Instrumentation in Raman Spectroscopy: Elementary Theory and Practice

6. Coupling with other technique

Raman-LINF-LIBS

JEAN DUBESSY, MARIE-CAMILLE CAUMON, FERNANDO RULL and SHIV SHARMA

Measurements on the same samples with a combination of two analytical complementary techniques generally enhances analytical performance for a comprehensive characterization of a complex sample. This is referred to as 'hyphenation' of two techniques. Such an approach is used widely in geosciences as well as in cultural heritage, Technological improvements are enabling the coupling of Raman spectroscopy with other techniques such as Laser-induced Break-down spectroscopy (LIBS) and Laser-induced Native Fluorescence spectroscopy (LINF).

EMU Notes in Mineralogy,**12** (2012) Chapter 3, 83-1721

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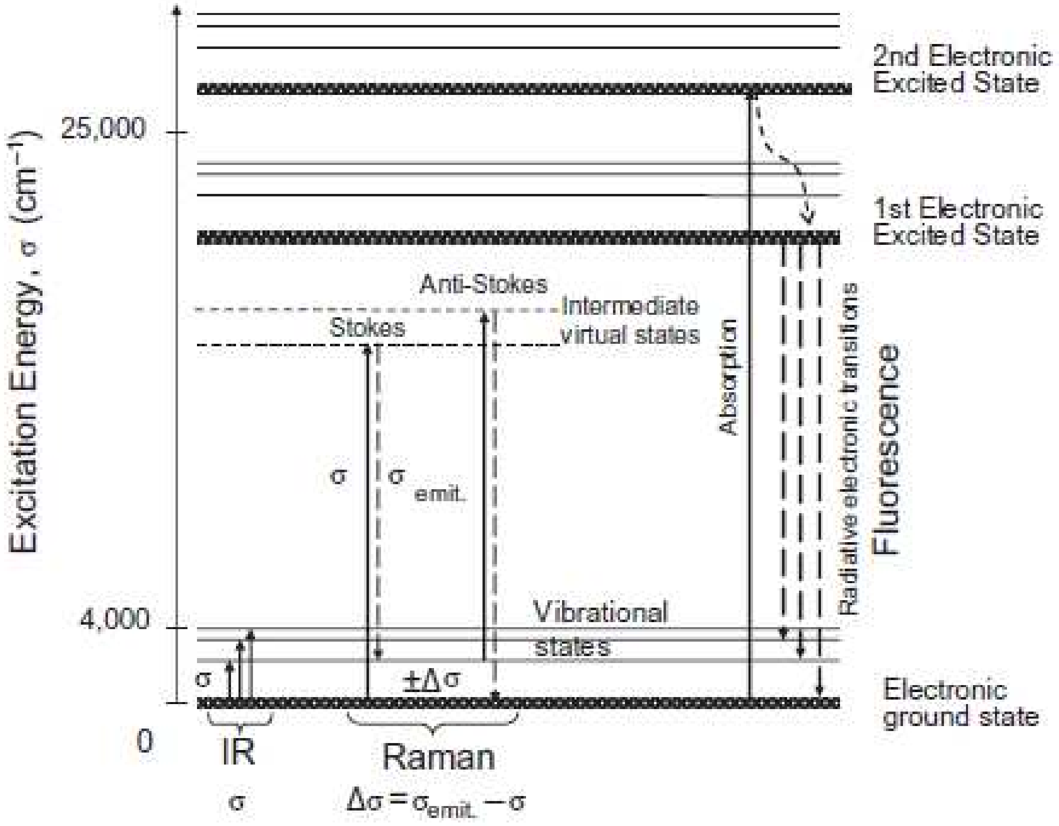
Outlines

- Time-Resolved Raman Spectroscopy
- Coupling of Raman With LIBS Instrument
- Coupling of Raman With LINF Instrument
- Raman Instrumentation for Ocean Study
- Conclusion

Jablonski Energy-Level Diagram



Raman lifetime = ~10^{-13} s

Fluorescence lifetime
= ~100 ps to several milli-sec

Panczer et al. (2012) EMU Notes in Mineralogy,**12** , Chapter 2, 1-22

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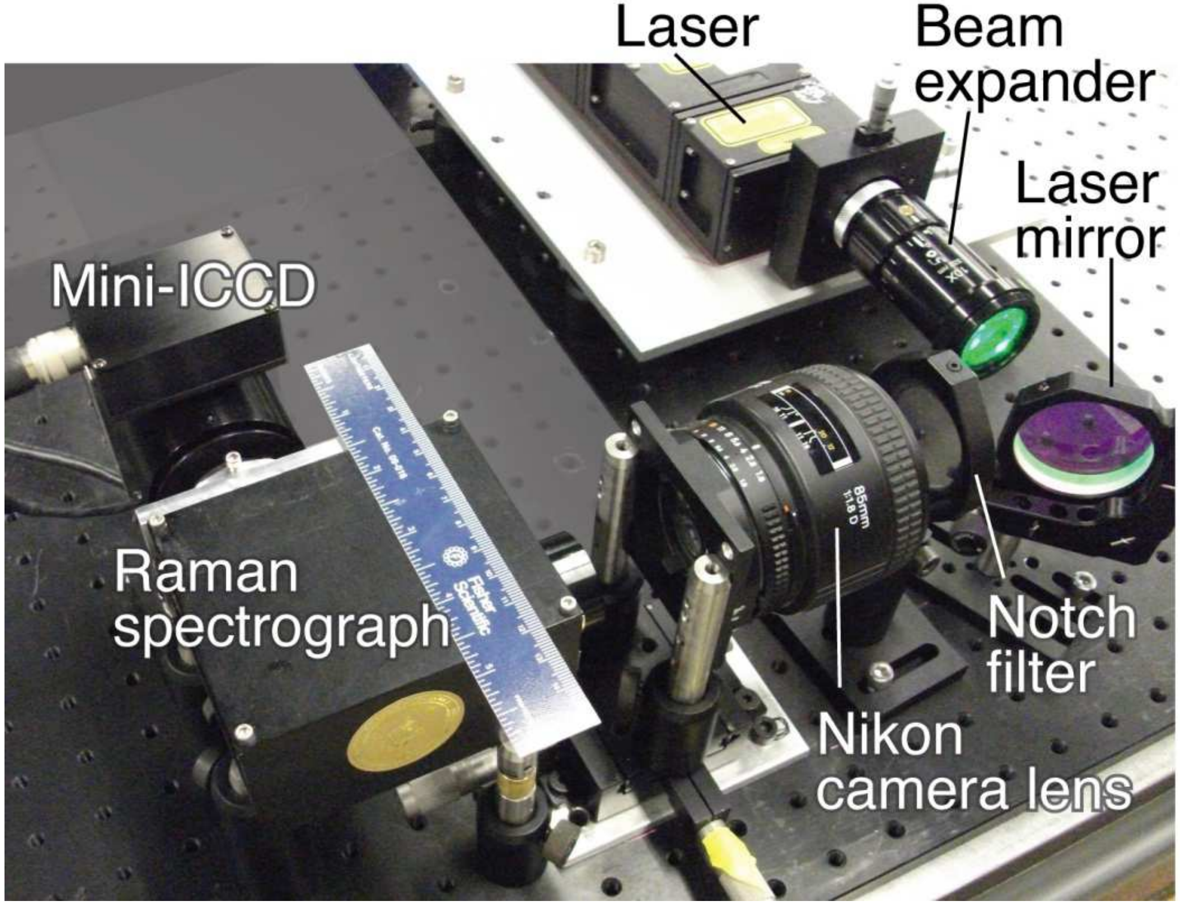
Photograph of the Compact Remote TR-Raman and Fluorescence System with Mini-ICCD

CCD chip 1392x1040 pixels
Pixel size 6.45 µm^2



Spectral resolution 15 cm^{-1} (0.43 nm) in the 100-2400 cm^{-1} and 13 cm^{-1} (0.37) in 2400-4000 cm^{-1} region;
LINF spectral range 533-700 nm
Spectrograph wt. = 631 g & ICCD wt. = 620 g (fabricated with aluminum body)
dimension 10 cm (length) x 8.2 cm (width) x 5.2 cm (high) is 1/14th in volume in comparison to the commercial HoloSpec (F/1.8) spectrograph from Kaiser Optical Systems

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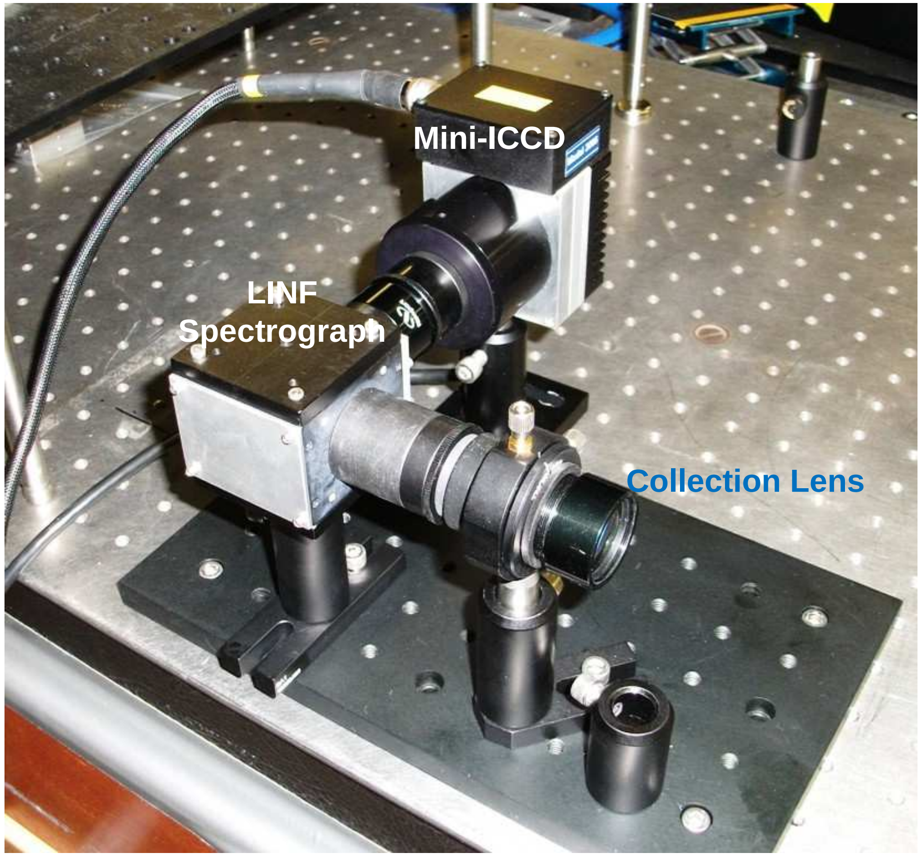
Photograph of the Compact Remote TR- Fluorescence Spectrograph

Also referred to as Planetary Compact Gatable (PCG) - LINF system with 355 and 532 nm laser excitation



Collection Optics 25 .4 mm
Spectral Range 380-800 nm
Spectral Resolution ~2.3 nm

Spectrograph Dimensions 50 mm^3
Spectrograph mass (Al metal body) =333 g
Mini-ICCD Mass (Al metal) = 620 g
Total mass (Al) = 953gm
Total mass (Mg body) =0.60 kg
Total mass (Be body) =0.64 kg

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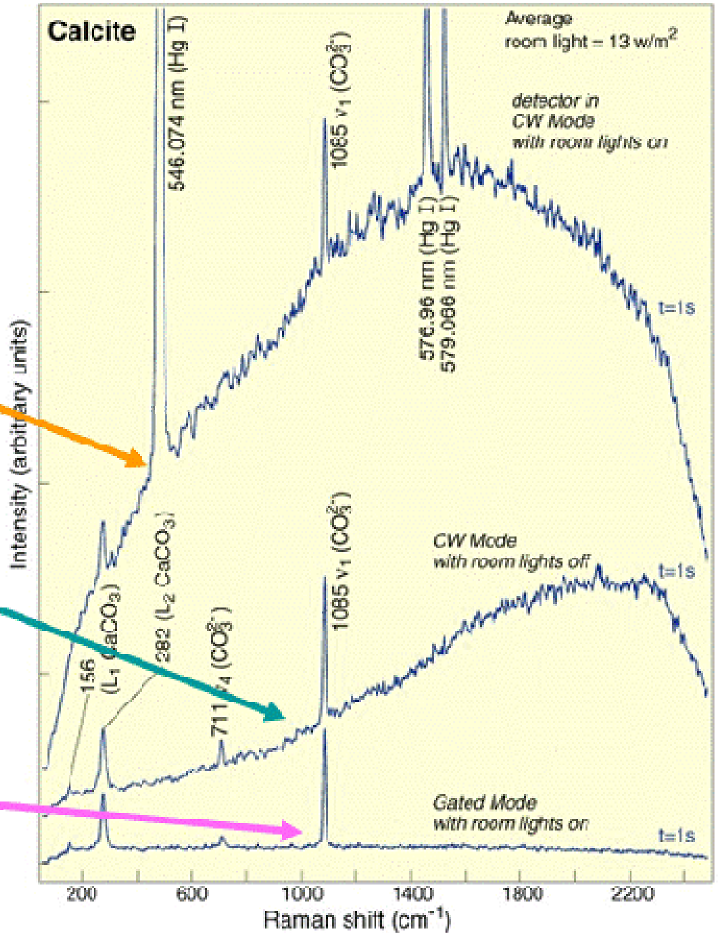
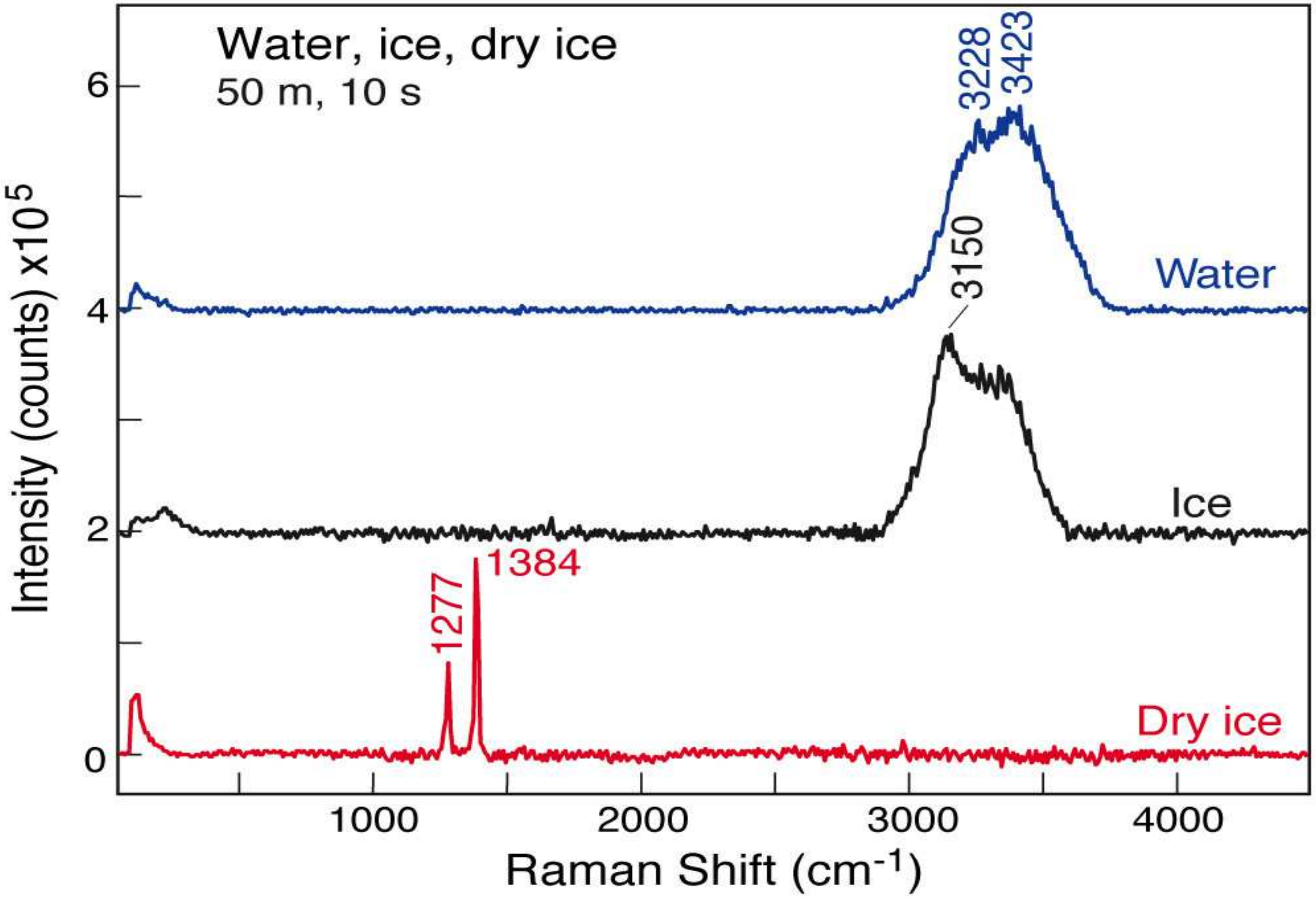
Comparison of CW & Time-Resolved Modes of Detection

Operating Modes:

- * CW (lights on)
- * CW (lights off)
- * Gated (lights on)
  (Gate 2 μs)



Raman Spectra of Water, Water-Ice and Dry Ice (CO_2 Ice) from a Distance of 50 m



Raman fingerprint bands of water and ice are in the 3000-3500 cm^{-1} region.
The Fermi doublet of CO_2 ice is observed at 1277 and 1384 cm^{-1}.

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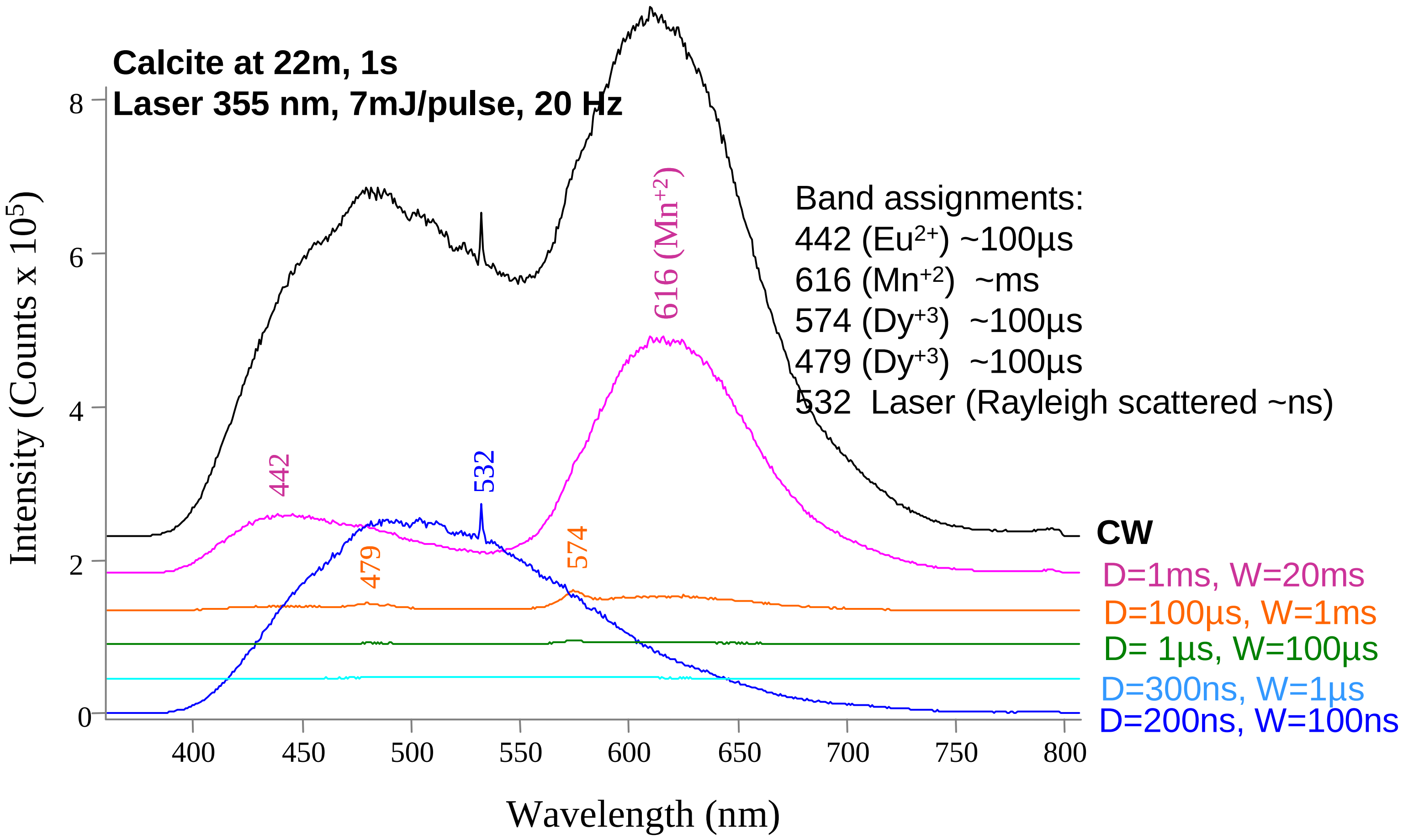
Laser-induced CW (continuous-wave) and Time-Resolved Fluorescence Spectra of Calcite Excited with 355-nm Laser



Calcite at 22m, 1s
Laser 355 nm, 7mJ/pulse, 20 Hz

Band assignments:
442 (Eu^{2+}) ~100µs
616 (Mn^{+2}) ~ms
574 (Dy^{+3}) ~100µs
479 (Dy^{+3}) ~100µs
532 Laser (Rayleigh scattered ~ns)

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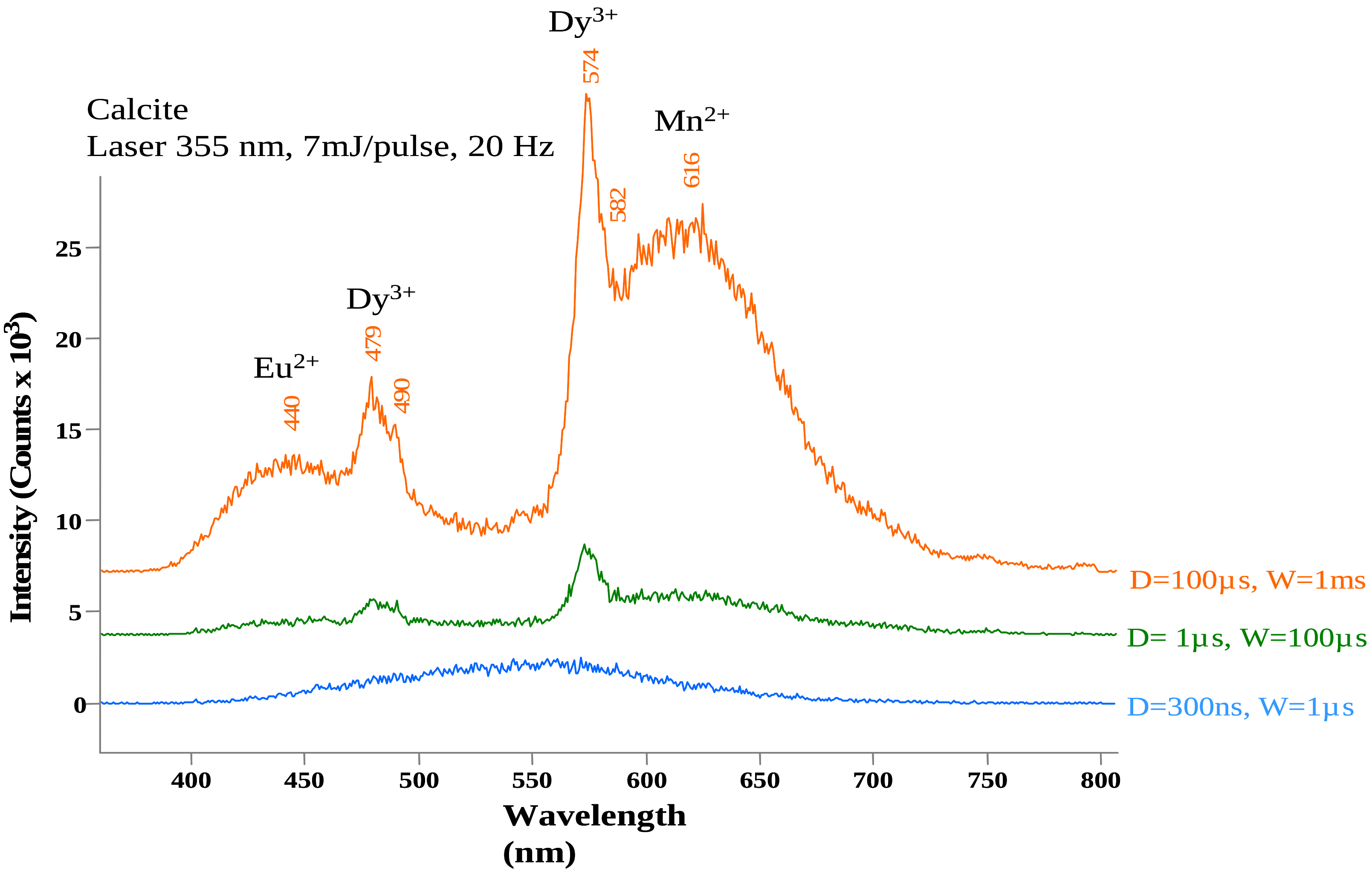
Time-resolved LINF spectral traces of calcite excited with 355-nm laser on an expanded scale along the Y-axis



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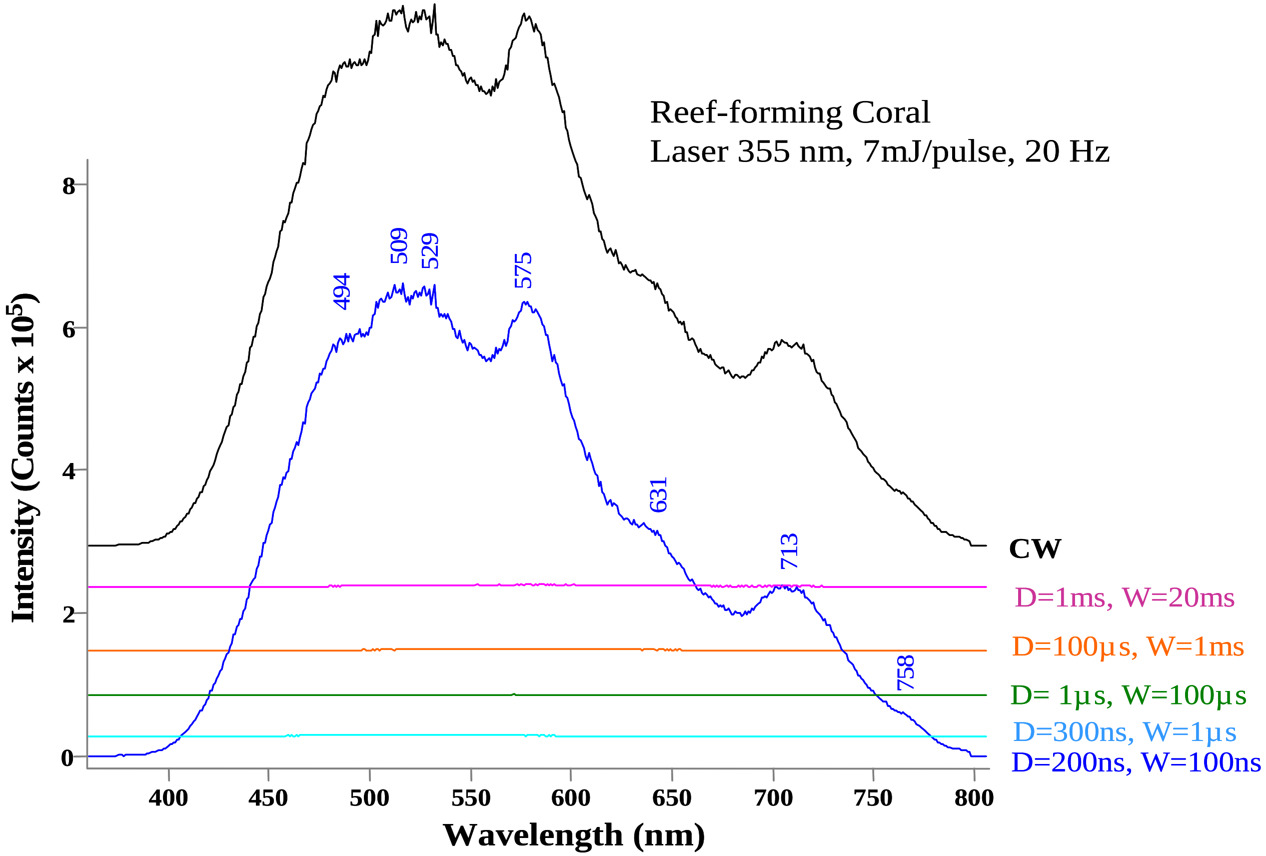
Laser-Induced CW (continuous-wave) and Time-Resolved Fluorescence Spectral Traces of a Reef-forming coral



Reef-forming Coral
Laser 355 nm, 7mJ/pulse, 20 Hz

494 nm =cyan fluorescent protein (CFP),
509 nm = green fluorescent protein (GFP), and
575 nm = orange fluorescent protein (OFP)
631, 713 and 758 nm LINF bands yet to be assigned.

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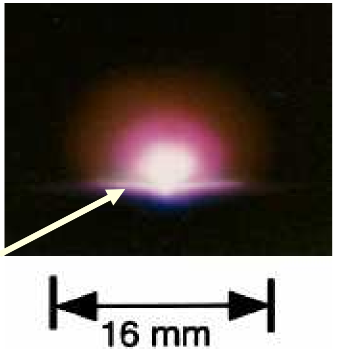
What is LIBS?

- **By Now You Know About Raman & Fluorescence Spectroscopy**

- **But What is LIBS?**



Laser-Produced
Surface Plasma

  - A form of elemental analysis that uses a laser-generated plasma
  - A laser pulse is focused on a solid target with > 1 GW/cm^2
    - Significantly Higher Energy Density Than Raman
  - A small amount of the target is ablated and atomized
  - The resulting atoms are excited to emit light
  - Emitting elements are identified by their unique spectral peaks
  - Yields semi-quantitative abundances of major, minor, and trace elements simultaneously
  - Laser ablation profiles through dust and weathering layers

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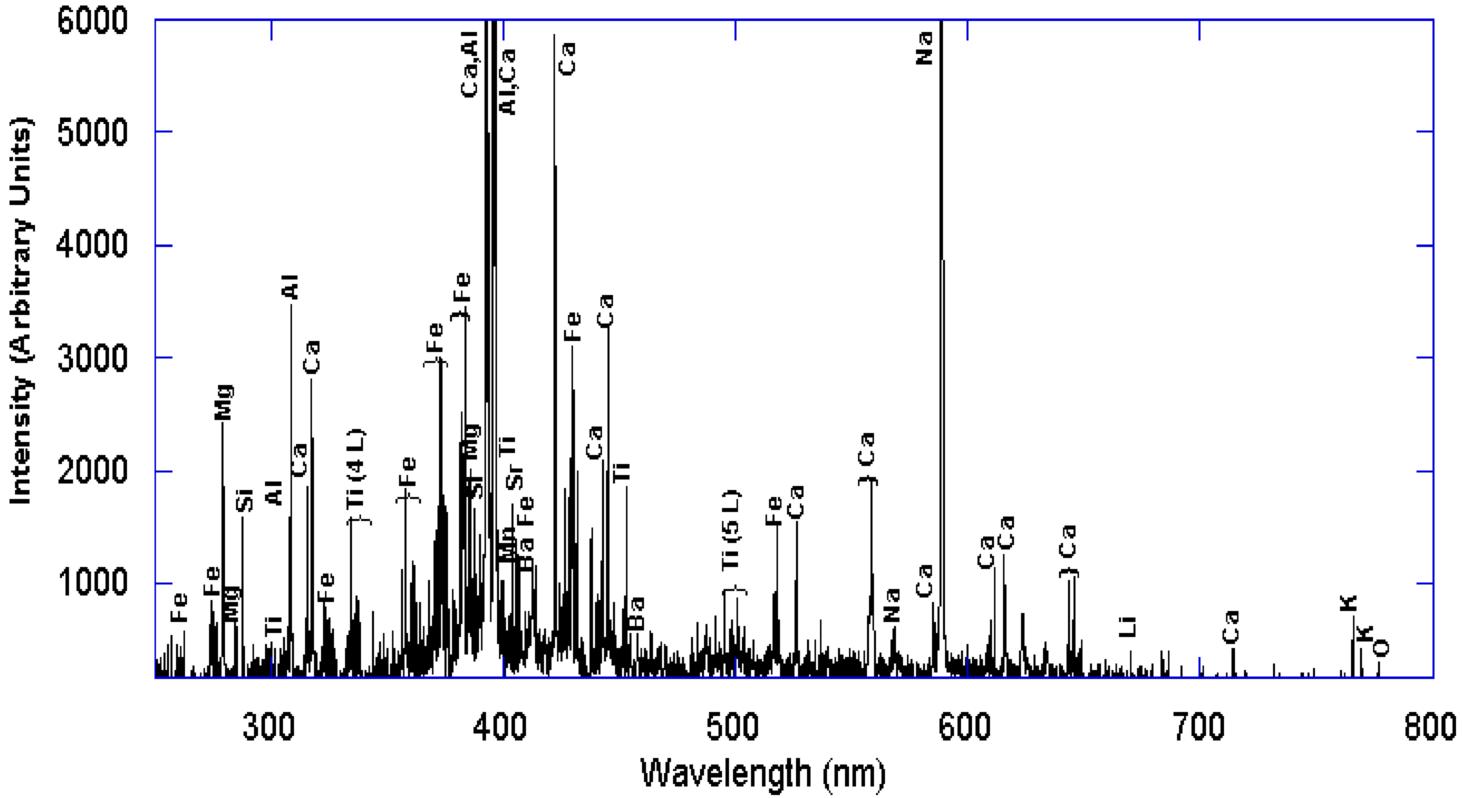
LIBS Spectra



- LIBS spectrum of basalt standard taken at 3+ m during a field test using a compact echelle spectrograph.
- Spectral resolution ($\lambda/\Delta\lambda = 2500$) is significantly higher than can be shown
- Average of 10 laser shots.

Combined Micro-Raman & LIBS Instrument

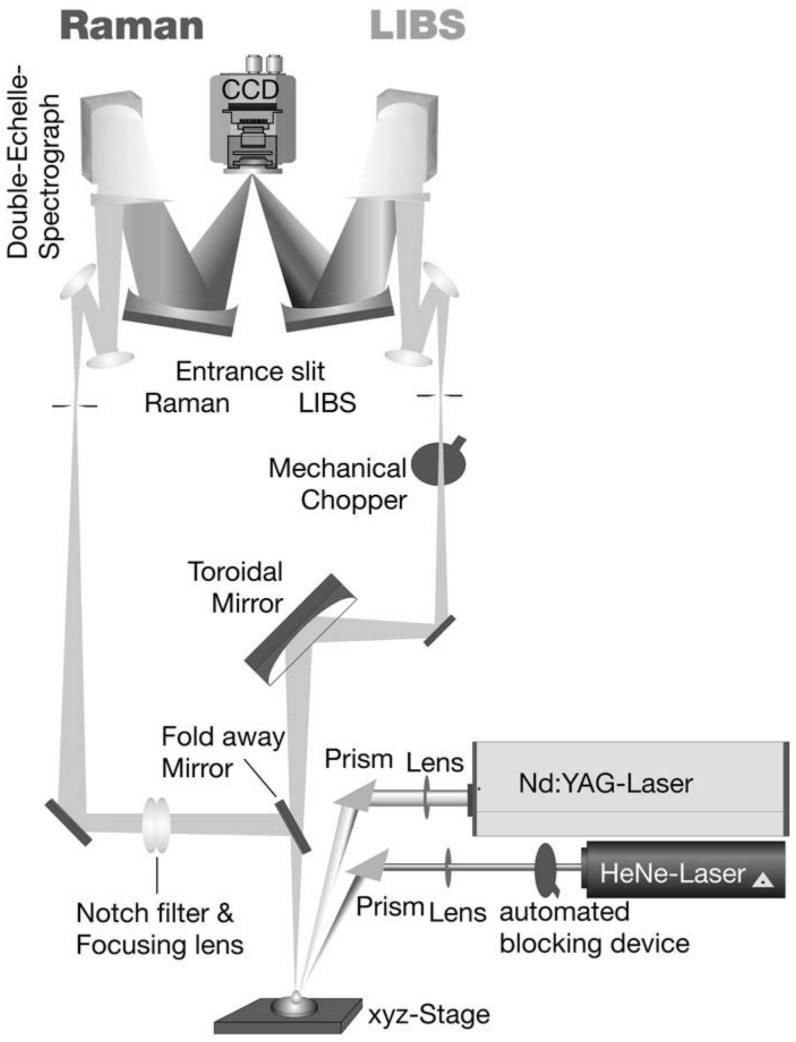
“Arielle Butterfly” Echelle spectrograph (LTB Lasertechnik Berlin GmbH, Germany), specifically modified to combine LIBS and Raman.

For Raman, the He–Ne laser line 632.8 nm (35 mW) is focused on the sample (spot size diameter ~50 µm) providing the irradiance of 1.5×103W/cm^2.

Spectral Resolution = 1.35 cm-1 at 700 nm;
slit 120x200 µm; $\lambda/\Delta\lambda$ = 10,000

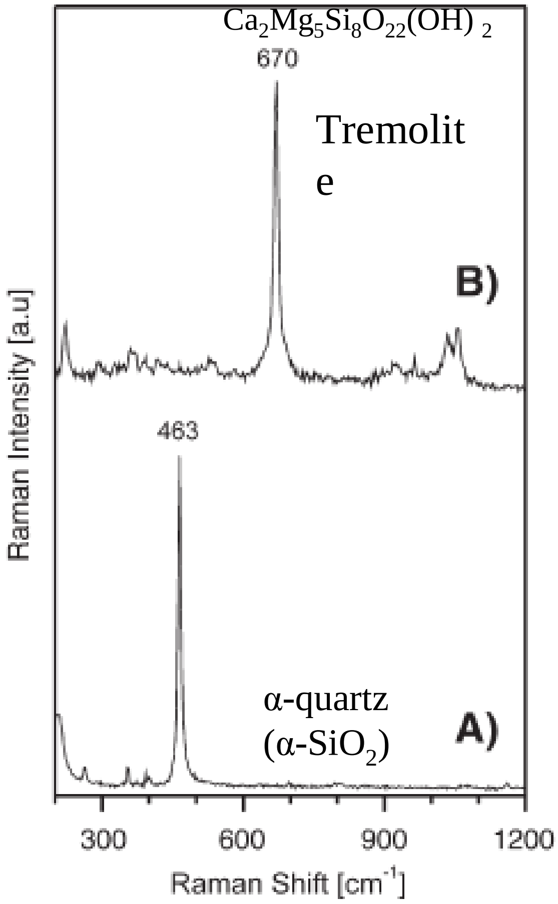
For LIBS, a frequency doubled Nd:YAG laser (max 200 mJ pulse energy at 532 nm, 7 ns pulse duration, laser beam on the surface is about 50 µm yielding an irradiance of 1.8×10^{11} W/cm^2.

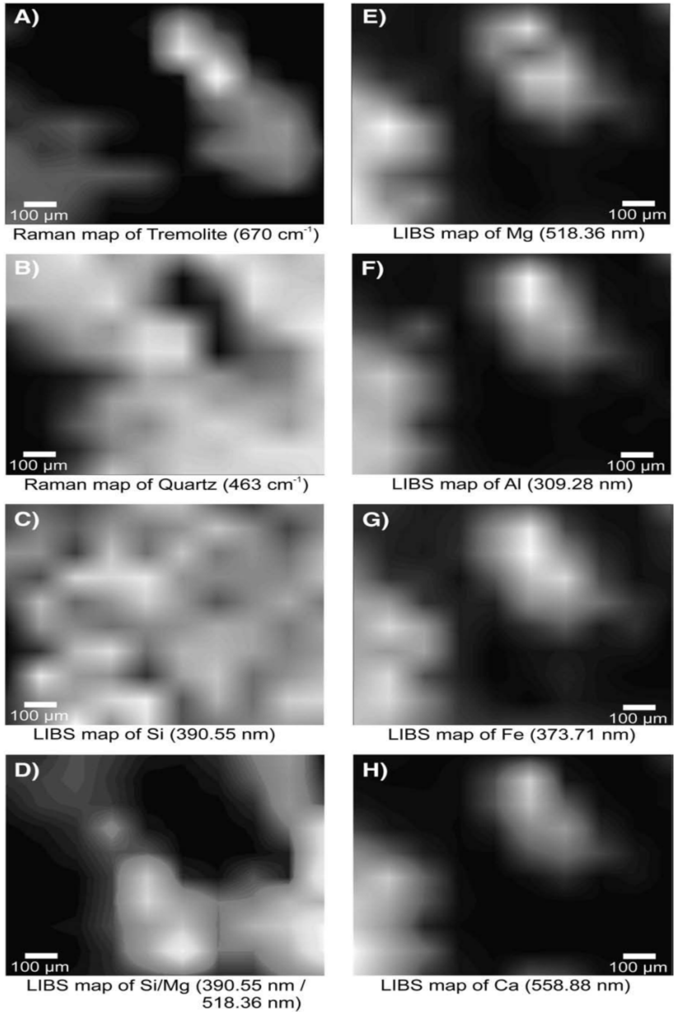
Slit = 50×50 µm^2, Resolving power $\lambda/\Delta\lambda$ = 15,000
Spectral range = 290-945 nm



Hoehse et al. (2009) Spectrochim. Acta , B64, 1219-1227

Raman & LIBS Spectra of Quartz & Tremolite Inclusions in Iron Ores





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Laboratory Raman & LIBS Instrumentation

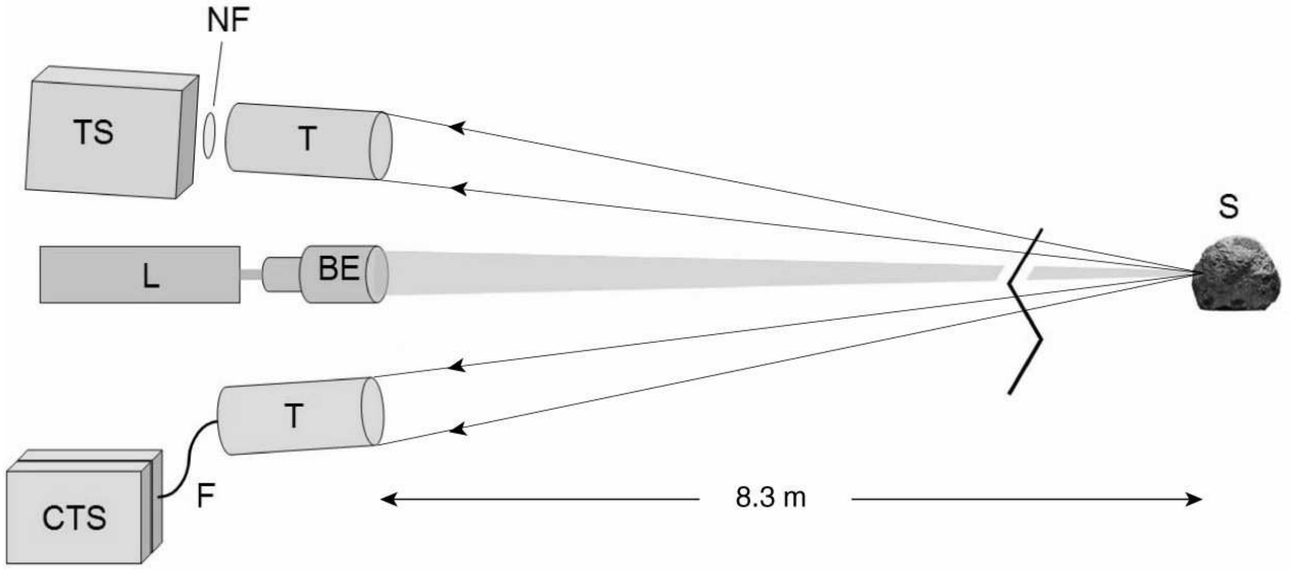
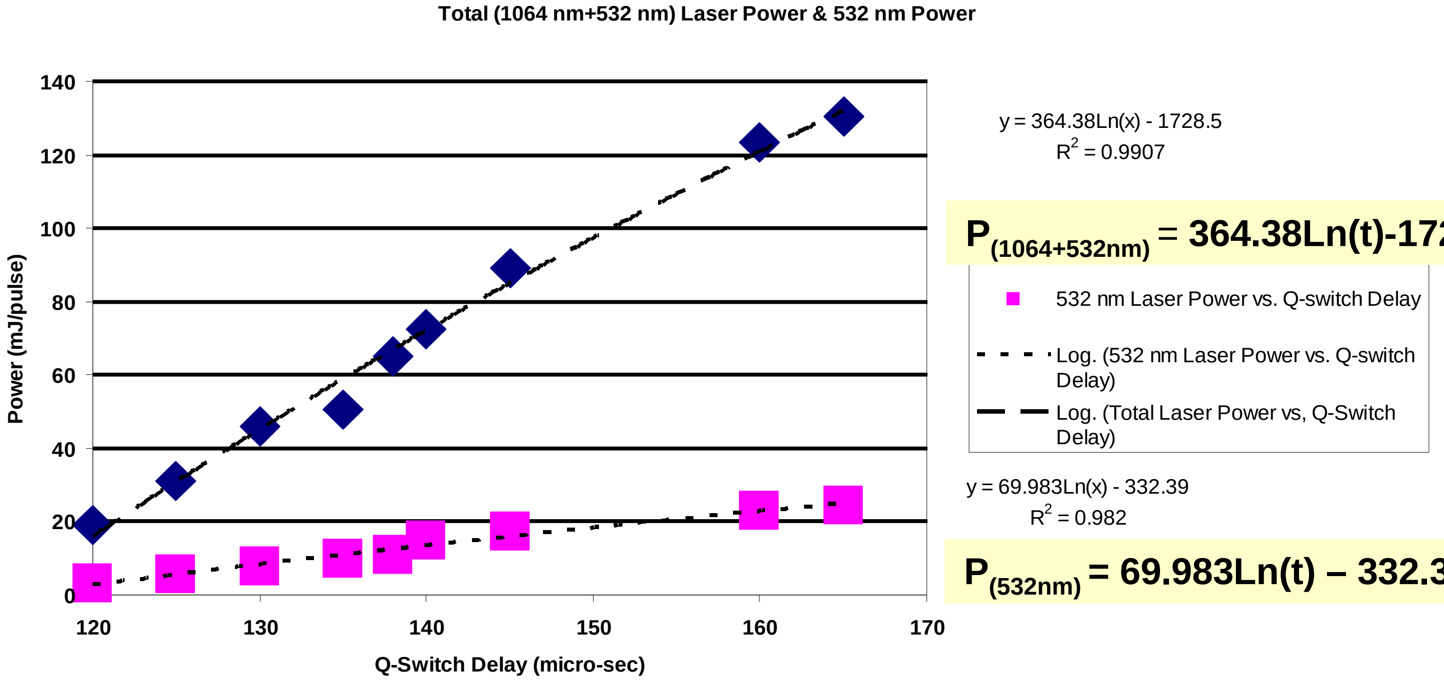


Fig. TS = Transmission-grating Spectrograph, NF = Notch Filter (532 nm), T = telescope, L = Surelite Continuum Nd:YAG laser, BE = 5X beam expander, S = sample, F = fiber optic cable, CTS = Czerny-Turner spectrograph. For the Raman spectroscopy measurements, the laser was used without the beam expander and only the transmission-grating spectrograph system was used. For LIBS, both telescopes collected light into respective spectrographs and was detected with two Ocean Optics HR2000 spectrometers configured for 225-320 nm (“UV unit”) and 385-460 nm (“VIS unit”) wavelength ranges, and the TS Raman spectrograph (533-699 nm).

Laser Power vs Q-switch Delay Time



$P_{(1064+532nm)}$ = 364.38Ln(t)-1728.5

$P_{(532nm)}$ = 69.983Ln(t) – 332.39

For Gypsum & Sulfur LIBS laser operated at: t= 132 µs Q-switch delay

$P_{(1064+532nm)}$ = 50.7 mJ/pulse; $P_{(532nm)}$ = 9.3 mJ/pulse

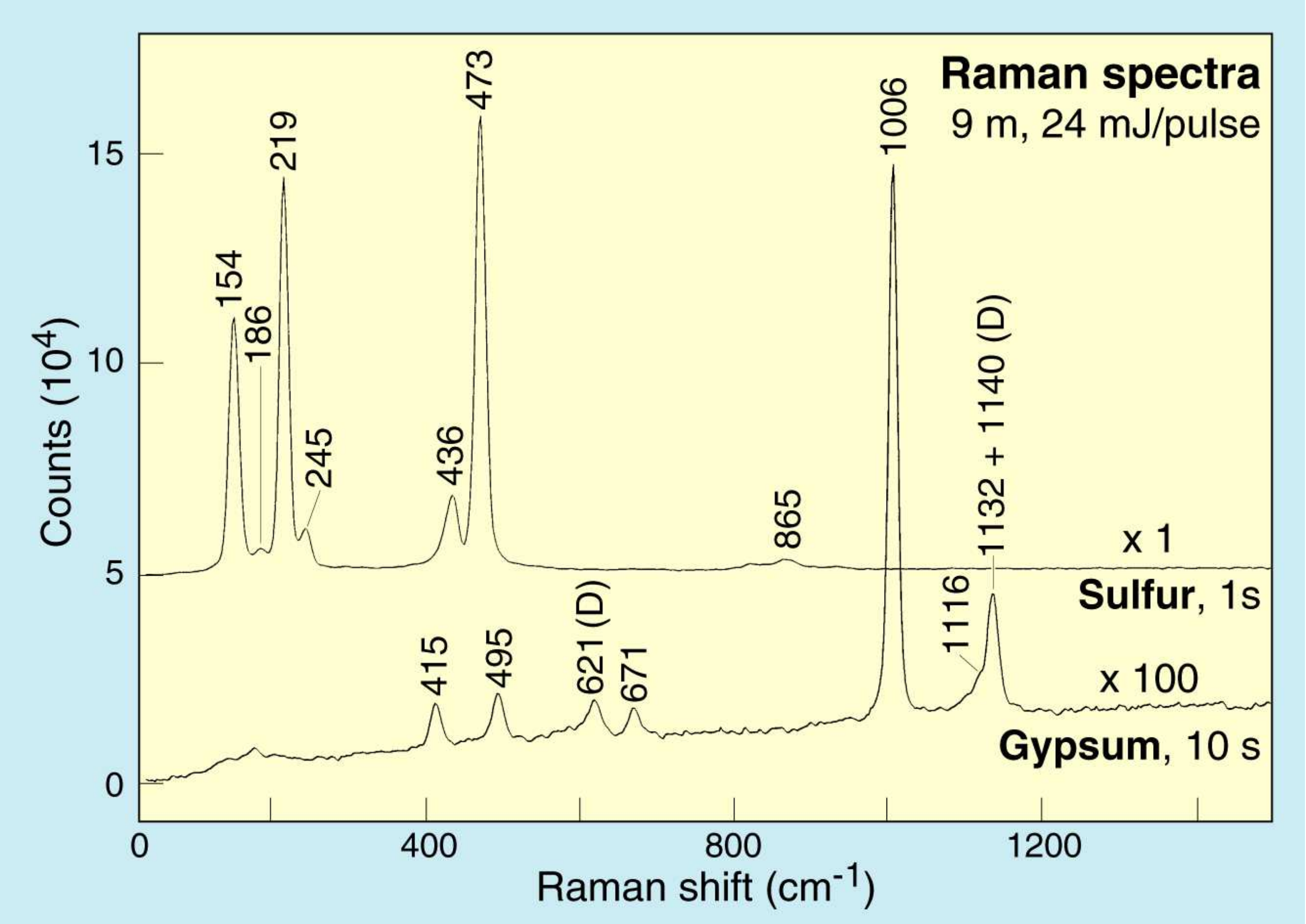
For Chalcopyrite **(t = 118 µs)**: **P $_{(1064+532nm)}$) = 39.5 mJ/pulse; $P_{(532nm)}$ = 7.2 mJ/pulse**

For Pyrite **(t = 112 µs)**: **P $_{(1064+532nm)}$ = 9.8 mJ/pulse; P $_{(532nm)}$** = 1.5 mJ/pulse

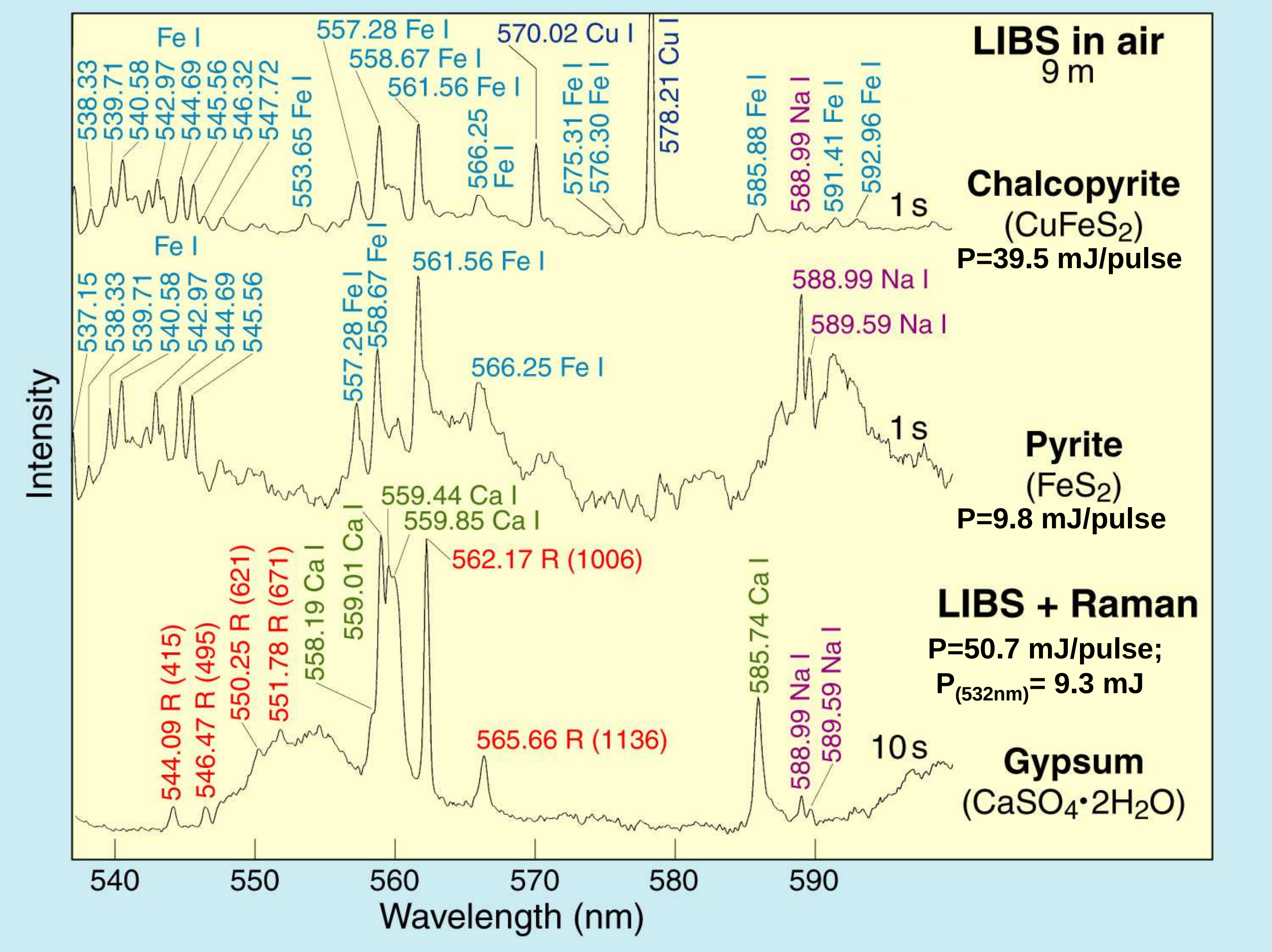
For Calcite (t=138 **µs**): **P (1064+532nm) = 66.8 mJ/pulse; P (532nm) = 12.4 mJ/pulse**

at t=142 µs Q-switch delay: the P_T = 77 mJ/pulse and P_{532}=14.4 mJ/pulse

Remote Raman Spectra of Sulfur (S) and Gypsum $(CaSO_4).2H_2O$



LIBS Spectra of Sulfur Bearing Minerals



- Main Cations Fe and Ca emission line detected.
- Trace amount of Na found on the surface of both gypsum and pyrite.
- No sulfur emission lines detected in air

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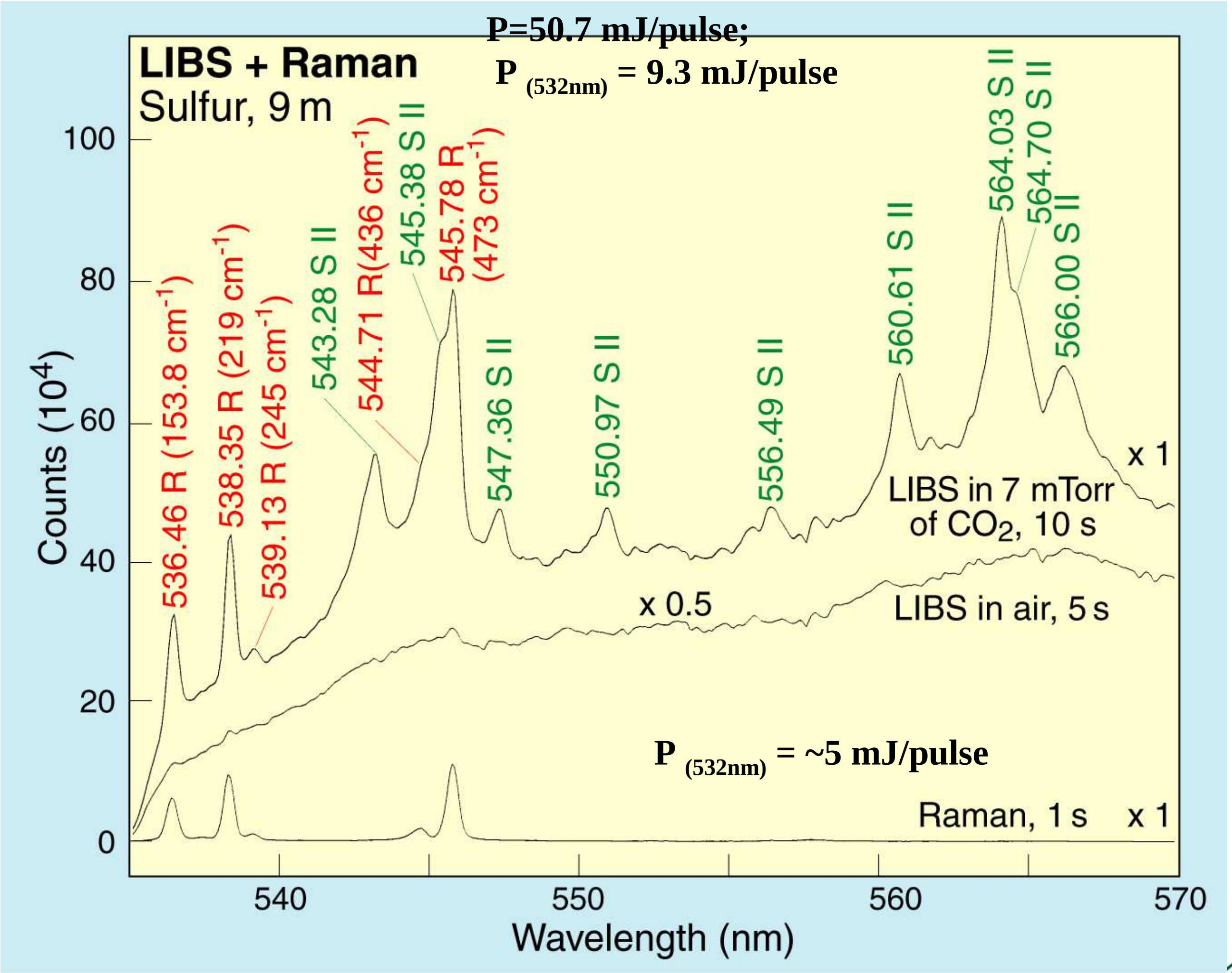
Remote LIBS & Raman Spectra of Sulfur



P=50.7 mJ/pulse;

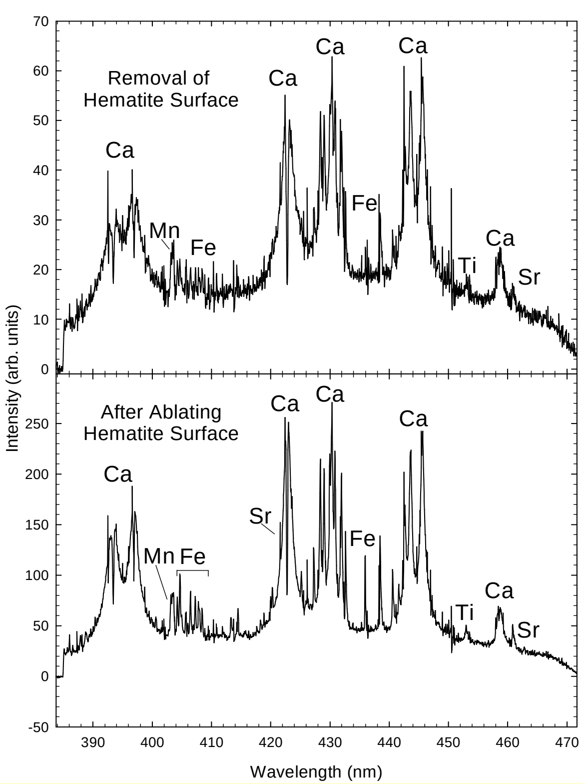
P $_{(532nm)}$ = 9.3 mJ/pulse

P $_{(532nm)}$ = ~5 mJ/pulse

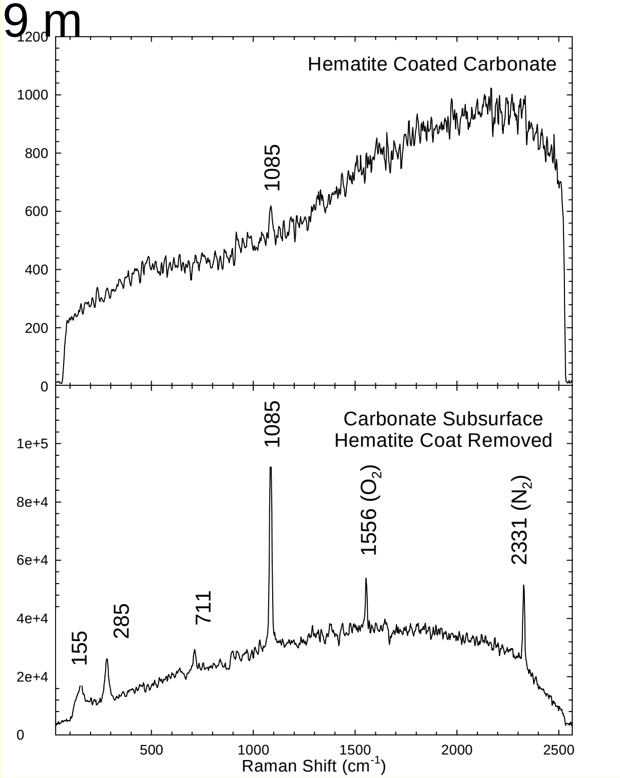
- No Sulfur emission lines in air.
- Both S emission lines & Raman lines of S detected in 7 mTorr of CO_2

Remote LIBS & Raman Spectra of Dog Teeth

Remote LIBS @ 9 m



Remote Raman spectra @ 9 m



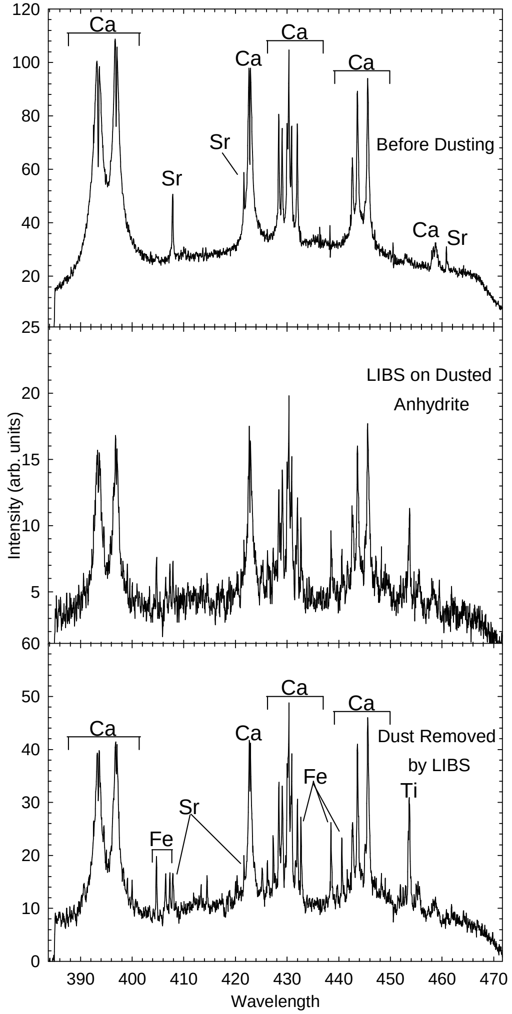
Hematite
Coated
Calcite

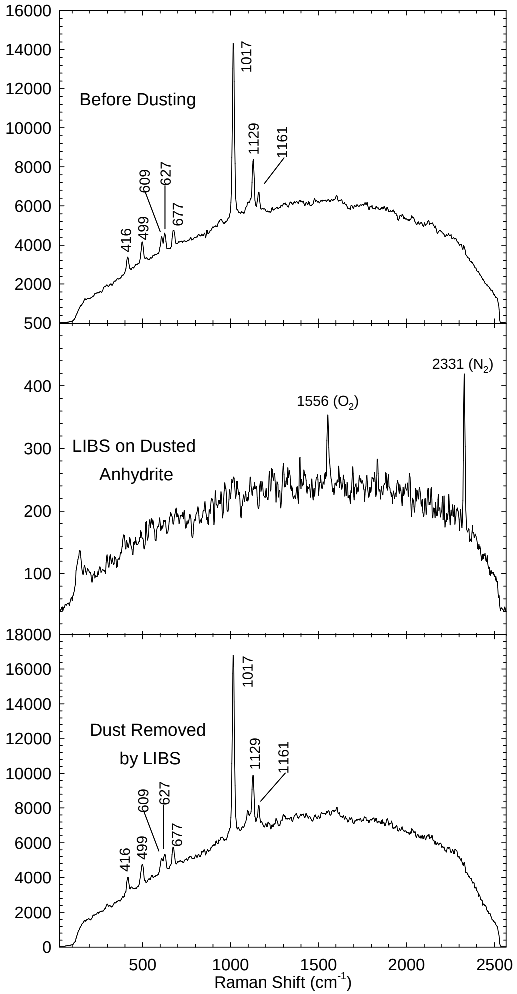
LIBS & Raman Spectra of Dusted Anhydrite

LIBS

Basalt Dusted Anhydrite

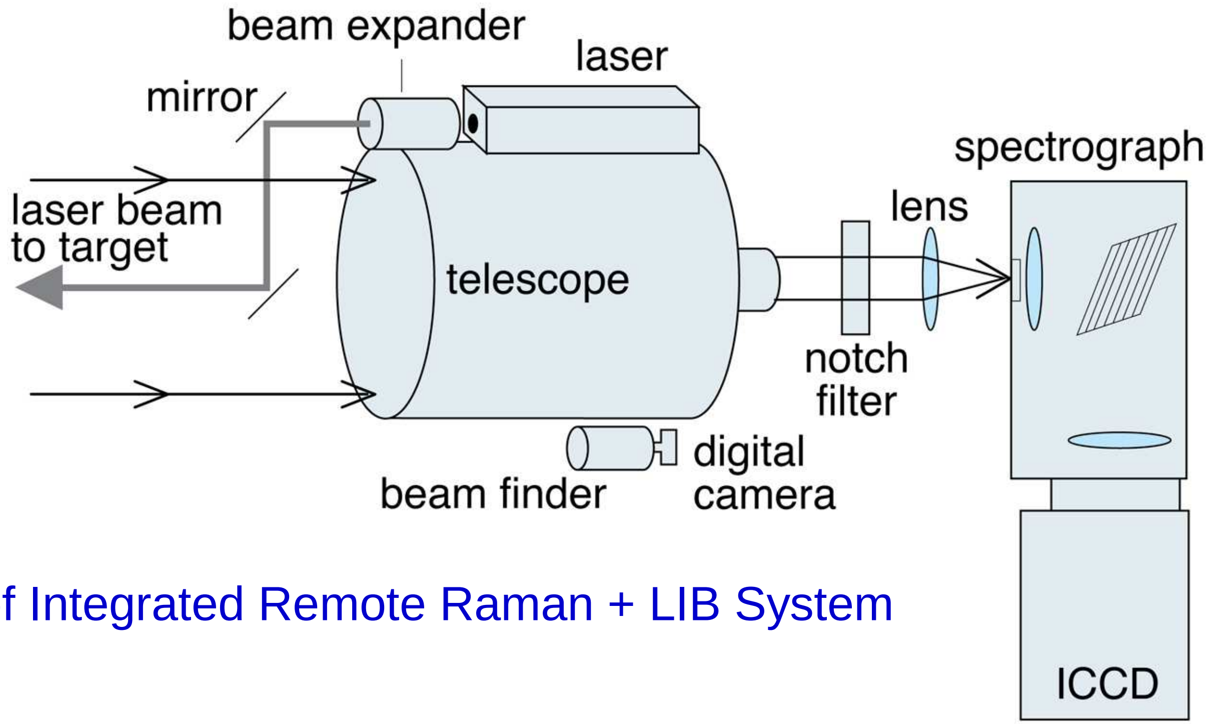
Raman Spectra





Raman + LIBS System Design

Coaxial directly coupled system



Schematics of Integrated Remote Raman + LIB System

Key Components:

(a) Dual Pulse Laser, 532 nm, 15 Hz, 100 mJ/pulse

(b) One detector (ICCD)

(c) One spectrograph with 3 high throughput VPH gratings (Range 450-850 nm)

(d) 8 inch Telescope

Sharma et al. (2009) *Spectrochim. Acta*, A **73**, 468-476

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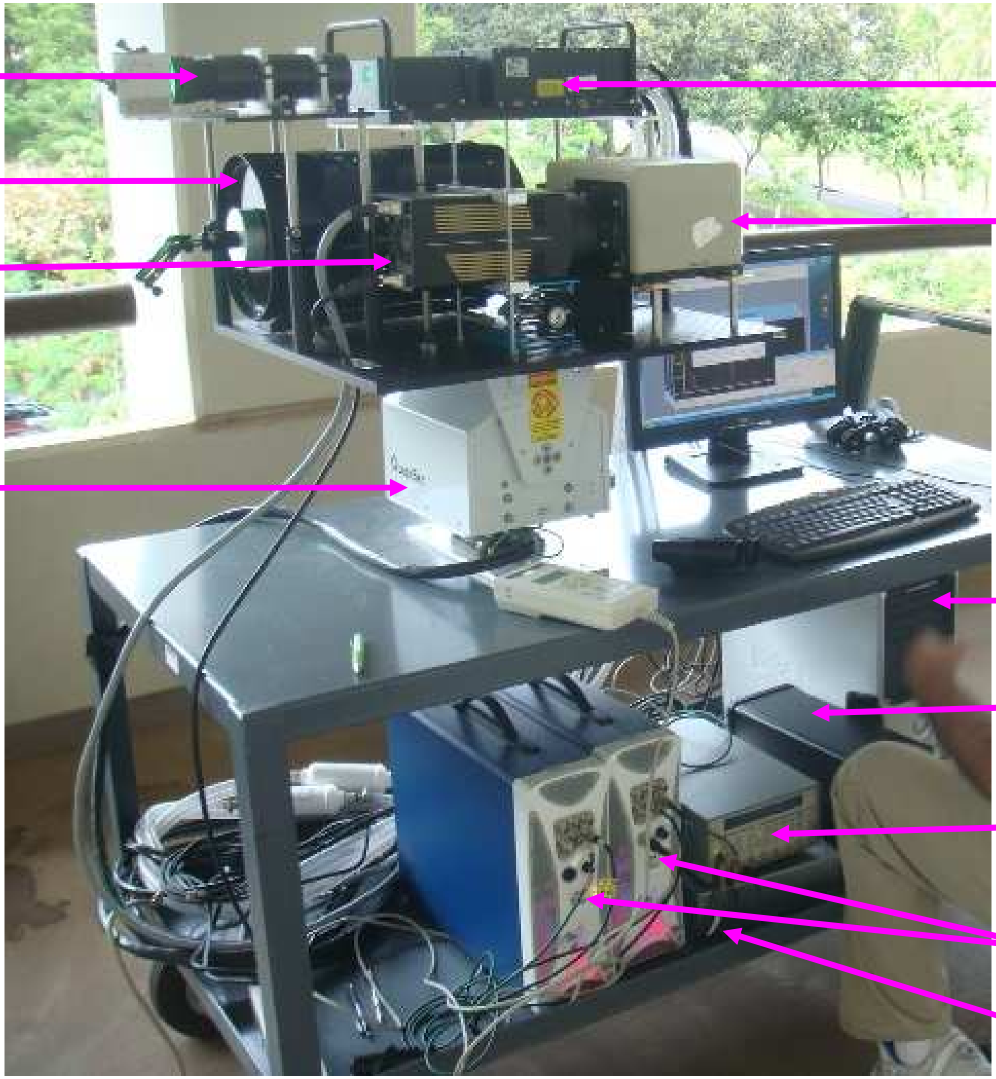
Stand-off Raman + LIBS System (532 nm)



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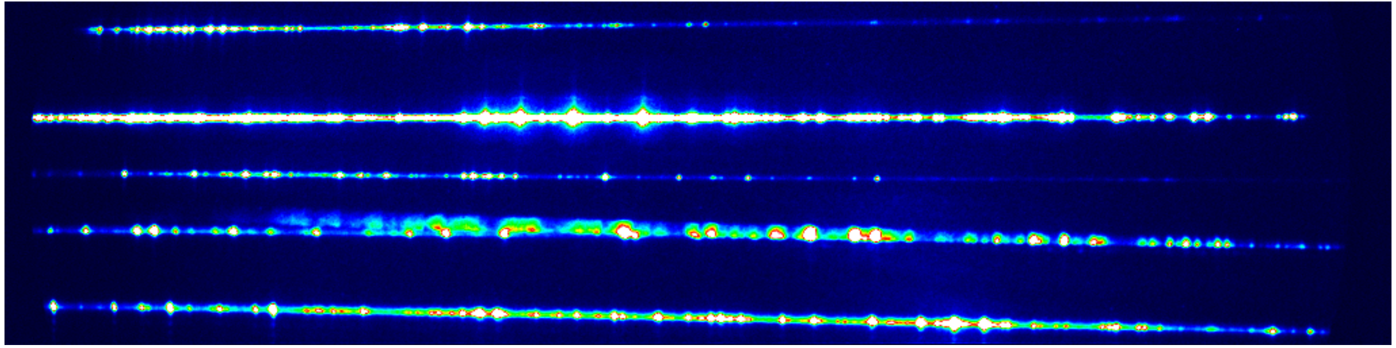
Raman+ LIBS Spectrograph with 3 VPH gratings

Iron (Fe), at 9 m, 1 double pulse, Pulse separation 1 µs, 100 mJ/pulse gate delay 2 µs, gate width 10 µs.

ICCD Image (1024 x 256 pixels)



Wavelength Range

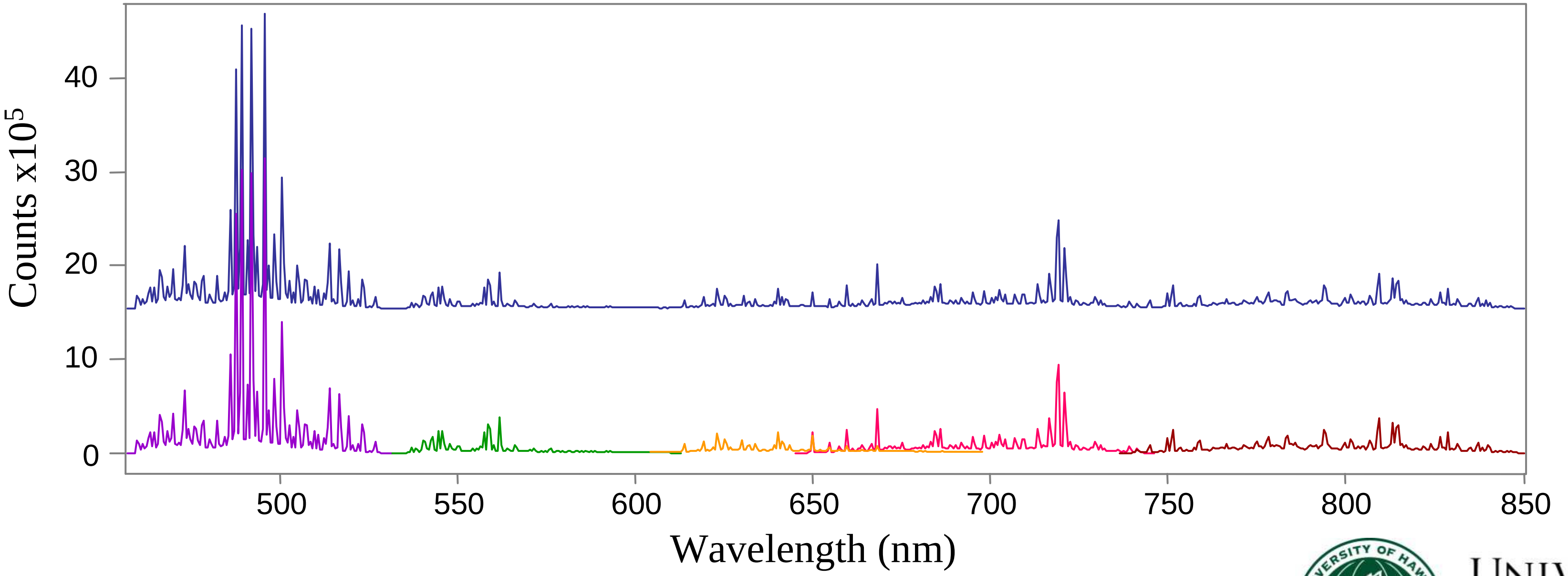
532.5 – 612.7 nm

457.3 – 530.9 nm

604.1 – 697.9 nm

736.5 – 850.2 nm

645.2 – 745.7 nm



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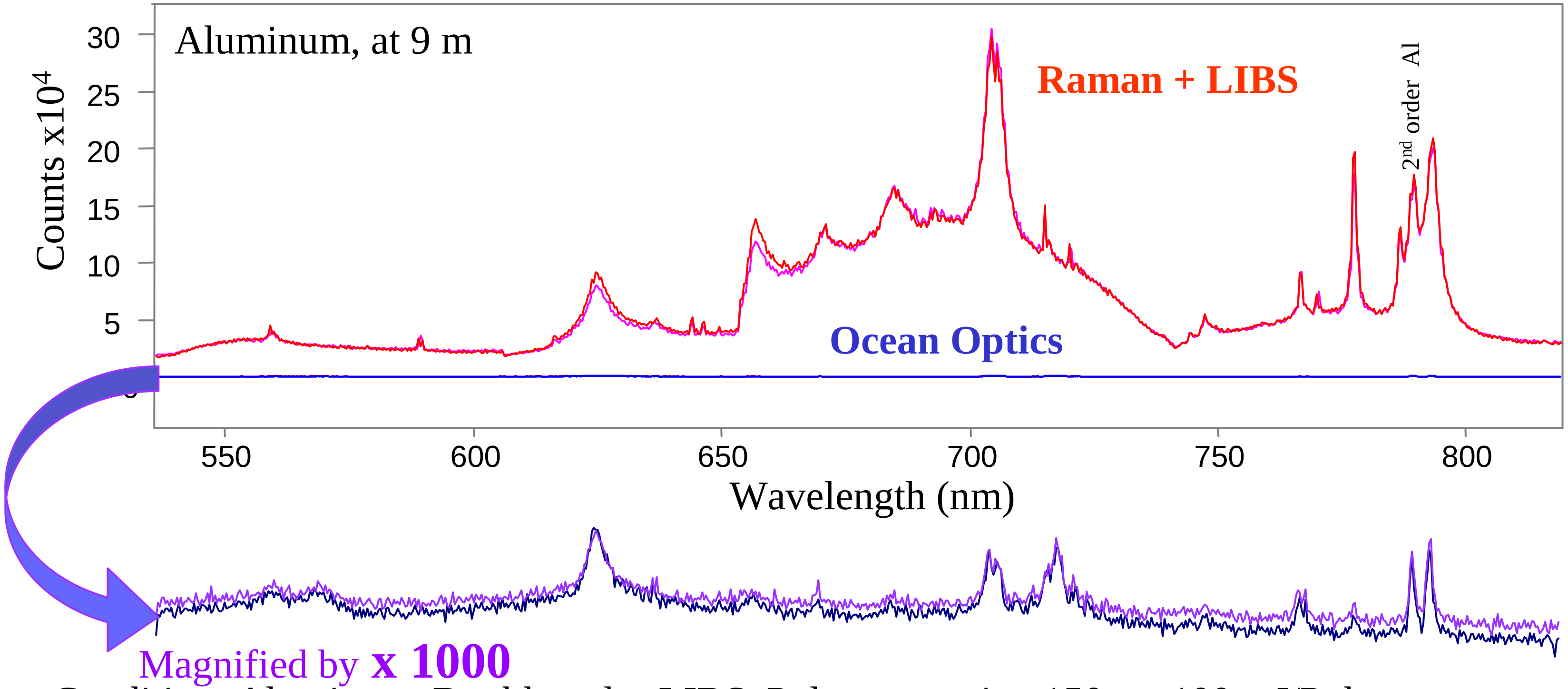
Comparison of Raman + LIBS spectrograph and Ocean Optics LIBS Spectrograph



Exp. Condition: Aluminum, Double pulse LIBS, Pulse separation 150 ns, 100 mJ/Pulse

Plot showing 2 spectra from both systems: good reproducibility.

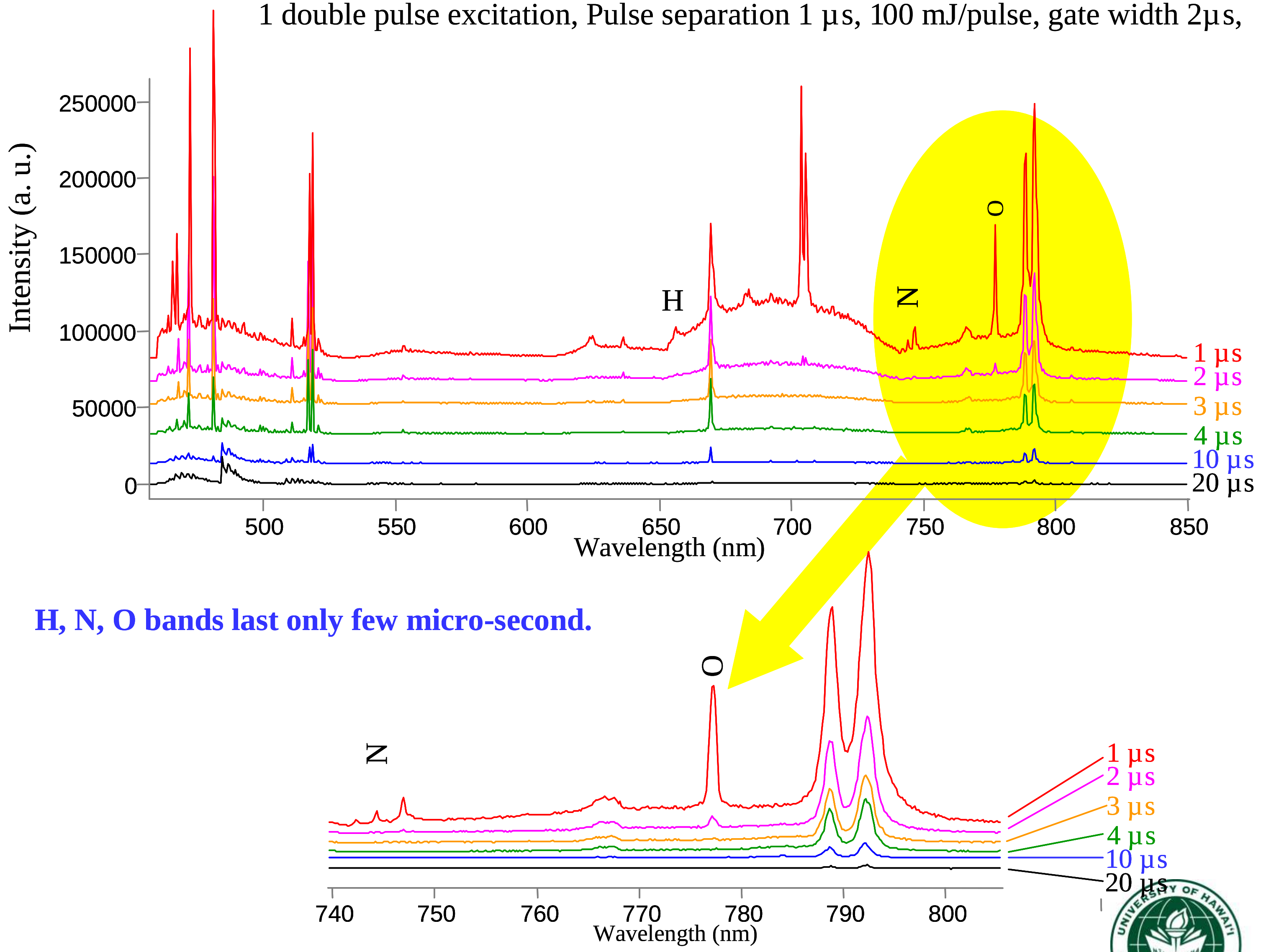
Raman + LIBS spectrograph: 8” Telescope, 1 double pulse, gate width 1 μs, delay 500 ns.

Ocean Optics Spectrograph: 8” telescope, fiber coupled, 10 double pulses (ave), gate width 1 ms, delay 1μs.

(Sensitivity difference due to : ICCD, VPH gratings, direct coupling used in the Raman + LIBS spectrograph)

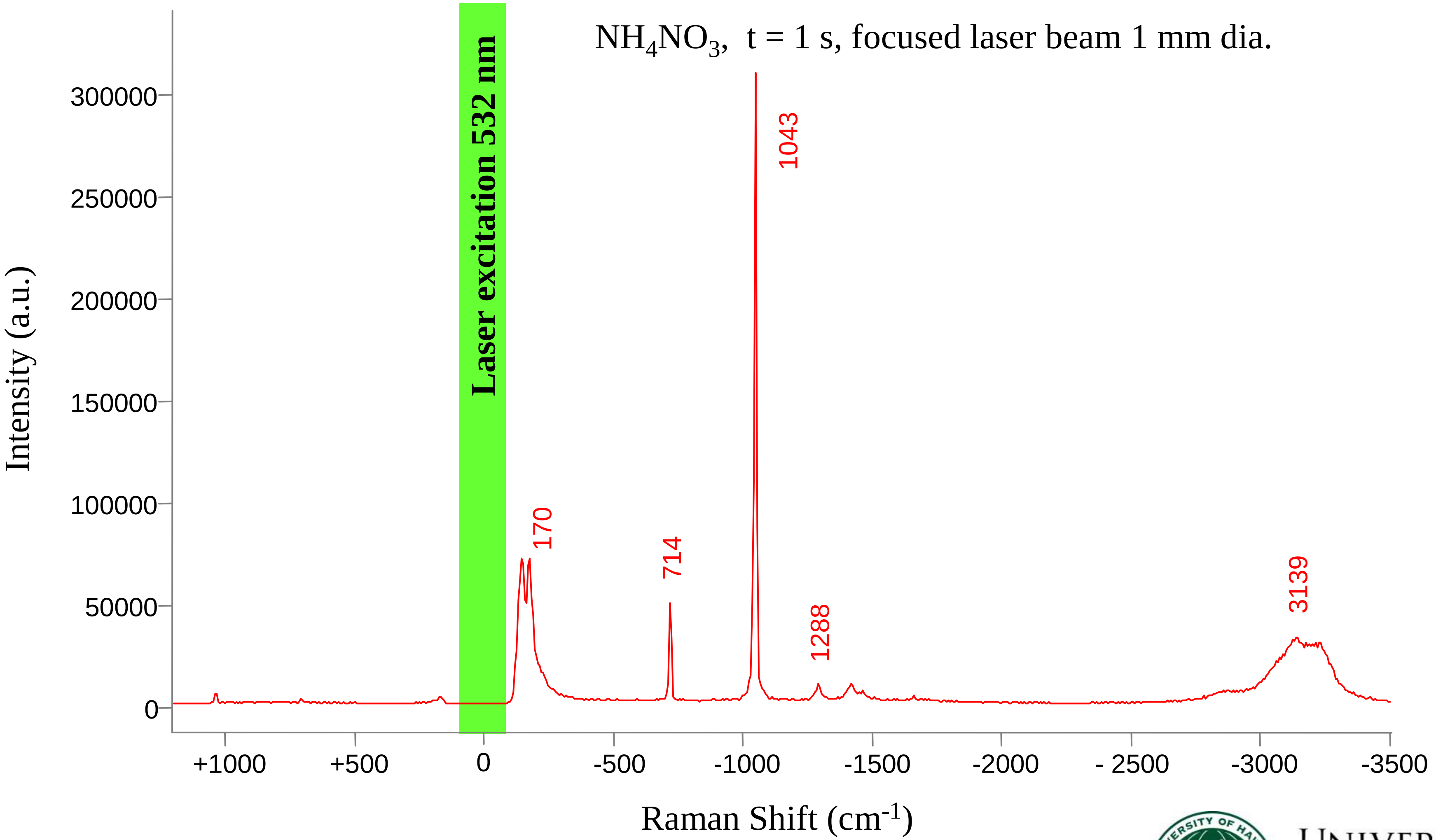
Variation in aluminum LIBS spectra at 9 m as function of gate delay from second pulse

1 double pulse excitation, Pulse separation 1 μs, 100 mJ/pulse, gate width 2μs,



H, N, O bands last only few micro-second.

Raman spectrum of Ammonium Nitrate at 9 m

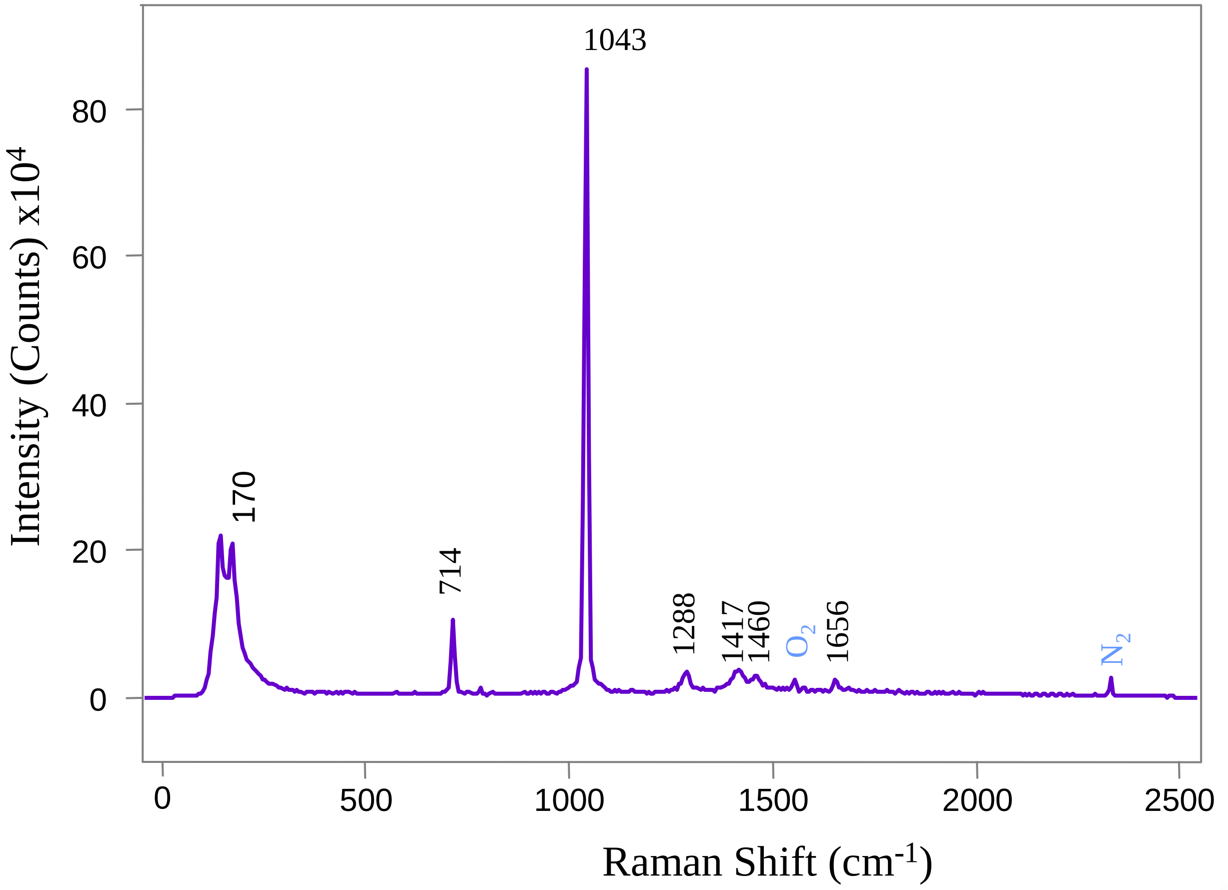


Gate width 1 µs, 50 micron slit

Raman Spectra of Ammonium Nitrate at 100 m

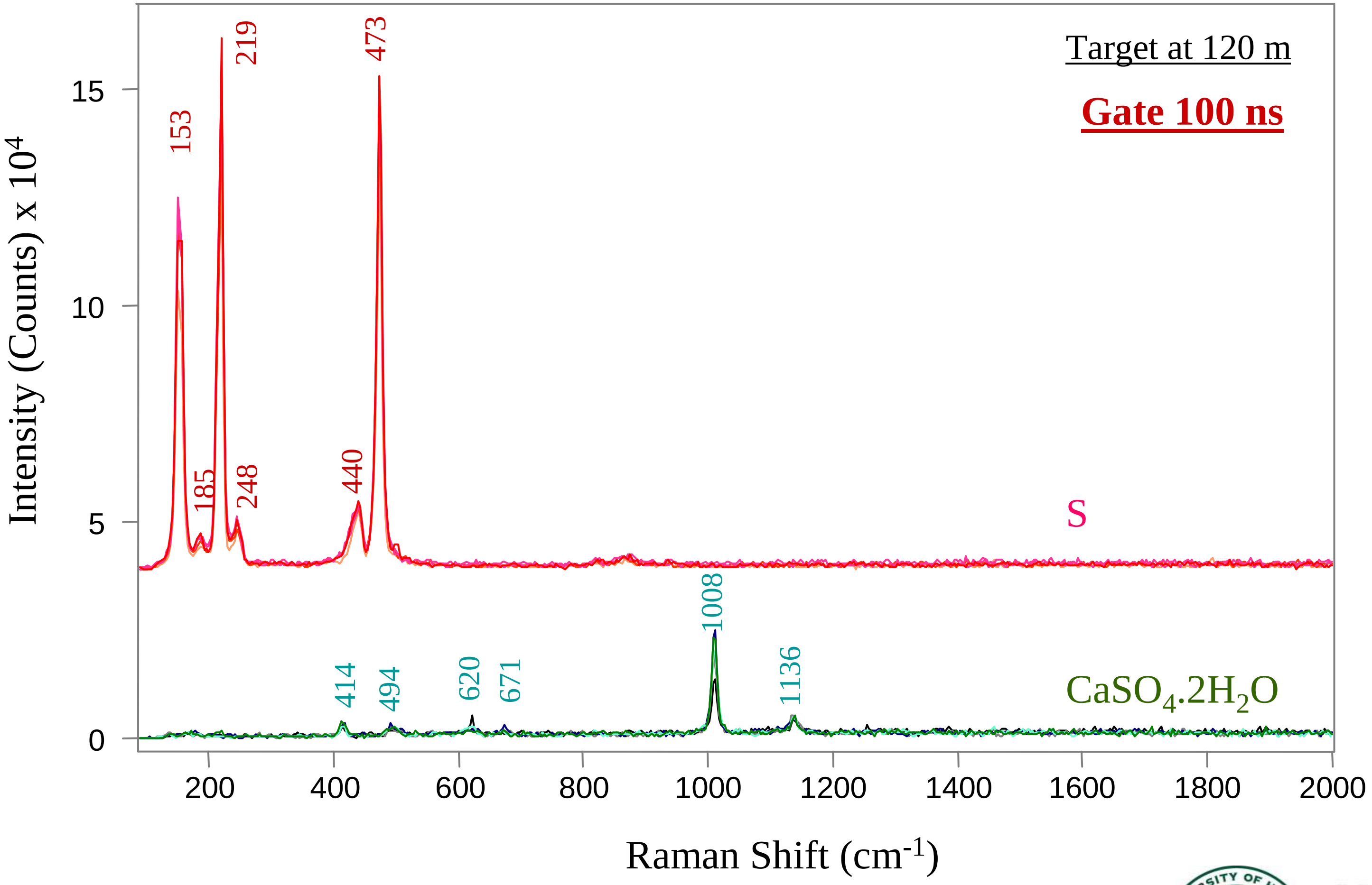
Ammonium Nitrate, 100 m, 1 s

double pulse, 38.6 mJ/pulse, 15 Hz, 532 nm, 50 micron slit



Single pulse Detection of Sulfur and Gypsum at 120 m distance

- *** Single laser shot excitation**
- *** Good reproducibility** (5 measurements shown)



110 mJ/pulse, 532 nm, 50 micron slit, laser spot size 1 cm (diameter).

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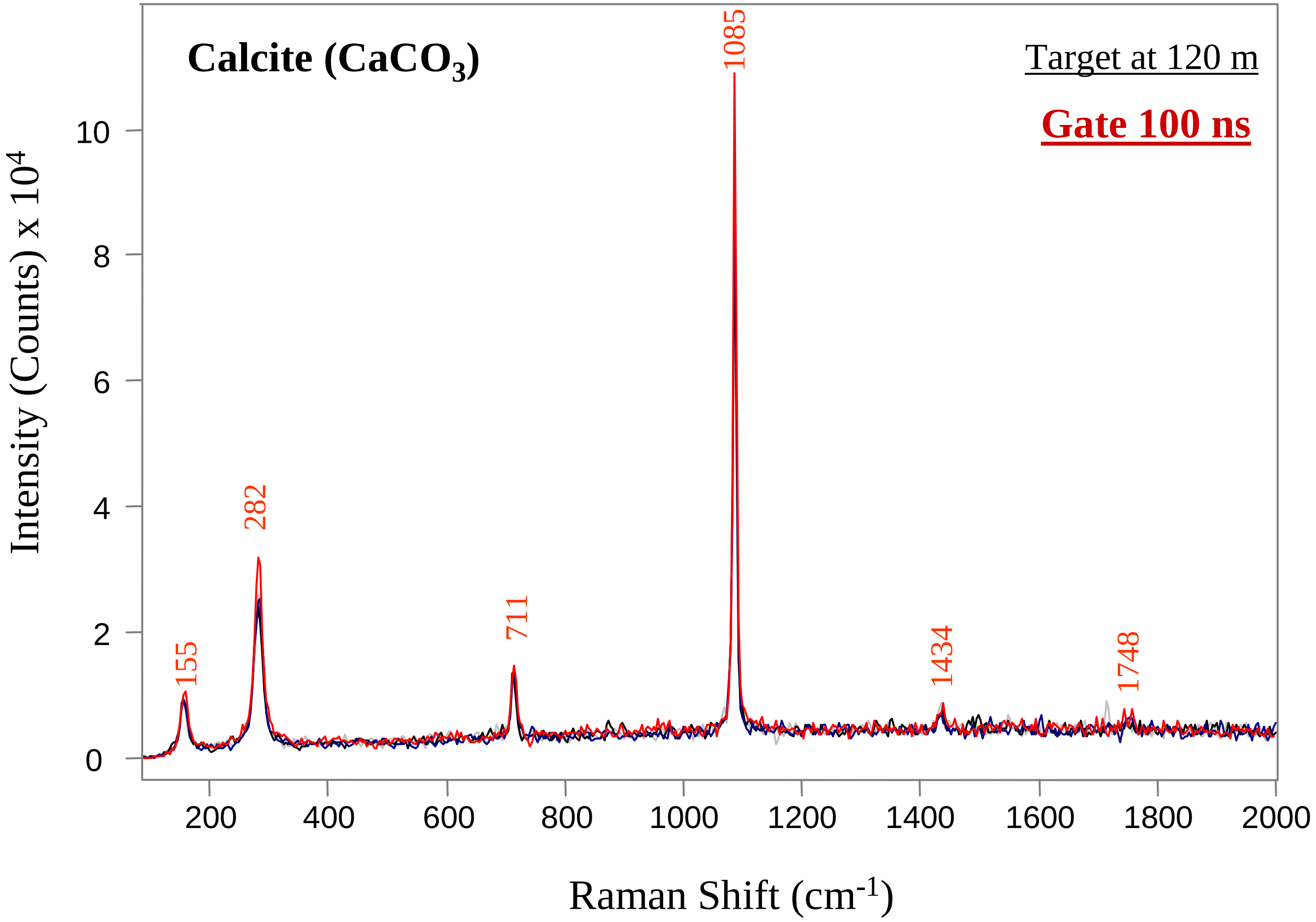
Single pulse detection of calcite at 120 m distance

- **Single laser shot excitation**
- **Good reproducibility** (4 measurements shown)



110 mJ/pulse, 532 nm, 50 micron slit, laser spot size 1 cm (diameter).
Gate width 100 ns, gate delayed to measure target only
(minimized atmospheric interference)

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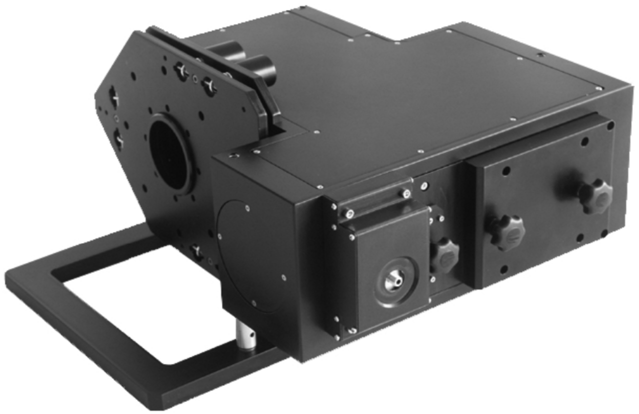
EMU (Echelle Multiplex Unit) Spectrograph

Catalina Scientific



EMU-65 VIS/NIR

EMU-65 UV/VIS/NIR

- Optimized for maximum resolution, up to R = ~50,000 (λ/FWHM)
- Optimized for maximum throughput, F/2 to F/4 at the camera focus
- Interchangeable cassettes (grating/prism), entrance slits, aperture stops

- For LIBS, Raman and photoluminescence at multiple laser wavelengths

Spectrograph wt. = 6.8 kg. Andore EMCCD Luca-R Camera wt. = 1,8 kg; 8x8 µ pixel, 1004x1002 pixel
EMCCD camera wt. = Andore iXonX3 885 10.9 kg; ; 8x8 µ pixel, 1004x1002 pixel

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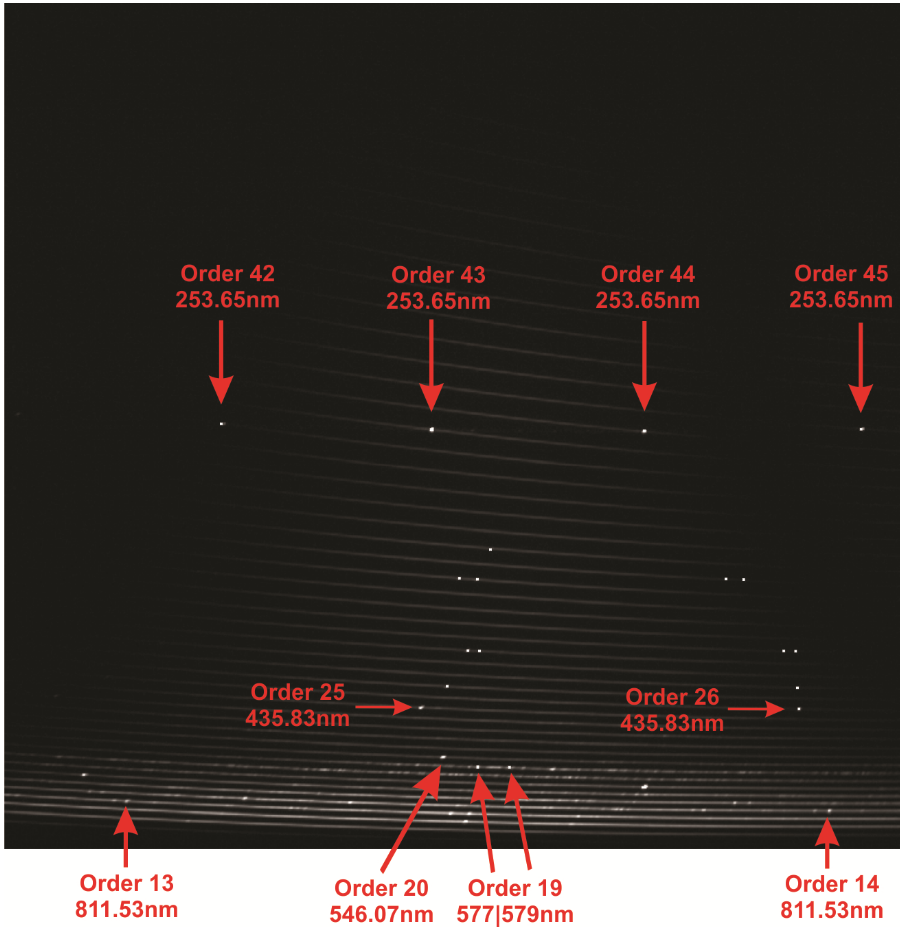
EMU-65 UV/VIS/NIR Image of Hg/Ar/Deuterium/Tungsten



- One echelle image covers a very broad wavelength range at high resolution with high throughput.

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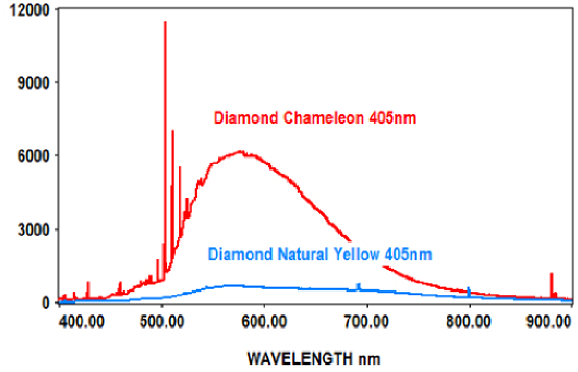
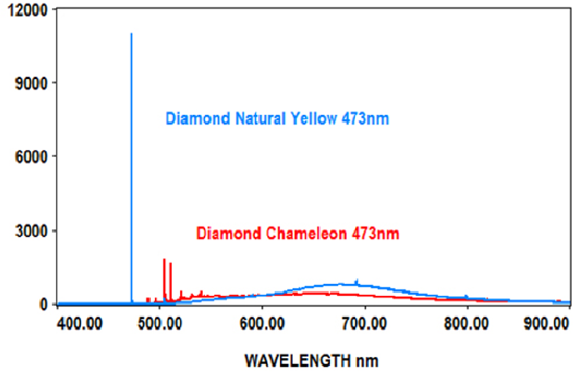
Photoluminescence with the EMU-65 VIS/NIR Catalina Scientific Spectrograph

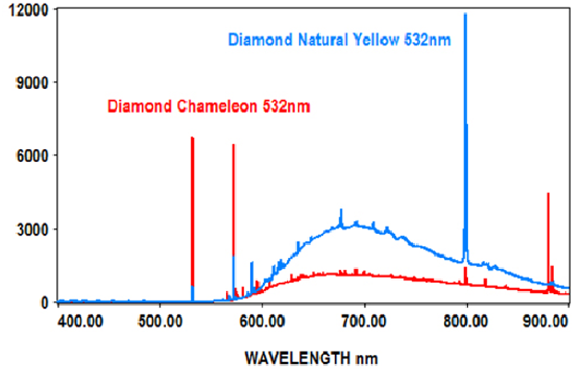
405nm Laser:



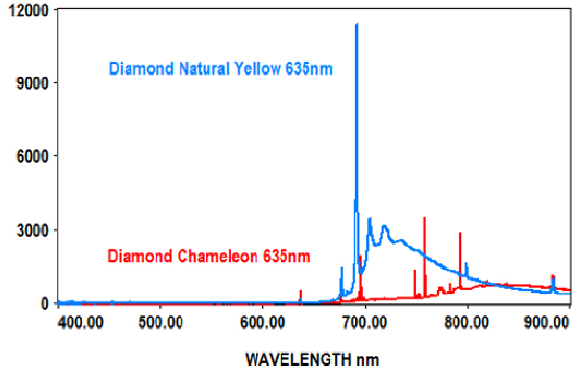
473nm Laser:



532nm Laser:



635nm Laser:



These diamond spectra at four different laser wavelengths are courtesy of Thomas Hainschwang at Gemlab (Liechtenstein) using an 8 x 80um slit with > 10,000 resolving power (ʎ/FWHM).

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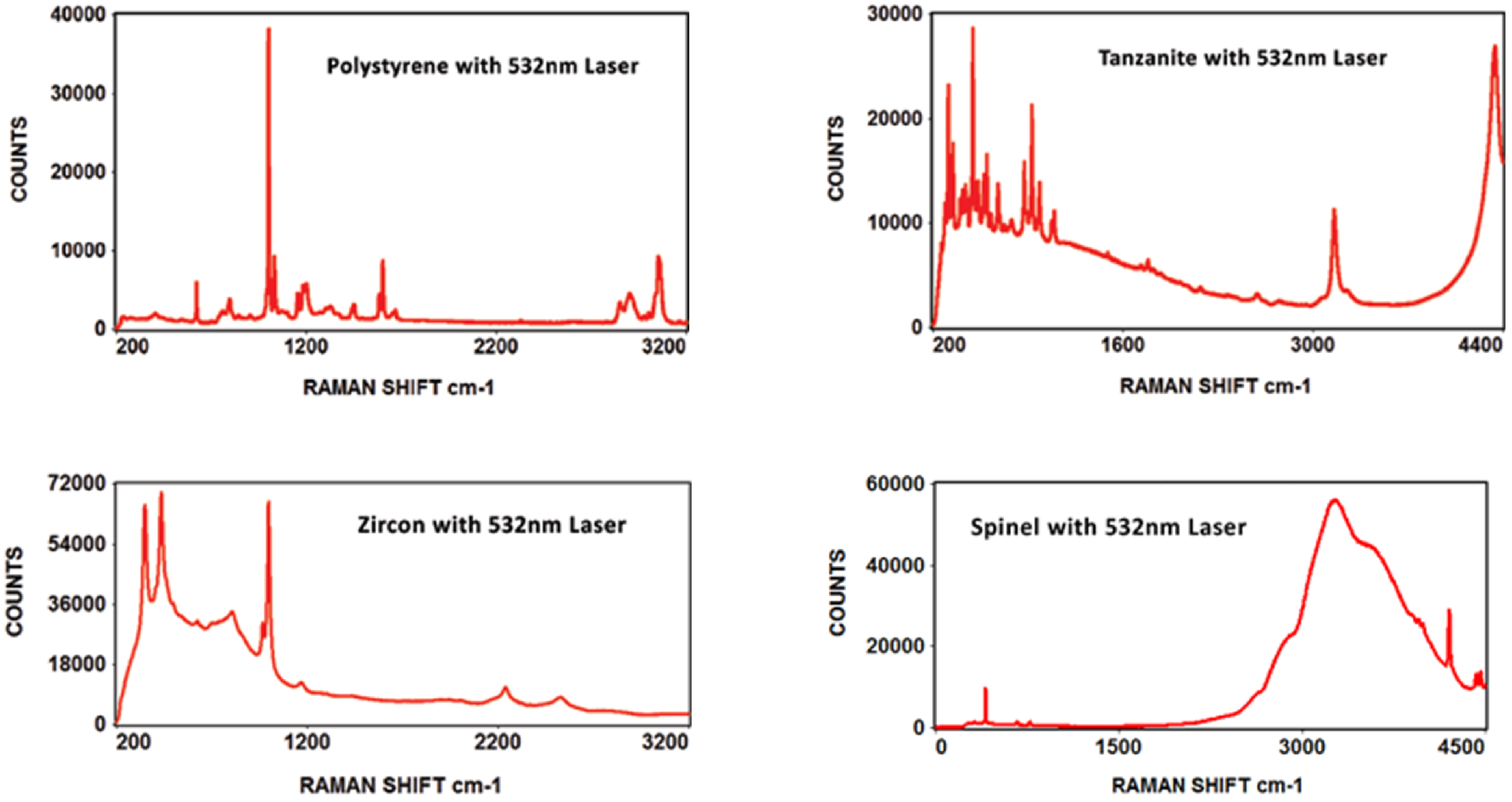
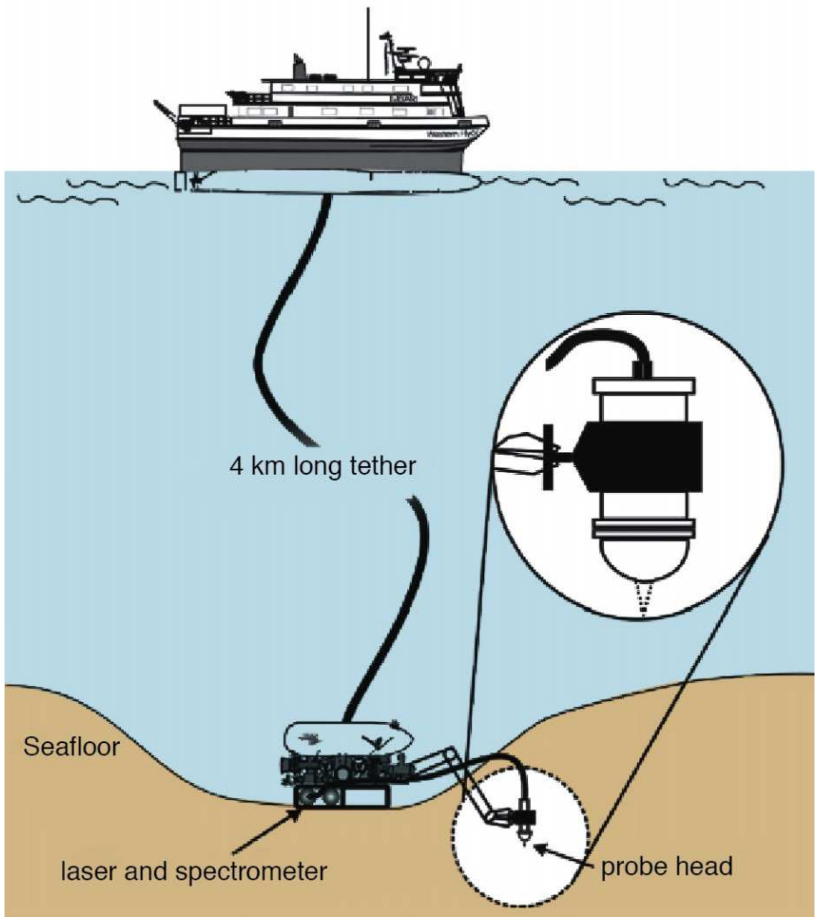
Raman with the EMU-65 VIS/NIR Spectrograph



All Raman spectra were acquired by Catalina Scientific using the EMU-65 VIS/NIR spectrograph and an EMCCD camera with an 8 x 80um slit at F/3.25 and resolution of 1 cm-1 FWHM.

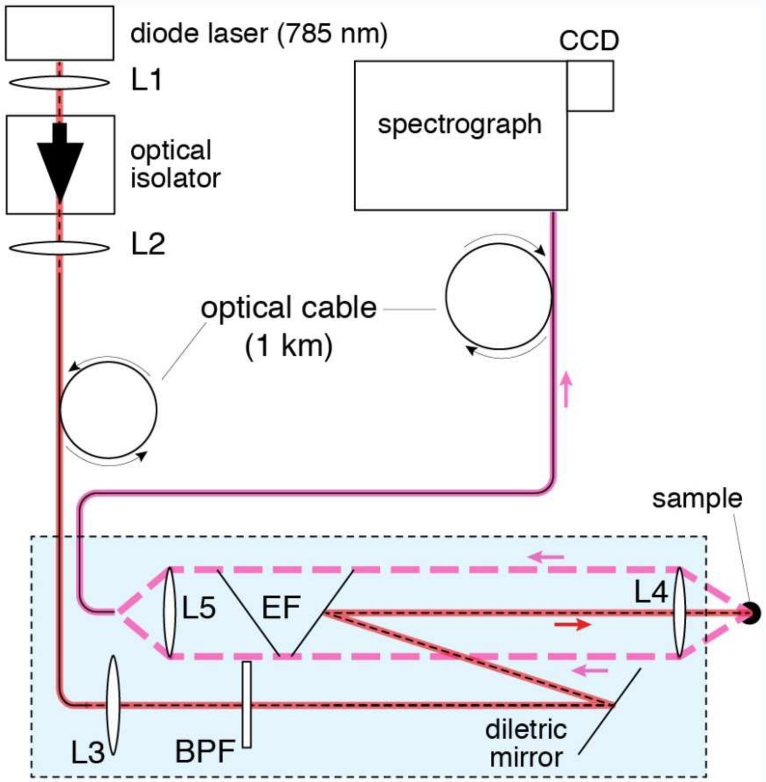
6.3. Raman instruments for ocean studies

1. Deep Ocean Raman *in situ* spectrometer (DORISS)



2.Kronfeldt, H.D. et al. (2010) Proc. S PIE, 7673, 7673B/ 1-8.

1.5 W BA DFB diode laser



1. Pasteris, J.D. et al. (2004) Applied Spectroscopy, 58, 195–208.
In Collaboration with Peter Brewer’s group at Monterey Bay Aquarium Research Institute, Moss Landing CA.

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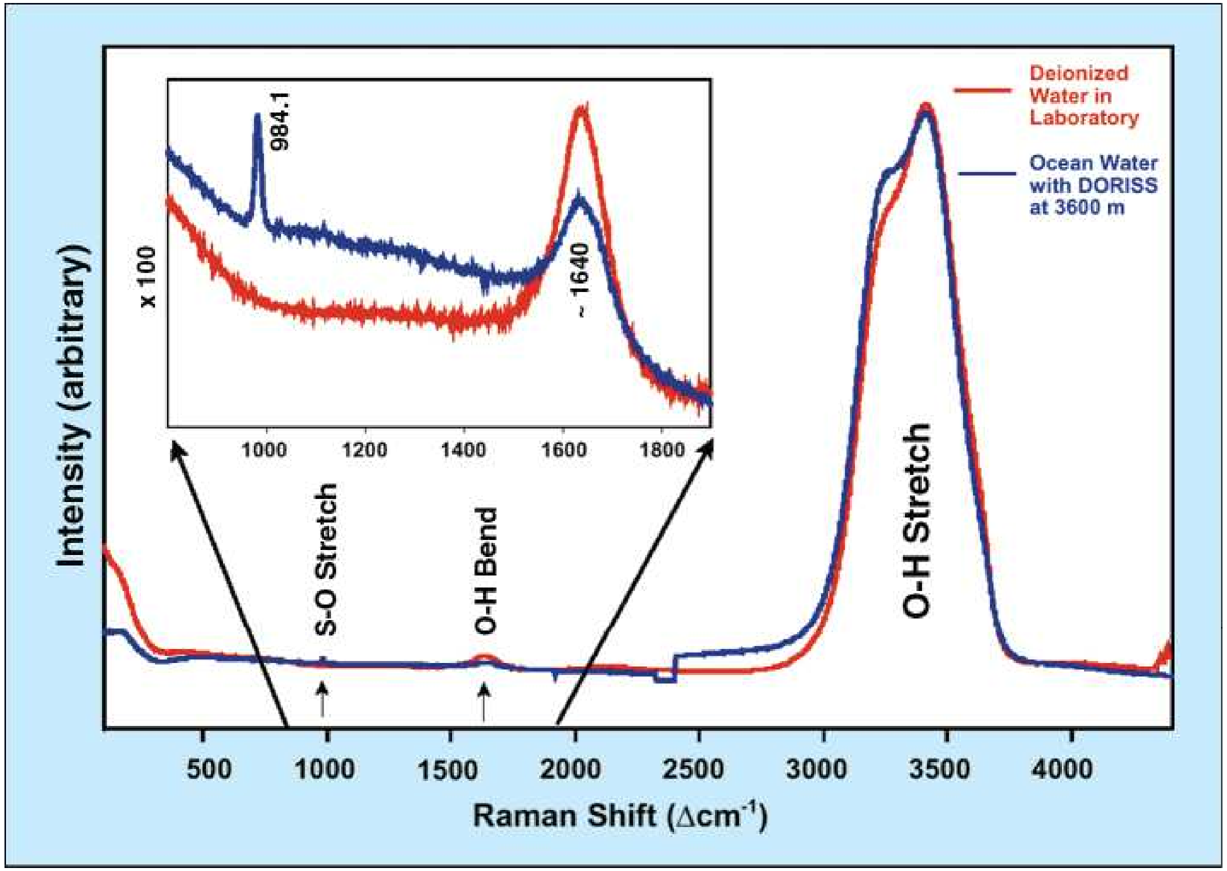
Raman spectra of deionized water at RT and ocean water (MBARI's DORIS System at 3600 m Depth and 4.8C).



Pasteris, J.D. et al. (2004) Applied Spectroscopy, 58, 195–208.

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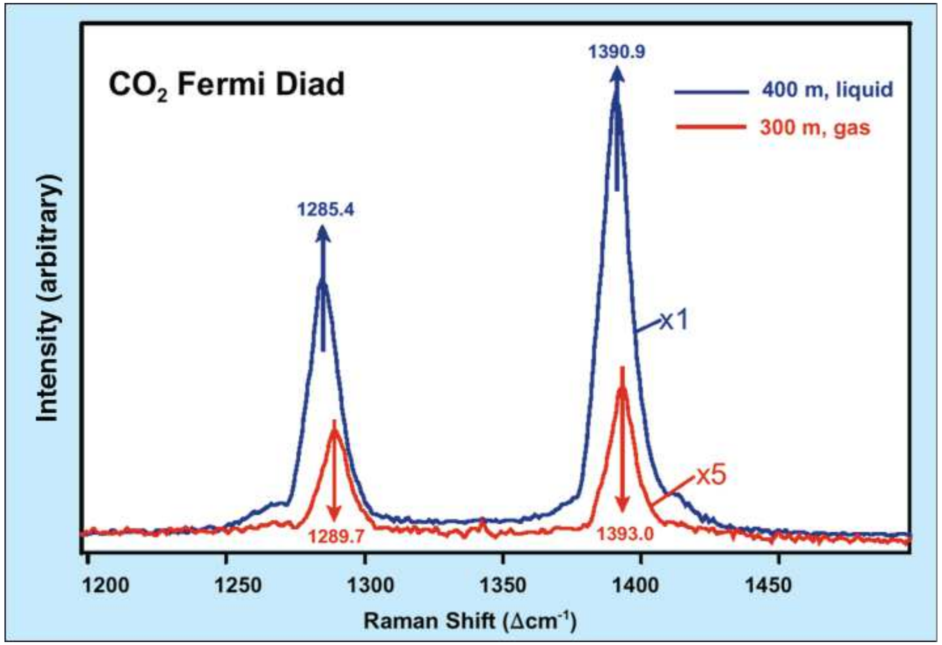
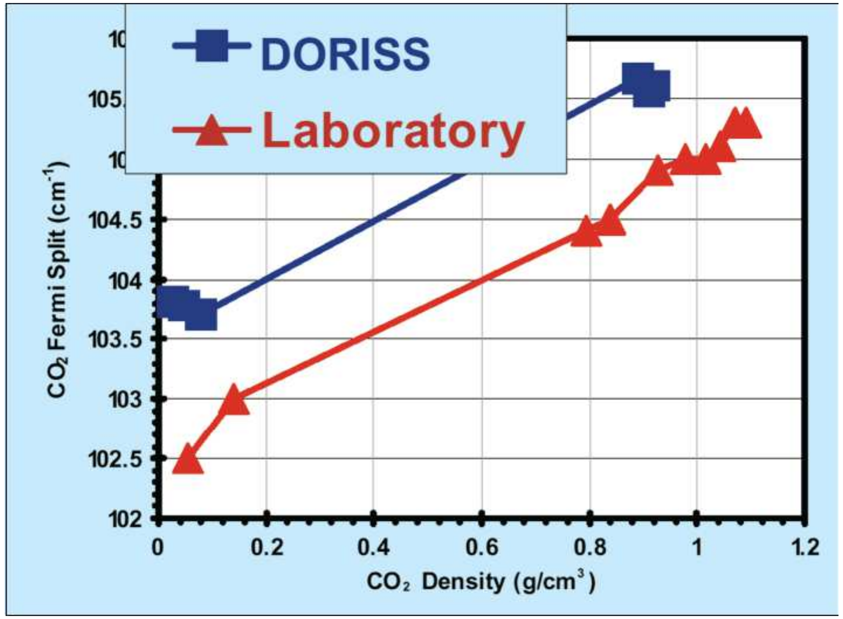
Raman Spectra of Carbon Dioxide Introduced into the Deep Ocean.





Raman offers one important means of monitoring the composition of a CO_2 stream that may be introduced into the ocean, e.g., in connection with studies of ocean sequestration of CO_2. Lab study 23 C, up to 700 bar.
Raman spectroscopy can be used to determine the concentration and speciation(e.g., into CO_3, and HCO_3) of CO_2 dissolved in water.

Pasteris, J.D. et al. (2004) Applied Spectroscopy, 58, 195–208.

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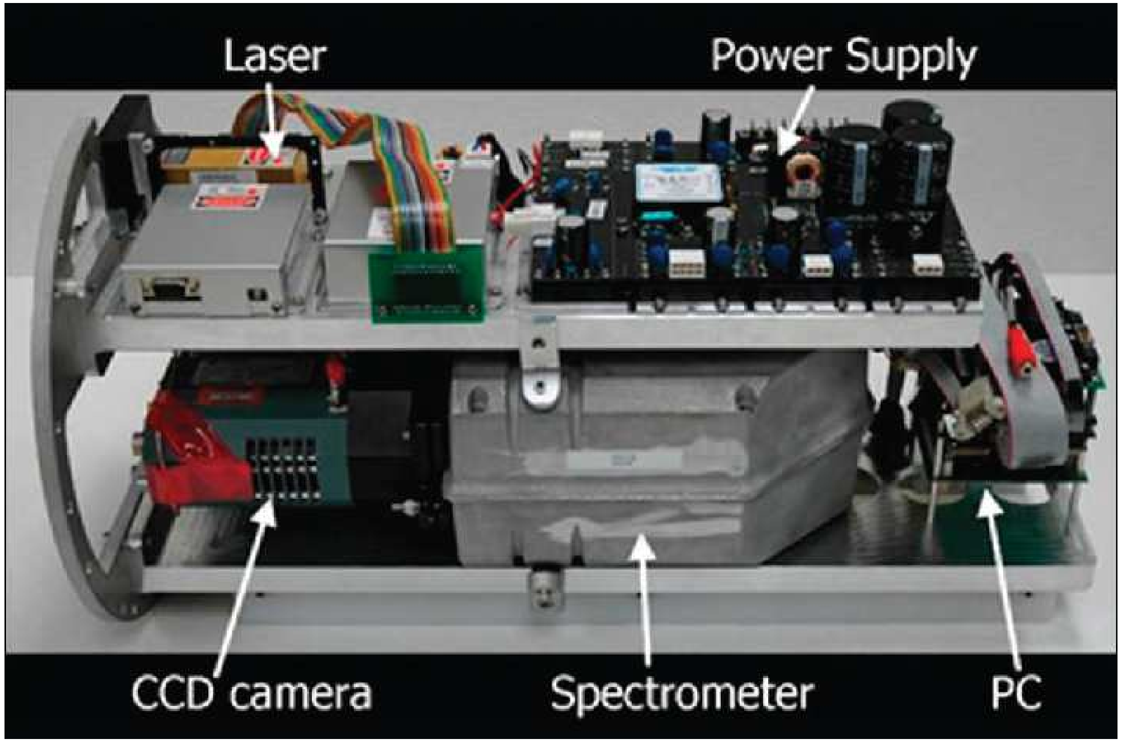
Open view of the DORISS II system designed by Kaiser Optical System & MBARI engineers.



Zhang et al. (2012) Appl. Spectroscopy, 66, 237-249)

Comparison of DORIS I & II Systems

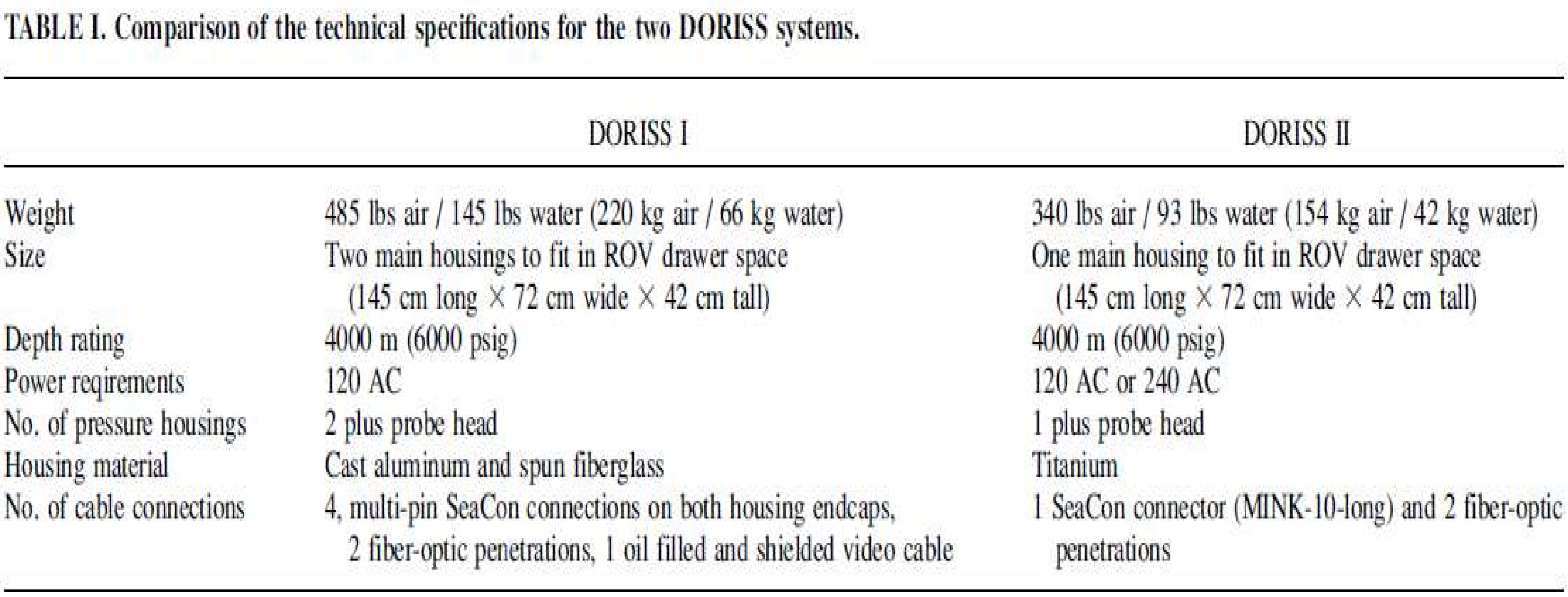
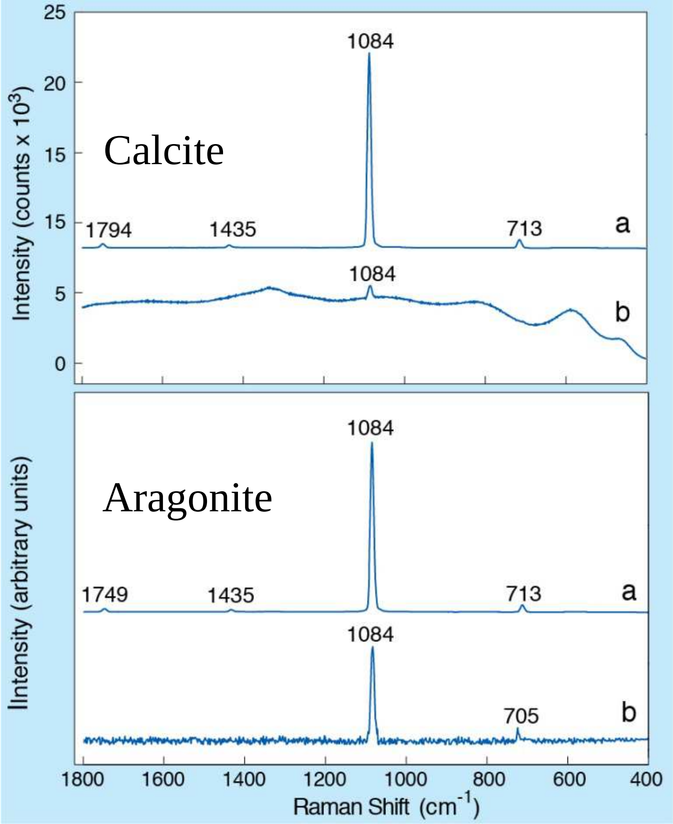


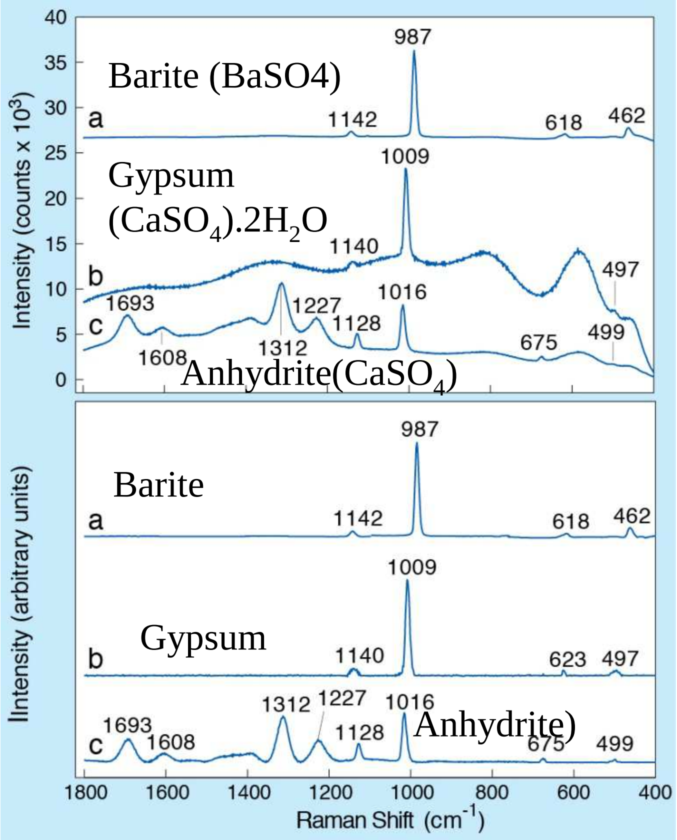
TABLE I. Comparison of the technical specifications for the two DORISS systems.

	DORISS I	DORISS II
Weight	485 lbs air / 145 lbs water (220 kg air / 66 kg water)	340 lbs air / 93 lbs water (154 kg air / 42 kg water)
Size	Two main housings to fit in ROV drawer space (145 cm long × 72 cm wide × 42 cm tall)	One main housing to fit in ROV drawer space (145 cm long × 72 cm wide × 42 cm tall)
Depth rating	4000 m (6000 psig)	4000 m (6000 psig)
Power reqirements	120 AC	120 AC or 240 AC
No. of pressure housings	2 plus probe head	1 plus probe head
Housing material	Cast aluminum and spun fiberglass	Titanium
No. of cable connections	4, multi-pin SeaCon connections on both housing endcaps, 2 fiber-optic penetrations, 1 oil filled and shielded video cable	1 SeaCon connector (MINK-10-long) and 2 fiber-optic penetrations

Zhang et al. (2012) Appl. Spectroscopy, 66, 237-249)

Raman Spectra Measured with 1 km Long Optical Fiber – 785 nm Laser





2.Kronfeldt, H.D. et al. (2010) Proc. S PIE, 7673, 7673B/ 1-8

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Summary

- **Combined Raman-LINF-LIBS system have been developed. The combined system uses only one laser, one telescope, one spectrograph and one ICCD.**
- **We have demonstrated that the combination of these remote sensing techniques are capable of identifying both the molecular and elemental signatures of geological samples.**
- **We have also demonstrated that the LIBS laser is a powerful tool when used to reveal the subsurface elemental and molecular structures. Consequently, surface materials can be removed that may interfere with the Raman probe, remove weathered surfaces revealing the nascent subsurface mineral, or provide a depth profile of the sample.**
- **Combined Raman-LINF-LIBS spectroscopy should have uses in many other research areas.**
- **Applications of Raman applications in deep ocean have become feasible with advancements in Raman instrumentation.**