

Technique for the collection of spatially resolved IR reflection-absorption spectra of molecular monolayers using an unmodified commercial IR microscope.

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I. Introduction

A. In this paper we describe a technique for collecting spatially resolved IR spectra of molecular monolayers using an unmodified commercial IR microscope. Spatially resolved spectra are useful for interrogating the homogeneity of monolayers and thin coatings with a spatial resolution determined by the the microscope system. The very basic InspectIR (Spectra-Tech/Thermo-Nicolet) instrument used for this work has a measured spot diameter of 94 μm , which may be reduced to about 64 μm by closing the aperture used in the FTIR. State-of-the-art microscopes available from manufacturers such as Bruker and Nicolet advertise diffraction limited resolution of 2.5 to 25 μm depending on the spectral range.(((ref their web sites))). Since the method described is capable of submonolayer sensitivity the technique extends the usefulness of standard microscopes to thinner films than they are typically used for and should improve performance when applied to films that are thicker than a monolayer.

B. Other methods for collecting vibrational spectra of monolayers with microscopic spatial resolution. (see notes)

The earliest description of microscopically spatially resolved IR spectra of monolayers appears to be the work of ___ using a grazing incidence IR microscope system (1991).(((ref))) At least one manufacturer (Bruker) now sells a grazing incidence microscope objective that can be used with some of their IR microscopes to obtain monolayer sensitivity on metal surfaces.(((Bruker web site))).

More recently work has been done combining a focal plane array IR detector with imaging optics to produce spectra of 200 μm wide lines across the irradiated area or the sample. This method allows some spatial resolution, with monolayer sensitivity and the ability to collect data with time resolution in the millisecond range.†Elmore, 2003 #778; Liu, 2004 #871; Elmore, 2004 #881; Kim, 2007 #882}

These techniques show good promise and are the authors' recommendation for those with the resources to to acquire or build such instruments. However, the method described in this paper will allow most people to achieve monolayer sensitivity with their current IR microscope.

II. Experimental

Octadecylsilanes on Aluminum and Silicon: Aluminum surfaces were 25 mm square front surface bare aluminum mirrors purchased from Edmund Optical. Silicon surfaces were electronic grade silicon wafers with one polished side cut into 25 mm squares or discs. Prior to octadecylsilane deposition these surfaces were plasma cleaned in 200 mTorr of water vapor for 10 minutes using a Harrick plasma cleaner. The cleaned substrates were immediately transferred to a 1 mM solution of octadecyltrichlorosilane in toluene and allowed to sit for 24 or more hours at 25°C. Upon removal the surfaces were rinsed with ethanol and then hexanes. To produce a monolayer with guaranteed position-to-position variation a silicon disc was dipped in the silane solution until about 2/3 submerged for 6 minutes. It was then rotated 90 degrees and 2/3 submerged for 6 more minutes twice more. This produced a sample with low but varied coverage. Higher varied coverage was produced by submerging this sample 1/2 way for an additional 18 hours.

Thiols on Gold: Evaporated gold surfaces were ~ 1000 Å of gold coated on silica windows (Esco) using a Denton Desk II sputter coater. Prior to thiol deposition surfaces were cleaned in a 100-200

mTorr air plasma for 10 minutes using a Harrick plasma cleaner or 20 minutes in “piranha solution” (3:1 conc. H_2SO_4 to 30% H_2O_2) followed by a water rinse. (((Need to include info on template stripped Au as well))). Samples cleaned by all methods were then transferred to stirred ethanol for 20 minutes to remove any metastable oxides formed during the cleaning.⁶ Cleaned surfaces were transferred directly to 1 mM octadecanethiol in ethanol and allowed to sit for 24 hours at 25°C. Upon removal the surfaces were rinsed with ethanol and gently blown dry with the purge air used in the FTIR spectrometer.

B. Technique.

Samples were mounted on the stage of an InspectIR Plus (Spectra-Tech/Nicolet) microscope using a custom machined holder that indexed the front of the sample to the same orientation each time (a thin front-surface mirror mount screwed to a metal plate cut to microscope slide dimensions). This microscope used a liquid N_2 cooled single element HgCdTe detector. The spectrometer bench was a Nicolet 670. Each spectrum was the average of 1024 scans at 2 cm^{-1} resolution referenced to cleaned substrates without monolayers grown on them. The reference spectra were the average of 2048 scans at 2 cm^{-1} resolution. Because of diffraction and interference effects in the beam path it was very important to get the sample distance from the objective to match the distance of the reference from the objective. This was achieved by maximizing the infrared interferogram intensity and then adjusting the height (focus) to minimize baseline oscillations (see Results for further discussion). Spectra of different spots on the same sample were collected one immediately after the other. Roughly 20 minutes elapsed between the start of collection of each spectrum. The cycle was repeated to collect multiple spectra at each spot (3-5) to guarantee reproducibility. The vernier scale on the microscope stage allowed positional reproducibility of about $10\text{ }\mu\text{m}$. The imaged spot size was $96\text{ }\mu\text{m}$ in diameter.

C. Data Processing

Spectra were generated from the interferograms by standard Fourier Transform IR processing. The baselines of all spectra were then corrected to account for instrument drift by subtracting a linear baseline from the data. The baseline correction was produced by linear-least-squares fitting to the spectra in the region $2800 - 3000\text{ cm}^{-1}$. Some of the samples on silicon required additional processing because the samples were so thin that reflections off the rough backside interfered with the reflections from the front side. This led to relatively high frequency periodic oscillations in the baseline (etalon fringes) that were removed by Fourier filtering (((ref?))).

D. Spot size determination.

The spot size was measured using Al traces on glass microscope slides. An Al coated slide was used as the background. The spot was focused on a $142\text{ }\mu\text{m}$ wide trace. When centered on the trace a flat spectrum was observed. The center of the spot (optical and IR images were aligned) was placed at the edge of the trace and then moved until the glass signal disappeared. All sides gave the same measurement, suggesting a nearly round spot.(((I am checking shape more carefully))) This provided the radius of the spot.

III. Results

The major impediment to observing monolayer spectra using standard IR microscopes is that the reflection-absorption spectra often exhibit baseline oscillations, which are similar in size to the signal from a monolayer. These oscillations vary with position on the sample and from spectrum to spectrum. The oscillations appear to result from small mismatches between oscillations in the reference and sample single beam spectra, and are probably caused by interference effects along the optical path. The

small differences between the sample and reference spectra thus reflect slight differences in focus and local surface angle. Most of the discrepancy can be corrected for by careful adjustment of the focus as shown in figure 1. The procedure used to adjust the focus was to initially focus the optical image. Then the focus was adjusted to maximize the interferogram signal. Then with the instrument set to repeatedly generate single scan but ratioed spectra the focus was further adjusted to minimize any observable oscillations. With practice this was usually enough. However, further improvement in the baseline could be achieved by collecting averaged spectra (16-32 scans) and making fine adjustments of the focus to minimize oscillations observed in the 2500-2700 cm^{-1} region where there are no peaks. With a computer controlled microscope stage this process could be automated by fitting the 2500-2700 cm^{-1} region of the spectrum to a line and adjusting the focus to minimize the χ^2 of the fit. The low-end microscope available to the authors did not have computer controlled focusing or positioning, so no attempt was made to automate this process. With these added steps it was possible to observe reproducible spectra of monolayers on solid surfaces with microscopic spatial resolution as shown later for octadecylsilanes on Si and Al and octadecanethiols on Au.

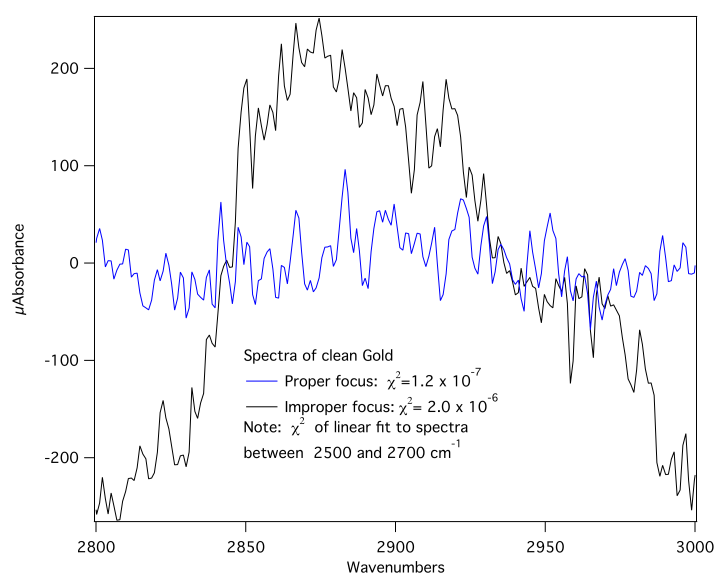


Figure 1: Baseline spectra (sample and reference the same) with the focus adjusted properly and improperly. The χ^2 of a linear fit to the 2500-2700 cm^{-1} region of each spectrum is also listed. Notice how much larger the improperly focused χ^2 is.

In addition to the procedure described above some adjustments to the microscope and FTIR beyond the typical alignment provided upon delivery can make it easier to collect spectra of monolayers:

- 1) Using a very clean flat front-surface metal mirror on the microscope stage the sample stage focus should be adjusted to maximize the interferogram. Then the visible (camera) image should be focused using adjustments on the camera mount/focus, not the microscope stage. This makes the optical focus and the interferogram maximum focus better matched, making it easier to find the optimal focus as described above.

- 2) If the FTIR instrument attached to the IR microscope has an adjustable aperture, the aperture should be closed as much as possible without reducing the interferogram intensity. The default aperture for most instruments is chosen based on the resolution. The beam path through many microscopes does not use the whole beam generated by the instrument. Closing the aperture reduces stray light which can sometimes add to the baseline oscillations. In the case of the instrument used for this study an

aperture of 30% was ideal, whereas 69% is the default for 2 cm^{-1} resolution.

A. OTS on Si

Figure 2 shows a sampling of spectra from different positions on a single Si disc coated with a good octadecylsilane monolayer. The quality of the monolayer is indicated by both the position of the antisymmetric CH_2 stretching at 2918 cm^{-1} (((ref))) and the reproducibility of the spectra as position varies on the sample. This result is typical of what is seen for a good monolayer on a very flat dielectric or semiconductor such as Si. The negative going peaks indicate an actual increase in reflected light at the frequencies of the absorptions. This is expected for an absorber at a non-conductive interface (((reff..optical text?))) Two spectra are shown for each position in the figure, they overlap so well that it is difficult to tell. More than two spectra were taken at each position verifying this reproducibility, but are not included in the figure to increase the visual clarity. As there were six positions sampled on this disc the duplicate spectra on each spot were separated in time by at least two hours (((double check this number))).

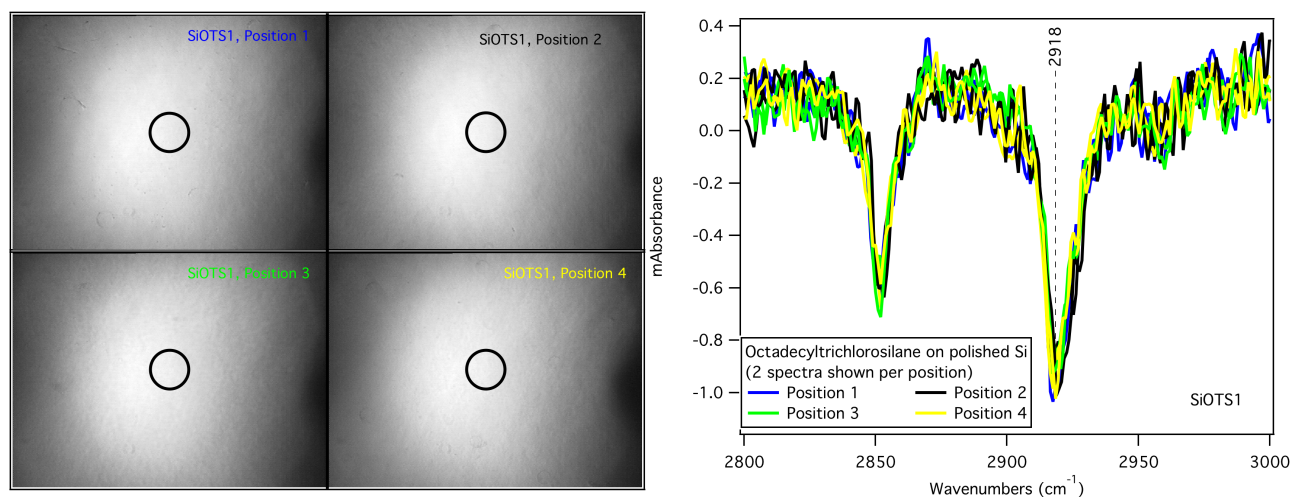


Figure 2: On the right: Spectra at different spots on a polished Si surface coated with a good octadecylsilane monolayer. Notice the observed peak at 2918 cm^{-1} and the reproducibility of the spectra versus position. On the left: Optical images through the same microscope objective of the sampled spots. The circle indicates the 96 μm diameter sampled spot.

As figure 3 demonstrates this method is capable of observing submonolayer coverages and seeing variations across the sample of incomplete monolayers. The sample was created by dipping a polished Si disc partway into the coating solution for short periods of time and then removing the sample and rotating it so that some areas were exposed to the solution for a maximum period of 19 hours and other for only a few minutes or hours. The spectra exhibit definite variation with position and the shift of the CH_2 asymmetric peak to higher wavenumbers indicate a poorly organized and incomplete monolayer. (((ref)))

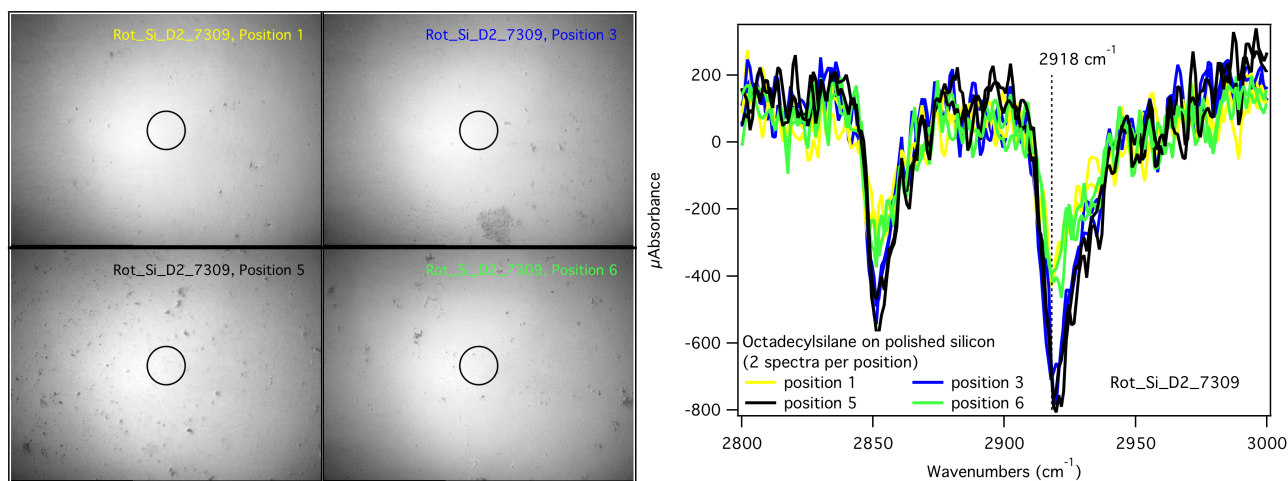


Figure 3: On the right: Spectra at different spots on a polished Si surface coated with an incomplete octadecylsilane monolayer. Notice the observed peak at greater than 2918 cm⁻¹ and the irreproducibility of the spectra versus position. On the left: Optical images through the same microscope objective of the sampled spots. The circle indicates the 96 μm diameter sampled spot. Notice that the optical images show signs of places with what appear to be lumps and might be multilayers. The sampled spots were chosen to avoid the "dirty" spots.

((do we need discussion of peak asymmetry or comparison with large area grazing spectra.)))

B. OTS on Al

All the Al mirrors suffered pitting and separation from the substrates during monolayer formation. Thus no uniform monolayers on Al were produced. In many cases it appears that multilayers were formed as well. This was suggested by the large signal from some spots and the fact that although there were significant spectral intensity variations versus position the CH₂ asymmetric peak appears at 2918 cm⁻¹ indicating the molecules are tightly packed.(((ref))) Spectra and images from one such sample are showing in figure 4.

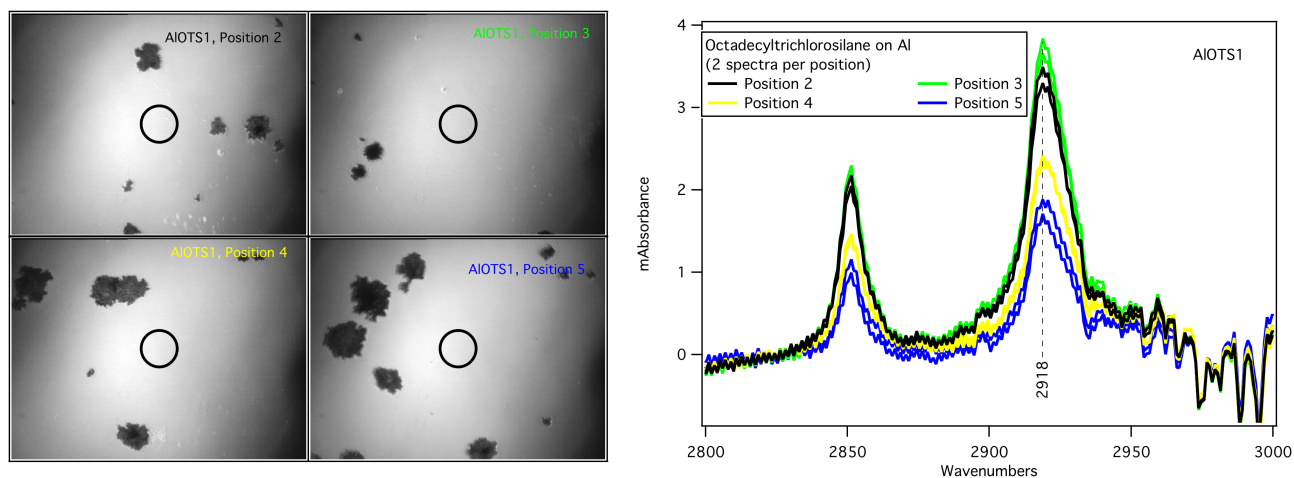


Figure 4: On the right: Spectra at different spots on a polished Al surface coated with octadecylsilane. Notice the irreproducibility of the spectra versus position. On the left: Optical images through the same microscope objective of the sampled spots. The circle indicates the 96 μm diameter sampled spot. Notice that the optical images show dark spots where the Al has lifted off the

substrate. Positions were chosen to avoid spots where the Al coating was obviously damaged.

C. Octadecanethiol on Au

On evaporated Au surfaces variation in signal was seen with position for both piranha cleaned and plasma cleaned Au surfaces. In these experiments the piranha cleaning appeared to produce somewhat larger variations with position (compare figures 5 and 6).

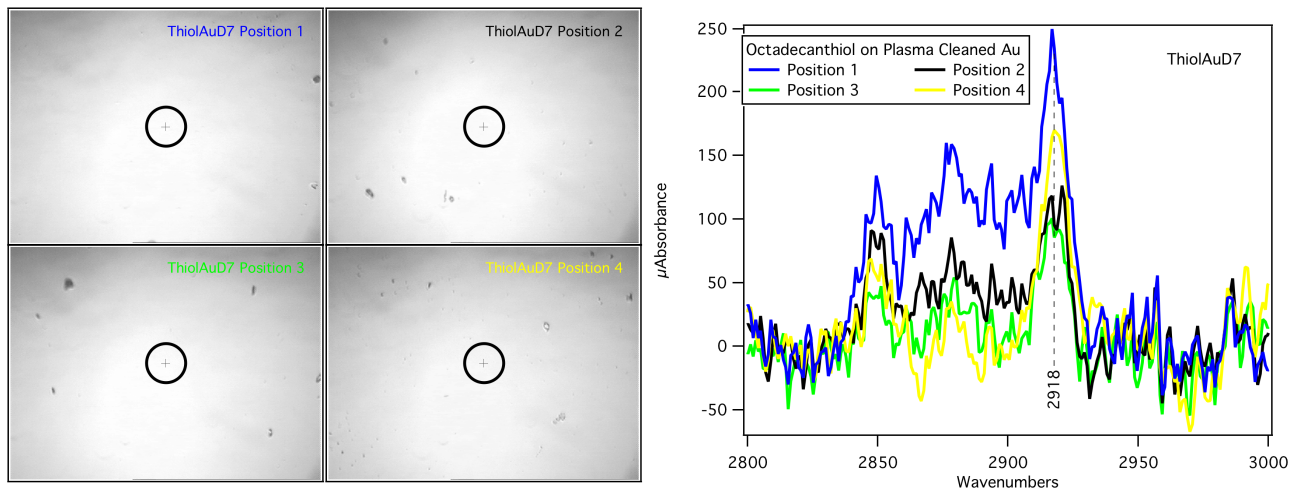


Figure 5: On the right: Spectra at different spots on a plasma-cleaned evaporated Au surface coated with octadecanethiol. Notice there is some variation of the spectra versus position although the peak position of 2918 cm^{-1} indicates a relatively ordered monolayer at each position. On the left: Optical images through the same microscope objective of the sampled spots. The circle indicates the $96\text{ }\mu\text{m}$ diameter sampled spot.

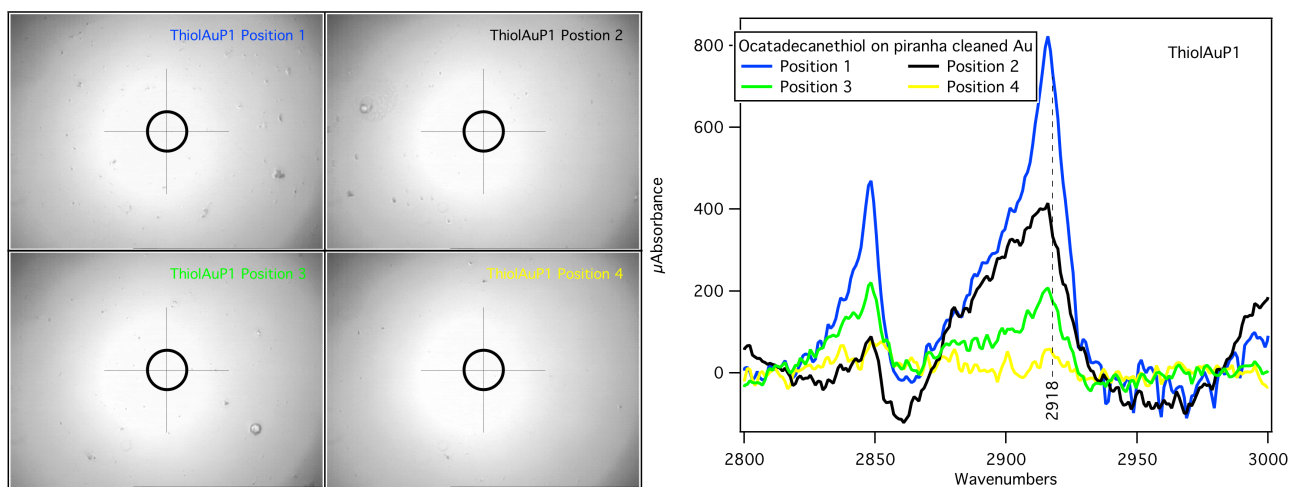


Figure 6: On the right: Spectra at different spots on a piranha-cleaned evaporated Au surface coated with octadecanethiol. Notice there is some variation of the spectra versus position although the peak position of 2918 cm^{-1} indicates a relatively ordered monolayer at each position. On the left: Optical images through the same microscope objective of the sampled spots. The circle indicates the $96\text{ }\mu\text{m}$ diameter sampled spot.

((4-16-09 sample is a good monolayer based on grazing...no signal above noise in micro...used 43009_m micro spectra with 41609 large area inset.)) On template stripped Au surfaces ((ref)) when large-area grazing incidence spectra indicated good monolayers (see figure 7) no signal was observed

in most microscopic spectra. Once in a while a spot would show signal that looked like the spectra more commonly observed on the evaporated Au surfaces. This is consistent with the metal surface selection rules that dictate the more upright thiols in a very good monolayer are difficult to detect without grazing incidence. However occasional defects (possibly grain boundaries) on the surface produce spots where some of the molecules tilt over more yielding a larger signal which can be observed using a standard IR microscope. Thus a good large-area grazing incidence spectrum of thiols on Au combined with IR microscope spectra at many positions with flat baselines that show no CH signals are a good indicator of a homogeneous thiol on Au monolayer.

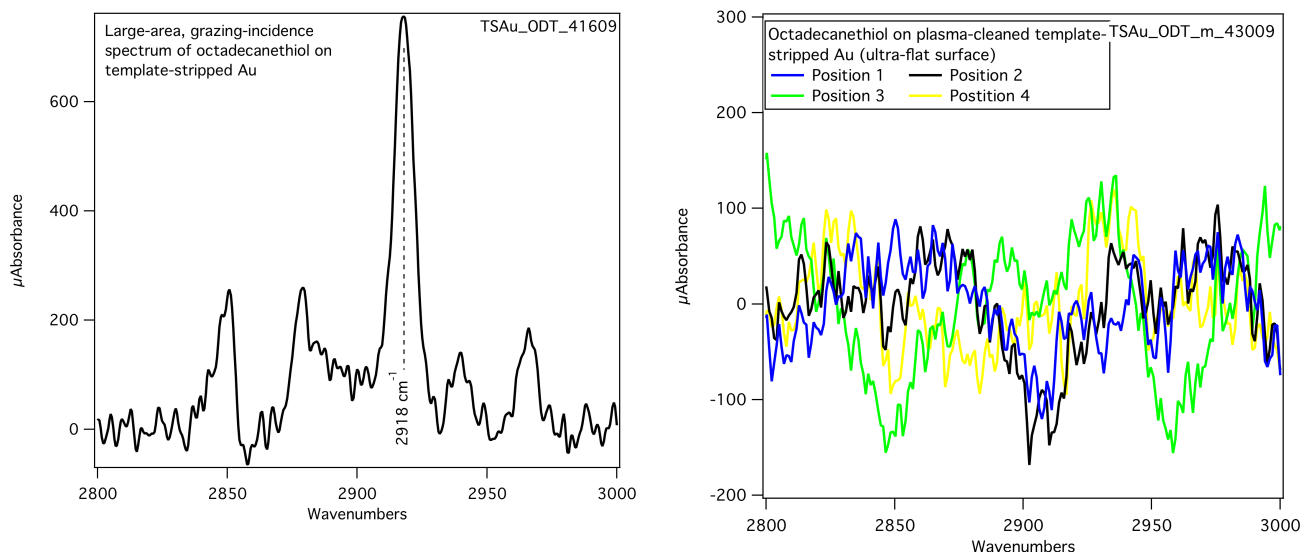


Figure 7: On the right: Spectra at different spots on a plasma-cleaned, template-stripped Au surface coated with octadecanethiol. Notice that there does not appear to be CH signal observable above the noise. On the left: Large-area grazing incidence spectrum of the same sample, suggesting that the surface is coated with a good thiol monolayer, based on the peak at 2918 cm^{-1} and the relative intensities of the other peaks. The visible micrographs have been left out as they look the same for each position. The sampled area is the same $96\text{ }\mu\text{m}$ circle as in the other cases.

IV. Conclusions

A. We report a technique which can be used with the unmodified installed base of commercial IR microscopes to achieve microscopic spatially resolved IR spectra of molecular monolayers. Using computer controlled microscope stages the technique could potentially be automated and used to produce IR spectroscopic images of monolayers. There are other techniques that can provide spatially resolved IR spectra of monolayers, but they require more specialized equipment, than the commonly available IR microscope.