Featuring PiFM & PiF-IR chemical analysis

Released: Jul 1, 2022

Whitepaper Article

PiF-IR vs FTIR: How Useful is Nano-spectroscopy?

Introduction

PiFM and PiF-IR are the next generation of infrared spectroscopy techniques. PiFM revolutionized atomic force microscopy by providing chemical mapping capabilities. PiF-IR is PiFM's sister technique used for measuring nanoscale spectra. However, PiF-IR is not just a companion nanoscale IR technique. It is an extremely capable spectroscopy technique that expands the horizons for all types of IR spectroscopy, including FTIR. As reliable and as versatile as FTIR spectroscopy is, it can no longer keep up with the spatial resolution and surface-sensitivity requirements of modern nanomanufacturing. The future needs extremely precise and sensitive analysis, and no other infrared spectroscopy technique can provide the same results as PiF-IR.

Background

FTIR (Fourier transform infrared) spectroscopy is a very well-known analytical technique that is used to detect and identify organic and inorganic molecules. It can effectively analyze solids, liquids, and gases. However, for comparison with PiF-IR, this discussion will be limited to solid materials.

FTIR instruments are typically spectrometers only. That means they offer a simple bulk measurement of the sample without preserving the spatial chemical heterogeneity. Unfortunately, this doesn't work very well on composite materials. Therefore, some companies couple an infrared microscope to an FTIR spectrometer which can be used to spatially resolve the chemical features in a sample. While this offers an improvement, FTIR is still limited to a spatial resolution of ~5 microns due to the diffraction limit of infrared light. Therefore, unless the sample is available in large quantities of pure material, the utility of FTIR can be limited.

PiF-IR is an AFM-IR technique that uses photo-induced forces (PiF) to analyze solid and thin-film samples at very high spatial resolution. AFM-IR instruments are based on atomic force microscopes, which inherently have a spatial resolution of a few nanometers. When infrared capabilities are added to such an instrument, the leap in spatial resolution and surface sensitivity is astounding. PiFM absorption maps can show chemical distributions with a lateral resolution better than 5 nm, and PiF-IR nanoscale spectroscopy can probe a volume that is at least one billion times smaller than FTIR. Therefore, measurements using these techniques are orders of magnitude more sensitive and localized than the best FTIR microscopes.

FTIR theory

The most fundamental parts of an FTIR instrument are the light source and detection scheme. All FTIR-based instruments have the same fundamental ingredients: a broadband light source, an interferometer, and a photodetector.

The interferometer acts as a sort of "tunable" detector which is not always intuitive to understand. As the IR light passes through the interferometer it is split into 2 pathways: one with a fix path length (stationary mirror), and the other with a variable path length (moving mirror). When the light from these two pathways converges at the sample, they interfere with each other. The photodetector records the intensity of all wavelengths of light, and that is plotted in the computer as a function of the moving

mirror's position. This interference spectrum is called an interferogram. The Fourier transformation (FT) is then applied to the interferogram to convert it into a spectrum.

One way to think about this process is that the interferometer encodes the light into a time-domain measurement, which is the interferogram. The Fourier transformation de-encodes the interferogram back into its spectral features as a function of wavenumber, which is in the frequency domain.

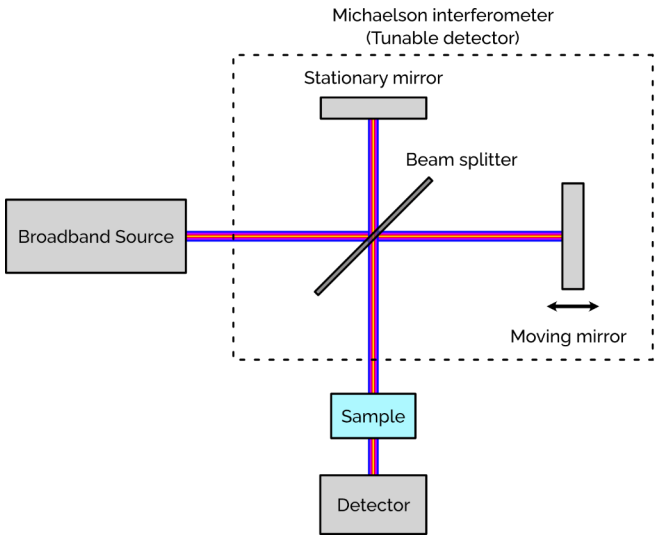


FIGURE 1. Schematic of an FTIR with a Michaelson interferometer. The light from the moving and stationary mirrors creates an interference pattern. This pattern interacts with the sample, and it is different for each position of the moving mirror. Since the detector collects the data as a function of mirror position, a Fourier transform is performed to recover the spectrum as a function of wavenumber, which is equivalent to frequency.

PiF-IR theory

PiF-IR is the spectroscopy component of PiFM measurements. These techniques rely on mechanical force detection of a sample's absorption to enable nanoscale chemical measurements. Because they are a class of AFM-IR measurements, the entire system is built on an AFM (atomic force microscope) so it can simultaneously measure the topography as well as the chemistry.

An AFM is a type of scanning probe instrument where an extremely sharp probe (~10 nm radius) is raster-scanned over the surface of a sample. Like a record needle, the AFM probe interacts with the sample and is deflected by the topography. However, instead of producing sound, this deflection is recorded to generate a heightmap of the sample's surface. This technique provides extremely high-resolution topographic maps, but they are in "black and white," meaning they are devoid of any chemical information.

To add "color" to the AFM topography, PiF chemical analysis techniques can be used simultaneously to identify and map out surface materials while beating the diffraction limit by 1000x. This is done by focusing a tunable infrared (IR) laser onto the tip of a metal-coated AFM probe. The metal-coated tip acts as a nano-antenna and creates a highly local enhanced field which excites the sample. The sample's optical response can be detected mechanically via dipole-dipole force interactions between the tip and the sample's surface.

By leveraging the field enhancement of the tip and a sideband bimodal™ detection scheme, these PiFM and PiF-IR measurements can have a resolution that exceeds that of the AFM topography for the same tip! Therefore,

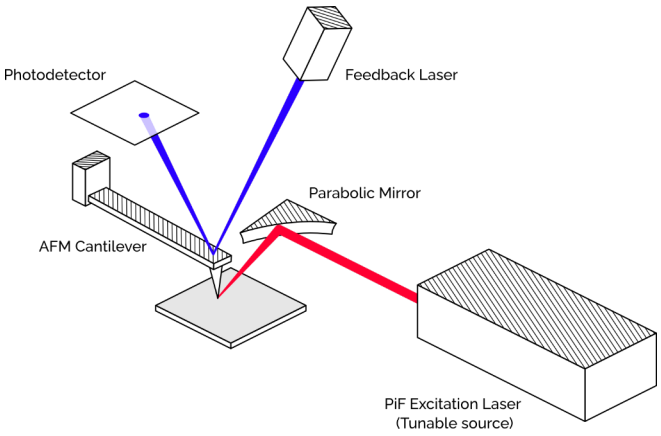


FIGURE 2. For PiF-IR and PiFM, a narrow-band tunable excitation laser is focused onto the tip of an AFM probe. The laser excites the sample, and the AFM probe mechanically detects the excitation at a resolution that beats the diffraction limit by 1000x.

PiF-IR spectra are the next-generation of FTIR-type spectroscopy because the advances in resolution offer much more utility when dealing with any small, ultrathin, or composite sample.

Comparisons

Background, baseline, and artifacts

FTIR provides accurate and repeatable spectra, making it the standard by which all new IR spectroscopic techniques are compared. However, it is not always as straightforward as one would hope for. While PiF-IR is a relatively new form of spectroscopy, it has fewer sources of error making it attractive for any application.

FTIR has many opportunities for errors to creep into measurements. FTIR data must be manipulated significantly which introduces more chances for error. For example, the physical setup of the instrument will have many inconsistencies that need to be accounted for. These include the power distribution of the broadband light source, contamination/degradation of the internal optics, and ambient water vapor and carbon dioxide in the light path. To make sure that all these factors are accurately subtracted out of a measurement, a background spectrum must be taken in the exact same conditions as the sample's measurement. This is usually done automatically, but it is the first major correction that must be applied to every measurement.

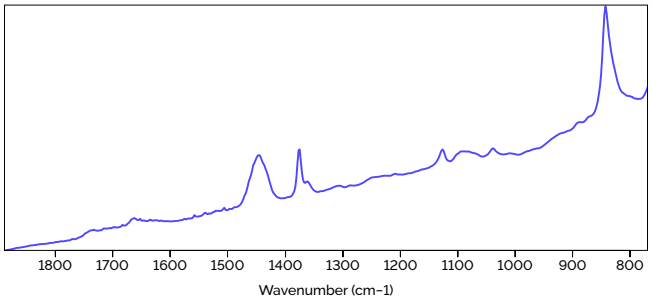


FIGURE 3. This non-uniform baseline shows how sensitive to deviations the interferometer in an FTIR instrument is. This will need to be corrected with some post processing.

Next, FTIR has some effects that change constantly, and therefore cannot be subtracted out using the background spectrum. The primary factors here are thermal drift and mechanical vibrations in the interferometer. Interferometers are extremely sensitive devices, so any deviations in the moving mirror's path is an issue and will cause an uneven baseline in the spectrum [Figure 3].

This effect is corrected using a baseline adjustment. Usually, a smooth function will be used to fit the baseline curve. Then, that function can be subtracted from the spectrum to make the baseline flatter. Again, many FTIR instruments do this automatically. However, this is a major correction to the data where more errors can creep in. Some subjectivity can also be a factor, especially if the SNR is poor.

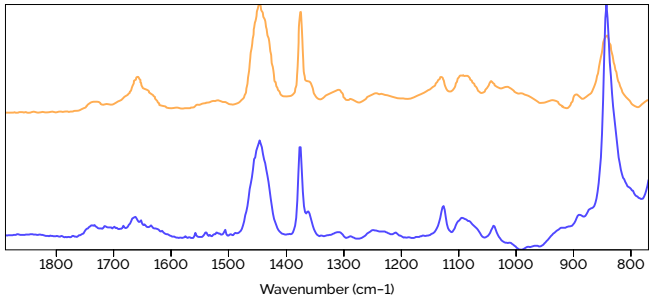


FIGURE 4. After baseline correction, this FTIR spectrum appears much flatter. However, the rise on the right-hand side doesn't look real and is probably an artifact. When compared to a spectrum from SpectraBase (top), there are still errors that aren't properly corrected in the bottom spectrum.

PiF-IR, on the other hand, can avoid these issues. First, PiF-IR spectra have no background to subtract. That may seem almost impossible; however, everything is taken care of before the spectrum is recorded. First, the laser is aligned onto the tip of the AFM probe to make sure that any differences in the probe itself are accounted for. Then, the background is measured, and the laser power is attenuated in real time to correct for errors. Once the system is aligned and setup (which it can do automatically), the background will be completely flat. This means that the

light that the tip sees is consistent across the tunable range of the laser. Therefore, the spectra taken will need no post processing.

PiF-IR spectra also don't suffer from thermal drift in any way because there is no interferometer. The most important alignment in a PiF-IR system is the focus of the laser onto the tip of the AFM probe. Because that is a very stable alignment once set, the system is immune to optical drift while taking spectra. The sample could drift and cause a spatial error; however, PiF-IR spectroscopy itself has no drift considerations. Therefore, multiple samples can be analyzed sequentially without issue.

PiF-IR spectra are not completely immune to all artifacts though. One common problem is an intensity issue from a mis-aligned laser tuner. Since QCL lasers have multiple tuners that are coaligned to cover a larger wavelength range, the alignment of those tuners is very important. If there is a misalignment, then the light from some tuners may hit the AFM tip differently. Luckily, this problem presents itself as a DC offset for the affected tuner. The wavenumber range of each tuner is known, and so the effect is not only easy to spot, but also easy to correct.

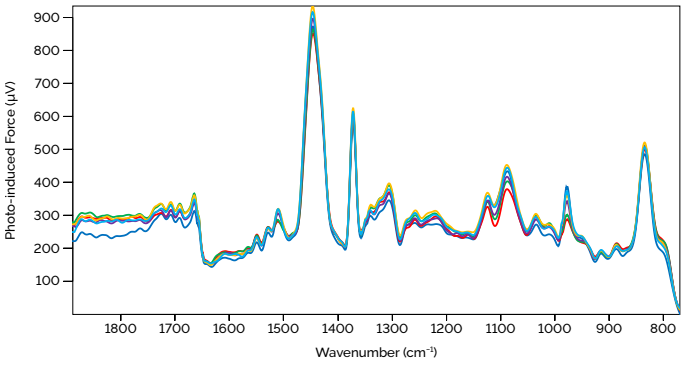


FIGURE 5. A tuner error in the range from 1880 cm^{-1} to 1670 cm^{-1} appears as a DC offset. This is a simple problem to correct, and a laser tuner alignment would fix this problem for all future data.

Another problem that could introduce inconsistencies into PiF-IR spectra is the interaction between the tip and the sample. Because the measurement is extremely dependent on the tip–sample gap, that distance must be held constant for accurate spectra. Therefore, if there is any instability in the AFM system, that can be seen as periodic noise in the spectra. When this happens, there is no way to correct the spectrum after the fact. However, this problem will be immediately noticeable since the stability of the AFM system will let the user know if spectroscopy is possible.

In general, while PiF-IR has some artifacts that can affect the spectra, they are usually easy to notice and correct unambiguously. FTIR on the other hand has many corrections that are required for each measurement, and that can introduce errors into the spectrum. Therefore, PiF-IR may be even more reliable than FTIR since very little data processing is required.

Spatial resolution for mapping and spectroscopy

Unlike FTIR-based instruments, PiF-IR is not limited by the diffraction limit of the IR light. Indeed, PiFM chemical maps show a resolution of sub-5 nm, and PiF-IR point spectra are at least sub-10 nm for their lateral spatial resolution. The detection techniques for PiFM and PiF-IR are the same, so why is the resolution different? Part of the reason is that the human eye is very good at pattern recognition. That means that small changes in the absorption map are much easier to see and measure than when analyzing full PiF-IR spectra.

As a demonstration of resolution, consider this example. Figure 6 shows a cross section of the cell wall from some spruce wood. The image is cropped slightly from a scan that is only 150 nm square, so the topography shows very little information [1]. Therefore, the focus will be on the PiFM images.

One image was taken at 1504 cm^{-1} which corresponds to an absorption peak in lignin. Cellulose has a peak in its spectrum at 1051 cm^{-1}, so that wavenumber was chosen for the next scan. These two PiFM chemical maps now show where there is more of each material on the surface. The topography is recorded simultaneously with each PiFM chemical map, so the combined PiFM image can be overlaid the topography to visualize the complete picture.

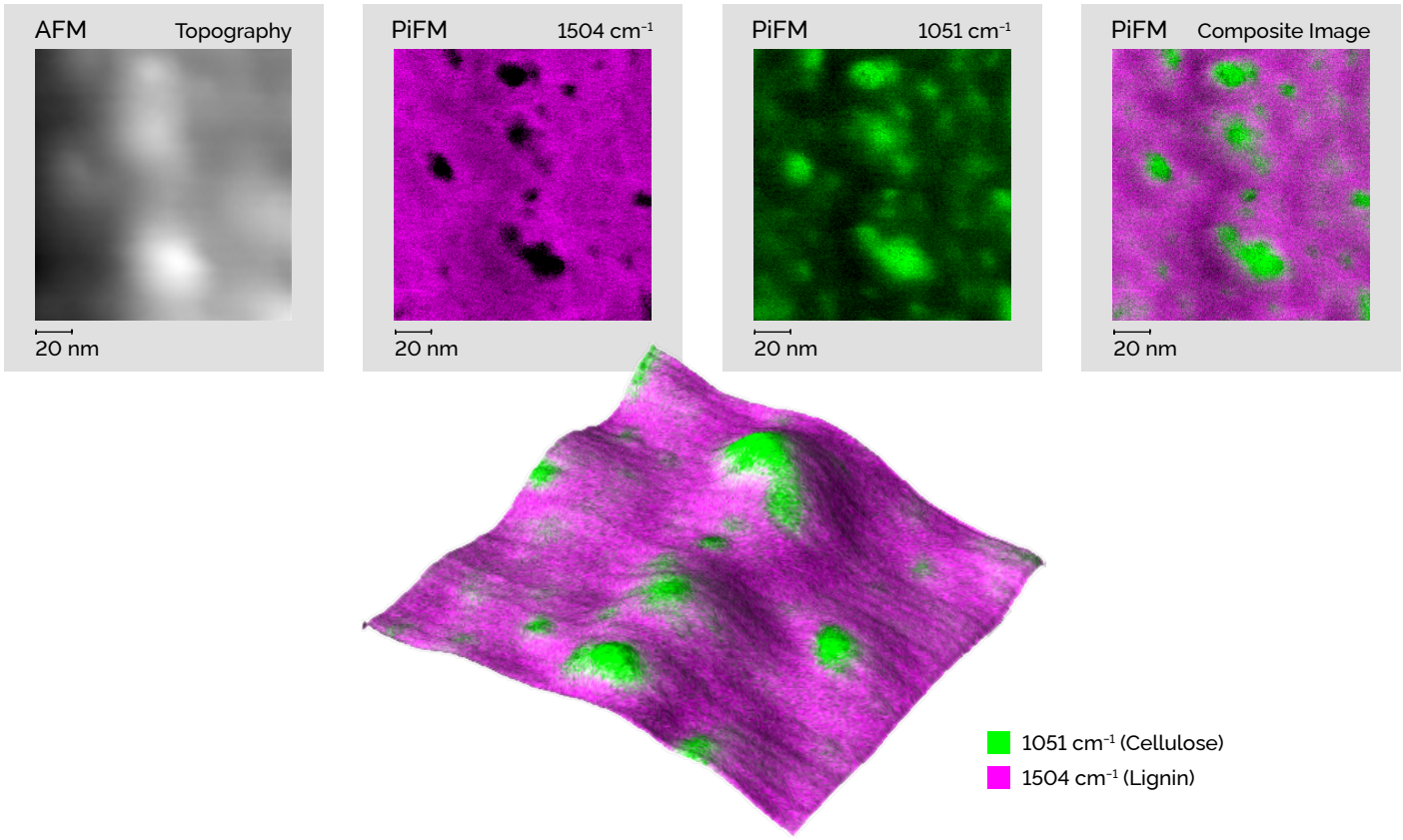


FIGURE 6. The AFM topography shows a 150 nm section of the cell wall from some spruce wood. PiFM chemical maps taken at 1504 and 1051 cm^{-1} show the distribution of lignin and cellulose on the surface, respectively. The combined PiFM chemical map can be used to show the chemical distribution on the 3D surface. Therefore, PiFM analysis offers an all-in-one solution for both physical and chemical scanning.

To measure the spatial resolution of these chemical maps, consider the intensity changes in the cellulose image. Figure 7 shows a line drawn on the image, and the absorption intensity along that line is plotted in the graph. A commonly accepted way to determine the resolution of something like this is to measure the distance required for the signal to go from 10% up to 90% of the peak maximum. Doing that, we see an astounding resolution of only 2.5 nm [Figure 7]!

To investigate the resolution of PiF-IR spectra, one needs to take multiple spectra very close together and inspect them for meaningful changes. An interface such as this is a great sample because the relative heights between the lignin and cellulose peaks can be compared where these two materials meet.

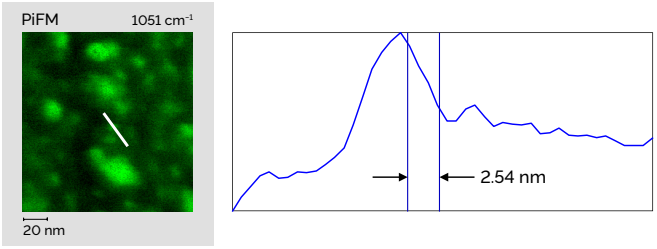


FIGURE 7. Measuring the spatial resolution of PiFM. The intensity in the image is plotted along the white line. The peak in the plot is the bright spot under the line. Measuring the distance required for the signal to go from 10% up to 90% of the peak gives a resolution of only 2.5 nm.

The three spectra in figure 8 were taken 10 nm apart. The first is on the bright spot in the cellulose fiber, so that spectrum has the greatest signal at 1051 cm^{-1} and the lowest signal at 1504 cm^{-1}. The last spectrum is taken where the lignin signal is high, so it has the intensity ratios. The spectrum in between shows the intermediate step across that boundary.

One interesting thing to note in figure 8 is that the PiF-IR spectra shown are notched. Because PiF-IR uses a tunable laser, the power supplied to the sample can be controlled individually for each wavenumber. Therefore, to get better SNR in spectral regions that have minimal absorption, one can simply increase the power in that region. This doesn't impact the data acquisition time, and it can provide much cleaner spectra without damaging the sample by using too much power at wavenumbers with strong absorption.

This demonstration shows the incredible resolutions of PiFM and PiF-IR, and it shows how these techniques could be used to analyze surface chemistry in ways that are otherwise impossible!

Sensitivity

There are many types of FTIR instruments available. Some of them rely on passing light through the sample itself. This can work well for some gases and liquids. However, it is generally impractical for solid samples (though it can be done with some complicated prep). An attenuated total reflectance (ATR) FTIR is one of the most surface sensitive types of FTIR instrument, and it solves this problem using a clever mechanism.

The sample to be measured is pressed onto the surface of the ATR crystal so the evanescent wave where the light reflects internally can tunnel into the sample. This interaction will attenuate the light and produce the absorption spectrum. The evanescent wave has a relatively small penetration depth for FTIR of about 0.5 µm to 5 µm. That is why this method is more surface sensitive than others [2]. However, even this method requires at least 100 nm of material to get a usable signal. Furthermore, on thin samples the substrate material will almost certainly contribute to the overall spectrum making isolating materials difficult. One way to solve that issue is to use a substrate like gold that is inactive in the infrared.

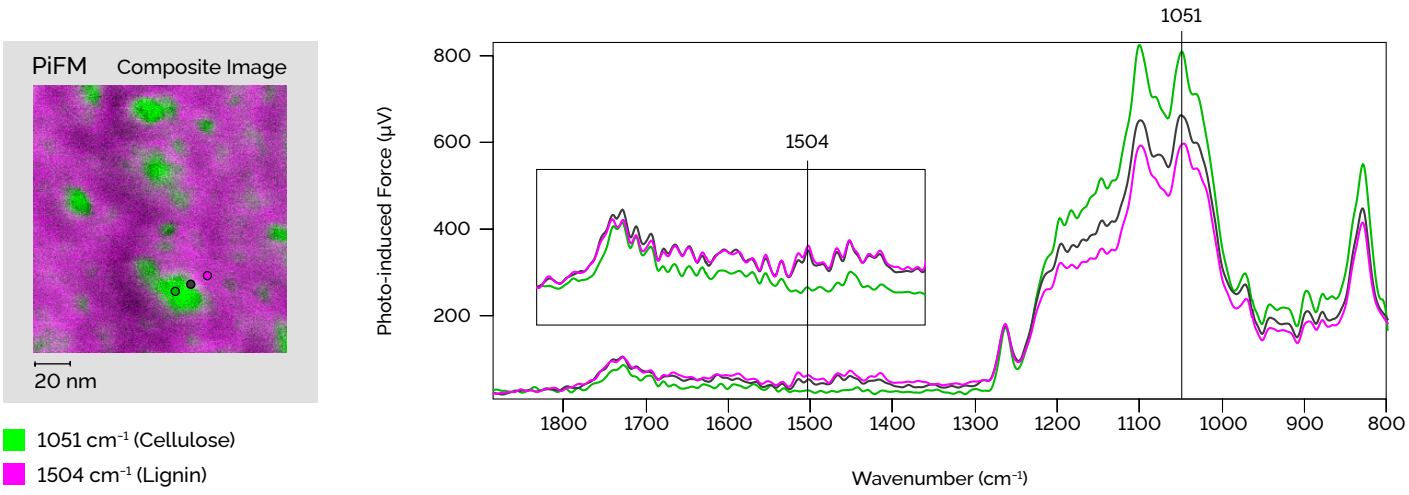


FIGURE 8. Three spectra spaced only 10 nm apart show significant differences in peak intensity. The spectrum taken on the cellulose (green) has the highest absorption at 1051 cm^{-1}. Conversely, the spectrum taken on the lignin (magenta) has the highest absorption at 1504 cm^{-1}. The spectrum in the middle (gray) shows the intermediate step. The region from 1880 cm^{-1} to 1360 cm^{-1} was notched and the laser power increased. This provides better SNR without damaging the sample by using high power at the strong 1050 cm^{-1} absorption peak.

Unfortunately, that is expensive and requires that the sample be prepared for ATR-FTIR spectroscopy ahead of time.

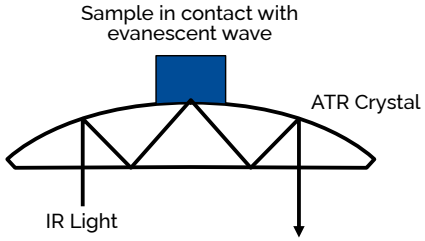


FIGURE 9. In and ATR-FTIR instrument the beam bounces inside a crystal with a very high index of refraction. At the points where the beam reflects internally, an evanescent wave tunnels and interacts with the sample pressed onto the crystal's surface.

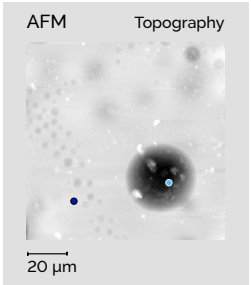
Another problem with this approach is that the sample will be squished. Because the interaction with the evanescent wave requires very good contact between the sample and the crystal, ATR-FTIR instruments generally have a strong clamp to hold the sample. This will change the surface of the sample and affect both the topography and the spatial chemical heterogeneity. Therefore, microscopy and other experiments should be done before the sample could be affected by ATR-FTIR measurements.

With all these considerations, FTIR is best suited to measure relatively large quantities of pure material. Chemical measurements in situ, or measurements on small quantities of material are difficult to perform and require special instrumental setups and procedures. Therefore, other techniques such as PiF-IR are preferable.

PiF-IR spectroscopy can detect extremely small amounts of material, down to even a monolayer deposited onto an otherwise clean surface.

PiF-IR has two different sensitivity modes: bulk and surface sensitive. The bulk sensitive mode is often referred to as direct drive because of how the laser is modulated in relation to the mechanical modes of the cantilever. Surface sensitive measurements are done using a side-band bimodal™ technique. The penetration depth of surface-sensitive PiF-IR and PiFM is about 20 nm. So, if there is at least that much material on the surface of the sample, then spectroscopy can be done without having to do any corrections for the substrate layer.

To analyze even thinner samples or monolayer deposits, then a combination of bulk and surface sensitive



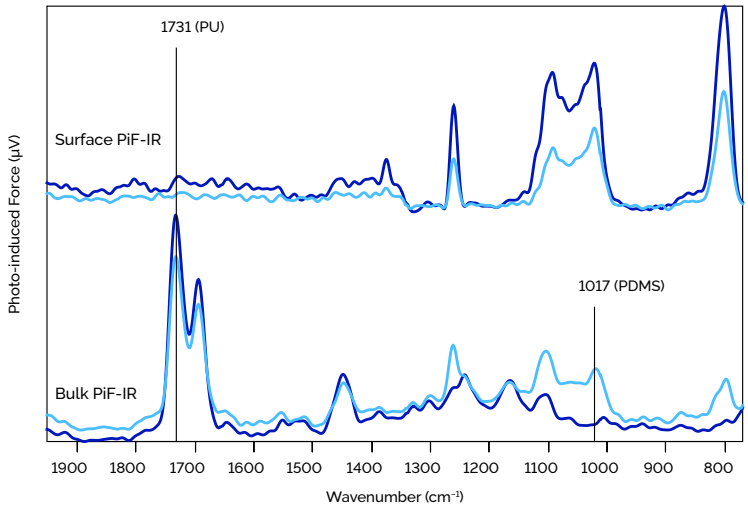


FIGURE 10. 3D analysis on an amphiphilic siloxane-polyurethane (AmSi-PU) coating. The matrix is rich in PU, and the circular island is rich in PDMS. Two surface sensitive spectra were taken, one on the matrix and the other on the island. However, both show only PDMS peaks, indicating that there is a layer of PDMS on the surface that is at least 20 nm thick. Bulk sensitive spectra taken in the same locations show the expected material difference.

modes can be used. In this case, the monolayer material will show up in the surface sensitive spectra along with any substrate material(s). However, in the bulk-sensitive mode the spectra will not see the monolayer at all. Instead, it will measure the substrate material with a much larger penetration depth. This could therefore be used like a background where the bulk sensitive spectra are subtracted from the surface sensitive ones to isolate the spectrum from the monolayer material.

This is part of what we call 3D spectral analysis, and it is an incredibly powerful technique [Figure 10]. For more information, we have a dedicated application note that expands on this idea further [3]. Also note that this analysis can be done on any sample, regardless of what the substrate material is. Other AFM-IR techniques sometimes show data that demonstrates a similar surface sensitivity; however, they often need to use a gold substrate to achieve this.

Ensemble average vs local chemistry

The difference between the ensemble average chemistry vs the local chemistry is a concept that typically does not need to be considered with FTIR. As an analogy, consider a computer or phone displaying an image of a yellow box. It looks yellow to the human eye, but if one zooms in to see the pixels it will become apparent that there is no yellow

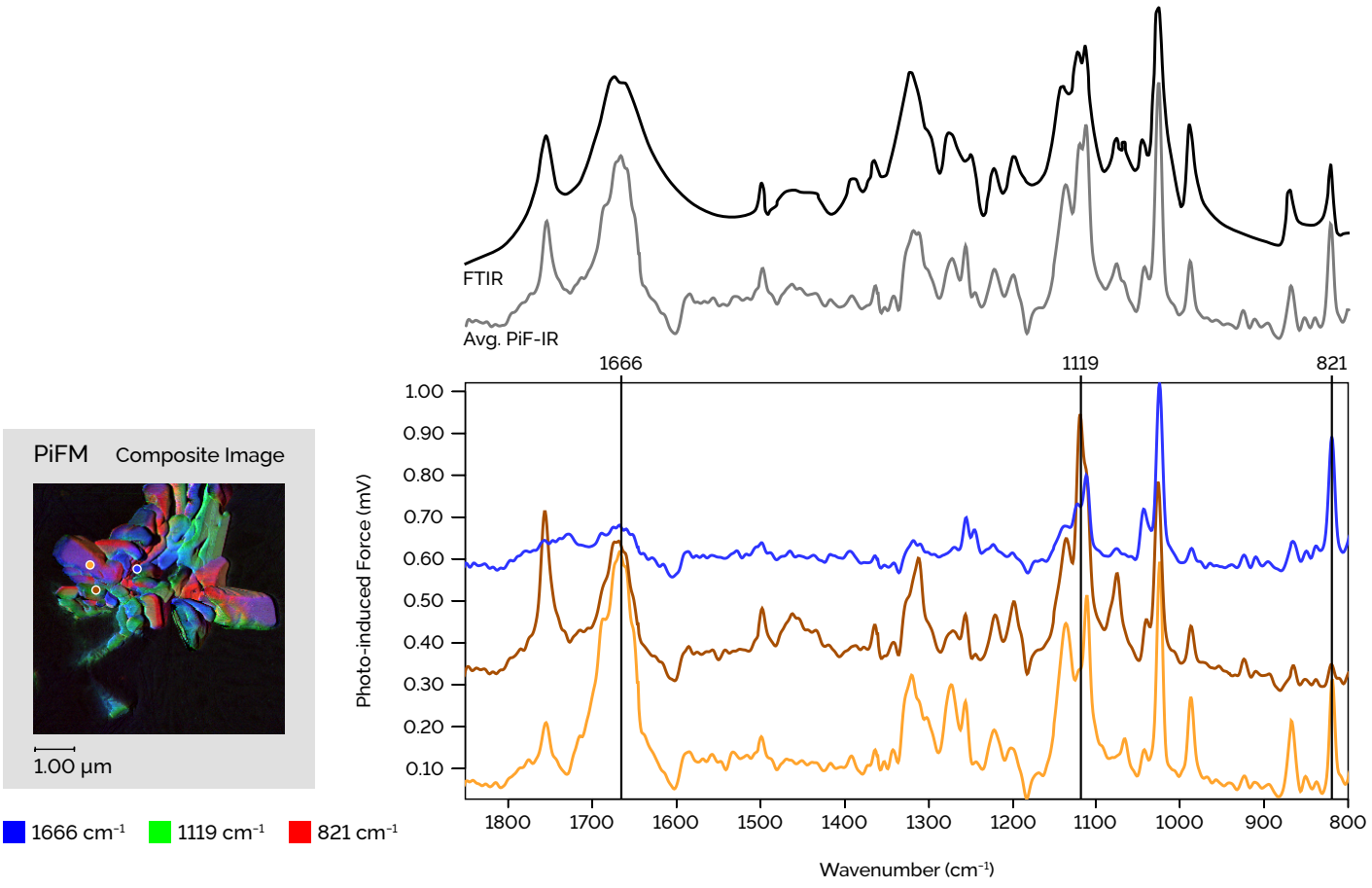


FIGURE 11. This vitamin C crystal embedded in a biodegradable polyester shows some polarization dependence. PiF-IR spectra taken on the crystal correlate well with FTIR, especially when averaged together. However, individually the PiF-IR spectra show some peak variance that is due to local differences in the crystal structure.

light being emitted at all. Instead, the LCD display is using a combination of red and green pixels to trick the brain. The human eye can't understand what is happening because the illusion is at a scale too small for it to resolve. This is the difference between FTIR and PiF-IR. FTIR can only probe chemistry at the ensemble average level. It can only see the combined effect of all the materials present with no way to separate them. However, PiF-IR can separate the components because it analyzes a volume that is at least one billion times smaller than FTIR.

The consequences of this are many. PiF-IR spectroscopy is unambiguous and precisely targeted. Additionally, PiF-IR spectroscopy can show local differences on pure materials. For example, PiF-IR acts somewhat like polarized FTIR. This is because the metal-coated tip of the AFM probe acts like a one-dimensional nano-antenna. The laser excitation light is usually polarized along this tip axis, and so the photo-induced force interactions show some orientation dependence. This means vibrational modes that are out of the sample plane are most sensitive. So, even if a sample is molecularly pure, PiF-IR will be able to see local differences due to molecular orientation. Additionally, this effect can be used to analyze different crystalline phases or other local chemistry that is impossible with standard FTIR [Figure 11]. For more examples see [4].

Another interesting thing to note is that PiF-IR has fantastic spectral resolution in addition to the incredible spatial resolution. In an FTIR instrument the spectral resolution is typically around 4 – 8 cm^{-1}. Higher resolutions are possible, but that requires more time to collect since the resolution depends on the mirror movement in the interferometer. PiF-IR generally has a spectral resolution of 1 – 3 cm^{-1} depending on the laser used. While such resolution may not by useful for ensemble measurements, this increased spectral resolution is useful to study the small spectral changes that matter for local chemical measurements.

Therefore, samples that look relatively straight forward for FTIR spectroscopy can present new opportunities when measured with PiF-IR instead. The highly local measurements show differences that are impossible to know about when looking only at the ensemble average provided by bulk measurements like FTIR.

Conclusion

PiF-IR spectroscopy is not just a clever way to identify nano-scale materials. It is an extremely powerful IR spectroscopy technique that stands on its own and offers incredible capabilities that expand what is possible with FTIR-like measurements. PiF-IR improves upon FTIR in almost every way possible: more precise spectral resolution, one-thousand times better spatial resolution, and a detection limit one-billion times more sensitive. PiF-IR can also analyze local chemistry that isn't possible otherwise. There is little room for ambiguity, so PiF-IR spectroscopy is stable, reproducible, and reliable. When all this is coupled with the wealth of information provided by PiFM chemical mapping and AFM topography, these techniques offer modern science the detailed and precise spectroscopy required for increasingly complicated research.

References

[1] Kesari, K.K., O'Reilly, P., Seitsonen, J. et al. Infrared photo-induced force microscopy unveils nanoscale features of Norway spruce fibre wall. Cellulose 28, 7295–7309 (2021).

[2] FT-IR Spectroscopy Attenuated Total Reflectance (ATR). PerkinElmer Technical Note. 2005.

[3] https://molecularvista.com/applications/3d-nanoscale-analysis-polymer-systems/

[4] https://molecularvista.com/applications/nanoscale-drug-delivery-systems-nano-ir-analysis/