



Raman Unit



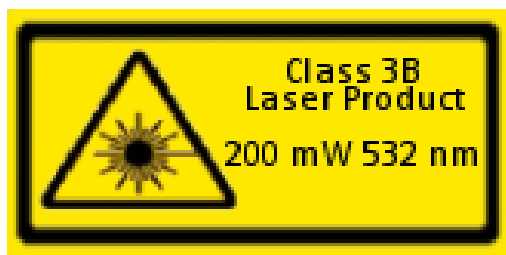
Technical Reference and User Guide

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1. Laser Safety

The laser included with the Raman Unit (RU) is safe to operate, provided the user pays attention to all safety warning and operates the device according to the instructions

1. This is a class IIIB laser device and up to 200 mW of 532nm (NIR) laser light is in use during data acquisition.
2. Only personnel trained in laser safety protocols should be allowed to use this instrument
3. Warning signs have to be posted in the area where the unit is being used.
4. Unauthorized personnel have to be kept out of the area where the unit is being used.
5. The device has to be shut off when not in use and cannot be left unattended while in operation.
6. Safety features cannot be circumvented, or altered.
7. Keep the device on a platform that has clear open area over it (this is the only direction where stray laser beam can be directed).
8. Never look down into the sample holder directly without wearing proper laser safety goggles.
9. This is a class IIIB laser device and up to 200 mW of 532nm (NIR) laser light may be emitted during data acquisition. Only personnel trained in laser safety protocols should be allowed to use this instrument.



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3. Device Information

3.1. Summary

Feature	Configuration	Detailed information
Laser wavelength	532 nm	Appendix A
Laser power	200 mW	
Detector	Ocean Optics HR2000	Appendix B
Spectral range	480 – 640 nm	
Raman shift range	0 – 3000 cm ⁻¹ Stokes-scattering	
Collection method	90° scattering (not configurable)	
Filter	540nm long-pass filter	Appendix C
Depolarization	Not installed	
Sample holder	1" diameter x 3" cylindrical (in-house made)	
Operating software	MATLAB Support package for Ocean Optics spectrophotometers OmniDriver (Ocean Optics) Windows 7 (USB connection) (not compatible with Windows 8!)	
Sample types	Gas, liquid, solid	Appendix F
Power requirement	110V 2A	
Safety features	<ul style="list-style-type: none">• Power switch• Key switch• Combination key switch• Sample holder tamper switch	Appendix D
Design	Self-containing closed box	
Connections	<ul style="list-style-type: none">• 110V power• USB-B female socket	Appendix E
Dimensions	10"x6"x15"	
Weight	3kg (6lbs.)	

3.2. Detailed Information

The **Raman Unit (RU)** is a low-cost Raman spectrophotometer which was built to support CHEM335L, specifically being able to capture the Raman spectrum of carbon dioxide (DryIce®). To that end, the design is restricted to limited feature set.

While the unit was specifically designed to capture the IR spectrum of DryIce®, it has been successfully tested on liquid samples and other solid samples (see Appendix F). The calibrations against these substances show remarkable accuracy with a consistent shift about $3\text{--}4\text{ cm}^{-1}$.

The inside view of RU is shown in Figure 3.1. The 200mW 532nm laser is mounted directly on the sample holder. The filter is mounted at right angle from the laser beam in a holder to which the detector is connected. The connections are SMA905 couplings.

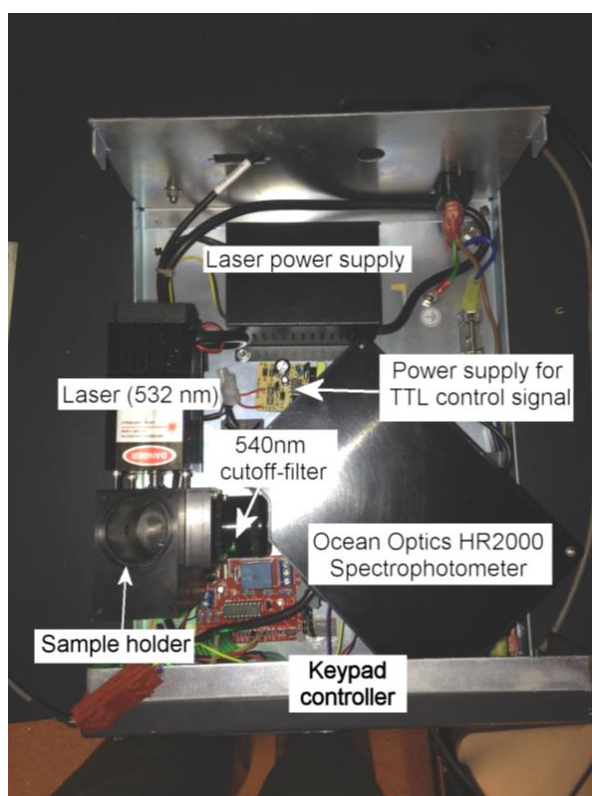


Figure 3.1. Inside view of RU.

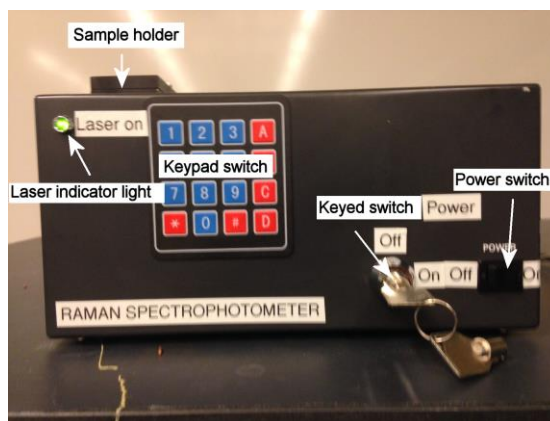


Figure 3.2 Front view of RU.

The sample holder is manufactured from aluminum and it is black anodized. The cover can be removed by lifting it and turning counterclockwise. Opening the sample holder disables the laser through a tamper switch. The sample holder can accommodate up to 1"x3" cylindrical sample or container (e.g. standard liquid vial), however for solid samples smaller sample is recommended to allow the laser to scatter to the detector (e.g. standard DryIce® piece).

The RU has a 540-nm long-pass filter to minimize stray light from the laser. Since the Anti-Stokes region is blocked by the filter, the device can only be used to observe the Stokes region.

The detector is an Ocean Optics HR2000 spectrophotometer with H9 gratings. This configuration is suitable to capture spectra between 480nm and 640 nm on 2048 pixel, which gives about 0.1 cm^{-1} resolution, however due to the laser 532 nm wavelength and the 540-nm long-pass filter, only the range above 540 nm can be effectively used.

No effort beyond has been made for optical alignment beyond basic manual tweaking as the power of the laser is sufficient even if there is considerable amount of loss.

The front view of the device is shown in Figure 3.2 with the controls. The power switch powers the entire unit. The cylindrical key switch provides the power to the controller of the electric lock. The keypad allows the user to key in the four-digit security code to enable the laser. The green indicator shows when the laser beam is active.

The RU is equipped with several safety features, including the power switch, the cylindrical key switch, the electric lock with a four-digit code combination, and the tamper switch which disables the laser when the sample holder lid is moved. Power switch powers the entire unit. A cylindrical key switch enables the 5V power for the controller of the electric lock through the tamper switch, therefore the power to the controller can be interrupted by the key switch or the tamper switch, which in turns disables the laser, the four-digit code has to be keyed in to enable the laser again. When the laser is on, entering "1" on the keypad also disables the laser.

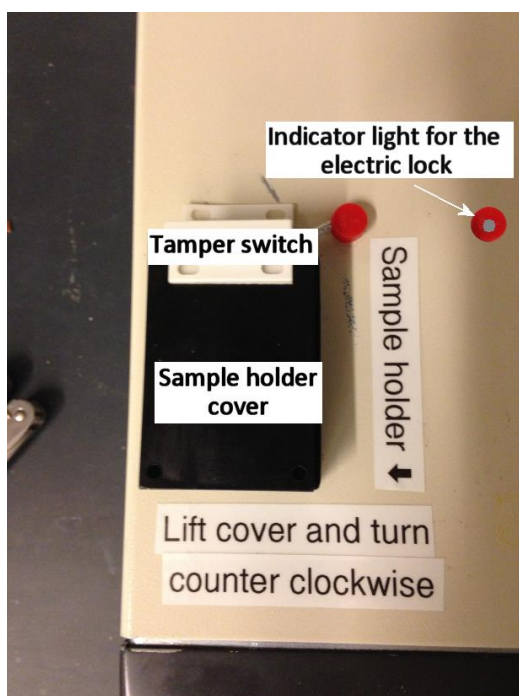


Figure 3.3 Top view of the RU

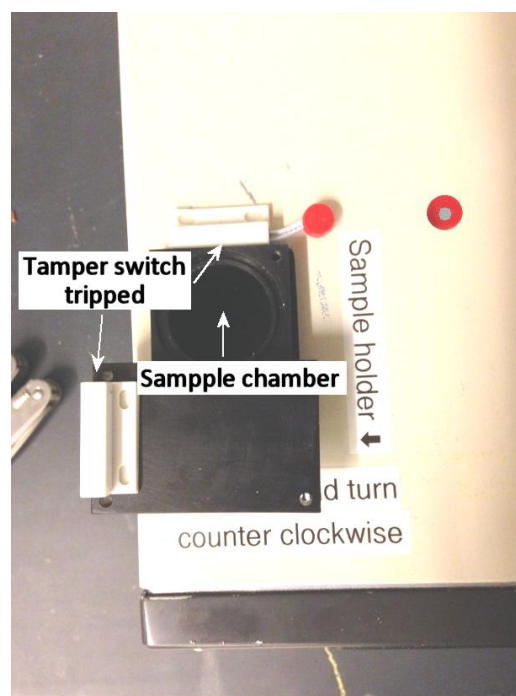


Figure 3.4 Sample holder opened

The top view of the device is shown in Figure 3.3. The sample holder can be opened by lifting the cover until the stop and turning it (Figure 3.4). Opening the cover trips the tamper switch and disables the laser. The electric key indicator displays status of the electric lock. The red and green LEDs are located on the circuit board and the indicator is a glass tube mounted in the cover that relays the light from these LEDs to the user.

The device has a standard power cord connector for 110V power (fused at 4A). It is connected to a PC with a standard USB cable (USB-B male/USB-A male). Both connectors are located at the back of the unit.

4. Software Environment

4.1. Software Installation

Since CHEM335L is heavily using MATLAB, only this venue has been investigated.¹ Setting up the software environment includes the following steps:

- Installing the OmniDriver package from Ocean Optics
- Installing the Ocean Optics Spectrometers Support Package
- Installing the MATLAB Instrument Driver

Please note, OmniDriver from Ocean Optics didn't work under Windows 8 (although theoretically it is supported), only on Windows 7. The steps of the installation are:

1. Install MATLAB with the Instrument Control Toolbox.
2. Download the OmniDriver package (OmniDriver-2.37-winXX-installer.exe) from the Ocean Optics website² and install it (no password needed for the end-user installation).
3. Download the Ocean Optics Spectrometers Support Package (oceanopticsspectrometers.mlpkginstall) from the MathWorks website³ and install it. Alternatively, in MATLAB the `supportPackageInstaller` command will invoke the Installer wizard and select the Ocean Optics Spectrophotometers from the list.
4. Download the Ocean Optics spectrometers - MATLAB Instrument Driver (OceanOptics_OmniDriver.zip) from MATLAB website⁴ and unzip it into a folder that it will reside (e.g. C:\Program Files\MATLAB\R2014a) and make sure that it is in the MATLAB path.
5. Configure MATLAB to use the Ocean Optics driver
 - a. From the folder that OmniDriver was unzipped, edit the file called `javaclasspath.txt` and add (if you used the standard folder when installed OmniDriver from Ocean Optics):
C:\Program Files\Ocean Optics\OmniDriver\OOI_HOME\OmniDriver.jar
and save it.
 - b. From the same folder, edit the file called `javalibrarypath.txt`, and add:
C:\Program Files\Ocean Optics\OmniDriver\OOI_HOME\

¹ The original OO_Base32 software (running on Windows XP or in a Windows XP emulator on a Windows 7 box has been successfully tested to run the device. Overture from Ocean Optics is supposed to run the device, however it has not been tested.

² 32 bit: <http://downloads.oceanoptics.com/OmniDriver/Release-2.37/Windows%2032-bit/OmniDriver-2.37-win32-installer.exe>

64 bit: <http://downloads.oceanoptics.com/OmniDriver/Release-2.37/Windows%2064-bit/OmniDriver-2.37-win64-installer.exe>

³ <http://www.mathworks.com/matlabcentral/fileexchange/42888?download=true>

⁴ <http://www.mathworks.com/matlabcentral/fileexchange/submissions/38572/v/6/download/zip>

and save it.

6. Restart MATLAB

Note: periodically MATLAB drops the OmniDriver folder from its path, and it has to be added manually.

4.2. Basic MATLAB Script and Function to Operate RU

The following MATLAB function captures a single spectrum (background or actual spectrum):

```
function [w s] = OO_Grab(xflag, iTime, iPass, iBox)
    %xflag: flag for type of return scale:
    % 'wl' = wavelength
    % 'wlCO2' = wavelength range relevant to CO2
    % 'wn' = wavenumber
    % 'wnCO2' = wavenumber range relevant to CO2
    %iTime = integration time (in s)
    %iPass = number of spectra to be averaged
    %iBox = number of points to be averaged in one spectrum

    spectrometerObj = icdevice('OceanOptics_OmniDriver.mdd');
    connect(spectrometerObj);
    disp(spectrometerObj);
    %integrationTime = 200000000;
    iTime = iTime*1e6;
    spectrometerIndex = 0;
    channelIndex = 0;
    enable = 1;
    numOfSpectrometers = invoke(spectrometerObj, 'getNumberOfSpectrometersFound');
    display(['Found ' num2str(numOfSpectrometers) ' Ocean Optics spectrometer(s).']);
    spectrometerName = invoke(spectrometerObj, 'getName', spectrometerIndex);
    spectrometerSerialNumber = invoke(spectrometerObj, 'getSerialNumber', spectrometerIndex);
    display(['Model Name : ' spectrometerName])
    display(['Model S/N : ' spectrometerSerialNumber]);
    invoke(spectrometerObj, 'setIntegrationTime', spectrometerIndex, channelIndex, iTime);
    invoke(spectrometerObj, 'setScansToAverage', spectrometerIndex, channelIndex, iPass);
    invoke(spectrometerObj, 'setCorrectForDetectorNonlinearity', spectrometerIndex, channelIndex, enable);
    invoke(spectrometerObj, 'setBoxcarWidth', spectrometerIndex, channelIndex, iBox);
    % invoke(spectrometerObj, 'setCorrectForElectricalDark', spectrometerIndex, channelIndex, enable);
    wavelengths = invoke(spectrometerObj, 'getWavelengths', spectrometerIndex, channelIndex);
    disp('=====');
    if strcmp(xflag, 'wl')
        w = wavelengths;
        disp(['Wavelength range: ' num2str(min(w)) ' - ' num2str(max(w)) ' nm']);
    elseif strcmp(xflag, 'wlCO2')
        w = wavelengths(934:1136);
        disp(['Wavelength range: ' num2str(min(w)) ' - ' num2str(max(w)) ' nm']);
    elseif strcmp(xflag, 'wn')
        w = (1 ./ (532*1e-9) - 1 ./ (wavelengths * 1e-9))/100;
        disp(['Wavenumber range: ' num2str(min(w)) ' - ' num2str(max(w)) ' cm^-1']);
    elseif strcmp(xflag, 'wnCO2')
        w = wavelengths(934:1136);
        w = (1 ./ (532*1e-9) - 1 ./ (w * 1e-9))/100;
        disp(['Wavenumber range: ' num2str(min(w)) ' - ' num2str(max(w)) ' cm^-1']);
    end
    disp('Capturing requested type of spectrum....');
    spectralData = invoke(spectrometerObj, 'getSpectrum', spectrometerIndex);
    if strcmp(xflag, 'wlCO2') || strcmp(xflag, 'wnCO2')
        s = spectralData(934:1136);
    else
        s = spectralData;
    end
    disp('Requested type of spectrum captured');
    disp('=====');
    %%
```


Input parameters:

xflag	Flag to determine the returned scale: wl = wavelength (nm) wlCO2 = wavelength range relevant to CO ₂ (nm) wn = wavenumber (cm ⁻¹) wnCO2 = wavenumber range relevant to CO ₂ (cm ⁻¹)
iTime	Integration time (ms). Typically 80-300ms seem to work.
iPass	Number of spectra to be averaged
iBox	Number of points to be averaged in one spectrum (moving average)

Returning data:

w	Wavelength or wavenumber vector
s	Spectral data vector

The following script can be used to collect a background and a spectrum:

```
clear
disp('Press any key to capture background!(Make sure that the laser is on!');
pause;
[w bg] = OO_Grab('wnCO2',320,40,1);
disp('Press any key to capture a spectrum!(Make sure that the laser is on!');
pause;
[w sp] = OO_Grab('wnCO2',320,40,1);
s = sp - bg;
plot(w,s);
```

To reduce the noise, the smooth function can be used (with different smoothing parameters, e.g. 7):

```
s = smooth(sp - bg,7);
```

For solid samples simple background correction typically is not sufficient. To use a more effective background correction, one can fit a polynomial on the corrected spectrum (background subtracted from the spectrum of the sample), and subtract the fitted values from the corrected spectrum (e.g. using an 11th order polynomial):

```
clear
disp('Press any key to capture background!(Make sure that the laser is on!');
pause;
[w bg] = OO_Grab('wnCO2',320,40,1);
disp('Press any key to capture a spectrum!(Make sure that the laser is on!');
pause;
[w sp] = OO_Grab('wnCO2',320,40,1);
s = sp - bg;
p = polyfit(w,s,11);
s_c = polyval(p,w);
plot(w,s-s_c);
```

This approach may result in some intensities being negative, however the peak locations are accurate. Also combination of the methods discussed above can also be used.

5. Operating the Instrument

5.1. General Setup

1. Connect the device to the power (Do not turn it on!).
2. Connect the device to a configured PC with a USB cable (USB-A male/USB-B male).
3. Start MATLAB. Collect a spectrum to test the setup.

Note: The detector will function without the power turned on since it is drawing power from the computer. If MATLAB cannot find the driver, add the path of the driver to the MATLAB path (see above).

5.2. Running a Liquid Sample

1. Obtain the four-digit code and the key to the key switch.
2. Turn on the power switch.
3. Turn the key switch to the ON position.
4. Open the sample holder by lifting it to the stop and turning it counter clockwise.
5. Place the vial used for blank in the holder.
Note: you may have to remove the cap from the vial if the cover cannot be closed properly.
6. Close the cover firmly.
7. Enter the four-digit code on the keypad. Press each key firmly.
 - a. The key indicator on the top of the device should blink red for each key entered.
 - b. The key indicator should blink a few times green after the successful entry of the code. Now the laser is on, the "Laser ON" light should be green on the front of the device.
 - c. If the wrong key was entered, the key indicator will blink red a few times.
Note: after three unsuccessful code entry attempts the electric key will be locked for a minute while it is not receiving an input.
 - d. If after entering the code the key indicator doesn't blink red or green, likely one or more key(s) was/were missed. In this case, press any key, until the key indicator blinks red a few times, and then attempt to enter the correct key.
8. Collect the spectrum.
9. Press "1" on the keypad to disable the laser.
Note: even if the key "1" was not pressed, opening the sample holder will trip the tamper switch and disables the laser.
10. Replace the vial with the sample.
11. Repeat steps 5-8 to collect the spectrum of the sample.
12. When done, turn the keys witch to the OFF position, remove and return the key. Switch off the power to the unit with the "Power Switch".

5.3. Running a Solid Sample

1. Obtain the four-digit code and the key to the key switch.

2. Turn on the power switch.
3. Turn the key switch to the ON position.
4. Open the sample holder by lifting it to the stop and turning it counter clockwise.
5. Place the vial used for blank (if there is one) in the holder. Place the vial as far as possible from the laser beam and the opening to the detector so that the laser can scatter from the sample into the detector (see Figure 5.1).

Note: you may have to remove the cap from the vial if the cover cannot be closed properly. Also, the vial shouldn't be more than $\frac{1}{2}$ " in diameter.

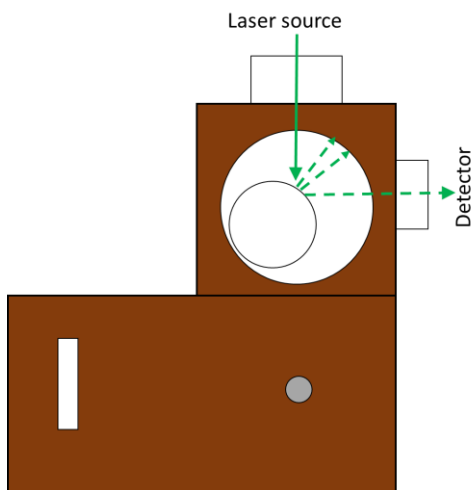
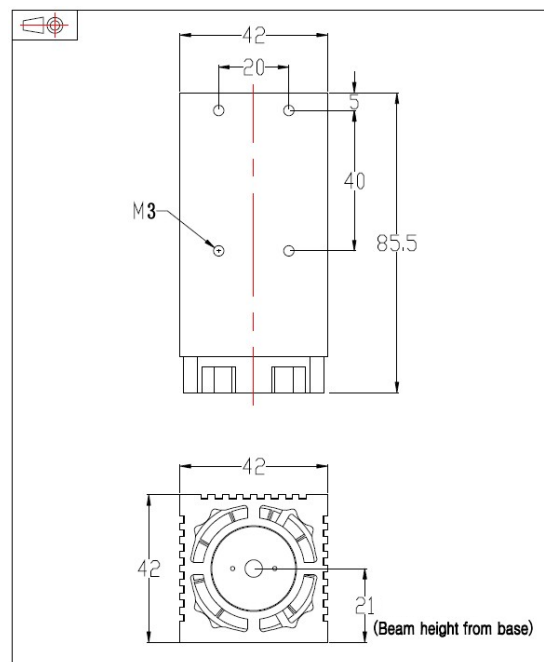
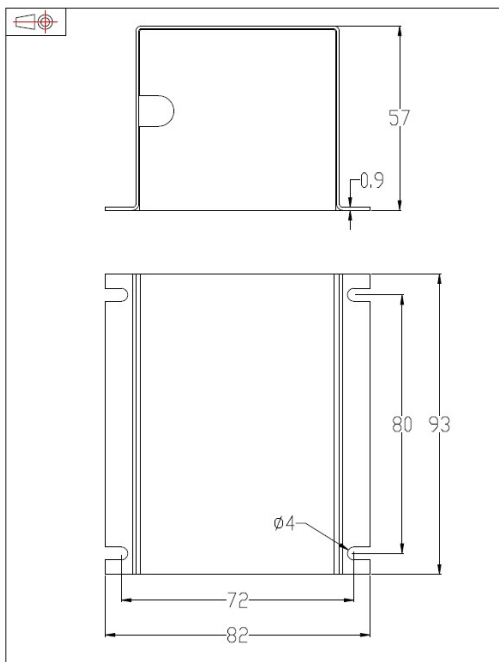


Figure 5.1 Placing solid sample in the sample holder

6. Close the cover firmly.
7. Enter the four-digit code on the keypad. Press each key firmly.
 - a. The key indicator on the top of the device should blink red for each key entered.
 - b. The key indicator should blink a few times green after the successful entry of the code. Now the laser is on, the "Laser ON" light should be green on the front of the device.
 - c. If the wrong key was entered, the key indicator will blink red a few times.
Note: after three unsuccessful code entry attempts the electric key will be locked for a minute while it is not receiving an input.
 - d. If after entering the code the key indicator doesn't blink red or green, likely one or more key(s) was/were missed. In this case, press any key, until the key indicator blinks red a few times, and then attempt to enter the correct key.
8. Collect the spectrum.
9. Press "1" on the keypad to disable the laser.
Note: even if the key "1" was not pressed, opening the sample holder will trip the tamper switch and disables the laser.
10. Replace the vial with the sample.
11. Repeat steps 5-8 to collect the spectrum of the sample.
12. When done, turn the keys witch to the OFF position, remove and return the key. Switch off the power to the unit with the "Power Switch".

Appendix A: 532 nm Laser Specifications

Model	G150
wavelength(nm)	532
Output power(mw)	>150
Transverse mode	TEM00
Operating mode	CW
Power stability (rms, over 4 hours)	<5%
Warm-up time (minutes)	<15
M2 factor	<1.2
Beam divergence, full angle (mrad)	<1.5
Beam diameter at the aperture (mm)	~3
Beam height from base plate (mm)	21
Polarization ratio	>100:1
Beam roundness	>90%
Operating temperature (°C)	10~35
Power supply (90~260VAC)	93(L)×82(W)×57(H)
Dimensions of Laser Head (mm)	85.5(L)×42(W)×42(H)
Modulation option	TTL/Analog modulation0-
Expected lifetime (hours)	5000
Warranty period	3+3 WARRANTY

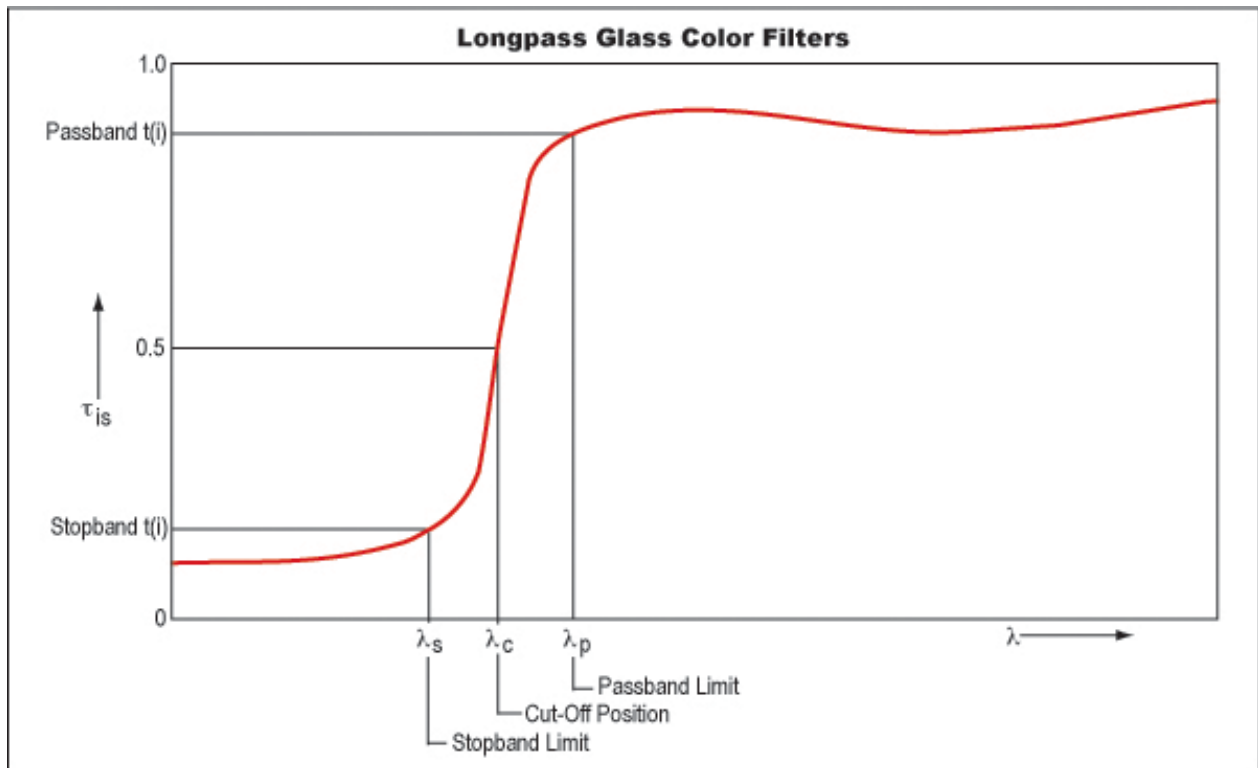


Appendix B: Specification of the Ocean Optics HR200 Spectrophotometer Detector

Dimensions:		148.6 mm x 104.8 mm x 45.1 mm
Weight:		570 grams
Power Consumption:		95 mA @ 5 VDC
Detector:		Sony ILX511 linear CCD array
Detector Range:		200-1100 nm
Pixel size:		14 μm x 200 μm
Optical bench:		f/4, 101 mm focal length
Gratings:	Grating number	H9
	Intended use	VIS-NIR
	Groove density	1200
	Spectral range	165-205nm
	Blaze Wavelength	Holographic VIS
	Best efficiency (<30%)	400-800 nm
Pixel elements:		2048
Entrance Aperture:		5, 10, 25, 50, 100 or 200 μm wide slits or fiber (no slit)
Order-sorting filters:		Not installed
Stray Light:		<0.05% at 600 nm; <0.10% at 435 nm
Dynamic Range:		2×10^8 (system); 2000:1 for a single scan
Fiber Optic Connector:		SMA 905 to single-strand optical fiber 0.22 NA)
Data Transfer Rate:		Full scans into memory every 13 milliseconds
Integration Time:		3 milliseconds to 65 seconds
Operating Systems:		Windows 98/ME/2000/XP, Mac OS X and Linux when using the USB interface on desktop or notebook PCs.
		Any 32-bit Windows operating system when using the serial port on desktop or notebook PCs.

Appendix C: Installed Long-Pass Filter

Brand	Edmund Scientific (#66-051)
Wavelength	VIS
Glass/Filter Number	Hoya O-54
Stopband Limit λ_s (nm)	498
Cut-Off Position λ_c (nm)	540 \pm 6
Passband Limit 1 λ_{p1} (nm)	570
Spectral Transmittance t_p (%)	95
Density (g/cm^3)	2.68
Transformation Temperature ($^{\circ}\text{C}$)	560
Color	Orange
Diameter (mm)	25.4
Diameter (inches)	1
Dimensional Tolerance (mm)	± 0.38
Thickness (mm)	2.5
Reflection Factor P_d	0.92
Surface Quality	80 - 50
Coating	Uncoated
Cut-On Wavelength (nm)	540
Substrate	Colored Glass
Type	Longpass Filter
RoHS	Exempt



Appendix D : Safety Keypad Configuration

D.1 Programming the lock

1. Power down the device
2. Install the jumper across the PG-GD pins
3. Key in “*22” (red LED blinks)
4. Enter a 4 digit code (green LED blinks)
5. Note: Lock feature can be programmed with “*11” (not used here)

D.2 Operating the lock

1. Enter the 4 digit code
2. Green LED blinks if code is correct, and turns on the laser
3. Red LED blinks if the code was not correct
4. Press “1” to shut off the laser

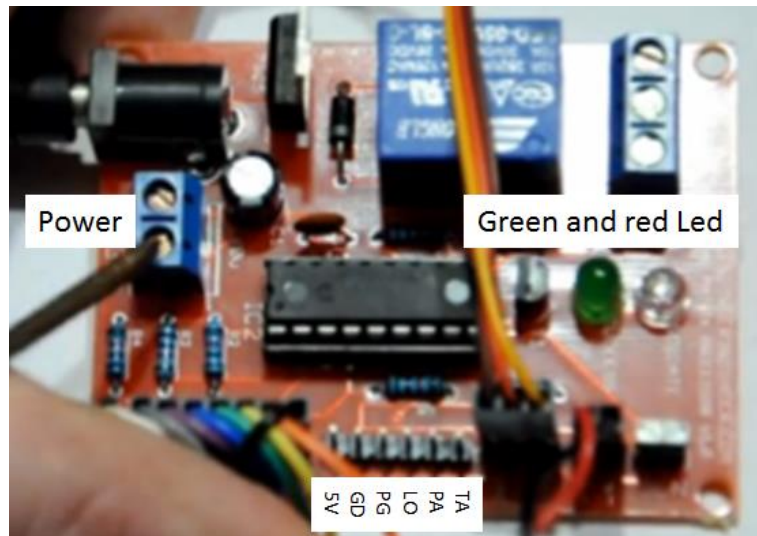
D.3 Notes

1. LEDs are visible on the top of the RU through the indicator light, right from the sample holder (look directly down when observing)
2. If wrong code was entered (red LED blinks), enter the code again. After three unsuccessful attempt the unit locks itself for 1 min.
3. If nothing happens after entering the 4 digit code, likely one or more digit was missed. In this case press any key until the red LED blinks, and enter the code again.
4. The device is programmed with **8546** at the time of writing these instructions
5. The GD and PA pins provide the 5V TTL signal for the power supply of the laser (see wiring diagram)

D.4 Keypad and controller of the safety lock

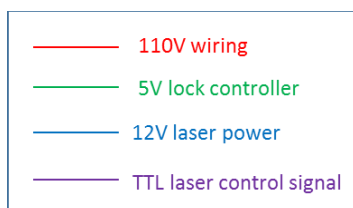
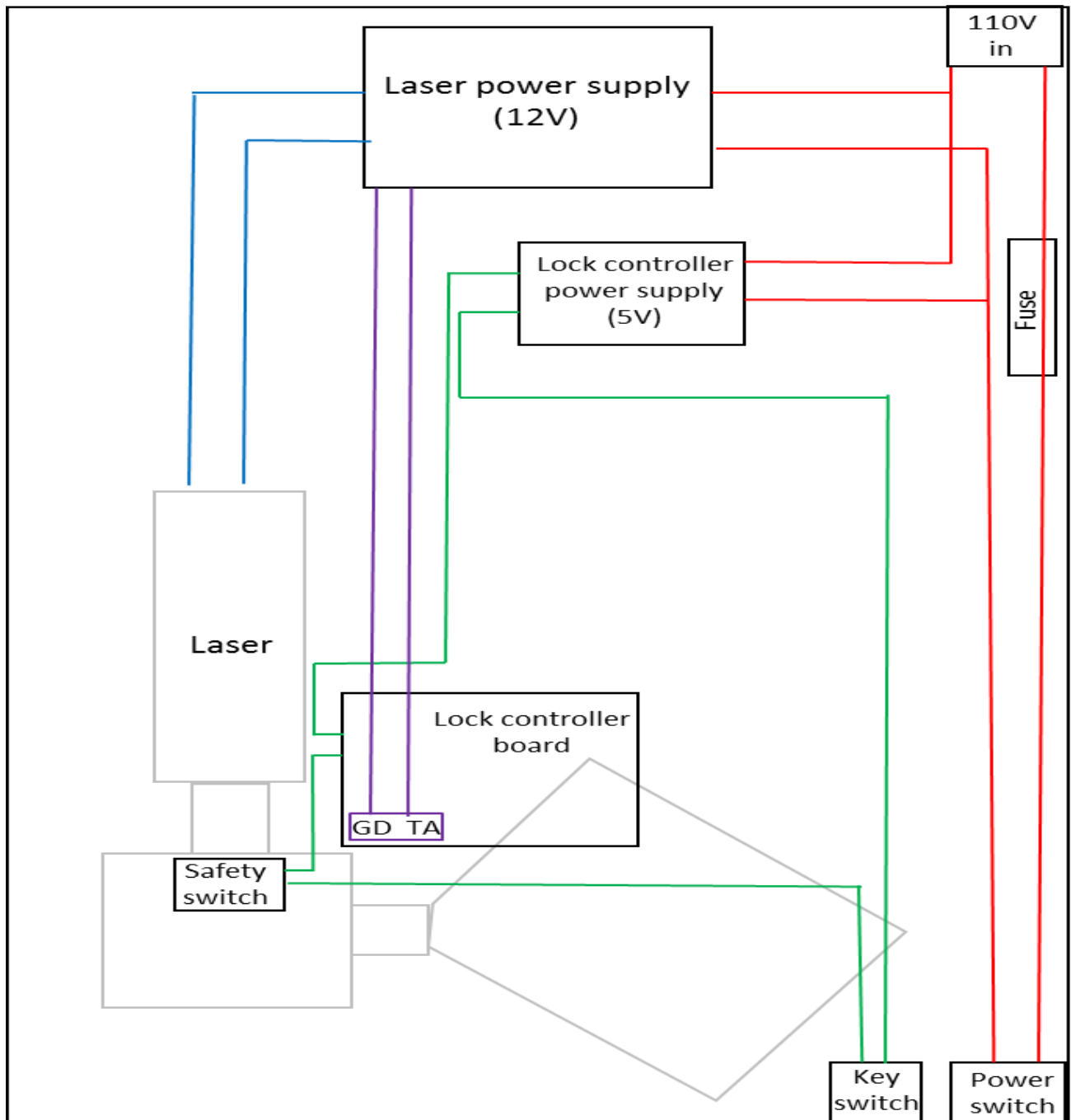


Security keypad



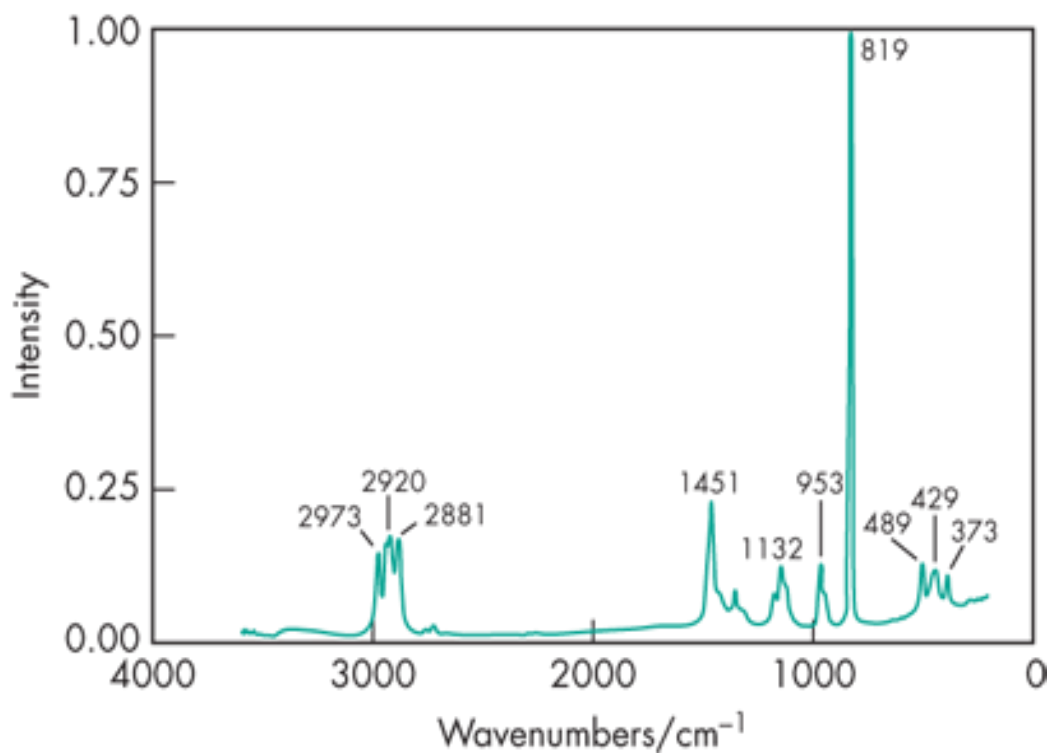
Pin layout and wiring of the keypad controller

Appendix E : Wiring Diagram of RU

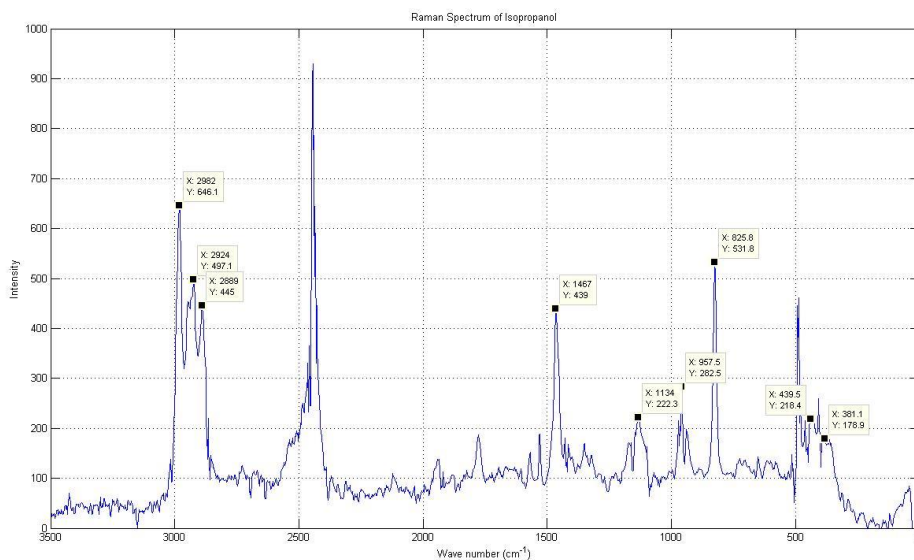


Appendix F : Calibration and Test Runs of RU

F.1 Calibration with Isopropanol (IPA)

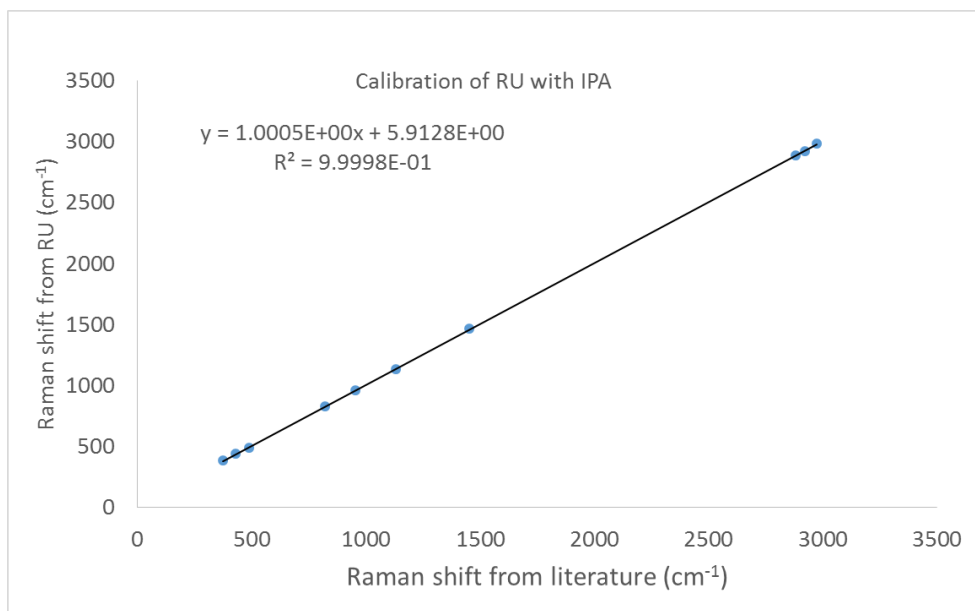


Expected Raman Spectrum of Isopropanol⁵



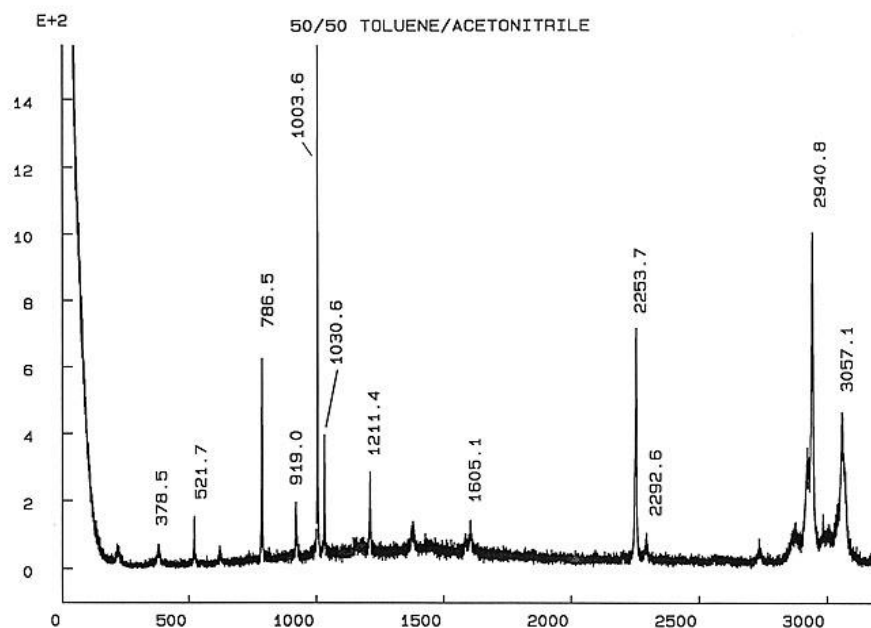
Experimental Raman Spectrum of IPA obtained with RU

⁵ https://www.medicinescomplete.com/mc/excipients/2012/Excisopropyl_alcoholR001_default.png

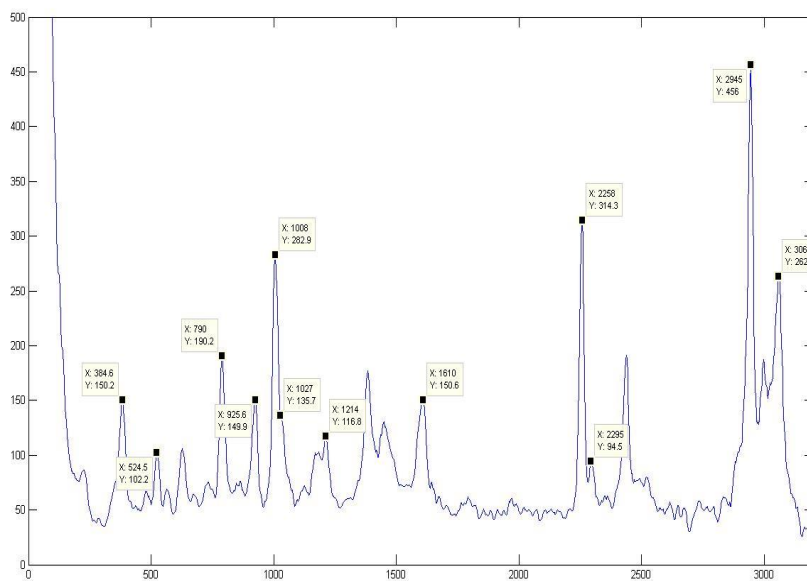


Calibration curve of RU against literature values for IPA

F.2 Calibration with 50% Acetonitrile/50% Toluene

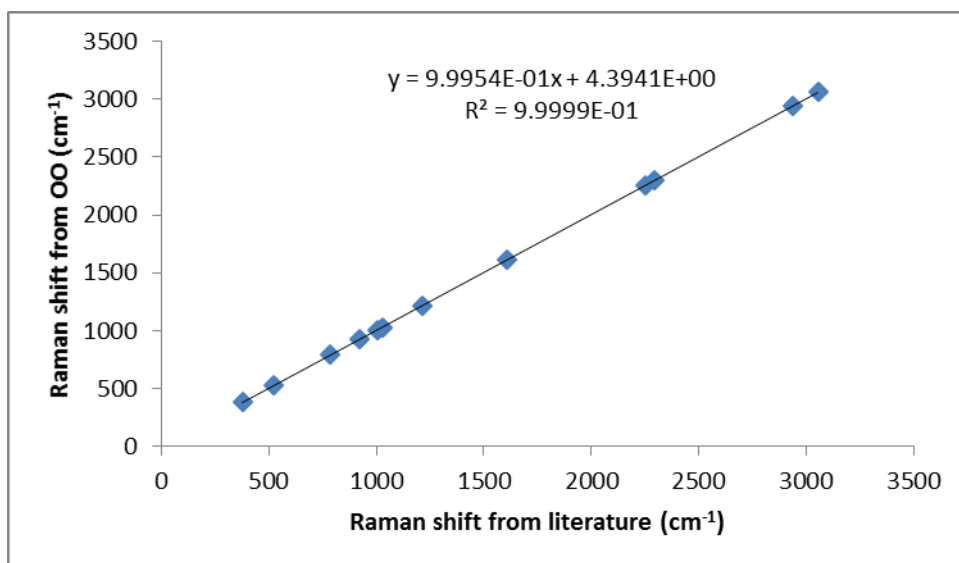


Expected Raman Spectrum of 50% Acetonitrile/50% Toluene⁶



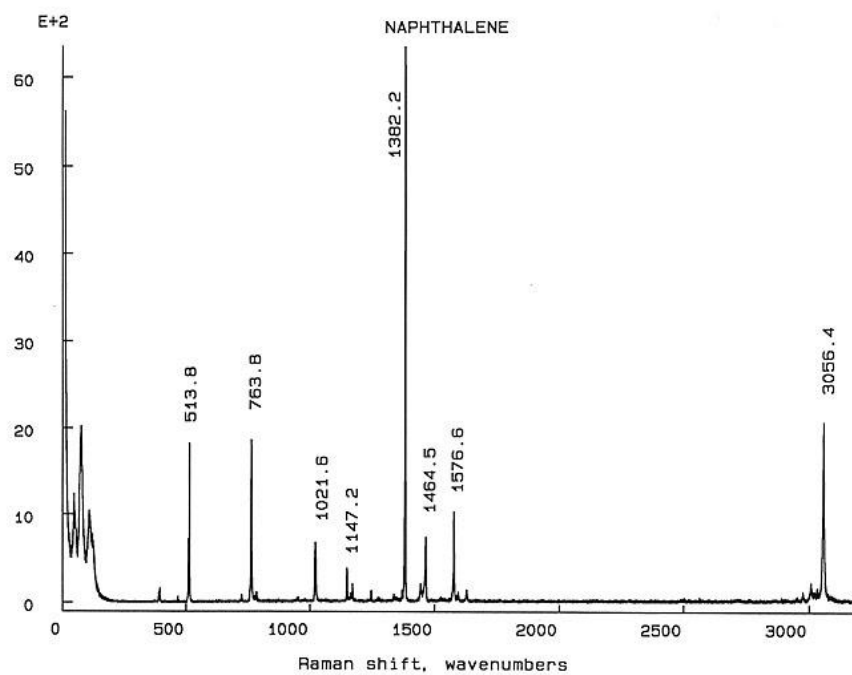
Experimental Raman Spectrum of 50% Acetonitrile/50% Toluene obtained with RU

⁶ <http://www.chem.ualberta.ca/~mccreery/ramanmaterials.html>

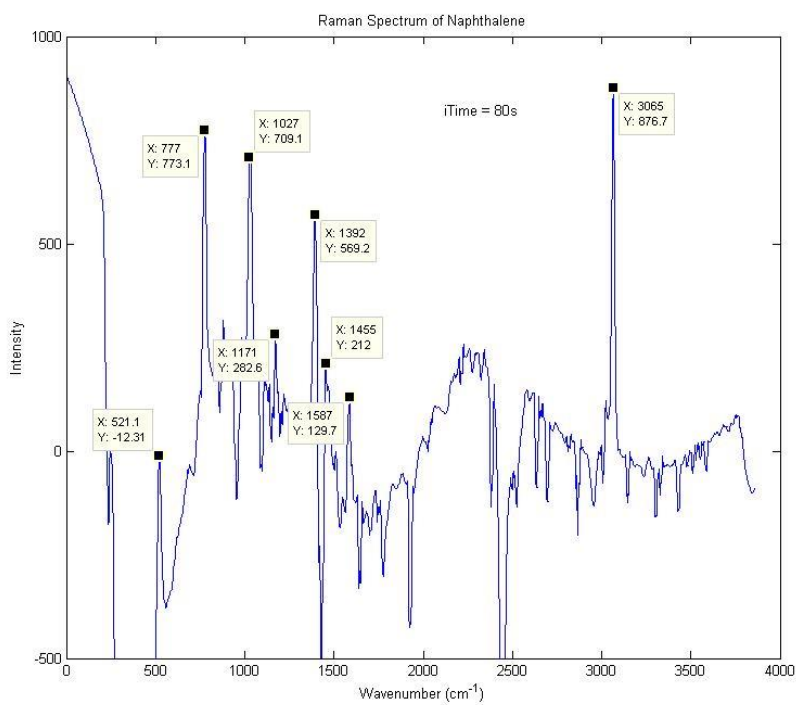


Calibration curve of RU against literature values for 50% Acetonitrile/50% Toluene

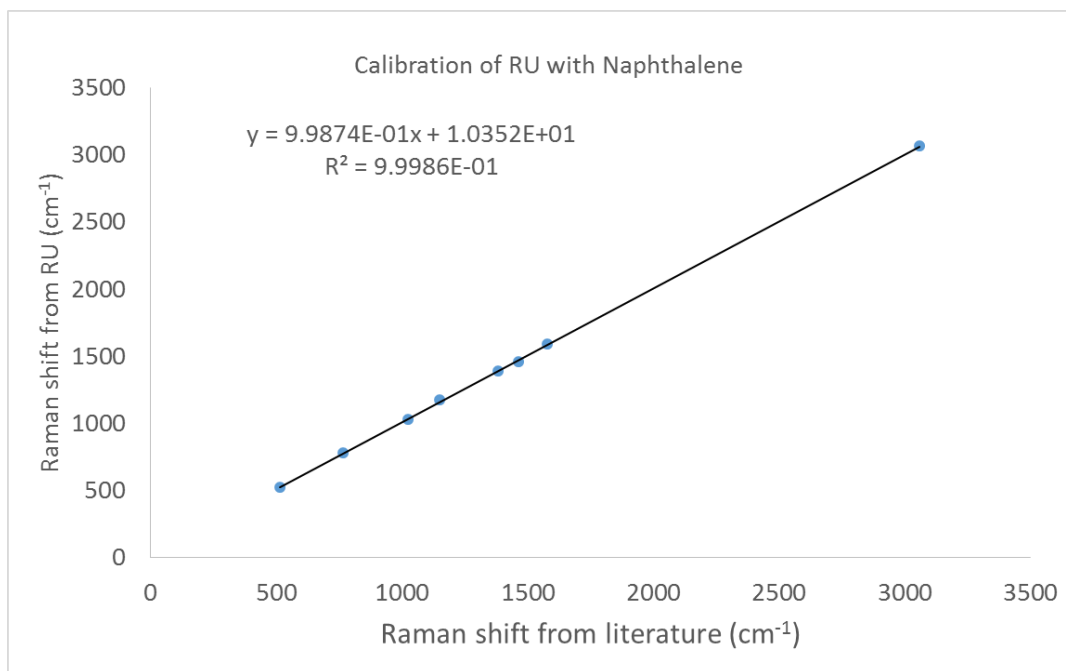
F.3 Calibration with Naphthalene (solid)



Expected Raman Spectrum of 50% Acetonitrile/50% Toluene⁶

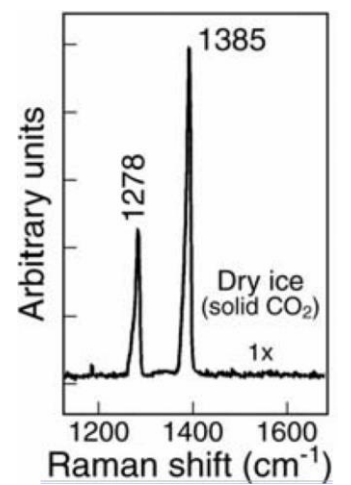


Experimental Raman Spectrum of Naphthalene obtained with RU

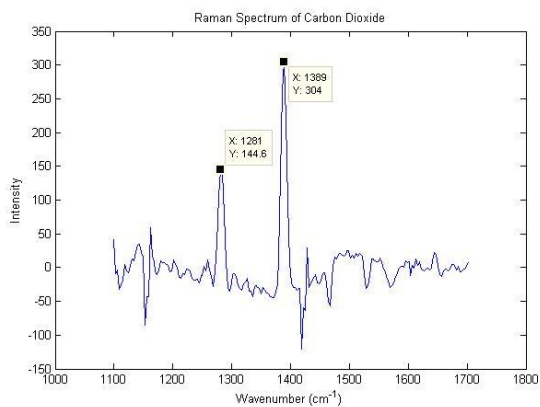


Calibration curve of RU against literature values for Naphthalene

F.4 Raman spectrum of CO₂



Raman spectrum of DryIce®⁷



Experimental Raman spectrum of DryIce®
obtained with RU

⁷ <http://www.lpi.usra.edu/meetings/lpsc2004/pdf/1929.pdf>