A. To collect a s-SNOM spectrum of a single segment
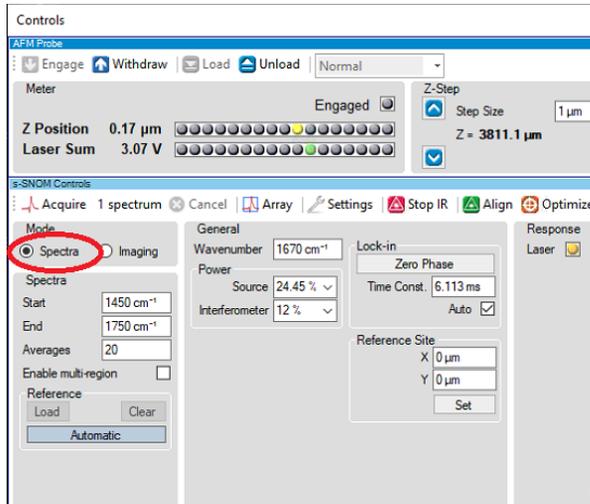
A single segment typically covers 200-300 cm^{-1} as the broadband laser has a FWHM (full width half maximum) of ~170 cm^{-1} and FWTM (full width tenth maximum) of ~300 cm^{-1}.

1. Select "Spectra" mode in the control panel

2. Use a snom probe (SNM-B or SNM-C) probe, and engage to the sample (for example, purple membrane on gold). Search for an area that shows purple membrane monolayer patches (5-7 nm thickness). Collect one AFM image that includes both purple membrane and gold substrate. Move AFM tip to the gold substrate.

3. Click "Align" and move the green laser spot to the tip location.

4. Type desired wavelength (for example 1600 cm-1) in the control panel. Click "Start IR". Typical "Source" power percentage is ~10% for 1600 cm^{-1}, 1-3% for 3000 cm^{-1} and 50-100% for 800 cm^{-1}. Confirm there is signal in the "MCT Intensity" data channel.

5. Confirm that the broadband laser is in "Broadband CW" mode. The Carmina software can be accessed from the nanoIR computer by "Remote Desktop Connection" at the address 192.168.200.31. The mode for the broadband laser (for example, "Broadband CW" is controlled by the analysis studio software, and there is no need to switch modes in the Carmina software.
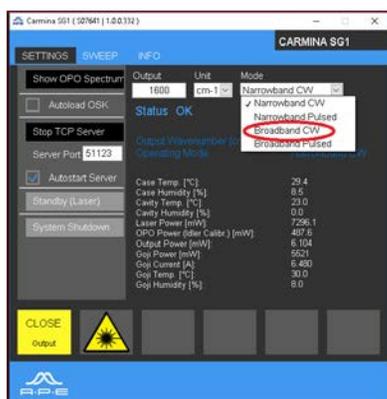
6. Optimize the near field signal from the tip side. Typically select "NF2" channel (or start with NF1 if the signal is too weak). The scanning speed of optimization is slower than AFM-IR as it uses OAP instead of fast mirrors M20/M30. The optimized spot typically has an elliptical shape and a size of ~25x50 µm. Adjust the IR focus number to get the ideal focused spot with the maximum peak to peak intensity (which is the difference between 615 and -105 in the following figure). Move the cursor to the center of the optimized spot (or center of gravity location in the case of two spots).
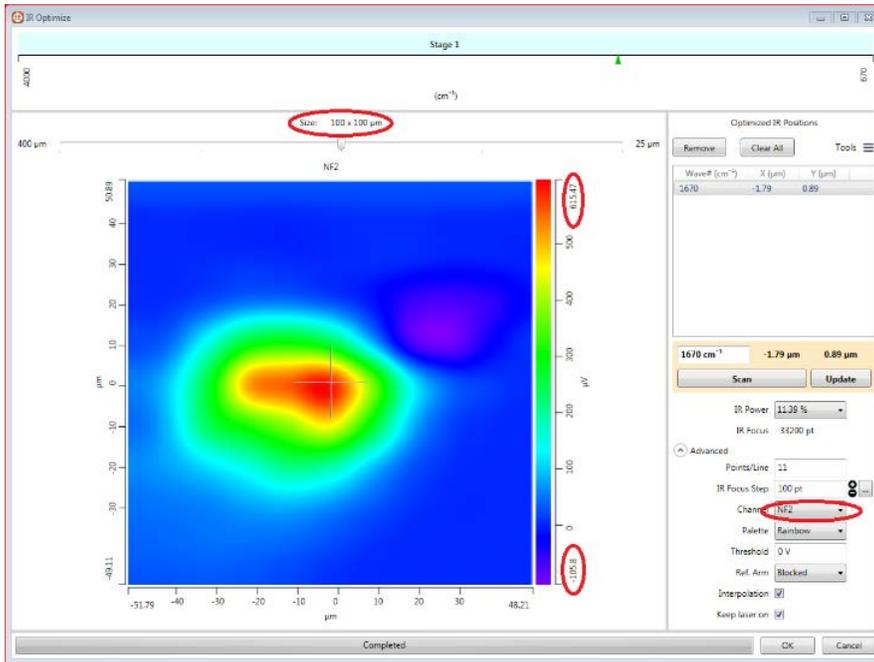

7. Click "Interferogram" in the main control panel to check interferogram. Normally a central burst is observed. If not, check interferogram in a large range of the Aerotech stage. In the "Settings" panel, set the values as -9000, 9000 and 300 for "Start", "End", and "Rate" (the End value may be less if it is set lower value in the "actuator.config" file.
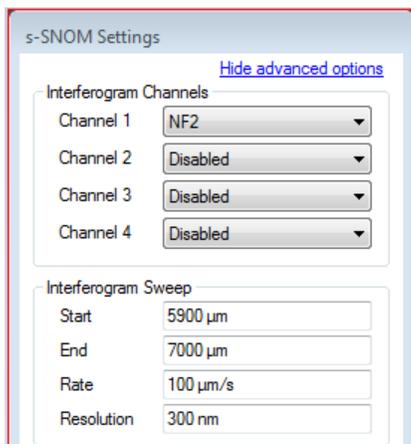
8. A wider range of NF2 interferogram looks like the following picture with a clear central burst. In the very rare case that no central burst is observed, check the interferogram of NF1 which has higher signal.
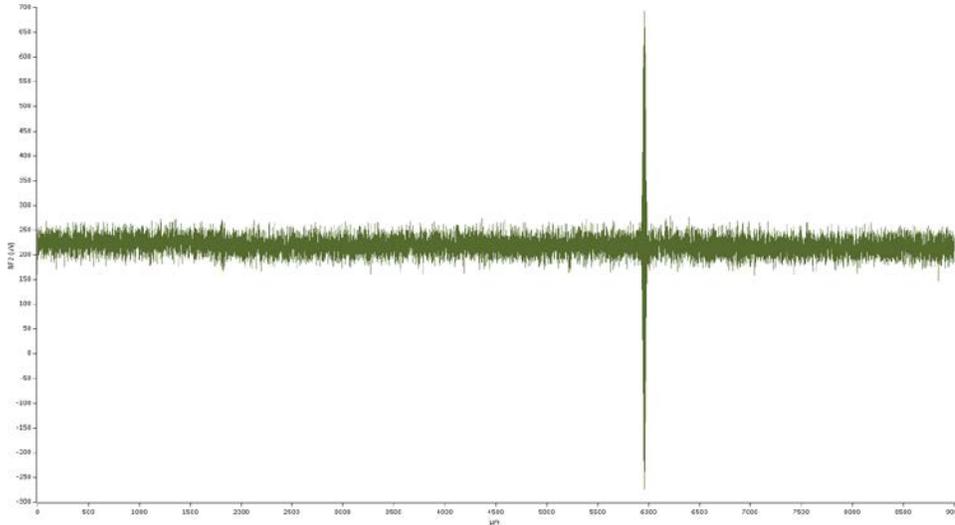

9. Click "Ref align" to maximize the peak to peak value of the interferogram. Set a sweep range of 100-200 µm and a rate of 100 µm/s. Adjust the MREFX and MREFY values to maximize the NF2 signal. On the gold substrate at 1600 cm-1, a peak to peak value of ~500 µV or more is expected for a MCT Intensity value of ~1V.
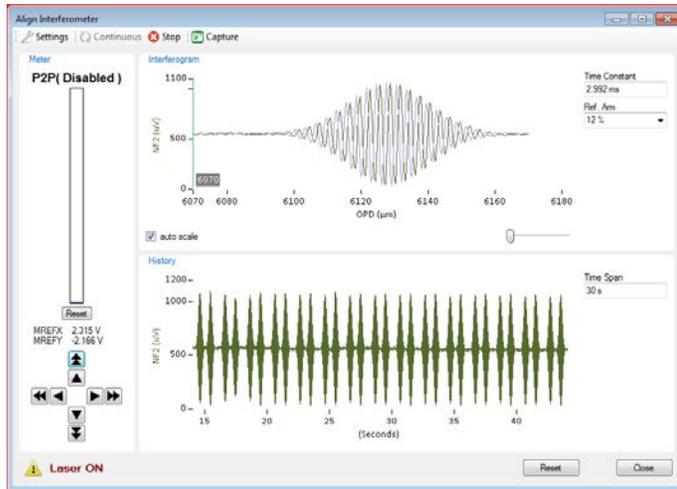
10. Set parameters for spectral range. The spectral range is set the same as the spectral width in the "Settings", with the middle of the range the same as the current wavelength. For example, for purple membrane we look for amide I at 1670 cm-1 and amide II at 1540 cm-1, therefore the center wavelength is set at 1600 cm-1. The spectral range is set as from 1500 to 1700 for a width of 200 cm-1, or from 1450 to 1750 for a width of 300 cm-1.

11. Set parameters for spectral resolution. The spectral resolution is determined by the sweep range of the Aerotech stage in the "interferogram sweep" parameters. The start

value is set 100-200 μm to the left of the beginning of the central burst, and the end value is flexible depending on the desired spectral resolution. For example, to achieve 4 cm-1 spectral resolution, the end value is set ~1200 μm to the right of the peak of the central burst. A sweep range of 1200 μm leads to an optical path difference of 2400 μm resulting in a spectral resolution of ~4 cm-1. In this case a typical sweep range of 1500 μm can be set as in the following figure. To achieve 8 cm-1 spectral resolution, the end value is set ~600 μm to the right of the peak of the central burst.
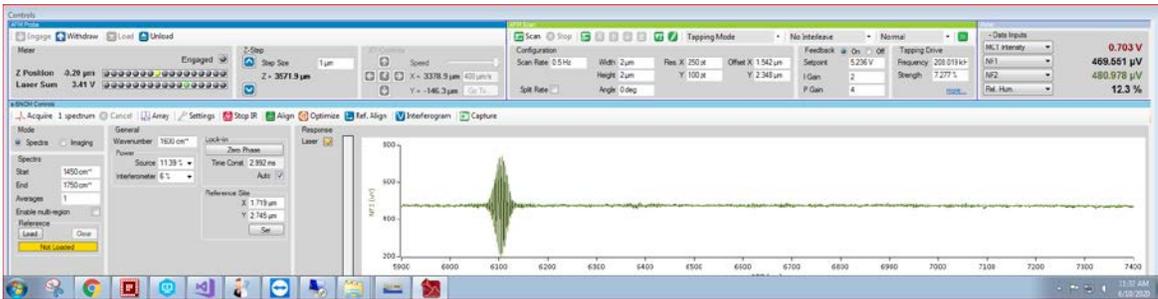

12. Set other parameters of snom spectrum. The sweep rate is typically set at 100 μm/s and the sweep resolution is set at 300 nm. A time constant of 3.3 ms can be calculated from the sweep rate and resolution. The spectral width is set at 200 or 300 cm-1, and overlap is set as 0. In the "advanced options" uncheck "Acquire Reference", and check "Show Raw Spectra" and "Keep Raw Data". Return to the main control panel, set the spectra "Average" to 10 or 20.

13. Acquire reference spectrum. Click "Acquire" to collect snom spectrum. This will collect 10 (or 20) interferograms from the substrate. Each interferogram takes ~15 seconds for a spectral resolution of 4 cm-1, so 10 interferograms take 2.5 mins. The green bar at the bottom left corner shows the progress of the interferograms, while the interferogram plot shows the real time averaged interferogram during the acquisition.

14. Load reference spectrum. After the interferogram on the substrate is done, click "Load" under "Reference" to load it as the reference.

15. Acquire sample spectrum. Move the tip to the purple membrane sample and click "Acquire" again. This will take another 2.5 mins to collect a co-average of 10 interferograms from the sample. The sample spectrum is acquired under the same conditions as the reference spectrum. The raw interferograms from the purple membrane sample has lower peak to peak value than from the gold substrate.

16. Displayed spectrum. After the spectrum acquisition is done, the software will automatically display the snom spectra acquired. The following figure showed two spectra, with spectrum 1 from the gold substrate which later on was loaded as the reference, and spectrum 2 from the purple membrane sample. Spectrum 1 showed two channels, raw magnitude and raw phase. Spectrum 2 showed six channels, including 2 channels for raw magnitude and phase from gold reference, 2 channels for raw

magnitude and phase from purple membrane, and 2 channels for calculated snom magnitude and phase spectra. The snom magnitude spectrum is calculated from the magnitude ratio of the two raw spectra, while the snom phase spectrum is calculated from the phase shift of the two raw spectra. The raw data channels will not be saved if "Show Raw Spectra" in not checked in the "Settings".
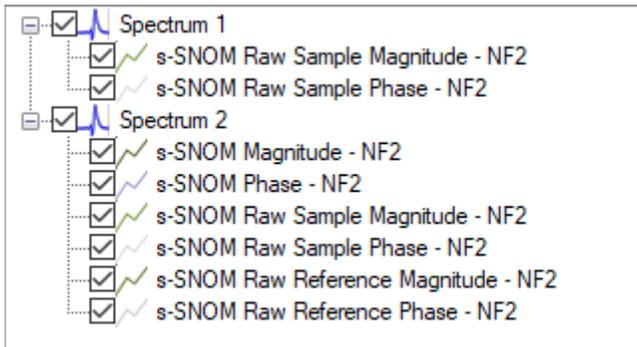

17. The phase spectrum may have a tilted baseline as the purple spectrum in the following figure.
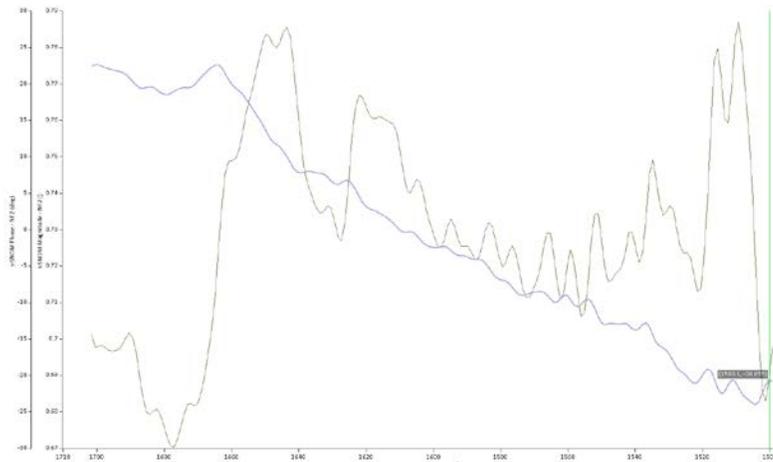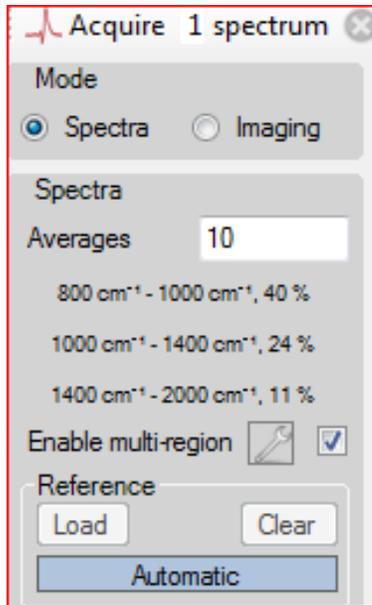

18. Correct slope and offset of snom spectrum. To correct the baseline of the phase spectrum, right click on "Spectrum 2" then select "Recalculate Single Channel Spectra". In the pop-up window change the wavenumber range so that it does not include the tails of the range that has very low output power. Use 0-30 for the "Drop first Points" of the interferogram where it shows mechanical noise from the Aerotech stage. Click the left or right arrow for "Phase Slope" to have a flat baseline for the phase spectrum. The corrected phase spectrum is the blue spectrum in the following figure which showed a

stronger amide I band at 1670 cm-1 and a possibly weaker amide II band at 1540 cm-1.
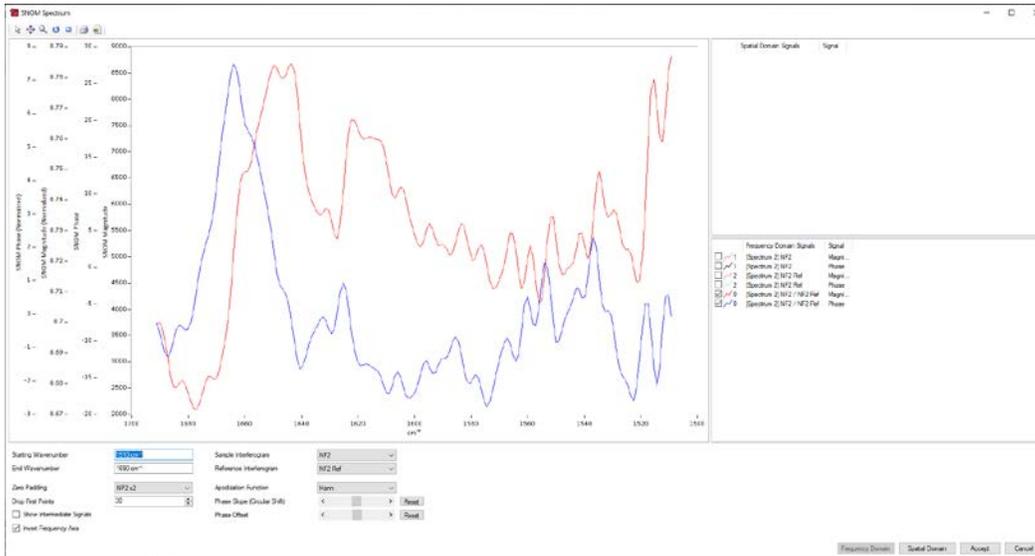

B. To collect a s-SNOM spectrum over a wider range (>200 cm-1)

1. Set snom spectral range. To collect a wider range snom spectrum, for example, from 1000-2000 cm-1, multi segments of snom spectrum will be collected, with the center wavelength of each segment step tuned across the whole range. If the spectral "Width" is set at 200 cm-1 and "Overlap" is set at 0 in the "Settings" parameters, the center wavelength will be step tuned at 1000, 1200, 1400, 1600, 1800 and 2000 cm-1, and the final spectrum displayed spectrum has the range of 1000-2000 cm-1.

2. Set overlap parameter. An "Overlap" parameter such as 50 cm-1 may be necessary between consecutive segments as the tails of each segment have lower output power and thus lower S/N. This can help correct the baseline slopes and offsets of different segments for the wider range snom spectra.

3. Enable "Multi-region". The laser output power varies across the tuning range and has a general trend of lower output power at lower wavenumber. To get approximately the same level of snom signal, different power percentages for the "Source" can be applied, as shown in the following figure.

Acquire 1 spectrum ⊗

Mode
- ⦿ Spectra   ○ Imaging

Spectra

Averages   10

800 cm⁻¹ - 1000 cm⁻¹, 40 %

1000 cm⁻¹ - 1400 cm⁻¹, 24 %

1400 cm⁻¹ - 2000 cm⁻¹, 11 %

Enable multi-region ☑

Reference

| Load | | Clear |

Automatic

4. Spectrum stitching. After finishing the multi segments of spectrum, highlight the spectra, click Analysis\Process\Stitch Spectra. A new window will pop up which allows to correct the slope and offset of each segment. A wider range of s-SNOM spectrum is obtained after corrections. Shown below is a s-SNOM phase spectrum of epoxy test sample over the range of 700-2000 cm-1, which shows characteristic bands of epoxy that are consistent with the IR bands observed in the AFM-IR spectrum.
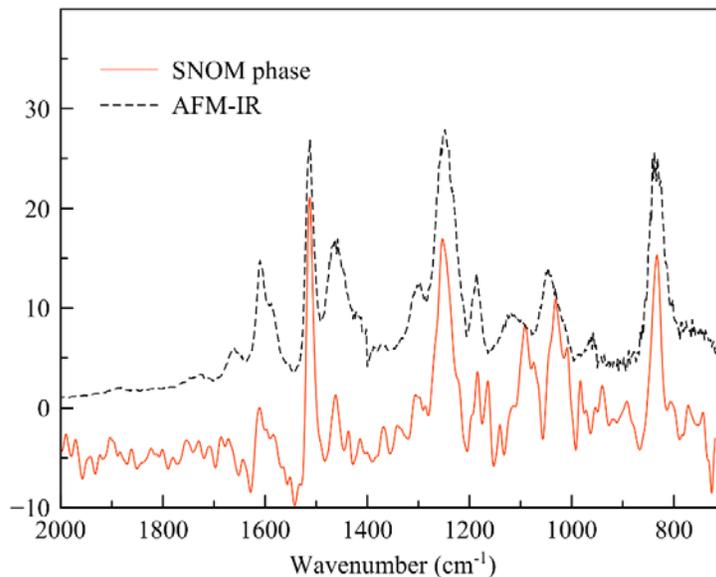
C. To collect a s-SNOM spectral array

1. After a reference is loaded, a s-SNOM spectral array can be collected in the same way as AFM-IR spectral array. The figure below shows one spectral array collected from the PMMA/epoxy test sample using ZnS substrate as the reference. The data was collected with a spectral resolution of 16 cm-1, and each spectrum was from one single interferogram collected in 10 seconds. As can be seen, the spectral array clearly resolves the PMMA particle which shows the carbonyl band at ~1740 cm-1 from the epoxy matrix which does not show the carbonyl band.
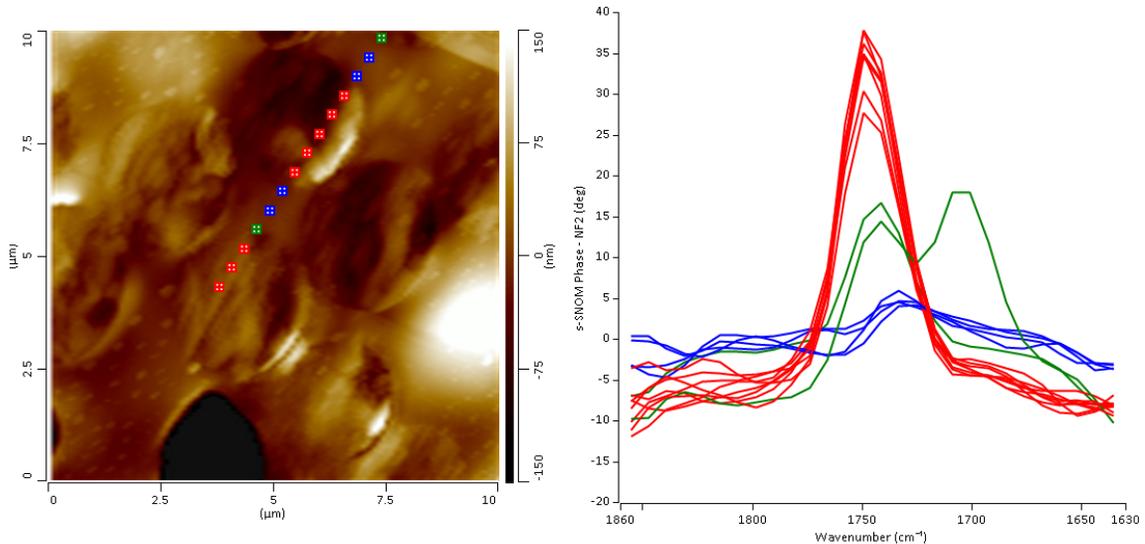

D. To collect a s-SNOM image

1. Select "Imaging" mode in the control panel.
2. Confirm that the Broadband laser is in "Narrowband CW" mode.
3. Optimize the near field signal from the tip side.
4. Click "Find ZPD" in "Settings". It will collect one interferogram and find Aerotech position which corresponds to the zero path difference, i.e, peak of the central burst of the interferogram. Wider Aerotech range may be needed to see the central burst.
5. Collect interferogram. Now with the Aerotech fixed at "ZPD" position, the reference mirror is controlled by the piezo which has a maximum sweep range of 9.8 μm, and the interferogram will be a sinusoidal wave over this narrow range.
6. Click "Ref align" to maximize the peak to peak value of the interferogram. Adjust the MREFX and MREFY values to maximize the NF2 signal.
7. Select "Reflection" or "Absorption" mode for s-SNOM imaging. Refer to nanoIR3-s manual (based on QCL laser) for more details of s-SNOM imaging.

8. Below is a reflection image of purple membrane on gold substrate at 1600 cm-1 showing lower reflectivity of the purple membrane patch than the gold substrate.
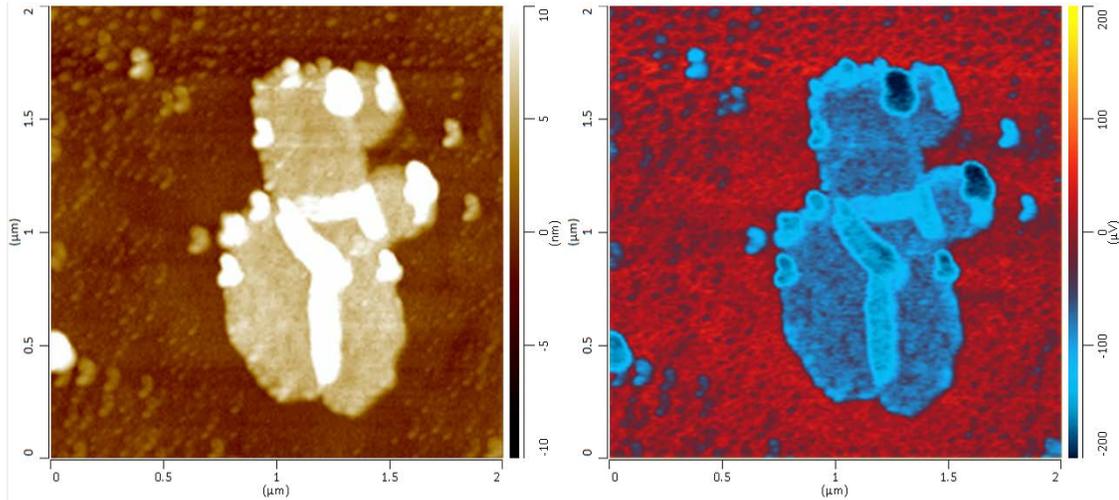
9. Below is a reflection image of hBN on silicon substrate showing the fringe pattern of the surface phonon polariton.
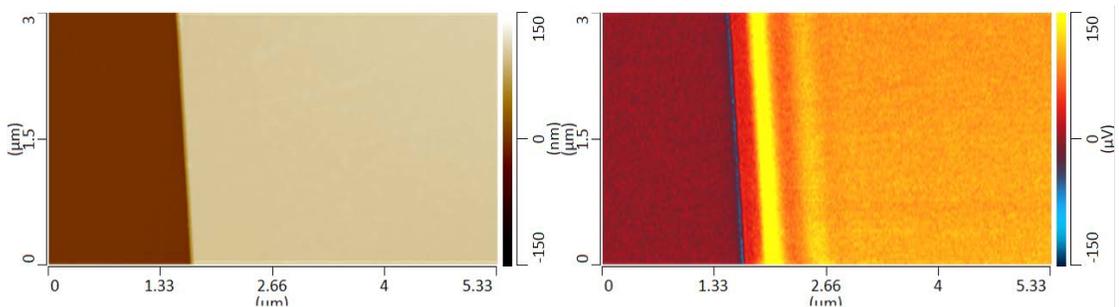
E. To switch sensor for Dual MCT detector

1. Some nanoIR3-s Broadband systems use MCT detector with two sensors. "B" sensor (photovoltaic) works for most of the IR range, from 4000 down to 800 (or even 720 cm-1 depending on the specific detector). "A" sensor (photoconductive) works for the low cm-1 range, from 1000 to 500 cm-1. "A" sensor only provides AC signal (such as NF1, NF2, but not MCT intensity value) and is only recommended for wavenumber below 800 cm-1. The two sensors are side by side inside the MCT, and are separate by a few mm. The "A" sensor is located to the left of "B" sensor when looking at the MCT detector from the front.

2. To switch to "A" sensor, replace the OAP in front of the MCT detector. The OAPs are on magnetic mounts and labelled as "A" and "B". Do not tilt the vertical or horizontal knobs of the OAP mounts as they were aligned during installation.

3. Swap the SMA cable from "B" sensor to "A" sensor.

4. Use NF1 or NF2 to optimize the signal for "A" sensor as it does not read MCT intensity value.
5. The rest of snom operations, including both spectroscopy and imaging, are the same as sensor "B".

F. To collect AFM-IR spectrum and image

1. "Narrowband Pulsed" mode. Confirm the broadband laser is in "Narrowband Pulsed" mode after switch to AFM-IR control panel. Do not change the laser mode in the Carmina software as it is controlled by the analysis studio software.
2. Spectral range. The full spectral range of the broadband laser is 670 - 2000 cm-1. Check the IRlaser.config file if that is not the case.
3. Sweep rate. The laser is typically swept at 20 or 40 cm-1/s.
4. Pulse rate. The laser pulse rate is in the range of 50-1500 KHz.
5. Duty cycle. The duty cycle is set at 50% all the time for stability of the output power.
6. Spectral resolution. The broadband laser has a typical linewidth of 10-15 cm-1 in narrowband pulsed mode for AFM-IR. The AFM-IR spectrum usually looks smoother than the spectrum collected with a QCL laser.
7. The rest of AFM-IR operations are the same as with a QCL laser.