

Nano-scale Fourier Transform Infrared Spectroscopy using a Thermal Source

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Abstract

Nano-scale imaging with chemical sensitivity is required to fully understand the formation, composition, and unique emergent properties of materials. However, many of the existing high resolution techniques are limited either by their spectroscopic bandwidth or by the classes of material compatible for study. Here we show that combining Fourier transform infrared spectroscopy with scattering-scanning near-field optical microscopy provides a non-invasive, broadband alternative to measuring these systems. We demonstrate that such an approach is capable of identifying chemical composition with a resolution better than 10 nm, and can be used to directly measure near-field phenomena. Considerations for optimization and construction of such a nano-FTIR spectrometer system are also discussed.

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1 Introduction

Fourier-transform infrared (FTIR) spectroscopy [1] is a crucial analytical tool employed by chemists, biologists, and physicists alike for the study and characterization of many classes of materials and chemical processes. While the rapid maturation of the technique has resulted in high-resolution, high-efficiency spectrometers capable of measuring and analyzing the composition of a sample in fractions of a second, its diffraction limited approach impedes its use in the advancement of many modern scientific and industrial objectives requiring chemical sensitivity on the nano-scale. A tremendous push has therefore recently emerged to combine FTIR spectroscopy with nano-imaging techniques such as scanning near-field optical microscopy (SNOM) [2] to realize nano-scale FTIR spectroscopy as a novel solution to these problems.

Because nano-FTIR spectroscopy uses a non-invasive approach to study organic and inorganic systems far beyond the diffraction limit, it offers a unique alternative to the considerably more complex and expensive techniques of scanning tunneling microscopy (STM), electron microscopy, or stimulated emission depletion spectroscopy (STED). Its broad applications in the characterization of nano-devices [5], the study of cells, viruses, and protein complexes [6,7,8,9], and analysis of quality control methods, make it an emerging dominant player in modern analytical chemistry and material science.

Nano-scale resolution is achieved by modifying the conventional symmetric interferometry in FTIR spectroscopy to instead conform to an asymmetric orientation with an atomic force microscope (AFM) at the end of one of the interferometer arms. This orientation is typically known as interferometric s-SNOM, and can be used in combination

with a lock-in amplifier to strongly enhance and isolate from the far-field background the minute radiation scattered back by the tip-sample region of the AFM [3,10]. This scattered radiation is what is used to generate spectra that reveal near-field phenomena and chemical information about the sample. Since the apex of the AFM's tip is around 10 nm, resolution far beneath the diffraction limit becomes achievable.

The quality of the spectra, of course, depends on many additional factors of the system which can limit the usefulness of nano-scale chemical information depending on the application. For example, low signal to noise ratios of tip-scattered radiation at the detector can make distinguishing spectral lines extremely difficult. A myriad of factors including misalignment or mismatched length of the interferometer arms, long beam path lengths, poor collimation, stability of the reference mirror or AFM, and so on, all contribute to the quality and feasibility of any FTIR spectroscopy system. The focus of this thesis will be primarily concerned with how the development and characterization of such a chemically sensitive nano-imaging system was undertaken to combat these issues, and to discuss the limitations and capabilities of this system by analyzing the data obtained in view of existing endeavors elsewhere [10]. It will conclude with a discussion of the ongoing steps to further develop and upgrade the nano-FTIR spectroscopy system, as well as the ongoing results.

2 Background

2.1 Nano-Optics and Scattering-Scanning Near-Field Optical Microscopy

The creation and study of novel and complex systems rely on a precise understanding of their interactions and properties at a fundamental level. The advent of nano-optics makes probing these small regimes of interaction possible by overcoming one of the traditional limitations of optical imaging, namely the diffraction limit. Though many techniques have been developed and refined over the years with this purpose in mind (STM, NMR, NSOM probing, etc.), one of the most successful and robust methods has been scattering-scanning near-field optical microscopy (s-SNOM). S-SNOM employs so-called 'aperture-less' probe tips in a modified Michelson interferometer to extract spectroscopic information about a sample with a theoretically arbitrary spatial resolution. It is a two-step process of scattering 'near-field' information produced by radiation interacting with the tip-sample region of an AFM, followed by enhancement of the scattered light for detection in the far field. To fully understand how s-SNOM is employed in this experiment, one must first become familiar with the generation of the optical near-field, atomic force microscopes, Fourier transform infrared spectroscopy, blackbody radiation, and finally how it all fits together via asymmetric interferometry.

2.2 The Optical Near-Field

The term 'near-field' refers to the electromagnetic waves that exist only very close to an object which is radiating and/or interacting with incident radiation in some fashion. An

example is the electric field described by an oscillating dipole,

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{(4\pi\epsilon_0)} \left\{ \frac{\omega^2}{c^2 r} (\hat{\mathbf{r}} \times \mathbf{p}) \times \hat{\mathbf{r}} + \left(\frac{1}{r^3} - \frac{i\omega}{cr^2} \right) [3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{p}) - \mathbf{p}] \right\}. \quad (1)$$

The terms going as $\frac{1}{r^3}$ and $\frac{1}{r^2}$ are considered the 'near-field' components since they disappear at large r . More generally, the near-field is taken to be the exponentially decaying *evanescent* waves defined by the form $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp\{i(\mathbf{k}\mathbf{r} - \omega t)\}$ with a wavevector $\mathbf{k}$ that is at least partially imaginary.

Evanescent waves are a common effect: they are a direct consequence of light interacting with inhomogeneities in materials, and can be easily detected using techniques such as photon-scanning tunneling microscopy [11]. As a brief explanation of their generation, we take the example of total internal reflection at a plane interface [12] (Fig. 1).

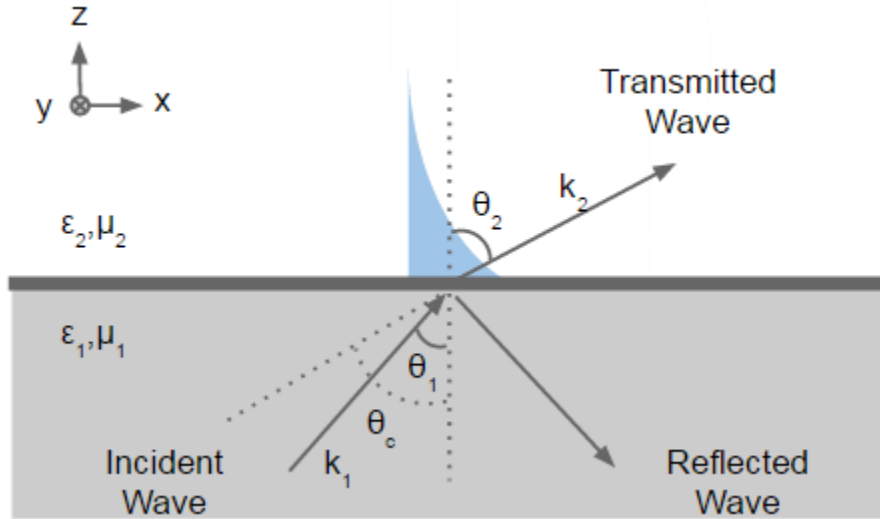


Figure 1: An electromagnetic wave encounters an inhomogeneity in the form of an interface between two materials with different permeability μ and permittivity ϵ .

It is clear from the figure that the general complex transmitted electric field is given by

$$\mathbf{E}_2 = \begin{bmatrix} -E_1^p t^p k_{z2}/k_2 \\ E_1^s t^s \\ E_1^p t^p k_{x2}/k_2 \end{bmatrix} e^{i(k_{x2}x + k_{z2}z)}. \quad (2)$$

where t is the transmission coefficient for (s) and (p) polarized light (we consider s perpendicular to the interface and p parallel to the interface in this case). The important thing to note is how we can write k_{z2} :

$$k_{z2} = k_2 \sqrt{1 - \frac{(k_{x2}^2 + k_{y2}^2)}{k_2^2}}. \quad (3)$$

And due to boundary conditions from Maxwell's equations $k_{x2} = k_{x1}$ and $k_{y2} = k_{y1}$ so that (3) becomes

$$k_{z2} = k_2 \sqrt{1 - \frac{k_1^2 \sin^2 \theta}{k_2^2}} = k_2 \sqrt{1 - \frac{\epsilon_1 \mu_1 \sin^2 \theta}{\epsilon_2 \mu_2}} \quad (4)$$

with $k_1 = \frac{\omega}{c} \sqrt{\epsilon_1 \mu_1}$ and $k_2 = \frac{\omega}{c} \sqrt{\epsilon_2 \mu_2}$. It is obvious for two different media that the fraction $\frac{\epsilon_1 \mu_1}{\epsilon_2 \mu_2}$ can be greater than one, and therefore that there exist angles $\theta \geq \theta_c$ for which k_{z2} is in fact imaginary (θ_c is of course the *critical* angle). For such imaginary k_{z2} , equation (2) then becomes

$$\mathbf{E}_2 = \begin{bmatrix} -E_1^p t^p k_{z2}/k_2 \\ E_1^s t^s \\ E_1^p t^p k_{x2}/k_2 \end{bmatrix} e^{ik_{x2}x} e^{-\gamma z} \quad (5)$$

where γ is just a decay constant for the transmitted wave. The above equation describes a wave that travels along x with a decaying field in the z direction in medium 2. This

decaying field is precisely the evanescent wave that exists only very close to the interface.

The importance of evanescent waves can best be understood by the *angular spectrum representation* for optical fields which tells us that a general field can be represented by a superposition of plane and evanescent waves [12]. The angular spectrum representation considers the electric field $\mathbf{E}(x, y, z)$ evaluated on a plane perpendicular to an arbitrary z -axis (at $z = \text{constant}$) along some direction of the scattering object (Fig. 2). This can be viewed as the Fourier transform of the reciprocal space $\hat{\mathbf{E}}(k_x, k_y; z)$, as

$$\mathbf{E}(x, y, z) = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \hat{\mathbf{E}}(k_x, k_y; z) e^{i(k_x x + k_y y)} dk_x dk_y. \quad (6)$$

We can then use the Helmholtz equation

$$(\nabla^2 + k^2)\mathbf{E}(\mathbf{r}) = 0 \quad (7)$$

to determine the spectrum $\hat{\mathbf{E}}$ at any point along the z -axis using the propagator

$$\hat{\mathbf{E}}(k_x, k_y; z) = \hat{\mathbf{E}}(k_x, k_y; z = 0) e^{\pm i k_z z} \quad (8)$$

with $k_z = \sqrt{k^2 - k_x^2 - k_y^2}$. Note that k_z is allowed to be imaginary so that equation (8) doesn't blow up at $z = \pm\infty$. By inserting equation (8) into (6), we see for a given k_x and k_y , that the exponent $e^{i(k_x x + k_y y \pm k_z z)}$ will be oscillatory for real k_z and decaying for imaginary k_z (as $|z|$ increases). The former is of course the plane wave solution, while the latter is the evanescent field. These two types of solutions are therefore enough to construct any desired field.

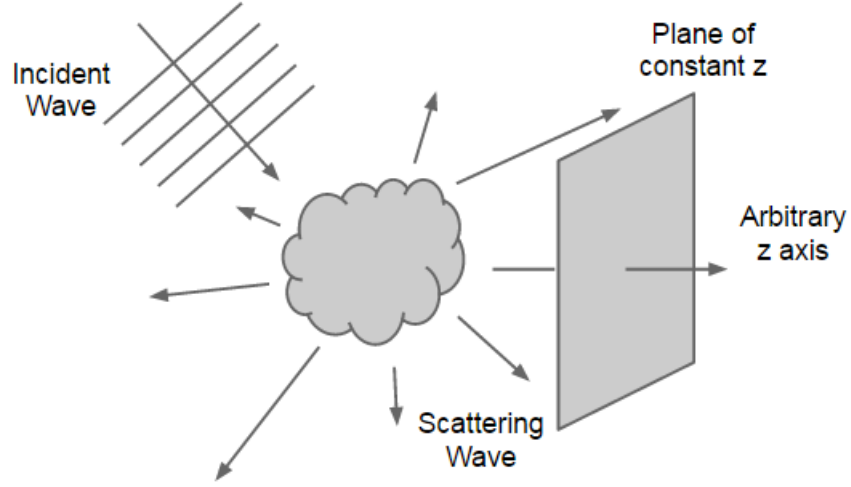


Figure 2: Light scatters off an object. The angular spectrum representation technique evaluates the resulting field $\mathbf{E}$ in planes of constant z .

It is clear from the above that evanescent waves contain information about higher spatial frequencies not normally accessible in the far field. When k_z is imaginary, the near-field must have $(k_x^2 + k_y^2) > k^2$. So if one has access the evanescent field information, then it is theoretically possible to obtain the infinite spectrum of spatial frequencies instead of being limited to the region $(k_x^2 + k_y^2) \leq k^2$ - the frequencies propagated to the far field by the plane waves. The significant result is that knowledge of both the plane wave frequencies and the higher spatial frequencies in evanescent waves makes possible the reconstruction of features far beneath the diffraction limit. It is exactly analogous to how one needs more and more (ideally infinite) high frequency sine waves to reconstruct a perfect delta function.

2.3 Atomic Force Microscopes

A beautiful system for extracting information from the near-field is the atomic force microscope (AFM). AFMs have been commercially available and developed since 1986 as a nano-imaging alternative for non-conductive materials previously unmeasurable by STM. They can reveal a plethora of sample information such as topography, adhesion forces, sample hardness, electrostatic forces (to name a few), and have found wide application in the life sciences, crystallography, and nano-technology [13]. Their ability to image over 1000 times smaller than the diffraction limit makes them an essential component to the s-SNOM system.

The basic operation of an atomic force microscope is easy to understand. As their name suggests, AFMs are concerned with precisely measuring the interaction of a 'probe' with a sample due to forces such as dipole-dipole interaction, Van der Waals forces, electrostatics, etc. Though many approaches exist, one of the most commonly used is the so-called *tapping mode* approach where the 'probe' (a metallic tip on the end of a cantilever) is driven by a piezoelectric to resonate at the cantilever's resonance frequency (Fig. 3). A photodiode laser is bounced off the cantilever from above to keep track of the oscillation amplitude, which is usually set to be anywhere from 100 - 200 nm. The tip is then brought close enough to the sample surface for interaction forces to significantly dampen oscillations down to about 50 - 70 nm. The AFM is now ready to raster-scan the surface while a PID loop maintains the tip-sample distance using information from the photodiode to try and keep oscillations at the preset dampened amplitude.

As the sample is scanned, the tip's oscillation will change rapidly due to the tip's

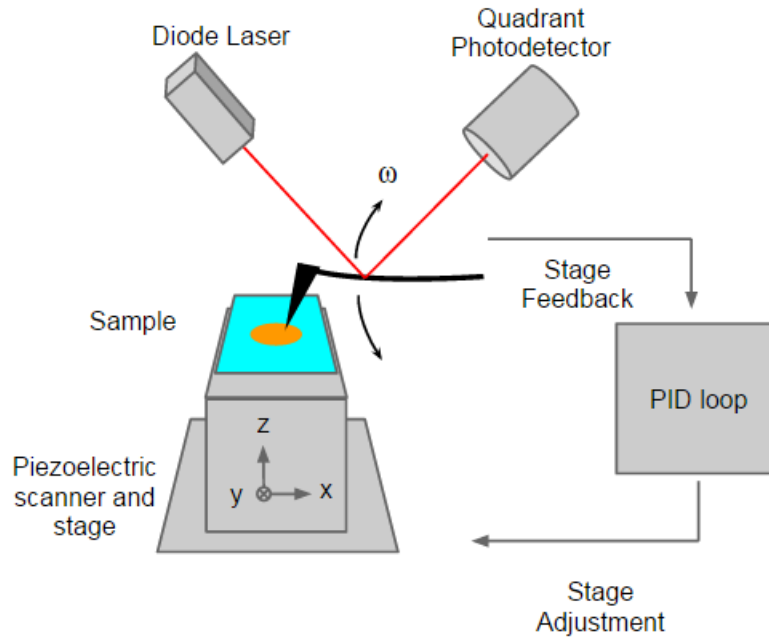


Figure 3: A diode laser and photodetector monitor cantilever's amplitude as it is driven at resonant frequency ω . A PID loop adjusts the stage to maintain a preset tip-sample distance. The tip on the cantilever is what is used to probe the surface.

high sensitivity to molecular forces and changes in sample topography. These changes are recorded by the photodiode to produce high resolution AFM images which are limited only by the tip radius which is usually on the order of 10 nm. Compared to a diffraction limited system using 10 μm light with a spot size $\sim \frac{\lambda}{2} = 5 \mu\text{m} = 5000 \text{ nm}$, AFM's offer a remarkable gain in resolving power (500 times as much in this example). It should be noted however that scanning must be very precisely carried out using piezoelectrics, leading to small scan ranges (on the order of microns rather than millimeters in STM) and long scan times (several minutes for a moderately resolved image).

In this experiment, the AFM tips will be the tool for extracting near-field information from a sample. When we illuminate the tip with far-field radiation, the electrons in the tip apex oscillate to form (approximately) a dipole field (Fig. 4). Bringing the tip in close

proximity to the sample surface will then solicit responses from charges in the material (an image dipole for example) that have the effect of strongly enhancing scattering in the far field by increasing the tip's effective polarizability [3,14]. The degree of enhancement will be governed by the unique intrinsic properties of the material and tip [15], which are generally dependent on the frequency of the incident radiation. It is this *contrast* in the intensity of scattered radiation between different materials at different frequencies that we wish to compare and measure. How broadband measurements of this type are made on such materials is the subject of infrared spectroscopy.

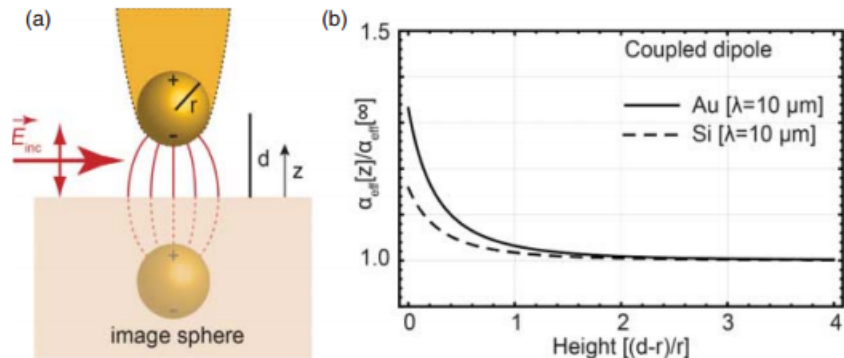


Figure 4: The probe tip can be approximated as a dipole [14]. (a) shows the dipole-dipole enhancement that occurs in close proximity of the tip to the sample, and (b) shows the enhancement of α , the effective polarizability of the tip due to this coupling which translates to larger scattering cross sections.

2.4 Infrared Spectroscopy

Infrared, or vibrational, spectroscopy is a standard tool for uncovering chemical information from a sample by exciting the vibrational modes of molecules and atoms in the infrared. The most straight forward way of accomplishing this is to shine light from a known source through a sample and measure the changes in transmission intensity for

each frequency using a slit. The result is a unique 'fingerprint' for the substance which can not only be used to identify future samples, but also uncover interesting properties of the material. Fourier transform infrared spectroscopy (FTIR spectroscopy) is a variant on this technique that allows a broad spectrum of frequencies to be measured *simultaneously* (Fellgett's advantage). They also offer more radiation throughput (Jacquinot's advantage) by doing away with the slit.

The invention of the interferometer around 1880 by Albert A. Michelson and Edward W. Morley marked the start of FTIR spectroscopy development. It was apparent at that time that modifying the fixed mirror in one arm of the interferometer by allowing it to translate (Fig. 5) would enable the experimenter to generate intensity profiles at the detector as a function of mirror retardation. These profiles, or interferograms, could then be Fourier transformed to reproduce the original frequencies of the source light, allowing interferometers of this type to play a unique role in spectroscopy.

This method can be illustrated by considering first, a perfectly collimated coherent light source of wavelength λ_{source} (in centimeters) passing through the interferometer at its zero path difference (ZPD) position. At the ZPD position the arm lengths are exactly equal in length, and the beam is interfering constructively at the detector. The wavenumber of our source is given by

$$\nu_0 = \frac{1}{\lambda_{source}}. \quad (9)$$

As the mirror moves through a distance $\frac{\delta}{2}$, the two beams of the interferometer will interfere destructively and constructively each time $\delta = \frac{n\lambda}{2}$ and $\delta = n\lambda$, respectively (n is an integer). It should be noted that when considering an ideal beam splitter, all the photons in the two beams pass back toward the source when there is destructive interference, and

similarly all the photons pass to the detector when the beams constructively interfere - the beamsplitter does not reduce the detectable radiation by 50%. The result is a sinusoidally varying intensity at the detector given by

$$I(\delta) = 0.5I(\nu_0)(1 + \cos(\frac{2\pi\delta}{\lambda_{source}})) \quad (10)$$

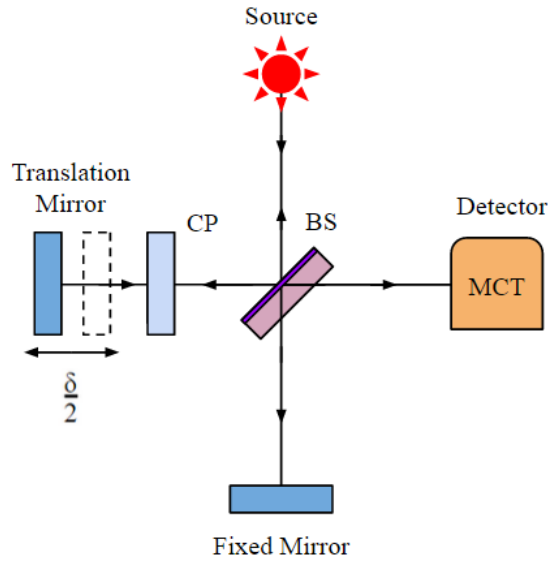


Figure 5: The basic setup of a Fourier transform infrared spectrometer. A BaF beam splitter (BS) splits a source beam along two orthogonal arms which exhibit interfere at the detector as their relative lengths are modulated. A compensation plate (CP) matches the dispersion of each beam so that each beam passes through a BaF medium exactly three times.

where $I(\nu_0)$ is the intensity of the source at wavenumber ν_0 . Keeping just the AC component and converting to wavenumbers, equation (2) simplifies to

$$I(\delta) = 0.5I(\nu_0)\cos(2\pi\delta\nu_0) \quad (11)$$

In a real experiment we need to multiply $0.5I(\nu_0)$ by a correction factor $N(\nu_0)$ to

account for imperfections in the beamsplitter, dispersion, noise, etc. We then lump the result into a corrected intensity expression $I(\delta)_{corrected}$ yielding

$$\begin{aligned} I(\delta)_{corrected} &= 0.5I(\nu_0)N(\nu_0)\cos(2\pi\delta\nu_0) \\ &= I(\nu_0)_{corrected}\cos(2\pi\delta\nu_0). \end{aligned} \tag{12}$$

The above result is just the cosine Fourier transform of $I(\nu)_{corrected}$, and can be extended to sources with many frequencies of light by superposition. The fundamental difference with such an extension however is that the spatial incoherence of broadband sources implies only interference at the ZPD position, producing a 'center burst' shape at the detector (Fig. 6) rather than a sinusoidal intensity pattern. The generalized result is then the following Fourier transform pair

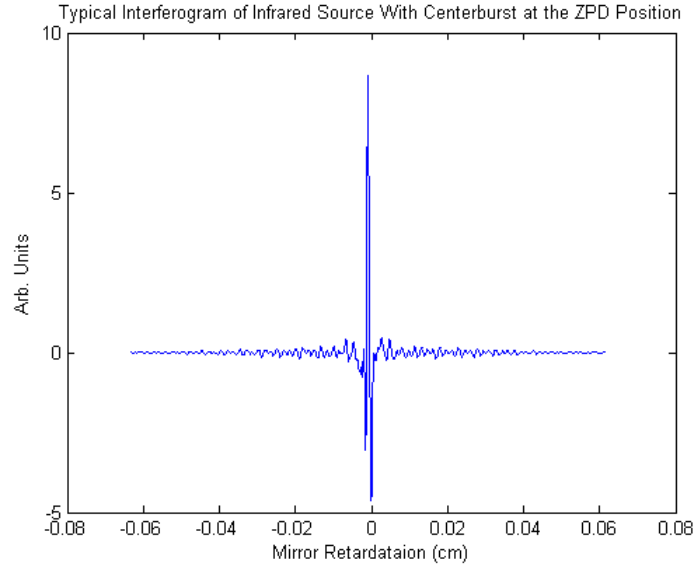


Figure 6: Typical interferogram showing a center burst where both beams interfere constructively at the ZPD position.

$$I(\delta)_{corrected} = \int_{-\infty}^{+\infty} I(\nu)_{corrected} \cos(2\pi\delta\nu) d\nu \quad (13a)$$

$$I(\nu)_{corrected} = \int_{-\infty}^{+\infty} I(\delta)_{corrected} \cos(2\pi\delta\nu) d\delta. \quad (13b)$$

We now have a method of extracting spectral information about the source from the interferogram produced by the translating mirror. It should be noted that in practice the integrals above cannot run all the way to infinity, and so apodization must be applied [1].

If we already *know* the spectral characteristics of the source, we can easily reveal unknown spectroscopic information about a material by simply placing it before the detector and measuring the deviation of the resulting spectrum from the source's original 'background' spectrum. It is for this reason that near-blackbody (or gray body) sources are used in this technique. Blackbodies not only have a known functional form, but can also provide the broadband source of infrared radiation need to perform vibrational spectroscopy and chemical analysis.

One of the last obstacles in the development of FTIR spectroscopy was to actually calculate the Fourier transforms above. In the days of Michelson and Morley, computing the Fourier transforms by hand was entirely impractical. Even with the advent of computers, Fourier transform proved a cumbersome and demanding computational burden. It wasn't until James Cooley and John Tukey developed an efficient algorithm for calculating these transforms (known now as Fast Fourier Transform or FFT) [16] that FTIR actually became feasible. This is the technique used in this experiment. A lot of improvements, like tracking the mirror position with an additional HeNe laser, precision control of the

moving mirror, increased versatility for analyzing gases and liquids, and reduction in cost has made an FTIR spectrometer an essential and common place instrument for industry and research all over the world.

2.5 Blackbody Radiation

Blackbody radiation was successfully explained by Max Planck in 1900 as an early result of the developing quantum theory of the time. Though his derivation is not overly complicated, I have omitted it on the basis that it is not especially illuminating in the context of this experiment. Rather, the results of the analysis are the important quantities of interest, namely *Wien's Displacement Law* $\lambda_{max} = \frac{b}{T}$ relating the peak wavelength to temperature (where b is Wien's displacement constant), the *Stefan-Boltzmann Law* relating power emitted per unit area to temperature $j = \sigma T^4$ (with σ the Stefan-Boltzmann constant), and of course the famous equation for the spectral radiance of a blackbody given by

$$I_\nu(\nu, T) = \frac{2h\nu^3}{c(e^{\frac{h\nu}{K_b T}} - 1)} \quad (14)$$

where h is Planck's constant, ν is frequency, K_b is Boltzmann's constant, and T is temperature.

After taking detectivity and emissivity into account, these equations will be useful for characterizing our thermal source to understand the amount of power we can push through our system.

2.6 Asymmetric Interferometry

The FTIR spectrometry and s-SNOM capabilities can now be combined into a single system to fully realize nano-imaging with chemical sensitivity. In this setup, a broadband thermal source of infrared light enters the apparatus and is split by a beam splitter to relay half the beam to a translatable mirror in the *reference arm*, while the other half arrives at an off-axis parabolic mirror that focuses onto the tip-sample region beneath the AFM cantilever (Fig. 7). It is this second half of the beam that interacts with the tip-sample region and scatters near-field information back into the far-field. The AFM arm of the interferometer therefore acts as the fixed mirror in the conventional Fourier transform spectrometer, and the resulting interference at the detector from this signal with the reference arm can be analyzed in the usual way to reveal spectroscopic information about the sample. Since this information can be obtained as the AFM images the sample surface, it is theoretically possible to then generate a corresponding 'chemical' or response map of the surface, limited only by the resolution of the AFM.

An first glance, it seems that there is a flaw with this idea. While the reference beam reflects straight back with nearly no loss, the intensity of light scattering back from the AFM is extremely minuscule. Furthermore, the light is immersed in a sea of background radiation not only from the ambient far-field, but also from other scattering centers on the tip and sample. The solution to this problem is a clever work around using demodulation of the detector signal at dither frequency of the tip.

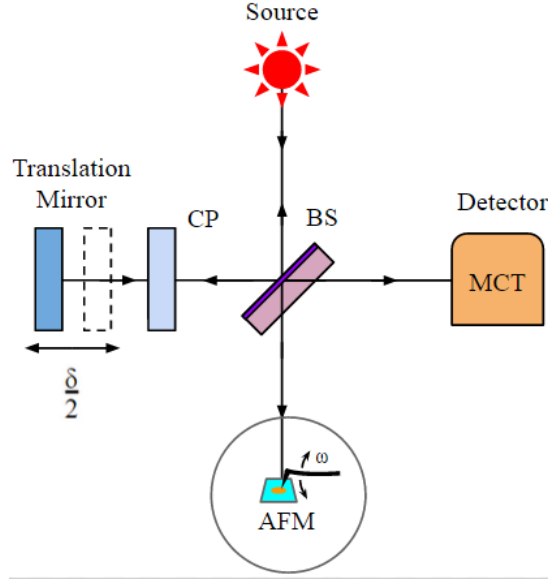


Figure 7: The FTIR spectrometer is modified with an AFM for performing s-SNOM.

Notice that the total power measured at the detector goes as

$$\begin{aligned}
 \mathbf{E}_{total}^2 &= (\mathbf{E}_s + \mathbf{E}_b + \mathbf{E}_r)^2 \\
 &= 2\mathbf{E}_s \cdot \mathbf{E}_b + 2\mathbf{E}_s \cdot \mathbf{E}_r + 2\mathbf{E}_r \cdot \mathbf{E}_b + \mathbf{E}_s^2 + \mathbf{E}_b^2 + \mathbf{E}_r^2,
 \end{aligned} \tag{15}$$

from the superposition of the tip-scattered (s), background (b), and reference (r) sources of radiation. (I am taking the simple case of real electric fields with identical phases for the sake of argument. I also consider only radiation from the reference arm capable of interfering at the detector. See chapter 4.) However if we lock-in detect using demodulation of the signal at the tip dither frequency, equation (15) reduces to

$$\begin{aligned}
 \mathbf{E}_{total}^2 &= 2\mathbf{E}_s \cdot \mathbf{E}_b + 2\mathbf{E}_s \cdot \mathbf{E}_r + \mathbf{E}_s^2 \\
 &= 2\mathbf{E}_s \cdot \mathbf{E}_r,
 \end{aligned} \tag{16}$$

where the last line follows from noting that $\mathbf{E}_s \cdot \mathbf{E}_b$ and $\mathbf{E}_s^2$ are negligibly small relative to the remaining term.

The result of equation (16) is that $\mathbf{E}_s$ (a small field) is dotted with $\mathbf{E}_r$ (a large field). When interfering constructively at the detector, the reference arm apparently has the effect of strongly enhancing the power detected from the scattered signal P_s by many orders of magnitude since $P_s \propto \sqrt{\mathbf{E}_s \cdot \mathbf{E}_r}$. Hence this design strongly enhances signals from s-SNOM.

The scattered light from the tip still contains a fair amount of background radiation however. This is primarily due to scattering centers along the tip shaft and cantilever that still oscillate at the tip dither frequency. To suppress this background, one must usually go a step further and optimize the 2nd or 3rd (or higher) harmonics of the demodulated signal to be confident that the signal is from the near-field interaction. This largely eliminates the unwanted background because the scattering enhancement described before decreases more rapidly with increased tip-sample distance for a higher harmonic than for a lower one [3]. Therefore, the higher harmonics will largely contain only the signal from the interaction at the tip apex since the other scattering centers are too far from the sample to be enhanced.

3 Experimental Design

3.1 Basic Layout

Figure 8 shows the completed nano-imaging FTIR spectroscopy system constructed over the course of several months in the lab. The evolution of the system was a long process that involved a lot of modifications along the way, resulting in a somewhat different looking layout than the figures shown in chapter 2. Therefore, it will be a useful starting point to consider the constraints and advantages of our system first from a macroscopic perspective.

We can see that fundamentally, the layout is still an s-SNOM system with a reference interferometer arm (left arm), a detection arm with a photovoltaic MCT (mercury cadmium telluride) detector (right arm), a source (top), and an atomic force microscope (bottom). The primary thermal source used in experiments was the EverGlo Thermo Fisher source which runs around runs at 880 K, though it is advertised higher. This was in place of the source that was originally going to be used, the Newport 6575 filament, because the latter had a very low emissivity past 1400 cm^{-1} . Details of these sources are discussed more in the next chapter.

To understand the deviations from the s-SNOM system shown in chapter 2, we begin with the constraint that the Veeco CP II AFM needs to be mounted such that the tip sample region is around the height of 10 cm off the optics table. Designing optical systems for this height is more or less standard due to the fact that most optical lab equipment is to only able to access 5 - 15 cm off the table and it is generally good practice to keep radiation

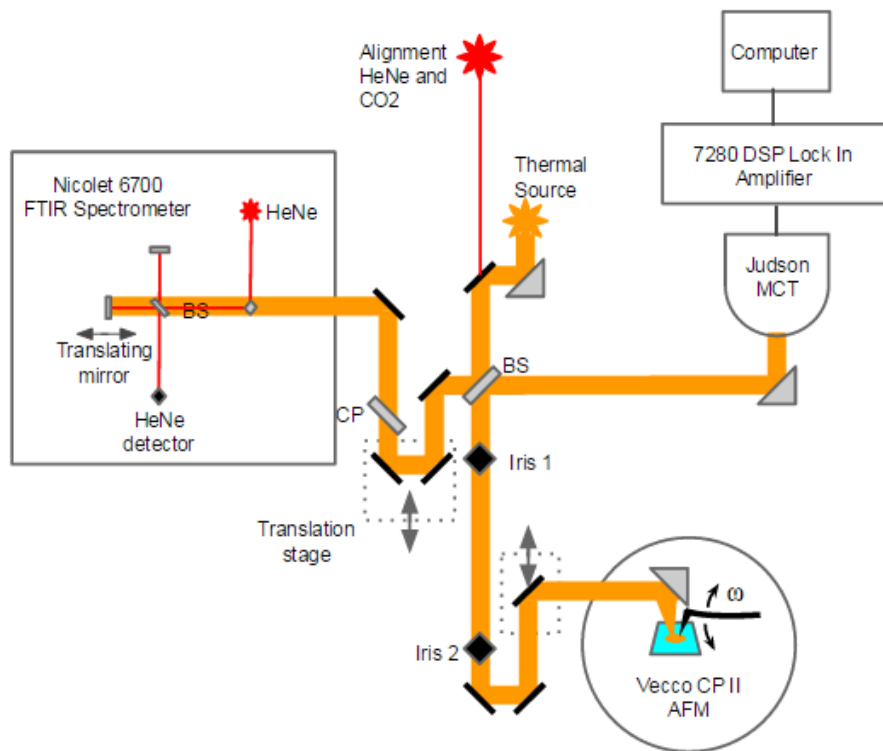


Figure 8: The design of the nano-imaging FTIR spectrometer. The path lengths for the reference and AFM arms are about 72.5 cm from the beamsplitter.

sources well below eye level for the user. The decade-old, 20cm+ Veeco CP II AFM is of course, *not* designed for this sort of system, and therefore needs to be mounted on the side of the optics table at the appropriate height. This was accomplished with an existing mounting system built by previous lab members.

The next essential piece of equipment was the translation mirror for the reference arm. This mirror needs to meet three primary requirements to be useful. Firstly, it needs to have the ability to move with extreme precision over a long distance. Resolution of the spectrometer in frequency space (after FFT) is just the reciprocal of translation [1]

$$\Delta v = \frac{1}{\Delta x_{max}}. \quad (17)$$

So ideally, the mirror will be able to translate as far as possible (while still reflecting the reference beam exactly back through the system) with minimal instability.

Secondly, the mirror's position needs to be tracked accurately. The signal from the MCT needs to be correlated to a reproducible mirror position so that an intensity value can be recorded. If the mirror's position is not known or is inconsistent over each cycle of translation, then there is no way to generate an accurate interferogram, and any integration of many interferograms will destroy the interference signal rather than enhance it.

The final requirement is that the mirror needs to move in extremely small steps so that many many data points can be taken along the path of translation. The number of data points will affect the *range* of frequencies that can be resolved. If the mirror takes 13 data points for example, it may have no problem measuring a low frequency sinusoidal intensity at the detector (Fig. 9), but it certainly would have a hard time picking up high frequency intensity changes.

To satisfy these requirements, advanced software and mirror tracking is needed. The fastest and most straight forward way to obtain this is to just *buy* a FTIR spectrometer (which comes with a mirror, software, internal HeNe for tracking, etc.) and modify it for our needs. This is the reason the reference arm with the translation mirror in the figure 8 has a box named "Nicolet 6700 FTIR Spectrometer" around it. We basically modify the instrument to reflect external sources of light directly back out, rather than using the internal IR emitter, allowing us to use the precision controlled mirror and interferogram collection software.

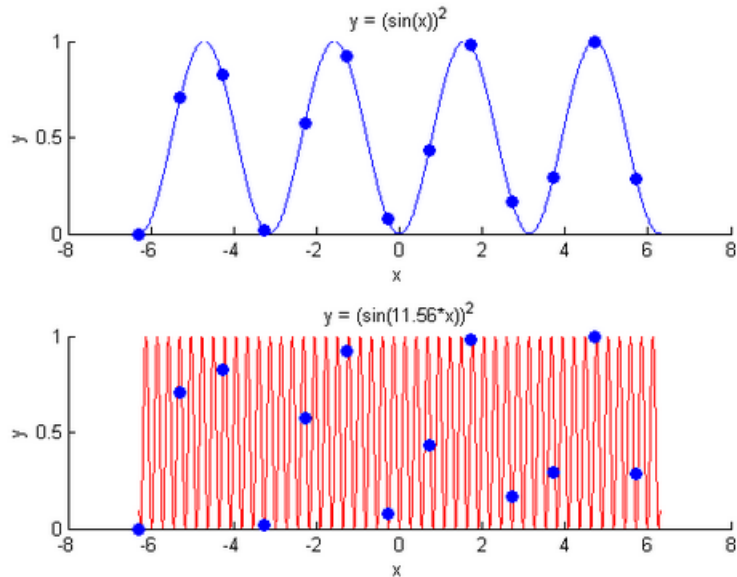


Figure 9: Both sinusoids go through the same set of points, but one is of much higher frequency. Without more data points, it is not clear if the signal is actually the higher frequency or the lower one.

Unfortunately, this spectrometer is a heavy and large piece of equipment. Since we are using it unconventionally with an external source, it requires that we pass in the thermal light through a relatively large distance inside the device, adding to the path length of the reference arm. Furthermore, to find the ZPD position, the reference arm needs to have adjustable length so it can match the length of the AFM arm. The translation mirror only changes the path length by about 0.25 cm for the standard 4 wavenumber resolution, so for a well centered interferogram, the arms need to be adjusted to have identical lengths within only a couple millimeters - impossible to do by eye. This is the reason for the translation stage in figure 8: we first align the light through the reference and AFM arms so that the path length is roughly identical (± 5 cm), and then use this translation stage to 'fine adjust' to the ZPD position. This stage must be in the reference arm because translation inevitably

leads to a slight change the in beam path (the beam is not hitting at perfectly 90 degree angles at the stage) and would almost certainly ruin the highly sensitive near field signal if implemented instead in the AFM arm.

The combination of path length due to the instrument, the need for a translation stage, and the fact that the mount for the AFM limits how close the FTIR spectrometer can be, all fix the lower bound for the length of the reference arm to be about 72.5 cm. This means that the AFM arm length needs to actually be *increased* to match lengths, making the second 'kink' in this arm necessary near 'Iris 2' at the bottom of figure 8.

A useful aspect of this system's design is the ability to switch sources by removing the second steering mirror of the thermal source. This allows us to first send an external *visible* HeNe laser through the system as an initial check that everything is roughly aligned by eye (including the focus of all parabolic reflectors). A CO₂ laser is then aligned to the HeNe (through an external alignment arm not shown) and passed through the system to perform diagnostics for s-SNOM. The focus of the parabolic mirror at the AFM and position of the MCT are now more finely optimized to maximize the near-field signal and check that the AFM and detector are working properly. (The parabolic mirrors at the AFM and MCT are on magnetic mounts and can be exchanged with flat mirrors to first check alignment along the optical axis before this optimization process). If we were careful to send the original HeNe beam through Iris 1 and Iris 2, then we need only align the thermal source through these irises (using a power meter) to be confident that it too is well aligned though the system. This technique is a necessary daily 'course adjust' that generally provides a tiny 1st harmonic signal as a starting point for thermal s-SNOM which can then be further optimized. Other general information about the system are listed in table 1

Typical Experiment Parameters	
Tip Type	Platinum Coated Arrow Tip
Tip Resonate Frequency	≈ 275 kHz
Tip Tapping Amplitude (free space)	100-150 nm
Tip Tapping Amplitude (in contact)	60-70 nm
Arm Path Lengths	≈ 72 cm
Detector Active Area	0.25 mm
CO ₂ power at Iris 2	0.5 - 7 mW
Thermal power at Iris 2	0.3 - 0.5 mW
Lock-In Time Constant	10 ms

Table 1: Additional system information and parameters

3.2 Instrument Modifications

Many more modifications needed to be made on the small scale to fully realize the nano-FTIR system. Most of this work involved the CP II AFM and the Nicolet spectrometer as described below in brief summary.

3.2.1 Veeco CP II

The primary modification made by previous students on the CP II was to cut away part of the top to allow a beam access to the tip-sample region for s-SNOM (Fig. 10). This required reconstructing new custom housing for the electronics and machining of mounts for the AFM's diode laser and quadrant photo-detector. At my time of arrival however, many of electronics needed to be fixed, making repairs in the head and the AFM's DAC (Digital Analog Controller) my primary task. Additionally, the piezoelectric scanner was replaced and carefully calibrated.

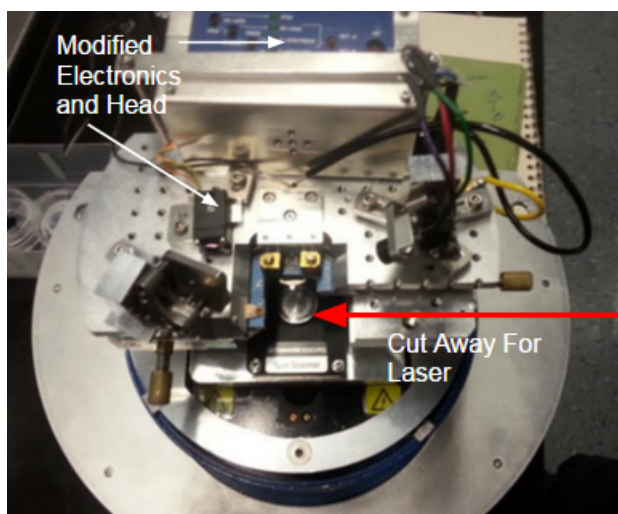


Figure 10: The CP II AFM modified for s-SNOM. The original head has been removed to allow for a laser to enter from the side. Custom mounting for the components became necessary for this modification.

3.2.2 Nicolet 6700 FTIR Spectrometer

Several modifications were made to interface the Nicolet spectrometer with an external detector and thermal source. First, the original internal beam splitter was replaced by a tiny (0.125 cm^3) beam splitter allowing the internal alignment HeNe to still track the translation mirror without splitting off the external thermal radiation (Fig. 11). This required machining a new high-precision mount for the new beam splitter, and coming up with creative ways of controlling the beam splitter's position to fractions of a millimeter while it sat inside the instrument.

Next, the signal from the Judson J15D12 MCT needed to be relayed to the instrument's computer so that it could correlate mirror position with measured intensity. After many attempts at clever cabling and software upgrades, the ultimate solution was to rewire the signal from the instrument's internal detector directly with our own, using a breakout box.

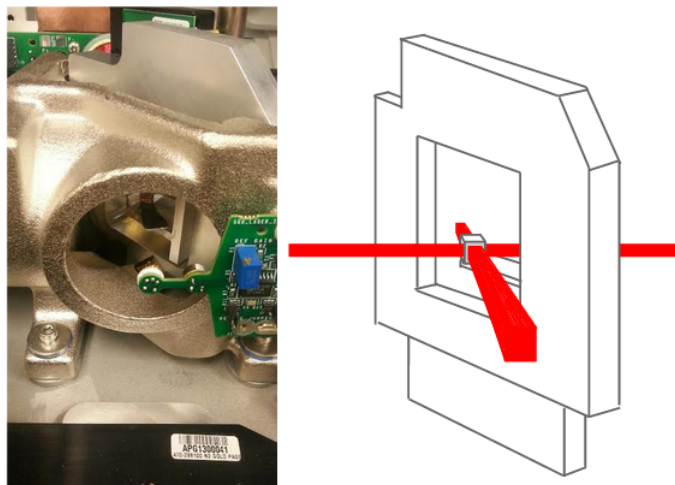


Figure 11: A tiny cubic beamsplitter needed to be mounted in a high precision aluminum mount to maintain mirror tracking capabilities. The beamsplitter needed to be rotationally and spatially aligned to fractions of a millimeter - accomplished by fastening the beamsplitter to a lever adjusted in tilt with wedges of individual layers of paper.

Finally, the internal Thermo Fisher infrared source for the Nicolet spectrometer was rewired externally as our thermal source. This source had the advantages of a long lifetime, high stability, and was computer controlled. However it seems that it did not run at the advertised temperature of 1000 K - 1200 K (see chapter 4).

3.3 Signal Recovery and Processing

The relatively simple signal recovery scheme required to extract the data from the nano-FTIR system begins with the Judson MCT in the detection arm of the interferometer. This MCT was chosen not only because it is highly sensitive in the mid IR around 10 μm , but also because it uses photovoltaic detection to maximize sensitivity to small signals - something deemed necessary after failure with a *photoconductive* alternative. Photovoltaic detection comes however at the cost of an increase in response time which originally added

a lot of complexity to the system prior to the implementation of the break out box.

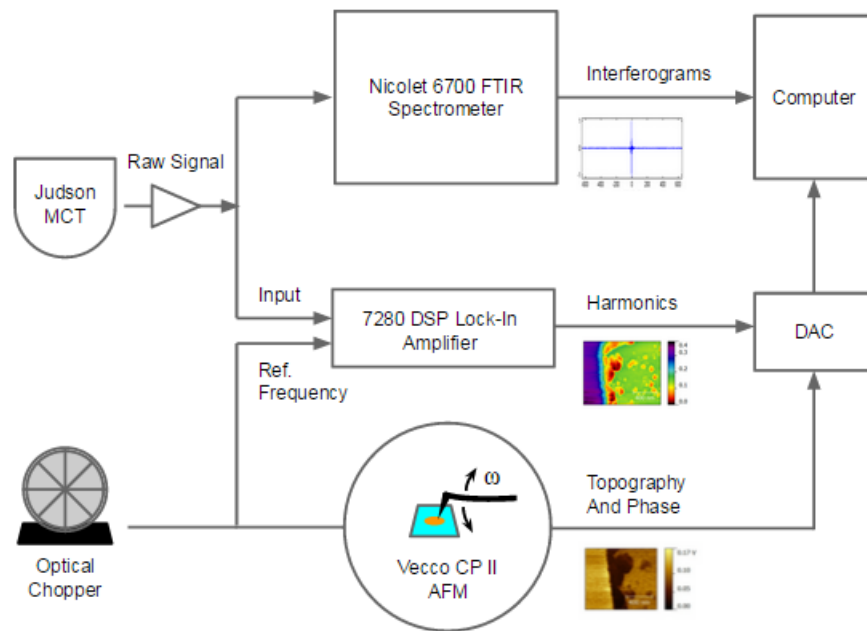


Figure 12: Signal recovery scheme for the nano-FTIR spectrometer. Raw signals are generated from the MCT and AFM which are then processed using the Nicolet's Omnic software, and the AFM's ProScan software.

The signal from the MCT is amplified and split with one half sent to the Nicolet 6700 and the other to the 7280 DSP lock-in amplifier (Fig. 12). A reference signal is sent to the lock-in either from a chopper or from the AFM, to isolate the signal from the background. When taking spectra without performing s-SNOM, the chopper frequency is used. For any near-field information extraction, the tip dither frequency must be used.

4 System Characterization

4.1 Parabolic Mirror Characterization

One of the major goals of our system is to maximize the interference of light at the MCT detector since it is this AC coupled signal from which our interferograms, and hence spectra, are derived. It is hoped that by more carefully thinking about divergence and spatial coherence of both the tip and thermal source, we can achieve higher signal to noise ratios than done previously [10].

Firstly, since we are using an incoherent source of radiation, we want to choose a 'collimation' optic for the thermal source with a focus spot size diameter on the order of the coherence length of the thermal emitter, $L_c \approx 10 \mu\text{m}$. Only the emitters in the region defined by L_c exhibit enough spatial coherence to contribute to the interference in the far-field. Thus a collimation optic that mostly excludes emitters outside of this coherence region is optimal for reducing noise at the detector from extraneous spatially incoherent rays.

For the optic at the AFM, we need as high a numerical aperture optic as possible to maximize radiation on the tip. This is because any confocal volume for even a diffraction limited system will be much larger than the tip apex volume when using infrared radiation. Since we are using one inch diameter mirrors for the beam path (affecting achievable beam diameter D), and a modified AFM with a fixed stage geometry (affecting minimum focus distance F), we are limited in practice by how high of a numerical aperture we can achieve with this optic.

Lastly, we must consider the fact that we image finite sources with finite beam waists, and this leads to inevitable divergence through the system. This divergence leads to Hädinger fringes at the detector [1], from which only the central one must be selected using a limiting aperture called a Jacquinot stop. In our case, this stop not necessary. This is in part due to the 4000 cm^{-1} range and 4 cm^{-1} resolution of our spectra, but primarily because our mirrors aperture the divergent beam due to our long beam paths. When choosing an optic for focusing into the MCT then, we just want to check that the area of its spot size is will fully fall on the detector element to maximize fringe contrast.

We now show that the optics we selected are adequate for the considerations discussed. All mirrors are coated in gold to maximize reflectance in the IR. We will determine experimentally, the beam waists (spot sizes) of these optics using a 632 nm HeNe laser, and then compare the results to theory. Then we recalculate with light of $10 \text{ }\mu\text{m}$ wavelength as an estimate for the thermal radiation used in the real experiment. To begin our approximate calculation of spot size radius, we note that

$$\theta \approx \arctan \frac{D}{2F} \quad (18)$$

by using D as an effective lens diameter and F as the effective focal length (Fig. 13). But the HeNe laser used in the tests is Gaussian, and so we also have an equation describing the beam profile given by

$$w(z) = w_0 \sqrt{1 + \left(\frac{z\lambda_0}{\pi w_0^2}\right)^2} \quad (19)$$

(defined by the $\frac{1}{e^2}$ drop off definition) where w_0 is the spot size of the beam waist, and λ_0

= 632 nm is the wavelength of the light used. It is clear from the plot (Fig. 14) that in the limit of large $|z|$, the angle for this beam is also

$$\theta \simeq \frac{\lambda_0}{\pi w_0}. \quad (20)$$

Since the measured $\frac{1}{e^2}$ diameter of the expanded HeNe beam is 8.695 mm, and F can be measured or looked up in the data sheets for each optic, we can simply equate equations 18 and 20 to get an approximation for the only unknown, w_0 .

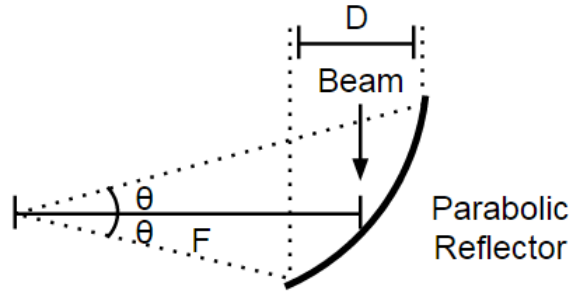


Figure 13: Geometry of a parabolic reflector. The effective focal length F is different than the actual focus of a full parabola.

Experimental verification of this result uses the knife edge technique to calculate spot size by sweeping a sharp blade in front of the Gaussian beam (Fig. 15). The blade is moved first to the x position where the power reaching the detector is attenuated by 90%, and then further to the point where the power is attenuated to 10% (the 90-10 version of the method). These x positions need to be related to the $\frac{1}{e^2}$ or ' x_e ' radius values of the Gaussian beam (about 86.5% and 13.5% attenuation) so that a plot of Δx vs. z can be compared to the theory given by equation (19) above (i.e. $x_e = w_0$).

As a brief description of how this conversion is done, we first observe that power as a function of blade translation is related to the total power by

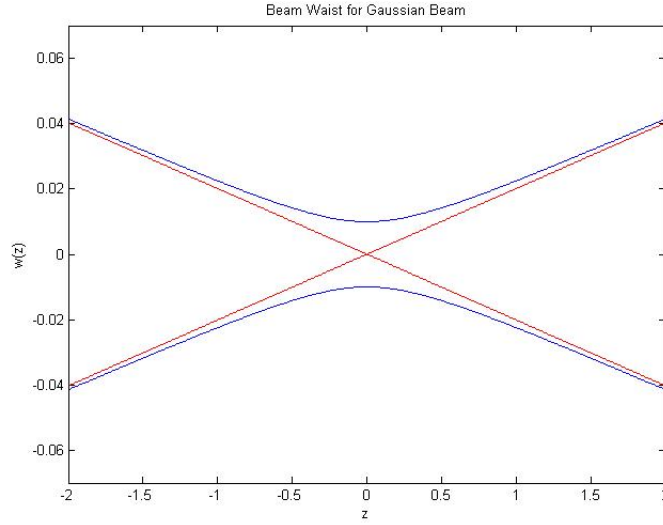


Figure 14: The focus of a propagating Gaussian beam by a parabolic mirror. The minimum separation between the bottom and top curves corresponds to twice the minimal beam radius, w_0 . Far from the waist, the beam expands linearly. The red curve shows this asymptotic behavior, while the blue shows equation 19 defining the waist.

$$P(x) = \frac{P_{total}}{2} \left(1 - \operatorname{erf}\left(\frac{x\sqrt{2}}{x_e}\right) \right). \quad (21)$$

This result is easily derivable from integrating a Gaussian with a boundary condition from the knife edge, but is omitted as it is not particularly interesting. We now simply plug in $0.1P_{total}$ and $0.9P_{total}$ in for $P(x)$ to obtain

$$\operatorname{erf}\left(\frac{x\sqrt{2}}{x_e}\right) = \pm 0.8 \quad (22)$$

respectively for the 90% and 10% power values. Using standard look up tables for Gaussian probabilities, we can compute that x for 10% is equal to $0.64x_e$ so that by symmetry the difference in x , Δx is just $1.28x_e$, or $x_e = \frac{\Delta x}{1.28}$.

Armed with correctly converted data, we can now fit a beam waist theory curve to our

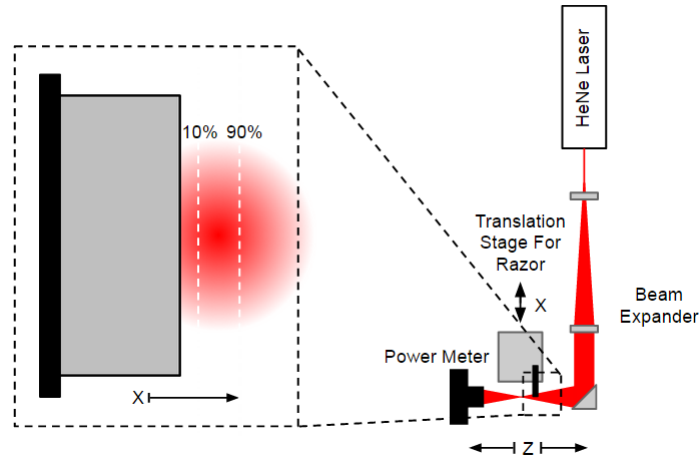


Figure 15: The knife-edge method for measuring a beam's diameter. The 10% and 90% attenuation values are recorded and then converted to get a sense of beam width.

knife-edge data and get an estimate for the parameter w_0 . The results are shown in figure 16 for each parabolic mirror. (This includes the Anasys AFM's parabolic to be used on the next iteration of the setup. See chapter 6). The results of the theory fit versus calculation are all tabulated in table 2.

Mirror spot size radius (w_0) from theory and experiment				
Parabolic	Focal Length	Theory, 632 nm	Experiment, 632 nm	Theory*, 10 μm
CP AFM	17 mm	0.80 μm	0.78 μm	4.96 μm
MCT	101.8 mm	4.71 μm	3.26 μm	25.64 μm
Anasys AFM	20.3 mm	0.95 μm	0.87 μm	5.69 μm
Thermal	20.3 mm	0.95 μm	0.91 μm	5.69 μm

Table 2: Mirror Spot Sizes. The experimental values are likely lower because the knife edge cut the Gaussian beam at an angle rather than perfectly perpendicular, leading to underestimates of spot size. *Theory for thermal light adjusted for 25.4 mm diameter beams.

The results agree reasonably well with theory. One source of error is the difficulty in measuring small spot sizes due to a limited translational resolution of about 10 microns.

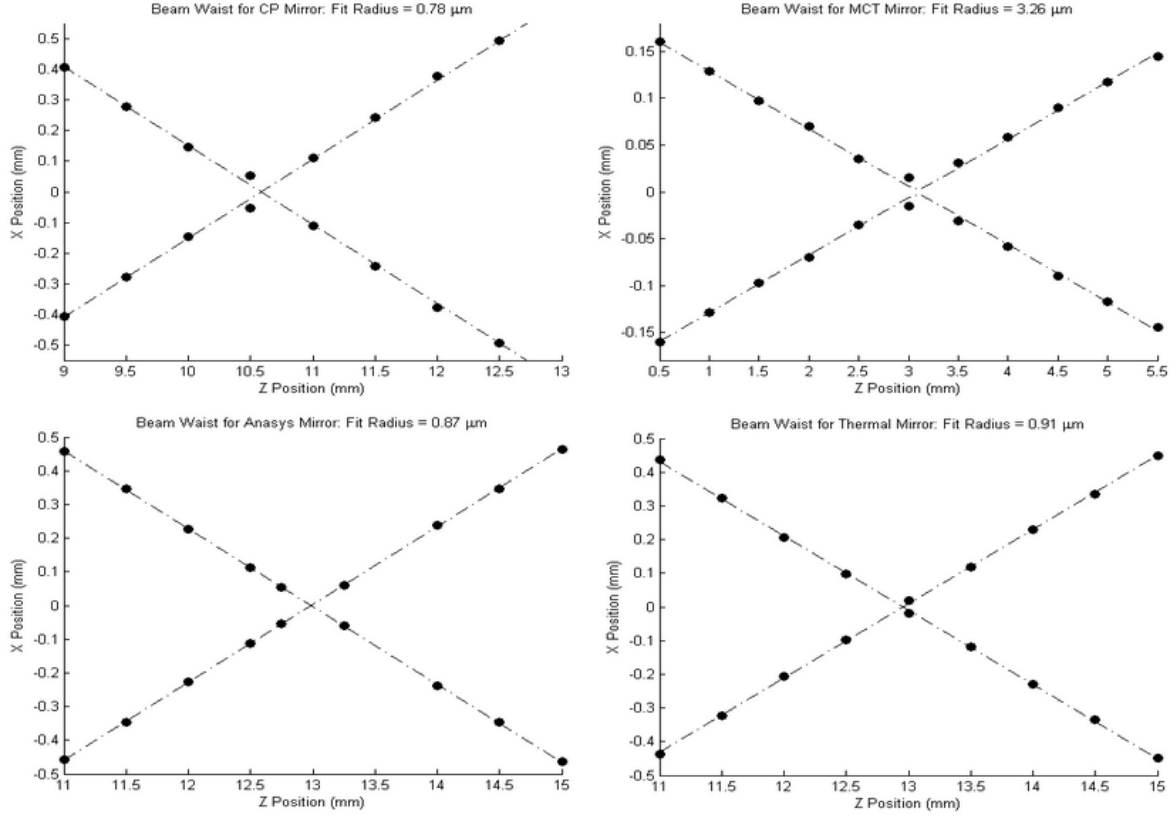


Figure 16: Parabolic mirror characterization plots showing the Gaussian beam waist fit (dotted line). The error in measurement is about 10 microns in both x and z.

Additionally, there is a systematic error due to slight misalignments in the beam and translation stage. Since these are not perfectly orthogonal, the knife-edge will cut the beam at an angle, reducing the effective spot size. It is clear from the table that our optic for thermal source collimation is on the order of a wavelength as we desired, the AFM optics are near their diffraction limited values for the given numerical aperture, and that the detector parabolic has a spot diameter of $\sim 50 \mu\text{m}$ compared to a detector diameter of $250 \mu\text{m}$.

4.2 Thermal Source Characterization

Characterization of the thermal source can now be done with the interferograms at hand by analyzing the resulting spectra against an ideal blackbody. This allows us to get a sense of the emissivity as a function of wavelength, and the peak temperature, from which other parameters can then be estimated. Since we are using the same source as the Nicolet's internal source, we can simply analyze a spectrum with the spectrometer itself. This spectrum will already be corrected for the detectivity of the internal detector (a DTGS pyroelectric detector) when it is processed by the software.

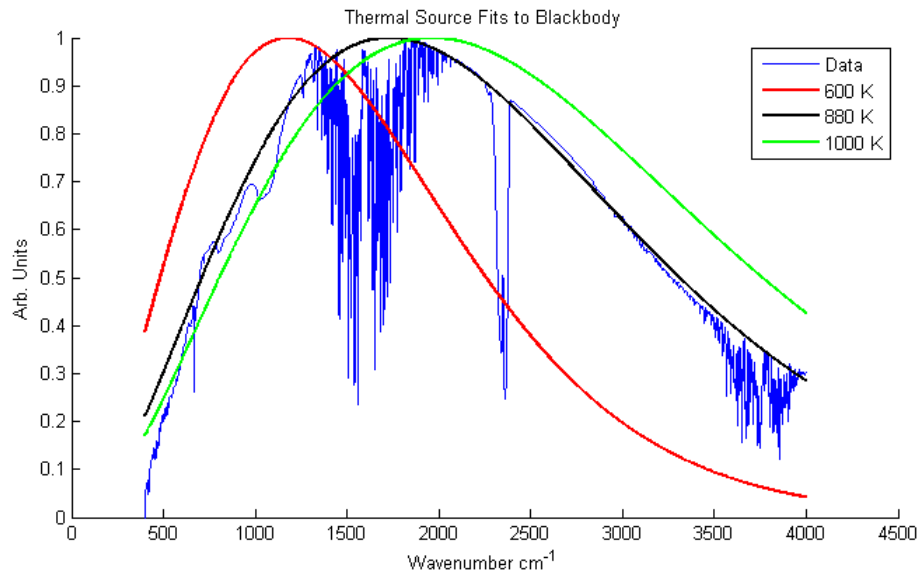


Figure 17: Spectral Radiance of Blackbody at 600, 880, and 1000 Kelvin.

We estimated the fit above using Wien's displacement law for a peak wavelength of $6.66 \mu\text{m}$ (1500 cm^{-1}), providing the 880 K value. Though this fit is not highly accurate, and the emissivity properties of the source are unknown, this value seems much lower than the 1000 K - 1200 K value advertised. We also tried the 6575 filament infrared emitter

source from Newport Corporation, however the emissivity was very low past about 6 μm (1666 cm^{-1} making it a less attractive option for broadband infrared spectroscopy).

It is clear that future systems will need to employ better sources. The power emitted per unit area in our 880 K source can be estimated as

$$j = \sigma * T^4 = 32002.7\text{ Wm}^{-2} \quad (23)$$

or

$$\begin{aligned} \text{Power} &\approx 32000\text{ Wm}^2 * 100(\mu\text{m})^2 \\ &= 3.4\mu\text{W} \end{aligned} \quad (24)$$

for our thermal mirror spot size. If the source ran at 1000 K and 1200 K, we could achieve powers of 5.67 μW and 11.8 μW respectively, underscoring the importance of temperature. In the future we will need to more carefully select our thermal options and verify that advertised temperature outputs are correct.

4.3 AFM and s-SNOM Characterization

To prove the strength of the near-field spectroscopy system, the more powerful ~ 10.2 micron CO_2 laser was used to optimize sensitivity to the infrared before putting in the thermal source. Platinum iridium5 and chromium coated silicon arrow tips were used to maximize diode laser reflectance and tip conductivity. These highly doped tips have a high Q-factor with a resonate frequency around 275 kHz, a free space tapping amplitude of about 110 nm, and an amplitude of about 65 nm when tapping near the sample sur-

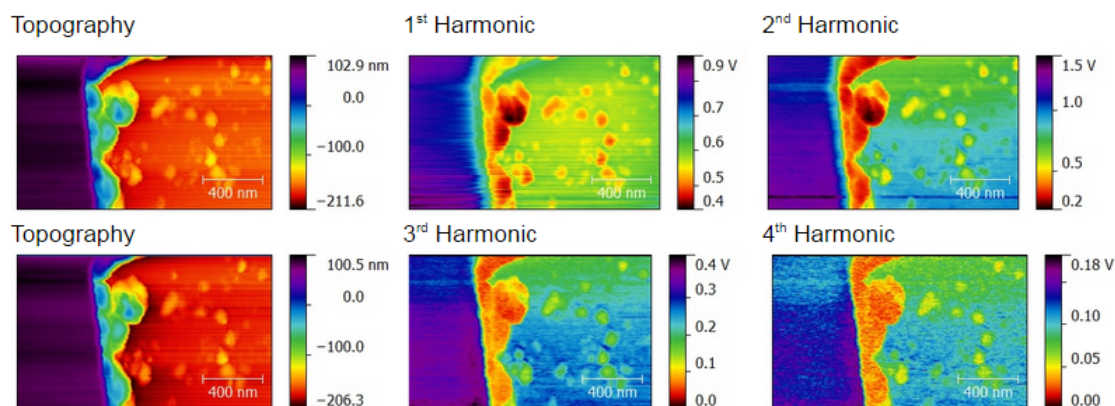


Figure 18: CO₂ near-field data from CP II AFM. Note that the first harmonic signal is significantly less than the second harmonic signal. This is due to different sensitivity setting on the lock-in amplifier, and the fact that maximizing the signal for the second harmonic does not necessarily imply a maximum first harmonic signal.

face. The results of figure 18 show that high signal to noise levels were obtained all the way into the fourth harmonic, indicating an efficient near-field imaging system. Furthermore, the minimal hysteresis of these multi-minute scans attest to a stable, well calibrated piezoelectric scanner.

These images have only been processed with a color scheme using Gwyddion and were taken three at a time because only two signals could be retrieved from the lock-in at a time (topography is retrieved from the AFM itself). The images are a small portion of a calibration grid of gold on a silicon substrate with a periodicity of 1.5 μm . One can clearly see that the topography is reproducible to within a few nanometers between the two sets. Furthermore, there is consistency in the contrast due to local variation in near-field scattering between all the harmonic images. It is not uncommon to see signals well into even the 6th harmonic for such a laser.

5 Results and Analysis

Many results of the nano-FTIR system have been very exciting, but also somewhat limited. Unfortunately, evidence of fundamental barriers to progress have become apparent through the evolution of the system that were not known previously. In this section I will discuss some of these successes and shortcomings. The strategy for overcoming these challenges, and the current work on the next iteration of the system will be the topic of the next chapter after these results.

5.1 Interferograms

A huge initial success of this system has been its ability to perform spectacularly as FTIR spectrometer. Figure 19 shows for example, the comparison of a single background spectrum of air with our system vs. the Nicolet using the Thermo-Fisher source, taken off the a flat mirror at the AFM. Note that there is large attenuation in the spectrum of the external source due to the use of a Barium Fluoride (BaF) beamsplitter rather than the KBr (Potassium Bromide) beamsplitter used in the Nicolet. BaF becomes strongly opaque below about 900 cm^{-1} . The interferogram for this spectrum also shows a high signal to noise ratio, and symmetry - indicating good interferometer alignment and dispersion matching (Fig. 20).

For a more quantitative analysis of system fidelity, we can also look at the results from the higher power CO_2 laser. Figure 21 shows the 1st harmonic, tip scattered spectrum of the laser from the interference of the 1st harmonic scattering from the AFM cantilever with the reference arm. We can see that the line width and shape behaves entirely as we expect

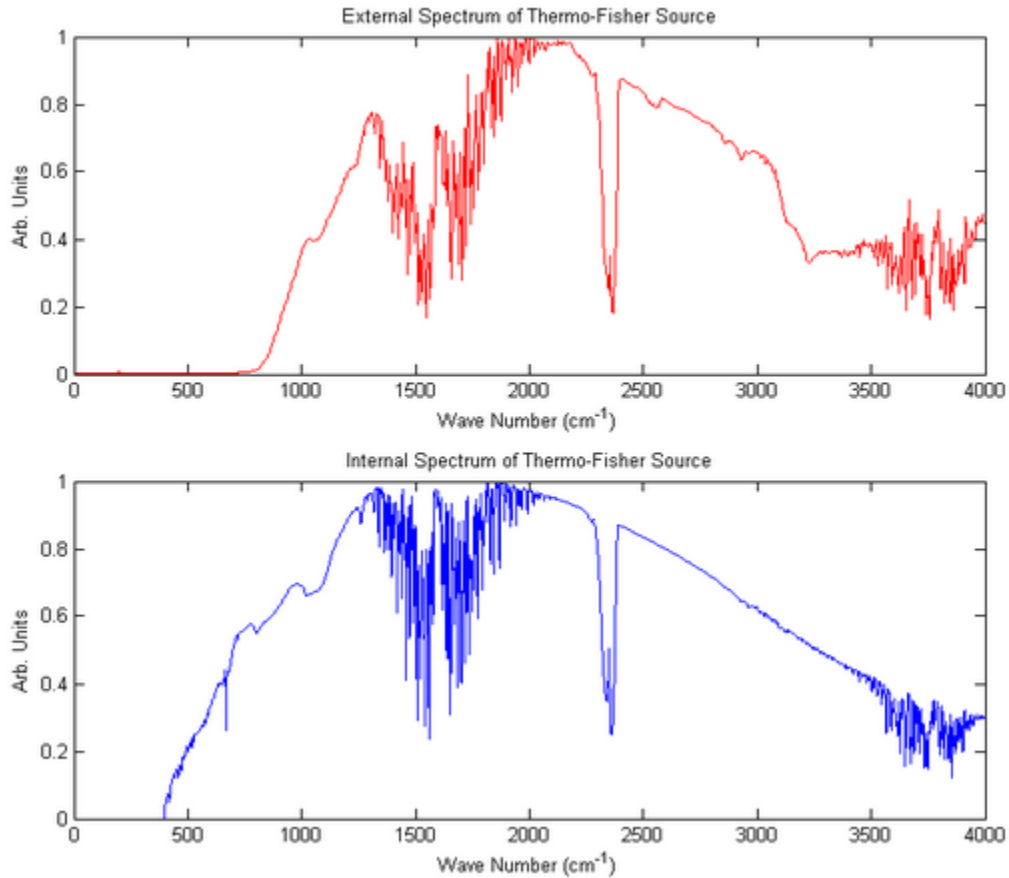


Figure 19: Comparison of the Thermo-Fisher spectra for the external (top) and internal (bottom) configurations. Both spectra were taken at 4 cm^{-1} resolution. 1 scan takes approximately 0.15 seconds.

after Fourier transform at a resolution of 4 cm^{-1}). The linewidth is about 4 cm^{-1} and fits a Gaussian (as expected from an imperfect laser). Happ-Ganzel apodization, and Mertz phase correction [1] also contribute to the lineshape and asymmetry, but these effects are seen to be minimal in this plot. Though the laser scatters appreciably more radiation from the tip than the thermal source, this data shows that the FTIR spectrometer aspects of this system are limited largely by source intensity and collimation rather than incorrect layout or misalignment.

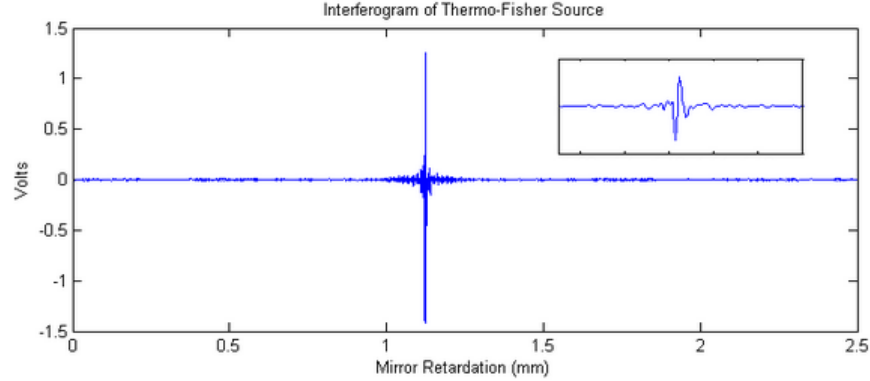


Figure 20: Interferogram of external Thermo-Fisher source. The close up shows a high degree of symmetry and signal to noise. The interferogram consists of 16384 data points over a mirror retardation amount of 2.5 mm.

5.2 Thermal S-SNOM

A lot of success was found when performing thermal s-SNOM as well. Often the procedure of co-linearizing the thermal radiation with the CO_2 laser, finding CO_2 near-field, and then switching to the thermal source, produced a small first harmonic signal from the tip with little effort. This again shows the experimental design to be both reliable and effective. Finding signal in the second harmonic however, proved to be a much bigger challenge.

Since the 1st harmonic signal can vary wildly due to scattering from all over the tip, tip holder, or cantilever, the signal should only be optimized up until the point a small second harmonic signal is seen. The maxima and minima of second and first harmonic signals are generally *not* at the same parabolic focus locations. With such a small first harmonic starting signal, the problem of finding second harmonic then reduced to a little bit of luck, and a lot of patience.

Second harmonic was found on several occasions however, and optimized to a point

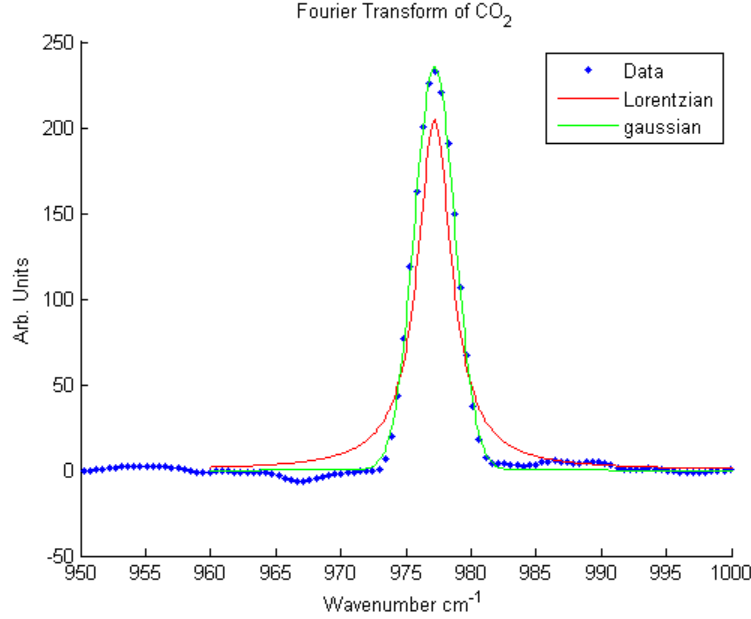


Figure 21: Spectrum of CO₂. This close up shows that for a resolution of 4 cm⁻¹, the system behaves nominally. The lineshape appears to be dominated by inhomogeneous broadening resulting in a Gaussian.

where contrast between materials of different dielectric contrast could be seen. For example, for the a gold-silicon step edge, we could see clear differences in the response of the materials in the first and second harmonics (Fig. 22).

These images are strong evidence for near-field signals, but certainly not conclusive. To be confident that this really is the near-field interaction we care about, we need to check several other parameters of the system. For example, we need to be confident that the AFM's tip is truly in 'contact' with the sample surface by checking that it has a stable dampened oscillation at this point. We also need to make sure the signal responds as we expect as we move in and out of close proximity (it decreases as we increase tip-sample distance, and vice versa). Even without tools like approach curves, we were reasonably confident that the above checks behaved as expected.

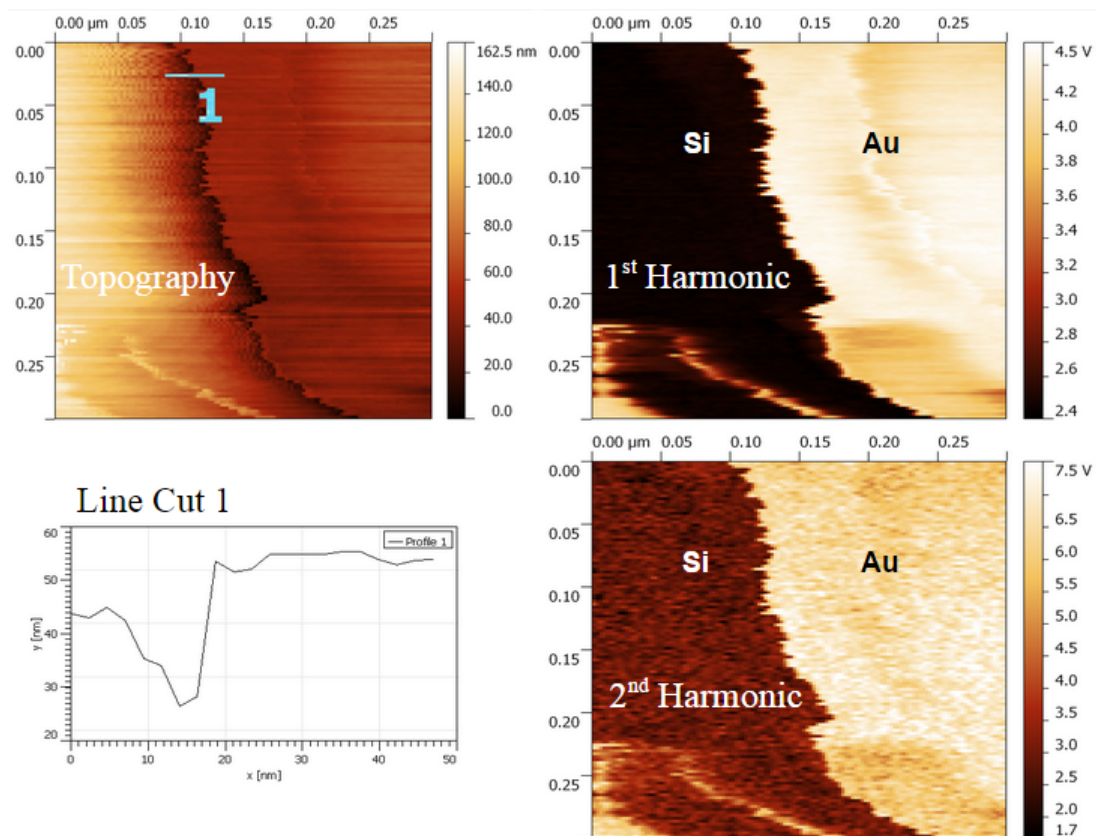


Figure 22: Near-field data for the first and second harmonics of thermal radiation on a gold silicon step edge.

5.3 nano-FTIR

It is clear that the system can operate as a good spectrometer, and reasonably well for s-SNOM. Combining the second harmonic and interferometry however, yields a big unanticipated problem. Even a highly optimized near-field signal is so weak that its interference with the reference arm will just barely show up in an interferogram taken with the Nicolet 6700. Since the software needs the signal to exceed a threshold above the noise to locate a ZPD location, it cannot integrate many interferograms over the same range, instead stopping and starting scans at random locations. This means any signal will be integrated out, rather than isolated from the noise.

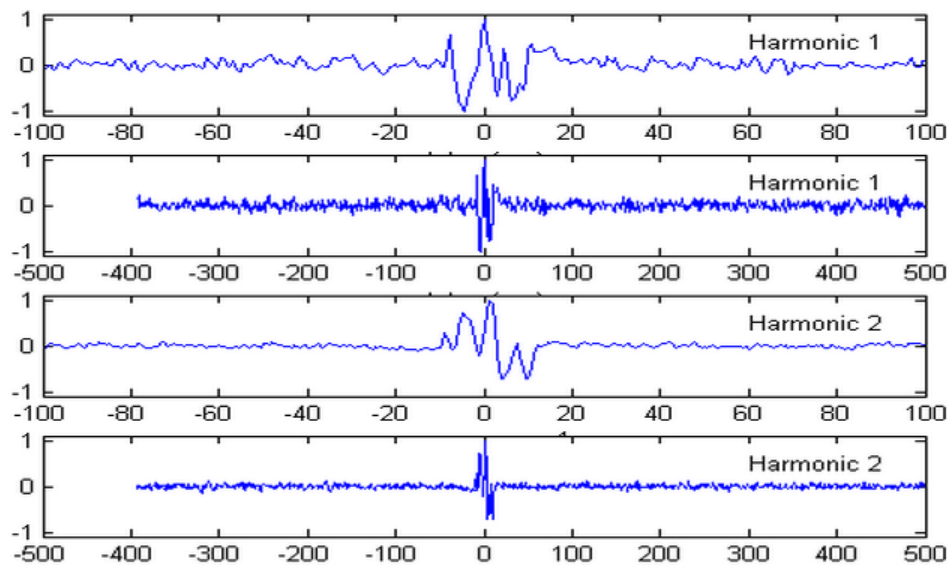


Figure 23: Interferograms for the thermal source on gold. Even with a 15:1 signal to noise ratio for the 1st harmonic and a 6:1 signal to noise ratio for the 2nd, the interferograms are barely detectable through the alternative channel in the Nicolet FTIR spectrometer.

Unfortunately, we could not reprogram the software to fix the center burst location as the ZPD position when a small signal was seen. My lab partners were able therefore at-

tempted to get interferograms (Fig. 23) going through a different channel in the Nicolet spectrometer. This method suffered from both a large amount of noise and signal cross talk, and also prohibited interferogram integration - making it more or less useless. This limitation ended up making integrated interferograms of the sample more or less impossible for the system when operating with only near-field signals.

It therefore became apparent that the system would need to be much more compact to further increase thermal signal, and that a new stage and program would be needed. As the plot in figure 24 shows, between Iris 1 and Iris 2 in figure 8, there is a decrease in power from 22.32 mW to 3.54 mW over just 33.02 cm. This is to be expected from an incoherent source with significant divergence, but underscores the importance of system compactness for maximizing power through the system.

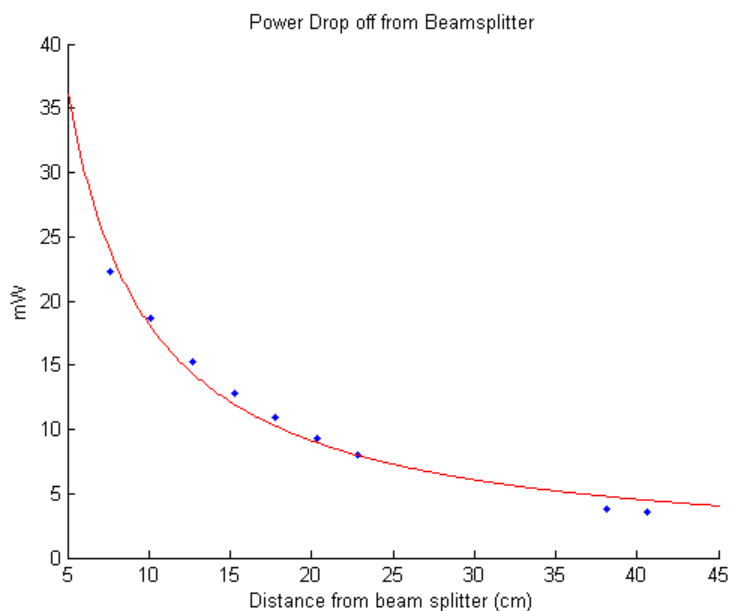


Figure 24: A large decrease in power is observed as one moves further from the thermal source. This power is compared to a $\frac{1}{r}$ drop off curve to show how it decreases with distance. The AFM is another — hole (convert to cm) away, making the power at the tip extremely minuscule.

6 Continuing work and Conclusions

6.1 Current Work

The nano-imaging system has recently been redesigned to overcome the challenges of its predecessor (Fig. 25). To start, an Anasys AFM has been put in place of the CP II. This AFM is capable of providing more diagnostics for near-field acquisition and system performance than the previous AFM. Next to this AFM is an extremely precise piezoelectric translation stage for the focusing parabolic reflector, which helps with the repeatability and quantification of moving the focus of the radiation onto the AFM's tip. The major changes however, are the decreased lengths of the interferometer arms, and the new translation stage for the retarding mirror. The arm lengths have been reduced from 72.5 cm to about 9.5 cm, and the stage uses LabView for more user control of the ZPD position, scan lengths, integration times, rapid scan, and so on. Hence the limit of the Nicolet's translation stage is no longer an issue for weak signals. Finally, the whole system is enclosed for nitrogen purging to suppress background absorbance.

A lot of the work put into constructing the system was done by myself and other grad students over the last month or so to machine new table mounts for the AFM, enclosure materials, and lay out all of the optics. Unfortunately, the beginnings of the exciting results to come out of this system have coincided with the deadline for thesis completion, so I can only include some of the early results taken by my lab partners near the beginning of March.

Instead of trying gold and silicon surfaces, enough signal was obtained to immediately

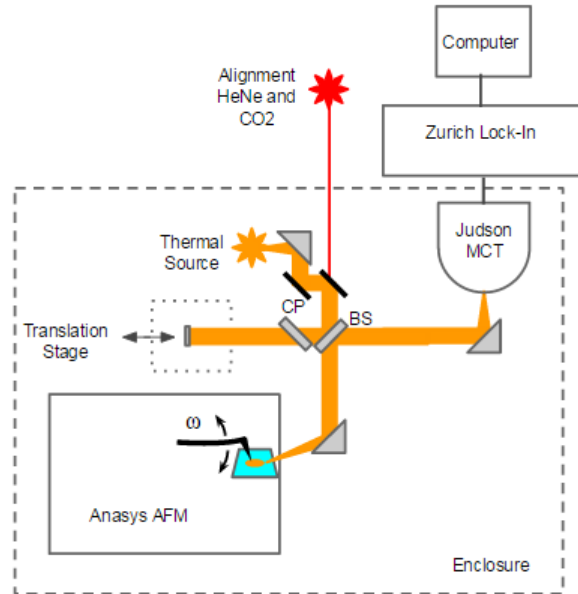


Figure 25: The new setup of the nano-FTIR spectrometer with an upgraded translation stage, AFM, and reduced arm lengths.

measure more interesting materials such as silicon carbide (SiC) and Boron Nitride (BN) (using the same Thermo Fisher thermal source). Figure 26 shows such an interferogram and spectrum of the distinctive surface phonon polariton resonance around 950 wavenumber for SiC. Note that the scans were taken with signals in the first harmonic, rather than with the second. We were able to use this harmonic because we could measure the near-field enhancement in the signal using a tool of the Anasys called 'approach curves.' This slowly brings the tip close to, and then far from the sample, to measure scattering enhancement. Since these curves indicated that a large enough portion of our demodulated signal was originating from the near-field, it was acceptable to use the first harmonic, and this is verified by the data. It is expected that continued improvements to signals in the higher harmonics will soon yield spectra from even better isolated near-field interactions.

Measurements on BN and other materials will soon follow with the intent of better

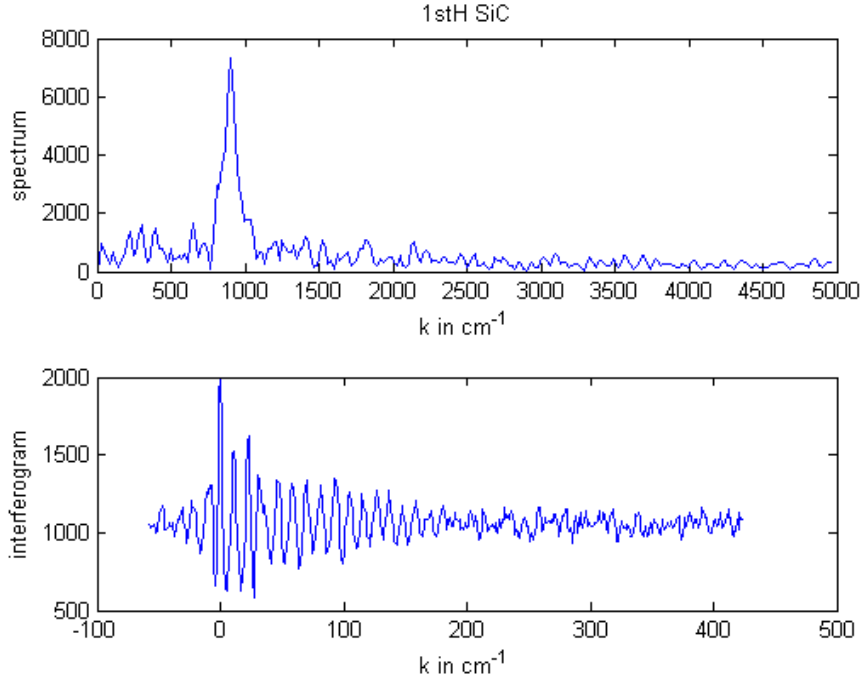


Figure 26: The above shows the spectra (top) and interferogram (bottom) of the familiar surface phonon polariton response of SiC around 950 wavenumber. This data was taken by integrating 20 scans at 42 cm^{-1} resolution.

characterizing them and fine tuning the new system. It will remain to be seen how this system compares to the work done previously [10], as we further consider better thermal sources and beam apertures.

6.2 Concluding Remarks

The development of the nano-FTIR spectrometer in this work marks an important step toward ubiquitous broadband nano-scale spectroscopy. The ability to perform non-invasive chemical mapping of materials on this scale not only improves upon some of the current applications of FTIR spectrometers, but also shows promise for studying new phe-

nomena unique to the nano regime. As such, nano-FTIR spectroscopy is expected to be useful in many engineering and scientific contexts.

We have shown definitively that such a system is capable of such applications. The results of this work demonstrate that our system can be applied both toward understanding emergent properties of matter on the nano-scale and for the determining chemical composition. However, more work is needed to realize the full potential offered by such a system. For example, the jump from the point spectra shown in the previous section to a full 2-D chemical map will likely require significant modifications to the AFM's cantilever system, as well as big improvements in image acquisition speed and scanner stability. More throughput will also be required to get radiation to the tip and enhance interference at the detector, requiring hotter running temperatures and perhaps larger beam path mirrors. Additionally, more careful management of beam divergence will be necessary to manage fringe contrast. These considerations will all help to reduce the integration times for reasonable signal to noise levels which currently limit this technique.

It will be very exciting to see how far the current system can be pushed as we continue to optimize components and designs. Even knowing it is possible to obtain meaningful signals from nano-FTIR spectroscopy is a tremendous step forward for the technology. We look forward to the new data still coming out of the upgraded system, and also to the bright future of nano-FTIR spectroscopy that is already starting to be developed for commercial systems.

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