

Nanoscale IR spectroscopy: From Principles to Nanoscale Imaging and Identification of Metal Soaps

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Oil paints are fine mixtures of pigments, drying oils and additives that together provide desirable properties such as slow drying, film flexibility and a pleasing appearance. Once dried, ideally oil paints should last for centuries; however, such complex mixtures are not completely inert and slow chemical reactions can deteriorate and damage works of art. A common reaction in oil paints occurs when metal ions from the pigments react with hydrolyzed triglycerides from the oil and additives forming metal carboxylates (soaps) which, over time may damage works of art. Metal soaps have been most commonly observed in Zn and Pb paints and have also been reported in paints containing Al, K, Ca, Cu, Cd, Mn.[1,2] However, despite substantial amount of research, metal soap formation and aggregation are not fully-understood processes. Not only each work of art is essentially a unique chemical experiment, with its own composition and history of environmental stresses, some commonly used characterization methods can miss important chemical details at the micro- and nano-scale. For example, μ -FTIR has proven very useful to identify the composition of metal-soaps; however, its spatial resolution is insufficient since it is typically limited by light diffraction to several micrometers.

In this talk, I will discuss two novel photothermal IR spectroscopy methods that overcome the diffraction limit of IR light and push benefits of IR spectral analysis to the nanoscale. Photothermal induced resonance (PTIR),[3,4] also known as AFM-IR, yields IR spectra and maps with 10 nm to 20 nm spatial resolution using an atomic force microscope (AFM) probe tip to transduce the sample photothermal expansion that is induced by the absorption IR laser pulses. Akin to PTIR, optical photo-thermal infrared spectroscopy (O-PTIR), yields IR spectra and maps with \approx 500 nm spatial resolution employing a visible laser (in place of the AFM cantilever) for probing, in a contactless way, the sample photothermal expansion due to absorption of IR laser pulses.[5] Similar to FTIR, the PTIR and O-PTIR signal is proportional to the amount of light absorbed in the sample at depths up to a few micrometers. For best results, our samples were prepared as very thin (200-400 nm) cross sections.

Here, I will discuss 2 application examples. I will use PTIR to determine the nanoscale distribution of metal soaps in a Zinc-containing oil paint of known average composition, Pre-tested Soft Titanium White (P250), that was prepared at the Grumbacher paint factory in 1995 and naturally aged for 23 years. PTIR reveal (Fig 1) that low density agglomerates of Al-stearate (AlSt_3) and a Zn-carboxylate complex with Zn-stearate nano-aggregates in proximity are distributed randomly in the paint. Notably, the gradients of zinc carboxylates are unrelated to the AlSt_3 distribution.[6] Next, I will leverage both PTIR and O-PTIR to investigate the distribution of chemical phases in the top layer of a French nineteenth-century painting (Gypsy Woman with Mandolin by Jean-Baptiste-Camille Corot, Figure 1, c. 1870) that contain lead white and cobalt green pigments along with and metal soaps alteration products.

Our measurements offer an unprecedented nanoscale composition-sensitive observation window on oil paints, revealing intermixing of metal-soap phases that are more complex and heterogeneous than previously known, and revealing the presence of rare species with low average concentrations. However, since spatial resolution comes at the expense of measurement throughput, making these novel methods most useful when used in combination with FTIR to provide a multiscale characterization.

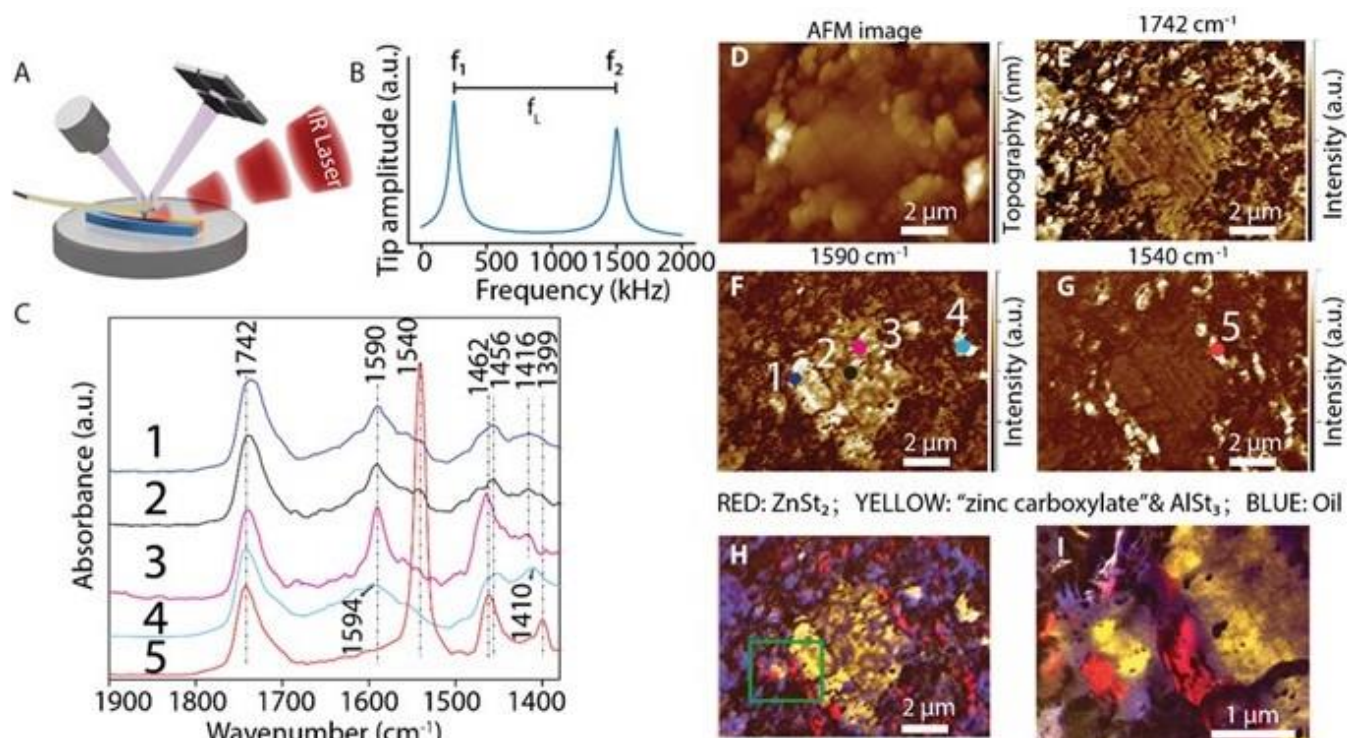


Figure 1. A) PTIR setup schematic, B) Tapping-mode PTIR signal detection is achieved by mixing the tapping motion of the AFM cantilever with the sample expansion due to non-linear tip-sample interactions. A piezo actuator drives the cantilever at its second mechanical resonance ($f_2 \approx 1550$ kHz), the PTIR signal is demodulated at its first mechanical resonance ($f_1 \approx 250$ kHz) while pulsing the IR laser with a repetition rate $f_L = f_2 - f_1 \approx 1300$ kHz. C) PTIR spectra at the color-coded marked locations in F and G (points 1-5), the spectra were normalized to the ester band at 1742 cm^{-1} and offset for comparison, D) AFM topography. PTIR absorption maps at E) 1742 cm^{-1} , F) 1590 cm^{-1} and G) 1540 cm^{-1} , H) Reconstructed qualitative color-coded image of PTIR absorption intensity: ZnSt_2 (G, red), “zinc carboxylate” plus AlSt_3 (F, yellow) and oil (E, blue). Colors are not displayed on a common intensity scale, I) Higher resolution image of the area delimited by the green box in H. This figure has been adapted from X. Ma et al.[6] with permission from Wiley, copyright 2019.

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