

Application Note

Understanding PiF-IR Spectrum

IR PiFM, with its ~ 5 nm spatial resolution holds tremendous potential for nanoscale chemical analysis. One major question about IR PiFM is whether PiF-IR spectra from nanoscale region agrees with bulk FTIR spectra. As seen in figure 1, PiF-IR spectra agree well with the bulk FTIR spectra when the sample is homogeneous in nanoscale. In figure 1, the PiF-IR spectra on the top four materials were generated on a bulk sample; even though PiF-IR spectra are generated from ~ 10 nm region, the agreement with FTIR spectra is exceptional. The PiF-IR spectrum on PEO (the last material in figure 1) was generated on a thin film of PEO. On PEO, while all the peaks agree well, a double peak near 1100 cm^{-1} is resolved in PiF-IR spectrum, and the smaller peak position matches the bulk FTIR peak position while the dominant PiF-IR peak position matches the left shoulder of the FTIR peak; this is likely due to the fact that a thin film may locally introduce preferential alignment of bonds such that PiFM senses a particular orientation of the bonds; due to the antenna enhancement from the tip geometry, the molecular vibrations along the tip axis will generate stronger signals (for P-polarization, which is the standard polarization used for PiFM).

The agreement between the PiF-IR and FTIR spectra will be different on samples that are inhomogeneous in nanoscale. Figure 2 shows spectra from laser toner particles, which consist of many chemical components. Toner particles were crushed to generate the light red ATR FTIR spectrum while PiF-IR spectra were generated from adjacent locations on a single toner particle glued onto a substrate. Three spectra colored green, red, and blue were acquired from locations shown in the inset topography image. The local PiF-IR spectra are characterized by subsets of IR peaks observed in the bulk FTIR; the green PiF-IR spectrum contributes dominantly around 1100 cm^{-1}

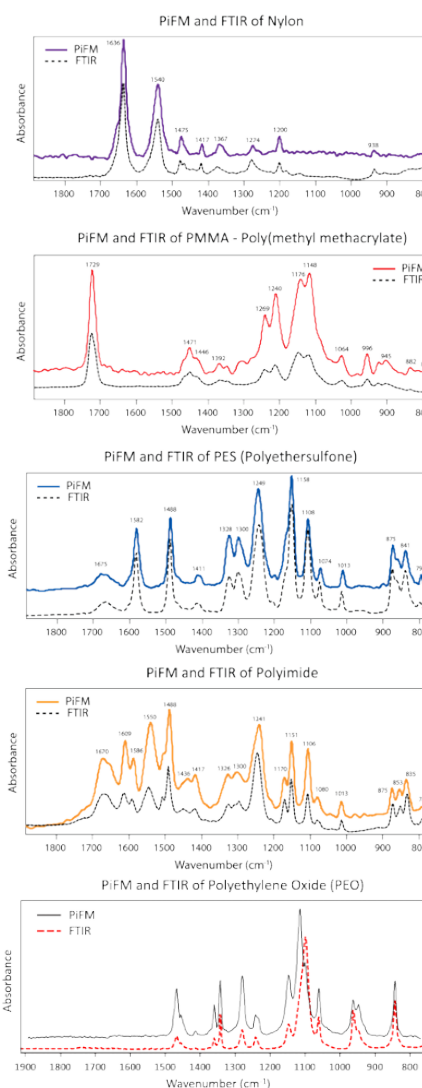


FIGURE 1: Comparison of bulk FTIR spectra and nanoscale PiF-IR spectra on various materials. The PiF-IR measurements on the top four materials were done on homogeneous bulk material whereas the measurement on the last material (PEO) was done on a thin film.^v

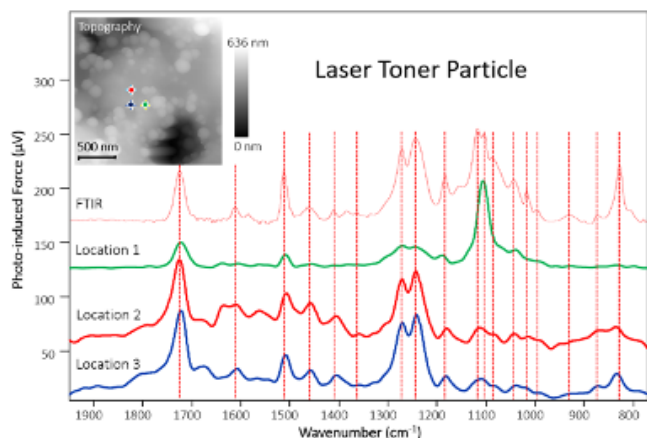


FIGURE 2: Comparison of FTIR spectrum on crushed laser toner particles and three nanoscale PiF-IR spectra from a single toner particle at adjacent locations.

whereas the blue contributes the peak at around 825 cm^{-1} ; the red spectrum contributes a bit more broadly around $1350\text{ to }1600\text{ cm}^{-1}$. Given the sampling volume of the bulk FTIR measurement, more than 10^9 nanoscale PiF-IR spectra need to be averaged to yield a bulk FTIR spectrum on samples that are heterogeneous in nanoscale.

Figure 3 shows the FTIR and PiF-IR spectra on polypropylene from the standard QCL and the optional OPO lasers (for higher wavenumber regions). Again the agreement between them is quite good.

Figure 4 shows the result of a search conducted with a PiF-IR spectrum acquired on polyvinylidene difluoride (PVDF) in an online spectral search library; the first candidate with the highest quality index is PVDF as expected. This highlights the potential use of PiF-IR to identify unknown nano organic and inorganic contaminants.

Figure 5 shows how PiF-IR spectra can be used to identify unknown nanoscale contaminants. On top of the figure is a $\sim 100\text{ nm}$ piece of Teflon that is $\sim 4\text{ nm}$ thick, which is easily identified by a clear PiF-IR spectrum even from such a tiny contaminant. On the bottom of the figure is a $\sim 20\text{ nm}$ silica particle, which has a distinct peak ($\sim 1100\text{ cm}^{-1}$) from the native silicon oxide peak ($\sim 1080\text{ cm}^{-1}$); the silica particle is most likely spherical in shape with $\sim 20\text{ nm}$ diameter, whose lateral dimension is inflated by the tip radius ($20\text{ to }30\text{ nm}$) in the topography. Note that both

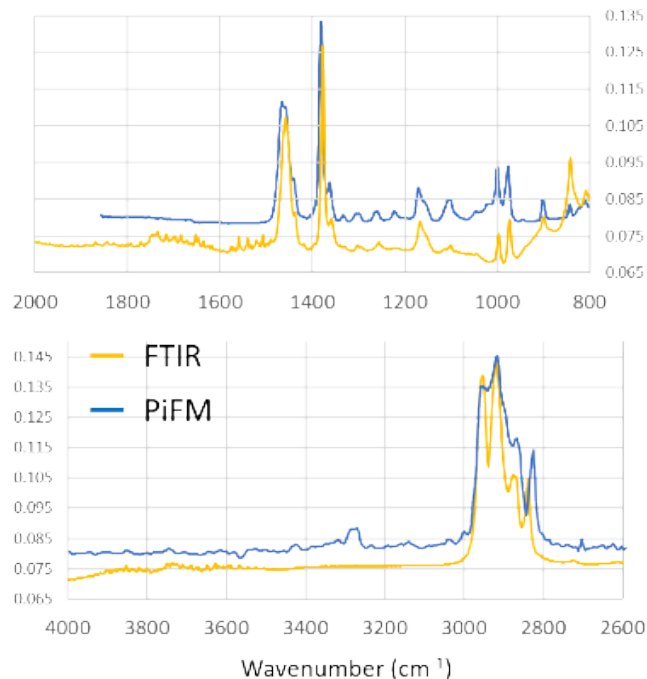


FIGURE 3: Comparison of bulk FTIR spectra and nanoscale PiF-IR spectra on polypropylene for the spectral range available from QCL (upper graph) and OPO (lower graph).

organic and inorganic nanoscale contaminants can be detected by PiFM.

Figure 6 shows 10 PiF-IR spectra with 50 nm spacing covering the C-H stretching modes across a fiber-resin interface. Spectra associated with regions away from the interface (spectra 1-2 and spectra 6-10) demonstrate the excellent repeatability of PiF-IR spectra. The chemical changes associated with the interface region are contained in spectra 2 to 6, showing that the interface region extends for about 200 nm .

Figure 7 shows five PiF-IR spectra on a thin film of lysozyme, an antimicrobial enzyme. While all five spectra show generally good correlation with the FTIR spectrum, each spectrum shows spectral features that express the second order structures of the enzyme underneath the AFM tip.

By using an IR laser polarization that is parallel to the AFM tip axis (p-polarization) or in-plane of the sample surface (s-polarization), PiFM can monitor selectively the molecular vibrations that are out of or in the sample plane,

respectively. Figure 8 shows PiF-IR spectra with p- and s-polarization on a thin film of polyphenylene sulfide.

In conclusion, PiFM can generate IR absorption spectra from nano-sized organic, inorganic, and biological samples that agree excellently with bulk FTIR spectra.

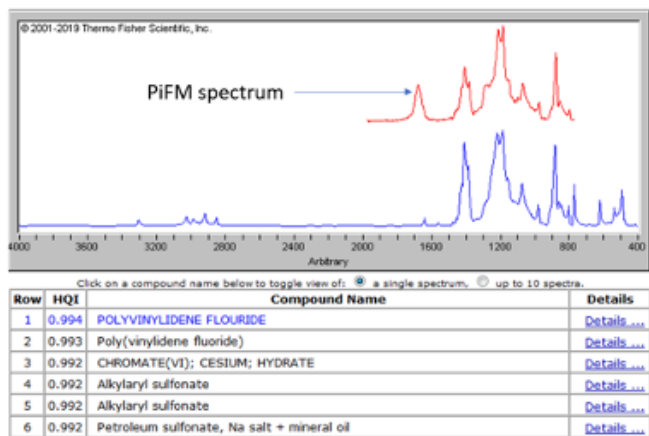


FIGURE 4: Search result from an online spectral search library.

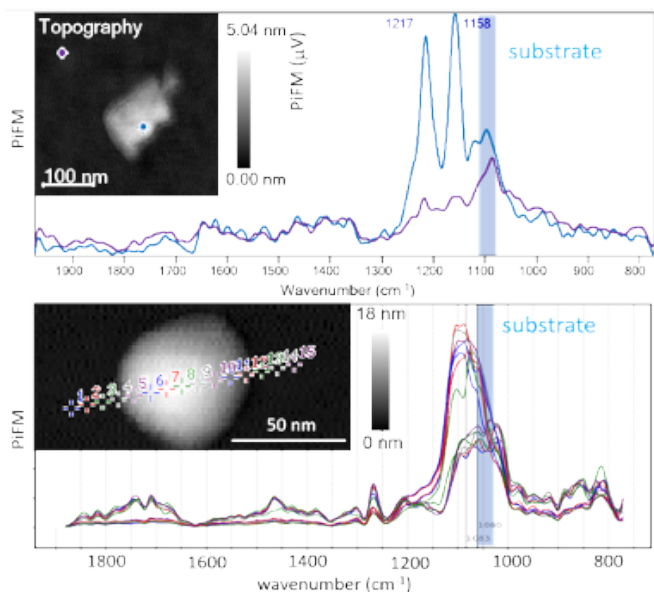


FIGURE 5: Topography images (shown as inset) and spectra acquired on two different contaminants: Teflon (top) and silica particle (bottom).

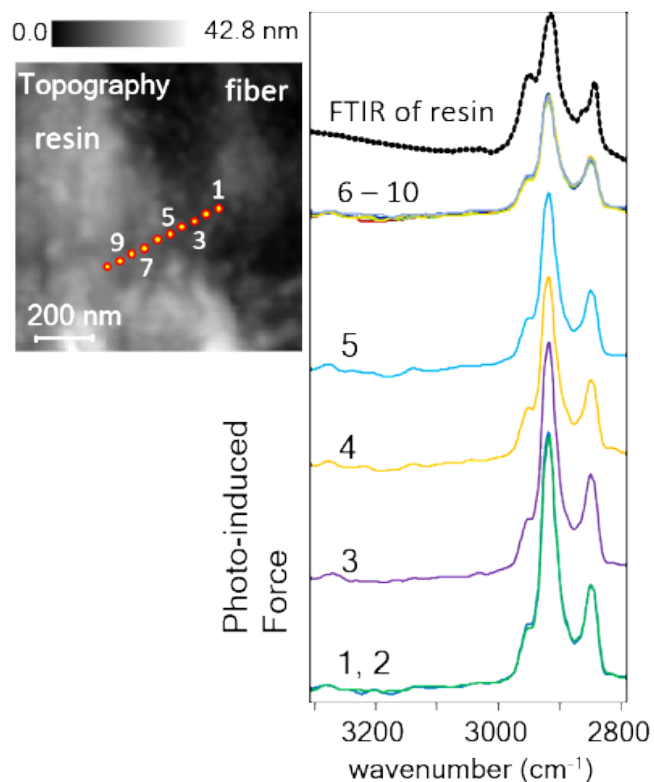


FIGURE 6: Topography and PiF-IR spectra across an interface between fiber and resin.

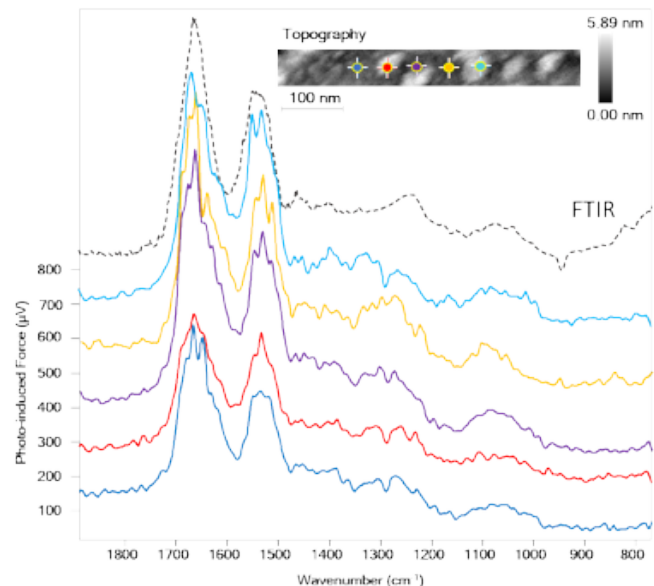


FIGURE 7: Topography and PiFM spectra on a lysozyme film.

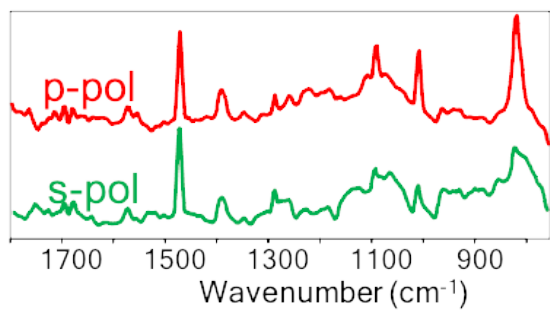


FIGURE 8: PiF-IR spectra with p (out of sample plane) and s (in sample plane) polarization.