AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?

Introduction

Nanoscale chemical analysis of surfaces and thin films plays a key role in modern research and development, putting a high demand for tools that provide chemical specificity of infrared (IR) spectroscopy and nanoscale spatial resolution of an atomic force microscopy (AFM). Two classes of such tools have been developed and are commonly known as nanoscale IR or simply "nano-IR". These are the techniques based on:

(i)   s-SNOM: scattering-type scanning near-field optical microscopy, and

(ii)   AFM-IR: atomic force infrared microscopy (also referred to as PTE, PTIR, PiFM & PiF-IR)

Both approaches are scanning probe techniques that combine AFM with IR illumination, but s-SNOM detects IR light scattered by the AFM probe, while AFM-IR records mechanical response of the illuminated sample using AFM detection. Both are capable of nanoscale IR imaging and spectroscopy but with their unique set of benefits. In the following, we discuss the benefits of each class with particular focus on tapping AFM-IR and pseudoheterodyne (PsHet) s-SNOM that offer comparable resolution and operate in a gentle intermittent contact (tapping) mode of AFM. This comparison primarily targets materials science applications at mid-IR spectral range and room temperatures.

Table 1. Brief comparison of neaspec s-SNOM and tapping AFM-IR

	neaspec PsHet s-SNOM	tapping AFM-IR^{+}
Materials & accessible properties	Works on all types of materials: • Complex refractive index, i.e. reflectivity & absorption • Free carrier density & conductivity • Amplitude and phase of optical fields • Carrier dynamics (pump-probe)	Excels on soft matter samples: • Infrared Absorption
Spatial resolution	• Typical ca. 5-20 nm for commercially available metallized AFM probes	• Typical ca. 5-20 nm for commercially available metallized AFM probes • Can depend on sample structure due to thermal diffusion
Depth sensitivity	• User-controlled: ca. 10-100 nm depending on the demodulation order & tapping amplitude • Can measure through membranes & capping layers	• Typically below 50 nm • Depend on the sample & technique used.
Analytical capabilities	• Relative material contrast (absorption & reflectivity) • Spectroscopic identification according to conventional IR references • Fully quantitative: demonstrated extraction of refractive index, absorption coefficient, and carrier concentration using well-established models	• Relative material contrast (absorption) • Spectroscopic identification according to conventional IR references • No quantitative results demonstrated
Tip-sample mechanics & influence of AFM parameters	• Optical signal detection independent from AFM imaging parameters	• Cross talk between mechanical & optical tip-sample interaction possible • Requires robust & stable mechanical tip-sample interaction (AFM operation) • Measurement depends on the specific probe and environmental conditions
Suitable substrate material	• Benefits from substrate enhancement on highly reflective substrates (Si, Au)	• Less reliant on substrate enhancement except for ultrathin samples • Good for measuring on glass and other IR transparent samples
Instrument preparation	• Easy system setup and alignment due to nonzero near-field signal on most samples • Requires interferometer alignment & detector cooling	• challenging on unknown samples, alignment sample beneficial
Tip contamination sensitivity	• Low: only probes within nano hotspot	• High: spectral artefacts are possible for standard tips; avoided with neaspec tips
IR sources	• CW or quasi-CW: QCL, OPO, broadband, synchrotrons	• Pulsed: QCL & OPO

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE+s?
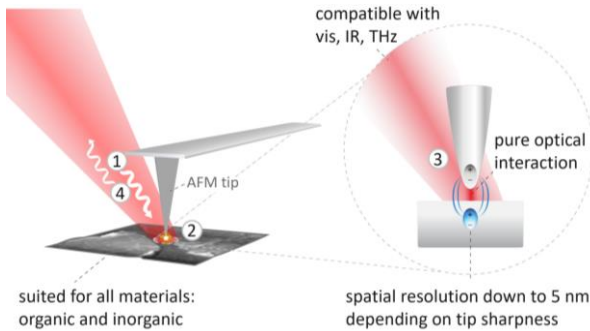
s-SNOM

Figure 1. Basic principle of s-SNOM: (1) focus light onto a sharp AFM tip; (2) illuminated tip creates strong near-field nano-focus at tip apex; (3) nano-focus probes optical properties of the sample modifying the tip scattering; (4) all-optical detection of tip-scatted light delivers complete information on sample dielectric properties.

Brief description

In scattering-type Scanning Near-field Optical Microscopy, or simply s-SNOM, the IR light is focused onto a sharp metallized AFM tip (see Figure 1). The illuminated tip creates a strong near-field nano-focus at its apex, which acts as an ultrasmall light source that probes optical/IR properties of the sample. The probed properties are then manifested in the tip scattering,

which is detected using interferometric detection that recovers both amplitude and phase of the tip-scattered light. As the result, s-SNOM delivers complete information about the sample's complex-valued optical response (e.g. absorption and reflectivity). Raster scanning the sample allows for recording e.g., nanoscale-resolved IR maps of sample surface simultaneously with the sample topography and mechanical information delivered by the AFM. Spectroscopic information is obtained by changing the IR wavelength, i.e. the "color" of the illuminating light or by utilizing broadband IR sources. Noteworthy, the spatial resolution of s-SNOM does not depend on the illumination wavelength but only on the tip sharpness, which allows for spatially resolved hyperspectral imaging. Resolution down to <10 nm has been routinely demonstrated with standard commercial AFM tips [1].

Modern s-SNOM microscope consists of an (i) AFM, (ii) an illumination source and (iii) an asymmetric interferometer where the tip and the sample are located in one of the interferometer arms (see Figure 2). Proper interferometric detection is the key for suppressing strong scattering background and disentangling the amplitude and phase of the tip-scattered light. It also provides strong interferometric gain for superb sensitivity down to single molecular complexes [2].

Figure 2. Setup schematics of neaspec s-SNOM (left) that measures amplitude and phase of tip-scattered light simultaneously to topography (right)
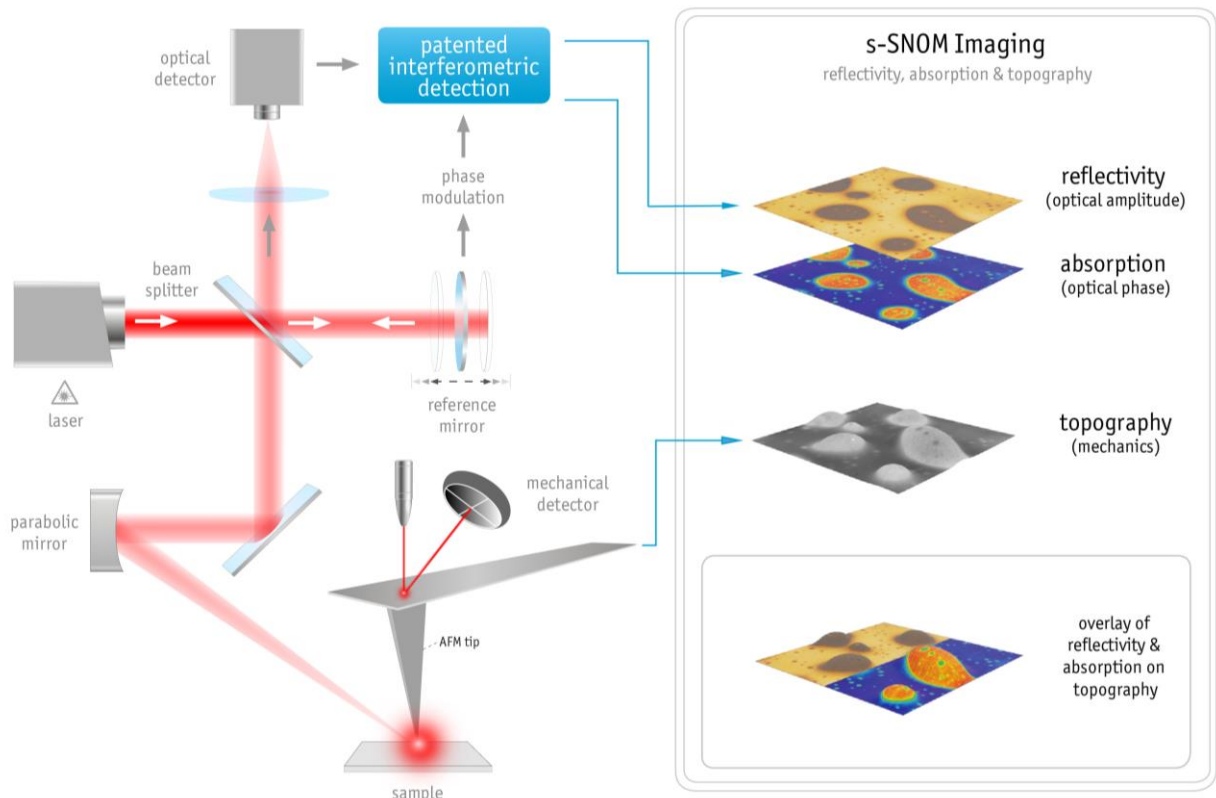
AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?

Traditionally, s-SNOM utilized CW sources to perform rapid nanoscale IR imaging of a sample surfaces. Spectroscopy was done using sequential imaging. However, this has changed since the introduction of s-SNOM point spectroscopy (P-Spec) by neaspec. In P-Spec the sample dependent tip scattering is measured as a function of wavelengths by sweeping a light source, thus rapidly recording IR spectroscopic signatures with nanoscale spatial resolution. P-Spec is currently the only commercial technique that provides s-SNOM spectroscopy using wavelength-tunable IR lasers with all the benefits of neaspec s-SNOM: delivering both amplitude and phase, complete background suppression and high sensitivity due to strong interferometric gain.

Currently, commercial s-SNOM utilizes CW illumination and quasi-CW sources with 10 MHz or above repetition rate to ensure high SNR and fast imaging speeds. Attocube offers two types of IR illumination sources: quantum cascade lasers (QCL) and widely-tunable optical parametric oscillator (wOPO) lasers. QCLs offer high power and narrow linewidth with flexible configurations that can be fit into specific budgets. wOPO offers an extended near-continuous tuning in the range from ca. 1.4 um up to 18 um[1]; it has the best value per wavelength but requires larger upfront investment compared to QCLs.

Note that s-SNOM has to be distinguished from the aperture SNOM (also known as NSOM or a-SNOM), which despite its name similarity is a different technique that utilizes fiber probes to probe the sample. NSOM is incapable of nanoscale mid-IR spectroscopy due to bandwidths and transmission limitations of fiber probes and will not be discussed in this article.

nano-FTIR – broadband s-SNOM variant

s-SNOM can also utilize broadband illumination sources. Combined with the detection principles of Fourier transform infrared (FTIR) spectroscopy [3], it enables nano-FTIR – the nanoscale analogue of conventional FTIR spectroscopy [4]. nano-FTIR is therefore an s-SNOM variant designed primarily for local spectroscopy and hyperspectral imaging. It is also the only commercial technique capable of nanoscale pump-probe spectroscopy at <100 femtosecond temporal resolution as a turnkey solution from attocube [5].

It has been a "workhorse" of nano-spectroscopy since 2012 serving hundreds of users including at IR beamlines of more than a dozen synchrotrons worldwide. An advantage of nano-

FTIR is a relative affordability of the tabletop laser sources, taking into account the offered IR spectral coverage (4.6 um - 15.4 um). The tradeoff is the inability of nano-FTIR to perform rapid chemical mapping of samples at an IR wavelength of interest.

Background-free detection in neaspec s-SNOM

While s-SNOM has been known since the last century, it only became available to the market about less two decades ago with the founding of neaspec. The main challenge was the extraction of weak near-field signal from the dominant scattering background originating primarily from the large tip shaft. Scattering background is often used to put s-SNOM in a negative light. However, over the last decades, several robust detection schemes have been developed that completely suppress scattering background. Thus nowadays, s-SNOM is an important reliable tool for nanoscale imaging and spectroscopy with several unique benefits not offered by any other nano-IR technology that will be discussed later.

To suppress scattering background, a so called high-harmonic demodulation scheme was invented [6]. In it, the tip gently taps on the sample with a small tapping amplitude of ~20 nm and the detector signal is demodulated at the higher harmonics of the tip tapping frequency. Tapping leads to the harmonic modulation of the tip height. The scattering background is largely insensitive to small height variations (much smaller than the IR wavelength) and primarily contributes to the lower tapping harmonics of the demodulated detector signal. In contrast, the near-field interaction depends on the tip-sample distance in a highly nonlinear fashion creating higher harmonics of the detector signal (2, 3, etc.).

High-harmonic demodulation alone is not sufficient to completely remove the scattering background[2]. This is due to the s-SNOM detector measuring power, which results in coherent interference of tip-scattered light with the scattering background. This results in an admix of a near-field – background product even at high demodulation harmonics of the detector signal [7]. This is known a "multiplicative background" and can lead to various imaging artefacts especially over large scan areas. neaspec technology eliminates the multiplicative background by using an interferometric detection scheme with modulated reference phase. Changing reference phase results in addition modulation of the near-field signal. Locking to this modulation allows for complete

---

[1] Tuning range specification of neaspec products is given here approximately, please contact our sales for the available configurations.

[2] Detection schemes that intrinsically rely on the direct detection of electric field, e.g. time domain spectroscopy do not suffer from multiplicative background

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?

suppression of multiplicative background that does not depend on the reference phase.

Note that utilizing proper interferometric phase modulation scheme for signal detection is of outmost importance in s-SNOM. While multiple detection schemes exist, only three commercial techniques deliver pure optical/chemical near-field maps & spectra free of mechanical artifacts:

- pseudoheterodyne (PsHet),
- nano-FTIR,
- synthetic optical holography (SOH),

all of which are patented and exclusive to attocube Systems AG. Further discussion will be focused on comparing PsHet s-SNOM – a golden standard for s-SNOM imaging and spectroscopy – to the tapping AFM-IR.

Note that neaspec s-SNOM detection technologies are robust proven and maximally user-friendly requiring no technical background for successful measurements. For example, neaspec PsHet can reliably perform nanoscale measurements even at visible wavelengths where the background contribution is particularly strong. While offering a series of unique benefits, s-SNOM requires an IR detector, an interferometer and a relatively good quality laser source (low noise, single mode, TM00 with low divergence), which come at higher cost compared to simpler detection methods such as AFM-IR or PiFM.

AFM-IR

Brief description

AFM-IR (Atomic Force Microscopy InfraRed) is a family of techniques based on detecting mechanical response of the AFM cantilever upon pulsed illumination of sample with IR light. AFM-IR family includes tapping and surface-sensitive AFM-IR, Photoinduced Force Microscopy (PiFM) as well as Photothermal Expansion Microscopy (PTE, PTIR). AFM-IR is primarily utilized for sample absorption mapping and spectroscopy of materials with relatively large absorption coefficient (polymers, organic materials, etc.).

In AFM-IR, sample is illuminated by a pulsed IR source (see Figure 3). Illuminated sample absorbs IR radiation and heats up, which leads to its thermal expansion. Sample expansion in turn, exerts a force/kick upon the AFM tip that stimulates the cantilever motion which is then detected using AFM (mechanical) readout. The specifics of the detection technology define the corresponding technique within the AFM-IR family.

Naturally, the sample thermal expansion depends on the intrinsic absorption spectrum of the sample material: stronger absorption results in larger expansion. Thus, AFM-IR is capable of sample absorption spectroscopy by changing the illumination wavelength. Alternatively, scanning the sample while illuminating at a specific IR wavelength allows for rapid mapping of the sample absorption profile, especially valuable for investigating the components distribution in heterogeneous samples.

AFM-IR techniques can be subdivided into contact and tapping depending on the AFM operating mode. Signal in contact AFM-IR techniques (PTE, PTIR, AFM-IR and surface sensitive AFM-IR) scales with the illuminated sample volume. Therefore, contact AFM-IR delivers strong signals on relatively thick, "bulk" samples (few hundred nm and above). While still capable of
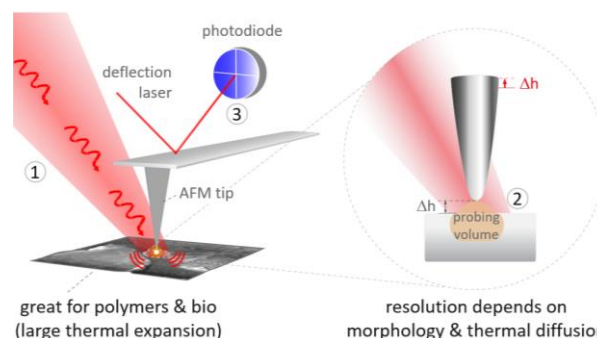

Figure 3. Basic principle of AFM-IR techniques: (1) pulsed IR light is focused onto the sample; (2) sample absorbs IR radiation and thermally expands, exerting force on the AFM tip and stimulating cantilever motion; (3) cantilever motion is detected using AFM, delivering thermal expansion maps and spectra.

investigating thin samples (ca. several nanometer) using enhancement provided by the cantilever mechanical resonances, contact AFM-IR is highly susceptible to the tip degradation and contamination, as well as causing sample damage due to direct contact with the tip.

Tapping AFM-IR techniques provide strong advantage on working in non-contact regime. Such AFM operation prevents tip contamination, degradation, and sample damage, making them ideal for an investigation of soft matter samples. Short tip-sample contact also helps reducing the probing volume, improving the surface sensitivity and lateral resolution. These benefits make tapping AFM-IR a preferred technique (vs. contact AFM-IR) for investigation of heterogeneous samples at the nanoscale. Therefore, in the following discussion will be focused on the tapping technique and more specifically, on the tapping AFM-IR$^+$ offered in neaspec microscopes.

attocube
WITTENSTEIN group

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?
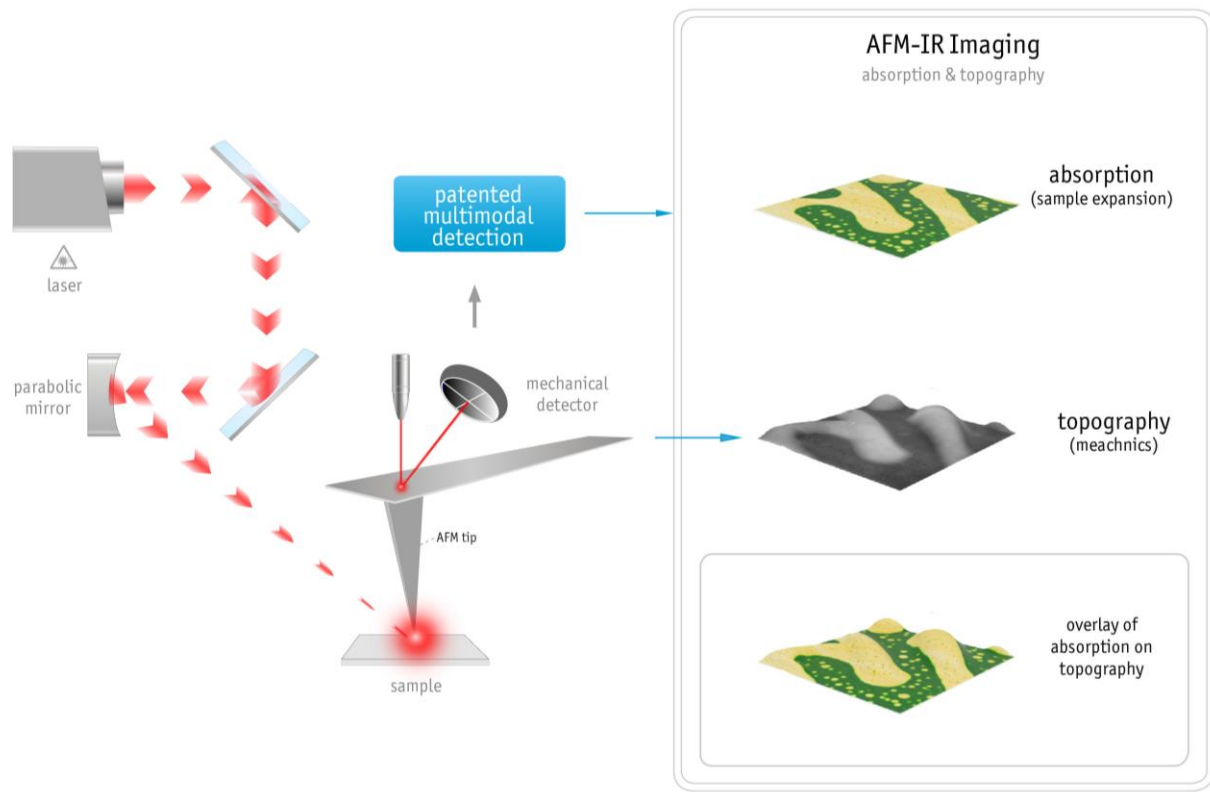
Figure 4. Schematic representation of neaspec tapping AFM-IR$^+$ (left) and typical measured data (right)

All AFM-IR techniques require pulsed IR sources with pulse rates of the order of 1 MHz. Standard neaspec QCL and OPO illumination sources are fully compatible with tapping AFM-IR.

tapping AFM-IR

Similarly to what is done in s-SNOM, in tapping AFM-IR$^+$ the tip gently taps the sample at a frequency corresponding to one of the cantilever resonances, f_1 (see Figure 4). This provides distance control between the tip and the sample, returning sample topography and mechanical properties. At the same time the sample is illuminated by an IR laser source pulsed at a frequency f_m. This pulsing exerts a periodically modulated force upon the tip[3], which induces cantilever oscillations at frequencies $f_2 = f_m \pm f_1$ among others (such a "frequency mixing" occurs due to nonlinear dependence of the interaction force on the tip-sample distance). Therefore, monitoring cantilever oscillations at the frequency f_2 allows for investigating sample's IR response. Namely, recording the

material response while changing the illumination wavelengths returns IR spectra of the material under the tip. Raster scanning the sample allows for recording nanoscale-resolved maps of the sample absorption.

A critical issue in tapping AFM-IR is the coupling of tip-sample mechanics into the optical AFM-IR channel, which is solved by neaspec bimodal approach and will be discussed in the next section.

Tip-sample mechanics and benefit of neaspec tapping AFM-IR$^+$

In neaspec tapping AFM-IR$^+$, frequency f_2 is chosen to correspond to the second cantilever resonance, which resonantly enhances the technique's sensitivity. Furthermore, the laser is pulsed at the sum frequency f_m, i.e. $f_m = f_2 + f_1$. Pulsing at the sum frequency provides higher laser repetition rate, which suppresses the thermal diffusion effects and

---

[3] Current consensus is that the dominant interaction force at mid-IR illumination is due to photothermal expansion. Here we focus primarily on describing the force detection disregarding

the nature of the involved forces. The detailed discussion on this is beyond the scope of this publication.

AFM-IR vs. s-SNOM: Applications Comparison

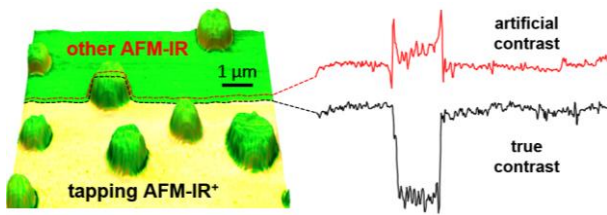What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?

Figure 5. neaspec tapping AFM-IR$^+$ helps suppressing mechanical artifacts associated with AFM detection. Left: tapping AFM-IR$^+$ image overlayed with sample topography (PS-LDPE polymer blend). Right: line profiles with (bottom) and without (top) mechanical resonance tracking.

provides better lateral resolution and surface sensitivity than alternative tapping AFM-IR implementations (e.g. PiFM).

Detection in tapping AFM-IR relies on the mechanical resonance enhancement provided by the cantilever. The latter is affected heavily by operating conditions (AFM operation parameters) and mechanical characteristics of the specific tip and most importantly by the local mechanical properties of the sample. Changes in the sample stiffness affect the mechanical interaction forces between the tip and the sample resulting in significant shifts of the cantilever resonance. If not compensated, this can cause mechanical artefacts in the IR images and/or spectra making materials appear more or even less absorptive than they actually are (see Figure 5).

To suppress the influence of varying tip-sample mechanics, the cantilever resonance shifts can be tracked and compensated for. One of the methods of achieving this is using a so-called phase locked loop (PLL). PLL monitors the mechanical phase of the cantilever oscillation and keeps it constant by adjusting the detection frequency of the tapping AFM-IR. This maintains maximum resonant enhancement of the tapping AFM-IR signal despite the resonance shifts, significantly reducing the artificial mechanical contrast.

neaspec tapping AFM-IR$^+$ utilizes patented bimodal AFM operation for reliable PLL performance. In it, a small modulation is added to the tip oscillation at the detection frequency f_2 in addition to the main tapping. Reliable operation of PLL relies on strong AFM-IR signal, which cannot be ensured in the spectral region where the sample does not absorb. This causes PLL failures and the reappearance of artificial mechanical contrast. Additional modulation in neaspec bimodal AFM provides sufficient signal for PLL even when the sample absorption is close to zero thus preventing the PLL failure.

Note that, s-SNOM techniques utilize a separate optical detector for monitoring sample response, which is not affected by tip-sample mechanics.

General Comparison

Spectroscopic chemical identification

tapping AFM-IR and s-SNOM are both highly suitable for spectroscopic IR analysis and capable of reference-free measurements (i.e. when no reference measurement is necessary to obtain a meaningful spectrum). More specifically for most relevant samples – i.e. those, where mid-IR fingerprint spectroscopy is a relevant technique for sample chemical analysis, such as polymers, biological and other organic materials – both techniques can measure high-quality spectra suitable for chemical identification according to standard FTIR databases. Importantly, both s-SNOM and nano-FTIR spectra can be directly compared to the FTIR databases without any need for s-SNOM modeling (see Figure 6). Small spectral shifts that can be found in literature are exhibited in all techniques that rely on the field enhancement provided by the sharp probing tip. This is true for both s-SNOM and AFM-IR on ultra-thin samples of few nanometers and reflective substrates [8]. In such cases, strong tip-sample interaction alters instrument spectral response, leading to minor alteration of spectral features. Notably, s-SNOM provides a clear benefit of being able to eliminate these shifts using well established models. The

same is unfortunately hardly possible for AFM-IR due to complexity of AFM detection modeling.
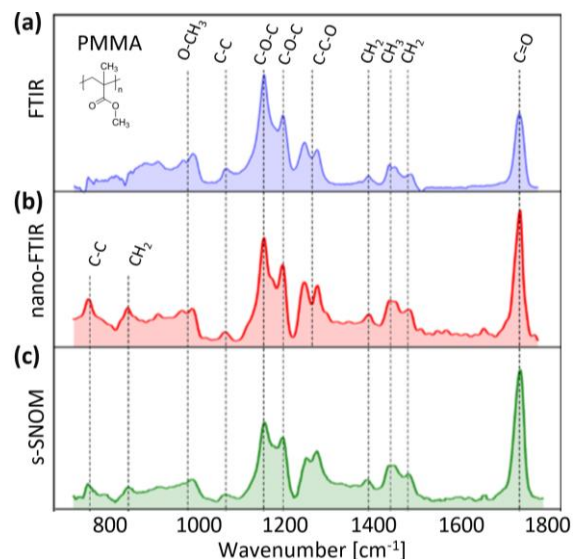

Figure 6. Comparison of FTIR absorption (a), nano-FTIR (b) and s-SNOM (c) phase spectra of PMMA. Both nanoscale spectra are in excellent match with their far-field counterpart, allowing for precise chemical identification of nanomaterials.

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?
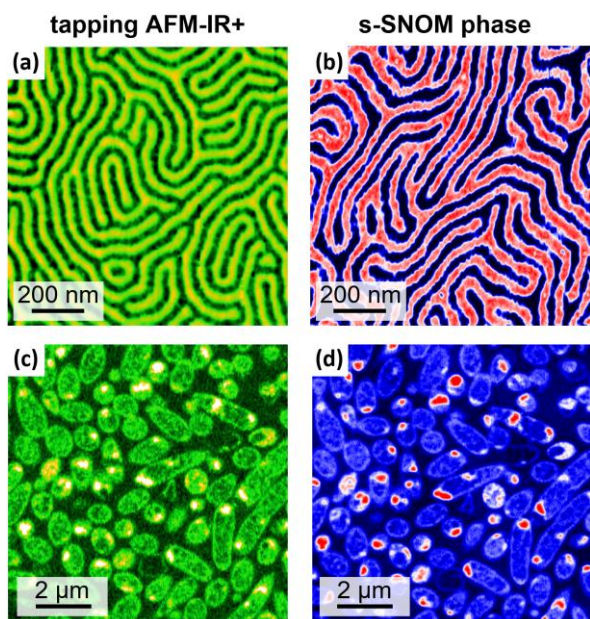

Figure 7. Comparison of tapping AFM-IR$^+$ and s-SNOM imaging on a PS-PMMA copolymer (a,b) and cross-sectional sample of E. coli embedded in resin (c,d). Top images are 1 μm x 1 μm and recorded at 1493 cm^{-1} wavelength with 5 nm pixel resolution, showcasing sub-10 nm lateral resolution for both techniques. E.coli images are recorded at 1530 cm^{-1} on the same exact sample location; sample is kindly provided by W. Duverger, Switch laboratory, VIB Center for Brain and Disease research, VIB-KU Leuven.

In general, it has been demonstrated previously that nano-IR spectroscopic measurements on crystalline materials can suffer from spectral peak shifts or distortions of line shapes compared to conventional FTIR spectra [9]. Materials such as Silica, SiC, BN, GaN, and other glasses and crystals exhibit strong optical interaction between the tip and the sample. Therefore, the reflectivity and absorption spectra as measured by AFM-IR and s-SNOM often reveal spectroscopic signatures with polaritonic resonances that cannot be excited in classic far-field experiments. Whereas is such cases, AFM-IR lacks a detailed understanding of how to relate measured nanoscale IR spectra to the specimens dielectric properties, s-SNOM can utilize well-established models to calculate dielectric functions, thus enabling the material identification and quantification of crystal lattice parameters [10].

Spectral resolution in both AFM-IR and s-SNOM is determined by the tuning step and linewidth of the utilized illumination source which varies from ca. 1 cm^{-1} to 4 cm^{-1}. An exception is nano-FTIR which offers variable resolution down to 0.25 cm^{-1} depending on the equipped modules.

Spatial resolution

s-SNOM and tapping AFM-IR have both demonstrated lateral resolution below <10 nm independently from the illumination wavelength and thus are fully capable of providing nanoscale chemical information (see Figure 7).

Probing depth & surface sensitivity

In s-SNOM the primary probing mechanism is through the highly enhanced hotspot with size determined primarily by the tip radius. Therefore, s-SNOM probes only the nanoscale volume of the material within the hotspot disregarding the sample thickness/structure. In addition, the high-harmonic demodulation is known to further localize the probing volume: the higher the demodulation order – the more surface sensitivity it provides. neaSCOPE records up to 5 harmonics simultaneously, allowing for the separation of surface contribution from bulk even after the data has already been recorded (see Figure 12). This way, s-SNOM is a highly surface sensitive technique with typical probing depths of ca. 10 to 100 nm depending on the tip curvature and tapping amplitude, providing user control of the probing depth and tomographic capabilities in postprocessing (see section Analytical capabilities).

A unique aspect of s-SNOM is the ability of sensing through thin IR-transparent membranes. This is particularly beneficial for sample investigation through a capping layer or for measurements in liquid. Namely, s-SNOM recently demonstrated in-vivo IR nano-imaging and nano-spectroscopy of bacteria [11].

IR probing in tapping AFM-IR relies on the photothermal expansion which scales with the total material thickness. Therefore, it picks up signals from absorbing components both at and below the sample surface without possibility of signals separation. This is especially true for contact AFM-IR techniques, where the probing volume can extend to hundreds of nanometers due to thermal diffusion, leading to strong signal yet typically poor surface sensitivity and spatial resolution that depends on the sample thickness and structure. Therefore, contact AFM-IR is often referred to as a "bulk-sensitive" technique providing probing depth and spatial resolution on the sub-micrometer scale.

Operating in tapping mode, effectively limits the AFM-IR signal acquisition time to the duration of the tip-sample contact which helps limiting the thermal diffusion, thus reducing the probing volume/depth. In addition, neaspec tapping AFM-IR$^+$ utilizes higher laser repetition rates than competing implementations, further decreasing the heat diffusion/probing volume to below 40 nm on par with s-SNOM. Therefore, tapping AFM-IR is a surface-sensitive technique vs. its bulk-sensitive contact AFM-IR counterpart. Note, that changing the probing volume in AFM-IR requires switching the operating mode and can't be done in postprocessing.

Product Line
neaspec

NANOSCALE ANALYTICS
advanced imaging & spectroscopy

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?
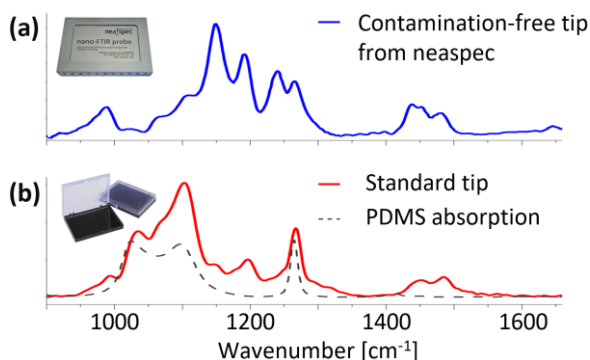
Figure 8. tapping AFM-IR spectra taken on PMMA sample with (a) neaspec contamination-free nano-FTIR tip and (b) with standard AFM probe. The contaminant signature (typically coming from PDMS used in tip handling and shipping) dominates the tapping AFM-IR spectrum making correct chemical identification challenging.

Note that tapping AFM-IR^{+} and contact AFM-IR (called PTE^{+} in neaspec products) have the same hardware requirements and thus are both available in *IR*-neaSCOPE systems.

Sensitivity to tip contamination

tapping AFM-IR is highly sensitive to the contamination such as PDMS that covers the entire tip and cantilever and occurs during tip manufacturing, handling, and storage. This is because despite being just a monolayer thick, the contamination often covers an entire tip and cantilever area, thus producing large overall thermal expansion effect. Therefore, tapping AFM-IR spectra are often dominated by the signature of the contaminant, which obscures the sample spectrum itself and decreases the accuracy of chemical identification (see Figure 8).

To tackle the tip contamination issue, neaspec supplies exclusive contamination-free nano-FTIR tips. These tips avoid contact with PDMS and other major contaminants during production and shipping enabling reliable chemical identification of sample materials.

Performance on Different Materials

tapping AFM-IR

Tapping AFM-IR excels on materials with high thermal expansion coefficients such as polymers and biomaterials. This is because these materials exhibit high thermal expansion coefficient, leading to strong AFM-IR signal (see Figure 9). For thick organic samples, AFM-IR, especially contact) could even outperform s-SNOM because it is affected by the whole sample volume, while s-SNOM only probes nanoscale sample volume in the hotspot disregarding the sample size/thickness). Nevertheless, on polymer and bio samples with relevant

Noteworthy, s-SNOM is less sensitive to the tip contamination. This is because due to the optical detection, s-SNOM (and nano-FTIR) only probes the analyte within the nanoscale-confined hot-spot under the tip. Thus, the contamination of the tip shaft and cantilever plays no role in the resulting data.

Power requirements

Another aspect of AFM-IR probing is that thermal expansion for ultrathin films and nanoparticles is very small, making measurements challenging and often requiring high illumination power (1-5 milli Watt) for high-quality measurements. In contrast, s-SNOM has been capable of high-quality imaging and spectroscopy even at very low illumination powers (below 100 micro Watt) and is highly suitable for nano-imaging and nano-spectroscopy on single monolayer/molecule samples [2]. Therefore, s-SNOM is gentler on samples and should be the technique of choice for materials that are easily damaged by heat (e.g. bio and soft-matter).

Instrument preparation

Preparing system for measurements in s-SNOM and AFM-IR involves optimization of beam focusing to maximize signal on the sample of interest. Tapping AFM-IR signal depends directly on the sample expansion upon absorption of IR light. Therefore, finding the optimal light focusing requires selecting a wavelength at which the sample is known to absorb, along with landing with the tip on the corresponding absorbing part of a generally inhomogeneous sample.

In s-SNOM, the signal magnitude is proportional to the tip scattering, which never vanishes. This ensures strong signal and thus straightforward focus optimization on any sample disregarding whether it is absorbing or not. This makes signal optimization on unknown samples with s-SNOM less challenging than in tapping AFM-IR.
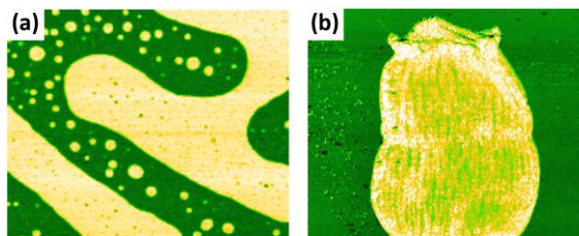

Figure 9. tapping AFM-IR^{+} images showing nanoscale resolution on soft matter samples. (a) PS-PVAC polymer film recorded at 1736 cm^{-1}, and (b) cable bacteria imaged at the Amide I band at 1642 cm^{-1}; sample is kindly provided by B. Smets, Dept. of Biology, U. Antwerp.

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+s}?

thicknesses both techniques are equally capable of delivering high-quality data with nanoscale spatial resolution.

s-SNOM

s-SNOM is a highly versatile technique that delivers high quality data on any AFM-ready sample – organic or inorganic (see Figure 10). This is because neaspec s-SNOM detects both amplitude and phase of the scattering signal, which are related to the sample reflectivity and absorption. This means that s-SNOM can be utilized on samples that are weakly/non-absorbing or exhibit only weak thermal expansion. This is particularly important for the investigation of crystals, as well as 2D and semiconductor materials where IR response originates primarily form phonon and/or electronic excitations. Data returned by tapping AFM-IR on such samples are often of low quality and noisy (see Figure 11).

An important ability of s-SNOM is the high sensitivity to the active free carriers (see Figure 10c-d). In combination with quantitative nature of s-SNOM measurements (see section Analytical capabilities below) and well-established interaction models, s-SNOM is an invaluable tool for free-carrier profiling in classic and novel semiconducting materials unmatched in capabilities by other techniques.

s-SNOM is also highly suitable for application involving field mapping. neaspec s-SNOM technology simultaneously detects amplitude and phase, delivering complete information about complex-value electromagnetic field distribution (see Figure 10f). It is thus a technique of choice for investigation of plasmonic and polaritonic materials, such as metallic nanostructures, van-der Waals and other 2D materials.

Challenging samples

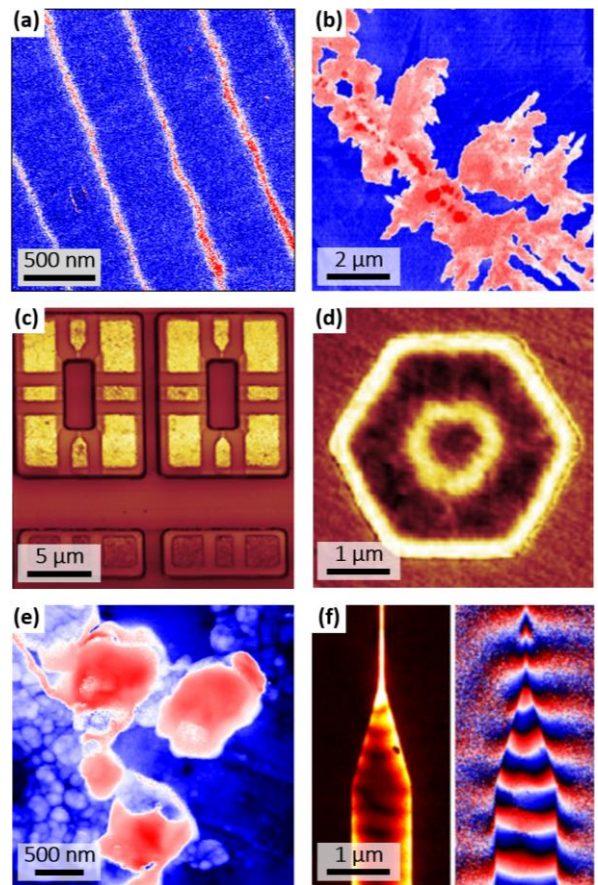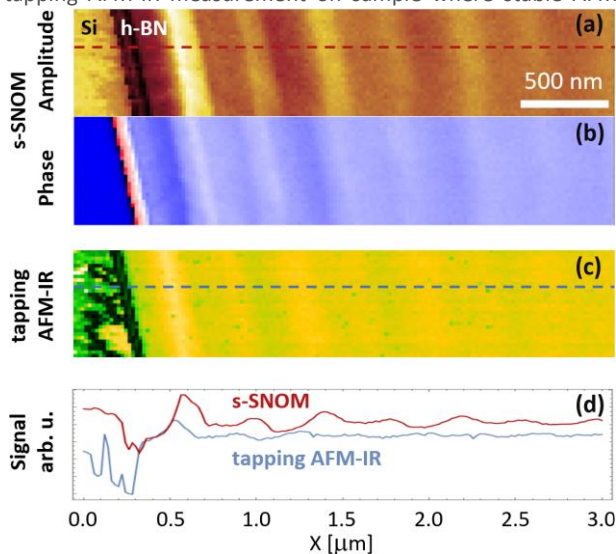Due to intricate dependence on the tip-sample mechanics, tapping AFM-IR measurement on sample where stable AFM

Figure 10. Applications of s-SNOM on diverse sample types: (a) absorption (phase) image of a packaging material cross section recorded at 1660 cm^{-1} resolving 20 nm thin polyamide adhesion layers; sample is kindly provided by Royal DSM. (b) absorption (phase) image of a self-assembled PEO monolayer imaged at 1123 cm^{-1} (asymmetric C-O-C stretching), in collaboration with Dr. O. Pop-Georgievski, Academy of Science, Czech Republic; (c), reflectivity image of SRAM device representing the corresponding doping map; (d) reflectivity image of a Bi$_2$Se$_3$ nanocrystal obtained at 10.2 μm and representing the carrier distribution map, Lu eta al, Adv. Electron. Mater. 2018; (e) phase image of copper oxide mapping CO$_2$ absorption at 648 cm^{-1}, sample is kindly provided by M. Johnson, KTH Royal Institute of Tech.; (f) amplitude and phase images of propagating polariton recorded at 1.5 μm wave in tapered IR waveguide (Zenin et al, Opt. Expr. 2016).

Figure 11. Mapping of hyperbolic phonon polaritons in hexagonal Boron Nitride (h-BN). s-SNOM delivers excellent data quality and maps both amplitude (a) and phase (b), providing complete information about complex-valued field distribution suitable for quantitative analysis. (c) tapping AFM-IR$^+$ map of the same sample region, also showing a detectable signal modulation on h-BN. (d) s-SNOM and AFM-IR line profiles showing much lower modulation depth and signal to noise in tapping AFM-IR. Note that optical field maps are the result of interference of multiple optical fields such as the actual polariton wave, incident light and surface scattering, thus requiring amplitude- & phase-resolved measurements to disentangle polariton properties such as wavelength, propagation length, etc. Such measurements can only be done by s-SNOM.

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?
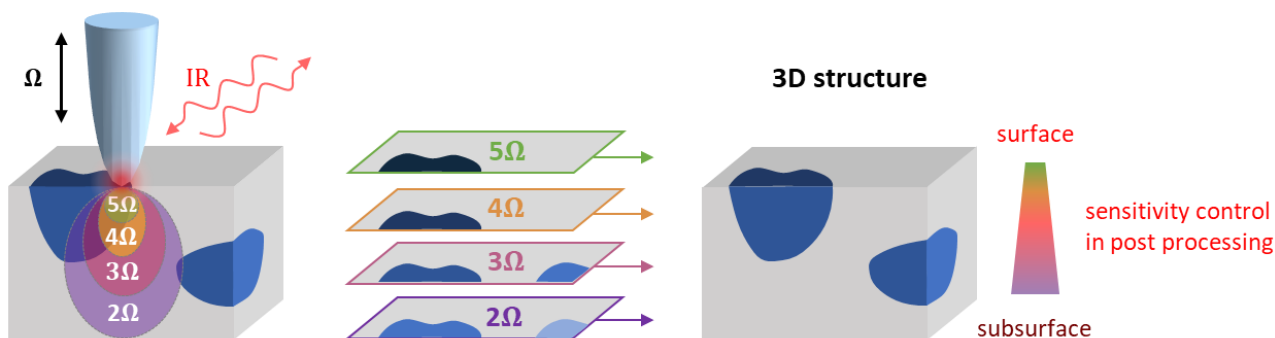

Figure 12. Schematic representation of subsurface nano-tomographic capability of s-SNOM. neaspec s-SNOM records simultaneously multiple signals that probe different subsurface volumes, which allows for user-controlled probing depth/surface sensitivity as well as tomographic analysis of samples in the postprocessing.

operation is hard to achieve (e.g. sticky, rough, etc.) might present a challenge. In contrast, s-SNOM signal is much less susceptible to the sample mechanics (thanks to the purely optical detection) making measurement more robust as long as a decent intermittent contact can be maintained.

Analytical capabilities

Note that in general, tapping AFM-IR signal is affected by multiple forces including due to photothermal expansion, photoacoustic effect, photoinduced force, sample reflectivity, etc. While current consensus is that the dominant interaction at mid-IR illumination is due to photothermal expansion, certain admix of other interactions is always present and cannot be fully decoupled from the sample expansion/absorption. Additionally, influence of tip-sample mechanics intrinsic to the AFM detection, can make the resulting data dependent on the measurement conditions/parameters, specifics of the utilized tips, etc. This negatively affects the experiment reproducibility making tapping AFM-IR a qualitative technique capable of spectroscopic material recognition but not quantitative analysis.

On the other hand, s-SNOM measures pure optical response, which is directly related to the sample IR properties. s-SNOM measurements are very well understood and can be accurately modeled. Furthermore, since amplitude and phase of the scattered light measured by s-SNOM relate to the sample reflectivity and absorption, s-SNOM provides complete characterization of sample complex dielectric properties. Particularly, s-SNOM (and nano-FTIR as its variant) allows for the extraction of sample refractive index and absorption coefficient or, alternatively, the real and imaginary part of the complex-valued dielectric function. This information is similar to what is delivered by IR ellipsometry and FTIR, yet with nanoscale spatial resolution [10], making s-SNOM an invaluable analytical tool capable of quantitative analysis.

Note that, when quantitative spectroscopic measurements are desired, nano-FTIR is the technique of choice. This is because nano-FTIR utilizes Fourier transform detection principles and measures the whole spectrum "at once". This makes the resulting nano-FTIR spectra independent form the emission profile of a specific laser ensuring correct ratios of spectral peaks.

Conclusions and Summary

Tapping AFM-IR, s-SNOM are powerful technologies for nanoscale imaging and spectroscopy with the spatial resolution of atomic force microscopy. They are all capable of chemical identification of relevant materials, each featuring unique application benefits and advantages summarized in the Table 1. Together, these technologies provide almost unlimited application potential for nanoscale sample analysis.

neaspec systems are the only microscopes engineered to fully integrate s-SNOM/nano-FTIR and AFM-IR technologies with maximum performance level, providing comprehensive analysis of chemical, optical, electrical and mechanical sample properties at the nanoscale. Best in class sensitivity and spectral coverage with unique IR sources (1.4 um to >18 μm) makes neaSCOPE product line a true leader in nanoscale analysis.

AFM-IR vs. s-SNOM: Applications Comparison

What technologies are behind *IR*-neaSCOPE & *IR*-neaSCOPE^{+S}?

References

[1]   S. Mastel, A. A. Govyadinov, C. Maissen, A. Chuvilin, A. Berger, and R. Hillenbrand, "Understanding the Image Contrast of Material Boundaries in IR Nanoscopy Reaching 5 nm Spatial Resolution," *ACS Photonics*, vol. 5, no. 8, pp. 3372–3378, 2018.

[2]   I. Amenabar *et al.*, "Structural analysis and mapping of individual protein complexes by infrared nanospectroscopy.," *Nat. Commun.*, vol. 4, p. 2890, Jan. 2013.

[3]   J. A. Griffiths, P. R.; de Haseth, *Fourier Transform Infrared Spectrometry*. New York: Wiley, 2007.

[4]   F. Huth, A. Govyadinov, S. Amarie, W. Nuansing, F. Keilmann, and R. Hillenbrand, "Nano-FTIR absorption spectroscopy of molecular fingerprints at 20 nm spatial resolution.," *Nano Lett.*, vol. 12, no. 8, pp. 3973–3978, Jun. 2012.

[5]   M. Eisele *et al.*, "Ultrafast multi-terahertz nano-spectroscopy with sub-cycle temporal resolution," *Nat. Photonics*, vol. 8, no. October, pp. 841–845, 2014.

[6]   R. Keilmann, F.; Hillenbrand, "Nano-Optics and Near-Field Optical Microscopy," A. House, Ed. Boston/London, 2008.

[7]   A. Cvitkovic, N. Ocelic, and R. Hillenbrand, "Analytical model for quantitative prediction of material contrasts in scattering-type near-field optical microscopy," *Opt. Express*, vol. 15, no. 14, pp. 8550–8565, Jul. 2007.

[8]   F. Lu, M. Jin, and M. a. Belkin, "Tip-enhanced infrared nanospectroscopy via molecular expansion force detection," *Nat. Photonics*, vol. 8, no. 4, pp. 307–312, 2014.

[9]   Y.-T. Lin *et al.*, "Photothermal Atomic Force Microscopy Coupled with Infrared Spectroscopy (AFM-IR) Analysis of High Extinction Coefficient Materials: A Case Study with Silica and Silicate Glasses," *Anal. Chem.*, vol. 94, no. 13, pp. 5231–5239, 2022.

[10]   A. A. Govyadinov, I. Amenabar, F. Huth, P. S. Carney, and R. Hillenbrand, "Quantitative Measurement of Local Infrared Absorption and Dielectric Function with Tip-Enhanced Near-Field Microscopy," *J. Phys. Chem. Lett.*, vol. 4, pp. 1526–1531, Apr. 2013.

[11]   K. J. Kaltenecker, T. Gölz, E. Bau, and F. Keilmann, "Infrared-spectroscopic, dynamic near-field microscopy of living cells and nanoparticles in water," *Sci. Rep.*, vol. 11, no. 1, pp. 1–12, 2021.