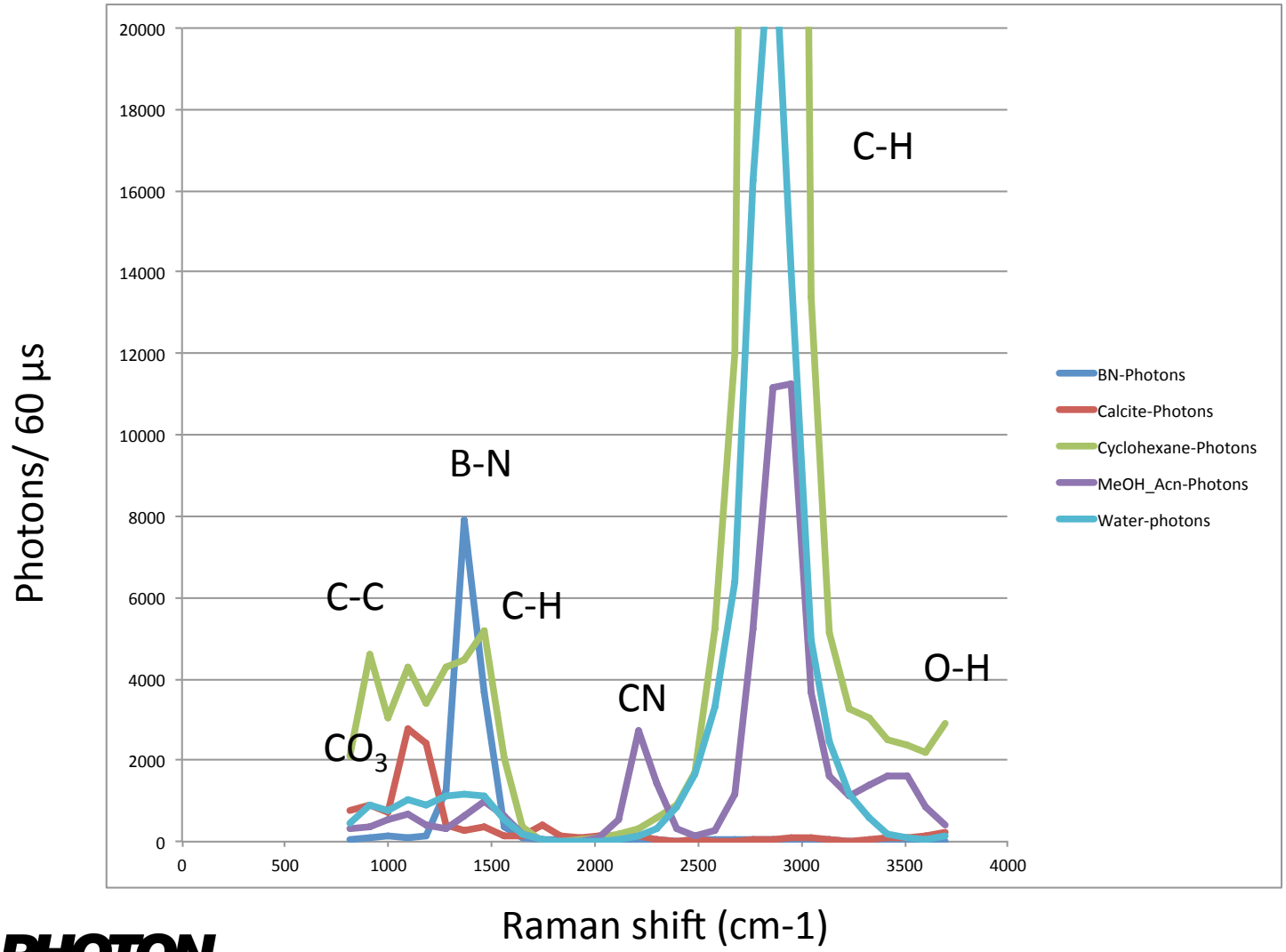
Single Pulse Raman Spectra
Gen 2.5 instrument, f=1.3 m (f/6.3)



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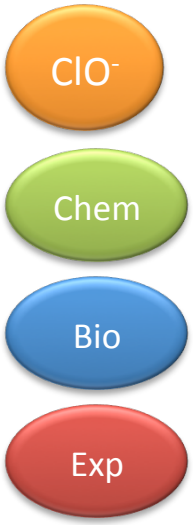
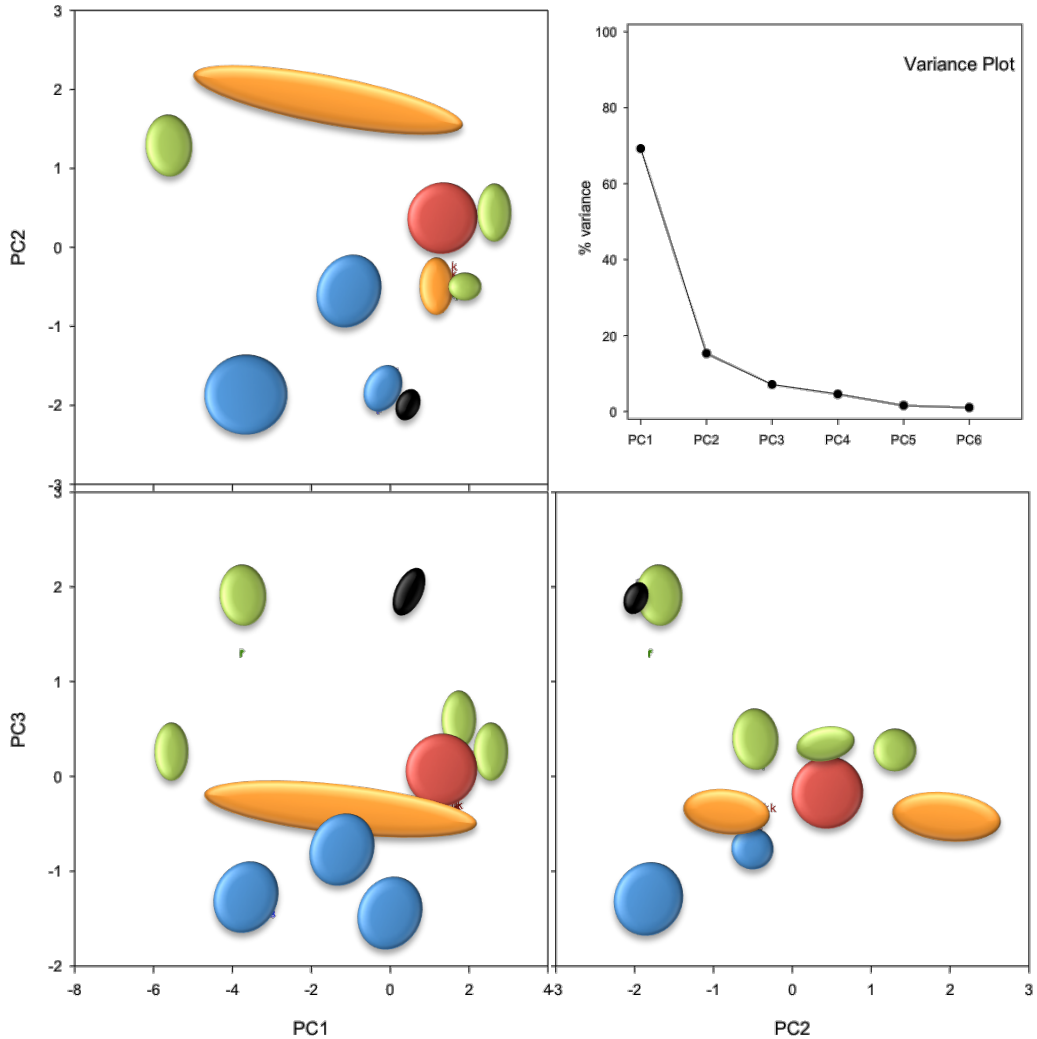
TUCBE Gen 2.5 Data: PCA

NEW IMAGES FROM NEW ANALYSIS PROGRAM

Raman & Fluorescence Spectra Normalized Independently





4-nitrotoluene
2,3 DNT
2,4 DNT
2,6 DNT
TNT
PETN
RDX

$KClO_3$
$KClO_4$
NH_4ClO_4

DIMP
DMMP
MES
TDG
TEPO

TSA
TSB
NSM
B. globigii (spores)

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