Infrared Imaging and Spectroscopy Beyond the Diffraction Limit

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Abstract Progress in nanotechnology is enabled by and dependent on the availabil- ity of measurement methods with spatial resolution commensurate with nanomaterials' length scales. Chemical imaging techniques, such as scatter- ing scanning near-field optical microscopy (s-SNOM) and photothermal- induced resonance (PTIR), have provided scientists with means of extract- ing rich chemical and structural information with nanoscale resolution. This review presents some basics of infrared spectroscopy and microscopy, fol- lowed by detailed descriptions of s-SNOM and PTIR working principles. Nanoscale spectra are compared with far-field macroscale spectra, which are widely used for chemical identification. Selected examples illustrate either technical aspects of the measurements or applications in materials science. Central to this review is the ability to record nanoscale infrared spectra because, although chemical maps enable immediate visualization, the spectra provide information to interpret the images and characterize the sample. The growing breadth of nanomaterials and biological applications suggest rapid growth for this field.

Keywords s-SNOM, PTIR, RE-AFMIR, nanoscale infrared spectroscopy, nanomaterials, chemical composition

1. Introduction

Over the past two decades advances in top-down fabrication methods ($\underline{1}$, $\underline{2}$) and in bottom-up nanomaterial synthesis (3–5) have enabled the preparation of a plethora of nanomaterials. Because nanomaterials typically provide novel properties or improved performance with respect to their macroscopic counterparts (6–10), they are of great interest in fields such as electronics (11), photovoltaics (12), biology (13), therapeutics (8, 14), and many more. However, harnessing the properties of nanomaterials in functional devices is not straightforward because their development and integration often require characterizing the material/device properties (electrical, chemical, thermal, etc.) at relevant length scales. This is particularly important for materials presenting phase separation, heterogeneity, interfaces, or degradation at the nanoscale.

Infrared (IR) absorption spectroscopy directly probes vibrational energy levels and phonons of materials, providing rich chemical and structural information (13, 15, 16), without any a priori knowledge of the sample. However, the diffraction of the long IR wavelengths (2.5 μ m to 20 μ m) limits the lateral resolution of IR microscopy to several micrometers (17, 18). In contrast, atomic force microscopy (AFM) (19) provides nanoscale-resolution images of the sample topography by scanning a sharp tip over the sample. Advanced AFM techniques can assess local mechanical (20–22), electrical (23), and thermal (24, 25) properties by exploiting various tip-sample interactions. However, they typically require complex modeling, a priori knowledge of the sample, or extensive (and tip-specific) calibration to extract information quantitatively. Ideally, nanoscale information should be immediately informative without necessitating complex calculations or prior knowledge of the sample.

Two techniques that combine the high spatial resolution of AFM with the high chemical specificity of IR spectroscopy are scattering scanning near-field optical microscopy (s-SNOM) (26, 27) and photothermal-induced resonance (PTIR) (28–30), also known as AFM-IR. IR s-SNOM (26, 27) measures the amplitude and the phase of light scattered from a tip in proximity to the sample. These quantities are functions of the sample index of refraction and absorption coefficient as well as some other parameters. Although s-SNOM technology benefits from 30 years of steady development, in the author's opinion, it became of general utility to the analytical chemist only recently, thanks to the ability of recording nanoscale IR spectra. Such an advance has been enabled primarily by the availability of continuous narrow-band lasers with broader wavelength

tunability (31–33) and by broadband sources with wider bandwidth (34–39). By comparison, PTIR (28–30) couples a pulsed, wavelength-tunable laser and an AFM cantilever to measure light absorption in the sample by transducing the sample thermal expansion into mechanical cantilever motion. Although of more recent development (\approx 10 years), PTIR received the immediate attention of analytical chemists because of its ability to record nanoscale spectra that are immediately comparable to far-field IR spectral libraries.

The intent of this review is to inform the reader on the fundamentals of near-field IR chemical imaging and spectroscopy, focusing on the current state of the art, rather than to provide a comprehensive history of technical development and a complete list of references. A few basic concepts pertaining to IR spectroscopy and microscopy are presented first, followed by the working principles of the s-SNOM and PTIR techniques. A few selected examples from the literature, illustrating either technical aspects of the measurements or applications, are discussed. Finally, a novel implementation of the PTIR technique, referred to as photo-expansion nanospectroscopy (40, 41) or resonance-enhanced AFM-IR (RE-AFM-IR), is described. Because IR analysis should be carried out by looking at a whole spectral pattern rather than a single peak or frequency, this review emphasizes the ability of collecting nanoscale IR spectra and their comparison with far-field spectra, commonly used for materials identification.

2. Infrared Spectroscopy

IR spectroscopy measures vibrational transitions of molecules and materials via electrical dipolar interactions with light, typically requiring photons with energies between 500 cm⁻¹ and 4,000 cm⁻¹ (20 μ m to 2.5 μ m). The IR optical properties of a sample can be described by molecular dynamics (42) at the molecular level, or by the complex refractive index (N) at the macroscale:

$$\mathcal{N}(\lambda) = n(\lambda) + i \cdot \kappa(\lambda), \quad (1)$$

where λ is the wavelength of light and n and κ are the real and imaginary parts of the index that are related to light scattering and absorption, respectively. For nonmagnetic materials *N*, n and κ are related to the dielectric permittivity (ϵ) of the sample by

$$\mathcal{N}(\lambda) = \sqrt{\varepsilon(\lambda)}, \quad (2)$$

$$Re[\varepsilon] = n^{2} - \kappa^{2}, \quad (3)$$
$$Im[\varepsilon] = 2 \cdot n \cdot \kappa. \quad (4)$$

Although *n* and κ could be considered as the fundamental parameters of absorptions peaks, experimentally they cannot be determined easily and they typically are not used for chemical identification.

At the molecular level, a sample is classically represented as a collection of point masses (nuclei) held together by weightless springs (bonds). Because intermolecular interactions are much weaker than intramolecular forces, in first approximation, the vibrational dynamic problem for a molecule can be solved by considering the molecule to be isolated (and treating the intermolecular interactions as a small perturbation). A molecule with nonlinear geometry composed of N atoms has 3N - 6 vibrational degrees of freedom (modes). To a hypothetical observer, the superposition of all these vibrations would appear as a complex convolution. However, by approximating the intramolecular potential with a harmonic function, it is possible to find a set of coordinates describing the motion of the nuclei for which all atoms reach the position of maximum displacement and pass through their equilibrium positions at the same time (42). Such coordinates (normal coordinates) are typically used in the theoretical calculations of IR spectra, and the vibrations they describe are known as normal modes, which are independent (normal) from each other. IR light can be absorbed only if the light electric vector oscillates at the same frequency as the molecular dipole moment modulated by a particular vibrational mode (and if these two vectorial quantities are not orthogonal to each other):

$$\left(\frac{\partial \overline{\mu}}{\partial Q}\right)_0 \neq 0, \quad (5)$$

where $\overline{\mu}$ is the molecular dipole moment and Q is the normal coordinate describing a normal mode. The absorption intensity of a normal mode is proportional to the square of the molecular dipole moment derivative with respect to the normal coordinate.

Internal coordinates describe vibrational modes independently of the molecule position and orientation in space, giving scientists a chemically intuitive description of molecular vibrations through changes of bond lengths and angles. Some vibrations are localized on a particular chemical group and always occur in a narrow frequency range, no matter how complex the rest of the molecule. The presence of functional groups in the sample can be easily determined by comparison with empirical correlation tables (29, 30). Other vibrations involve many atoms (skeletal vibrations) and are characteristic of the whole molecule.

The most important aspect of IR absorption frequencies is that they are the equivalent of fingerprints for chemical identification and, typically, allow the identification of unknown samples by comparison with IR spectral databases. Additionally, the perturbation of the molecule's intramolecular potential by intermolecular interactions (43), electronegativity of neighboring atoms (44), intramolecular conformations (45, 46), or mechanical coupling with other vibrational modes (44) can cause frequency shifts and intensity changes to the absorption peaks. Advanced use of IR spectroscopy takes advantage of these perturbations to extract important chemical and struc- tural information. Because of these complexities, IR characterization should not be carried out by looking only at a specific peak, but rather by analyzing the entire spectral pattern.

An implicit consequence of considering isolated molecules for calculating IR spectra is that the spectra are determined purely by absorption (not scattering), which is an approximation for solid samples. In general, IR spectra are nontrivially related to n and κ (i.e., absorption and scattering), with relative contributions that depend on the sample preparation and experimental conditions (transmission, reflection, etc.). However, provided that the samples are prepared correctly and consistently (i.e., diluted sample measured in transmission), the resulting spectra are determined mostly by absorption and are, in practice, very useful for chemical identification.

In transmission, neglecting the reflection losses, the transmitted light (*T*) is a function of the absorption coefficient (α abs) and of the path length of light in the sample (*l*):

$$T = \frac{I}{I_o} = e^{-\alpha_{abs} \cdot l}, \quad (6)$$

where I_0 and I are the light intensity of the incident and transmitted beams, respectively. The absorbance is defined as:

$$A = \gamma \cdot l \cdot c = -\log T. \quad (7)$$

Where $\alpha_{abs} = \gamma \cdot c$, γ is the molar absorptivity and *c* is molar concentration of the absorbing species. Equations 6 and 7 are good approximations if (a) the sample is homogeneous, (b) the sample is weakly absorbing, (c) scattering is negligible, and (d) n and κ of the sample are independent. Under these approximations, the absorption coefficient is related to n and κ by

$$\alpha_{abs} = \frac{4 \cdot \pi \cdot n \cdot \kappa}{\lambda}.$$
 (8)

However, in the vicinity of sharp IR absorption peaks, *n* commonly shows a strong dispersion (i.e. depends on κ), (47) and equation 8 should be regarded only as an approximation.

3. Infrared Microscopy

Fourier transform infrared (FTIR) spectrometers coupled with IR microscopes enable scientists to routinely obtain spectral information from small sample areas and chemical images. Given the broad application of IR spectroscopy, the use of IR microscopy is also widespread and has been the subject of recent reviews (48–51). Commonly, IR microimaging setups consist of a broadband thermal light source, an FTIR spectrometer, an optical microscope with reflective optics, and an IR focal planar array (FPA) detector. The availability of FPA detectors (with up to 256×256 elements) has been a truly enabling technology for IR chemical imaging, allowing for the simultaneous recording of more than 65,000 location-specific IR spectra. The lateral resolution of IR microscopes, limited by light diffraction, can be estimated by the Rayleigh criterion:

$$\xi = \frac{0.61 \cdot \lambda}{NA}, \quad (9)$$

where ξ s the lateral resolution and NA is the numerical aperture of the microscope objective. From Equation 9, two significant drawbacks are immediately clear. First, the lateral resolution is comparable to λ , which in the mid-IR is too large to capture nanoscale details. Second, the wavelength-dependent lateral resolution can limit the utility of IR analysis when mapping the chemical distribution of components with characteristic peaks in different spectral regions or when calculating intensity map ratios. The lateral resolution can be improved by a factor of four by using germanium (n = 4) attenuated total reflection objectives (49), but it is insufficient to reach the nanoscale range. Recently, FPAs with pixel sizes smaller than the optical diffraction limit have significantly improved image quality at the expense of lower signal-to-noise ratio (SNR) (52). High-brilliance light sources such as synchrotrons (18) and quantum cascade lasers can compensate for the lower SNR of those detectors (53, 54). Recently, a synchrotron source that combines multiple beams (55) was used in combination with tomographic reconstruction algorithms to extend IR microscopy to 3D.

Although the utility of IR chemical imaging is undeniable, it is also commonly recognized that differences (peak shifts, baselines distortions, etc.) exist between IR spectra from the bulk or from

a microscopic portion of the sample. These differences arise mainly from the scattering and transmission of light at interfaces with characteristic length scales comparable to the IR wavelengths (56). In other words, spectra recorded with IR microscopes contain information related to both n and κ that should be decoupled to obtain pure local chemical information independently of morphology (i.e., scattering). Thanks to FPAs, far-field IR microscopy provides full spectral information within every pixel over relatively large areas, thus enabling high throughput. However, the poor lateral resolution hampers its utility in nanoscale science and technology.

4. Scattering Scanning Near-Field Optical Microscopy (s-

SNOM)

In the quest for subwavelength imaging, earlier works (57–59) employed scanning probes with small (\approx 50 nm) apertures to illuminate the sample locally. Because the power transmitted through the aperture scales as $\sim \lambda^{-4}$ (60), this approach proved to be challenging in the mid-IR. In contrast, IR s-SNOM (26, 27) measures the light scattering from a scanning probe tip in proximity to the sample and has been applied to characterize several materials including plasmonic antennas (61–67), nanowires and nanotubes (32, 68–70), polymers (26, 34, 35, 71), small-molecule thin films (72), minerals (36, 37, 74), graphene (75–77), hexagonal boron nitride (78), and biological samples (79–81). In-depth instrumental and theoretical details of s-SNOM are available in former reviews (82–85). Although different s-SNOM setups have been reported, they commonly require a light source (spectrally narrow or broad), far-field optics to focus and collect light, a sharp scanning probe tip operating in tapping mode, and an interferometer with an IR-sensitive detector for measuring the amplitude and phase of the scattered light (**Figure 1a**). Additionally, a measurement scheme to amplify the weak near-field signal and to discriminate it from the broad, nonlocal background is necessary. A spectrally flat reference material (such as Si or Au) is typically used to compensate for the instrument spectral response.

The tip is crucial in s-SNOM because, in addition to the sample topography, it provides the electric field confinement and enhancement necessary for achieving subwavelength resolution ($\approx 20 \text{ nm}$) (82). In s-SNOM, the tip-mediated light-sample interaction changes the amplitude and

phase of the scattered light as a function of the local complex index of refraction. Because the amplitude and phase of the scattered light are not simple functions of κ (33), the resulting s-SNOM spectral line shapes may not correlate with far-field IR spectra. In general, this makes the identification of unknown materials and the interpretation of small spectral shifts or intensity changes challenging tasks requiring tip-specific modeling (27, 86) to accurately describe the tip-sample-substrate interactions in the near field. Although rigorous, tip-specific modeling of light scattering is necessary to interpret fine details in s-SNOM experiments, calculations typically approximate the tip as a sphere of radius (r) comparable to the tip apex (**Figure 1b**). This simple model allows interpretation of a large fraction of s-SNOM data with reasonable accuracy. According to this model, for weakly dispersive (i.e., weakly absorbing) modes, the s-SNOM phase provides spectra that resemble far-field IR spectra (34, 37, 61, 87). The sphere field scattered (*E*_s) is modeled as a point dipole:

$$E_s \approx \alpha_{eff} \cdot E_{inc}, \quad (10)$$

where E_{inc} is the incident electric field and α_{eff} is the effective polarizability of the tip which is a function of the dielectric properties of the tip (ε_{tip}) and of the sample (ε_s) (26). Under the assumptions that: (a) the sphere is polarized only in the sample direction, (b) the sample is polarized only by the sphere dipolar field, (c) there no retardation effects and (d) $r \ll \lambda$:

$$\alpha_{eff} = \frac{\alpha}{1 - \left(\frac{\alpha \cdot \beta}{1 - \left(\frac{\alpha \cdot \beta}{1 - \alpha \cdot (r + d)^3}\right)}\right)}, \quad (11)$$

where *d* is the distance between the point dipole and the sample, α and β are the polarizability of the sphere and of the point dipole induced by the tip in the sample, respectively:

$$\alpha = 4 \cdot \pi \cdot r^3 \cdot \frac{\varepsilon_{tip} - 1}{\varepsilon_{tip} + 2}, \quad (12)$$
$$\beta = \frac{\varepsilon_s - 1}{\varepsilon_s + 1}. \quad (13)$$

Because ε_s , ε_{tip} , α , α_{eff} and β are complex-valued quantities, characterized by an amplitude and a phase shift with respect to the incident light, s-SNOM measurements rely on interferometric techniques. For IR absorption (linear process) the s-SNOM signal increases approximately with the second power of the near-field enhancement (80). Tips providing spectrally flat enhancement (via the lightning-rod effect) like dielectric tips or non-resonant metal coated (Pt, Au) tips are preferred for measuring near-field spectra. For imaging at a fixed wavelength, noble metal tips

exhibiting λ -matching plasmonic or antenna resonances can provide higher sensitivity (84). Metallic substrates under a thin sample can further increase the local field-enhancement (85).



Figure 1: (a) Example of a s-SNOM setup: A fiber laser emits a pulse train (1.55 μ m) (blue) together with a broadened redshifted beam (green) that are superimposed in a DFG unit resulting in a mid-IR continuum beam (red) that illuminates the s-SNOM tip. The backscattered light is measured with an asymmetric Michelson interferometer comprising a beam splitter and a reference mirror (RM). Panel a adapted with permission from Reference 34. Copyright (2012) American Chemical Society. (b) Schematic for the point-dipole model: The s-SNOM tip is replaced by the point dipole generated by a sphere with radius (*r*). According to this model, the scattered light depends on the tip-sample distance (*d*) and on the dielectric functions of the tip (ε_{tip}) and of the sample (ε_s), but the sample thickness (*z*) probed is limited to $\approx r$. (c) Modeling the tip as an ellipsoid of length 2*L* and apex *r* can better reproduce the dependence of the s-SNOM signal as a function of *z*. Abbreviations: AFM, atomic force microscopy; DFG, difference frequency generation; s-SNOM, scattering scanning near-field optical microscopy.

Despite the field enhancement, the s-SNOM signal typically is much weaker than the non-local scattered background. To discriminate the two contributions, the near-field interactions are periodically modulated by driving tip oscillations (of tens of nanometers) close to the cantilever bending mode frequency (Q). Although the background is essentially unaffected by the modulation, the nonlinear dependence of the near-field signal on the tip-sample distance (see Equation 11) introduces higher harmonics in the scattered signal. The near-field signal is retrieved with a phase- sensitive lock-in detection of the harmonics of the tip oscillation frequency. As a rule of thumb, for the second and higher harmonics, the near-field signal typically exceeds that of the background. The selective excitation of the tip apex via adiabatic surface plasmon polariton nanofocusing is an interesting novel approach to reduce the unwanted background scattering that exploits the spatial separation between the illumination location and the tip apex (90–92).

Homodyne (32, 93) or pseudoheterodyne (94) interferometric techniques are typically used to amplify the near-field signal and determine its phase with respect to a known reference field. In the case of homodyne amplification, the harmonics of the s-SNOM signal amplitude are measured for two reference phases shifted by 90°, thereby enabling the determination of the near-field magnitude and phase of the scattered light. In the case of pseudoheterodyne amplification, a continuous (sinusoidal) phase modulation is applied to the reference field, which results in improved background suppression and allows the determination of the real and imaginary components of the near-field signal.

Graphene attracts interest in several applications because of its unique combination of properties. However, electrical transport and plasmon propagation in graphene are negatively affected by grain boundaries and other defects (75) and are typically difficult to characterize with conventional techniques. s-SNOM tips were used to launch surface plasmons in graphene and to visualize grain boundaries, invisible in AFM topography, by revealing the interference between the plasmon waves launched by the tip and the wave reflected by the grain boundaries or other defects (75, 76). s-SNOM was also used to image plasmon propagation in graphene flakes, revealing plasmonic wavelengths (tunable by electrical gating) that are up to 40 times shorter than in free space (77). Similarly, surface phonon polaritons were measured in hexagonal boron-nitride flakes (78), revealing long (10 μ m) propagation lengths with wavelengths (tunable as a function of the material thickness) that are up to 25 times shorter than in free space. Even higher wavelength confinement (up to \approx 70 times) was observed in boron-nitride nanotubes (70).

One common application of s-SNOM is mapping the amplitude ($|A_z|$) and phase (Φ_z) of the electric field component perpendicular to the plane of plasmonic structures (61–67, 95). The modes of two plasmonic structures with similar resonant frequencies in proximity hybridize (96), forming symmetric (bright) and antisymmetric (dark) collective modes (97). Whereas symmetric bright modes have a large electric dipole and interact strongly with light, dark modes have a small net electric dipole because the electric polarization vectors are in opposite phase in the two structures. However, dark modes typically lead to stronger near-field enhancement because of their reduced coupling with free space. s-SNOM provided the first direct experimental visualization of the interference between bright and dark plasmonic modes (**Figure 2**) (62). These experiments used a continuous-wave CO₂ laser that has a high brilliance but limited wavelength tunability, thus preventing the acquisition of near-field spectra. However, by measuring the phase of the scattered

field, s-SNOM images can distinguish between bright-mode (in phase) and dark-mode (out of phase) excitations, as exemplified in **Figure 2c** where the rods extremities are 180° out of phase, indicating a dark-mode excitation.



Figure 2: (a) Scattering scanning near-field optical microscopy (s-SNOM) measurement scheme. The Π structure is side illuminated with s-polarized light, and light scattered by the tip is measured with an interferometer yielding both amplitude and phase near-field images simultaneously with topography. (b) Numerically calculated reflection spectra for horizontal (blue) and vertical (red) polarization as indicated in panel a. The letter Q marks the wavelength used to acquire the near-field images with horizontal polarization in panel c; the red letters mark the wavelengths used to acquire s-SNOM images for vertical polarization (data not shown). The inset shows the topography image. (c) Experimental (top row) and calculated (bottom row) amplitude ($|A_z|$) and phase (Φ_z) images for horizontal polarization at 10.2 µm. Figure adapted with permission from Reference 62. Copyright (2011) American Chemical Society.

Quantum cascade lasers have wider wavelength tunability (a few hundred wavenumbers) than CO₂ lasers, enabling the acquisition of near-field IR maps and spectra (31–33, 63). Even broader spectral coverage in s-SNOM was achieved using a thermal source, similar to those used in FTIR (98), but the low brilliance of this source limits its applicability. The availability of brilliant coherent sources based on difference frequency generation of femtosecond pump pulses (34–36) (see **Figure 1a**) has enabled the acquisition of broadband IR s-SNOM spectra covering up to $\approx 800 \text{ cm}^{-1}$ in the 700–2,100 cm⁻¹ spectral range (**Figure 3**) (34). For weak IR absorption peaks, the s-SNOM phase spectra resemble, in good approximation, far-field IR absorption spectra, thus enabling material identification (**Figure 3c**) (34). Furthermore, using the same setup and more sophisticated modeling to analytically invert the near-field scattering problem, both $n(\lambda)$ and $\kappa(\lambda)$ can be determined for weak absorbers, in good agreement with FTIR and ellipsometry measurements (35).



Figure 3: (a) Topography image of a scratched PMMA film on a Si substrate. (b) Tapping-mode atomic force microscopy phase image, where the strong contrast designates a particle consisting of neither PMMA nor Si. (c) s-SNOM absorption ($A_{abs} = |A|\sin\Phi$) spectra of PMMA (from position P_3) and of the particle (P_4), identified by its IR spectrum as PDMS. The acquisition time was 7 min, and the spectral resolution was 13 cm⁻¹. Figure adapted with permission from Reference 34. Copyright (2012) American Chemical Society. Abbreviations: PDMS, polydimethylsiloxane; PMMA, poly(methyl methacrylate); s-SNOM, scattering scanning near-field optical microscopy.

Very recently, broadband synchrotron sources (37, 39) enabled the acquisition of near-field amplitude images (showing contrast in the sample refractive index) and amplitude (|A|) and phase (Φ) spectra across the full mid-IR spectral range (from 700 cm⁻¹ to 5,000 cm⁻¹) (37). These setups were used to measure SiO₂, CaCO₃ polymorphs, dried proteins (37), and semiconductors (39). For a SiO₂ sample (**Figure 4**), the spectra reveal spectral shifts at the SiO₂ step edge, which are attributed to changes in the sample thickness and/or to changes in the tip-sample interaction for the sharp interface (37).

According to the point-dipole approximation, the field enhancement under the tip is confined to a depth comparable to the tip radius, thus limiting the utility of the s-SNOM analysis to only the top (\approx 25 nm) portion of the sample. This is a good approximation for nontransparent samples. However, at IR frequencies, s-SNOM can image high index materials under a low index transparent layer up to 80-nm thick (89, 99). Optimization of the imaging conditions of buried objects is still the subject of investigations (100), but the point-dipole approximation is insufficient to interpret those results (101). For an SiO₂ film on Si, calculations that approximate the tip as a spheroid of length 2*L* and radius r ($r \ll 2L \ll \lambda$) show that the saturation of the s-SNOM signal occurs only for sample thicknesses (*z*) comparable to *L* (**Figure 5**), in better agreement with experiments (101).



Figure 4: (a) Atomic force microscopy topography and (b) broadband scattering scanning nearfield optical microscopy (s-SNOM) amplitude image of an SiO₂ disk on Si. The insets show the profiles of topography and s-SNOM intensity across the SiO₂ edge corresponding to the white lines. *D* indicates the distance along the white lines. (c) Amplitude and (d) phase line scans along the white line in panel *a*, consisting of 30 spectra (each 16-cm⁻¹ spectral resolution, 1-min acquisition time). (e) Amplitude and (f) phase spectra obtained at the three marked locations in panels *c* and *d*. The spectra have an offset for clarity. Figure reproduced with permission from Reference 37.



Figure 5: (a) Experimental scattering scanning near-field optical microscopy (s-SNOM) spectra for different SiO₂ film thicknesses obtained from the absolute value of the third harmonic scattering amplitude (*A*₃) normalized by the signal from the bare Si wafer. Inset: topographic atomic force microscopy image of 18-nm-thick SiO₂ sample (top) and corresponding near-field image acquired at 1,130 cm⁻¹. (b) Theoretical results for the spheroid model with r = 30 nm and L= 15r (see **Figure 1**c). (c) Theoretical results for the point-dipole model with r = 30 nm and b =0.75r, where b is the distance between the position of the point dipole and the bottom of the tip. (d) Calculations of the thickness dependence of the *A*₃ intensity for different tip models: point dipole with r = 30 nm (blue), point dipole with r = 50 nm (green), and spheroid model with r = 30nm and L = 15r (red). Black circles indicate data derived from the experiments shown in panel aafter some smoothing over of fluctuations. Figure adapted with permission from Reference 101. Copyright by the American Physical Society.

In far-field transmission experiments, the positions of IR bands are used to identify the sample chemical composition, and their intensities (proportional to the molar concentration, Equation 6) are often used to quantify the relative amounts of chemical species in a mixture via multivariate analysis. Although experimental validation on heterogeneous samples is needed, significant progress in relating s-SNOM spectra with far-field FTIR spectra was recently accomplished

through analyses of the amplitude (*A*), phase (φ), and absorption ($A_{abs} = |A|\sin\Phi$) signals as a function of thickness in PMMA films on highly reflective substrates (Si) (102). Peak intensities in the phase spectra increased with thickness, and their positions (blue-shifted by \approx 3 and 9 cm⁻¹ with respect to far-field grazing angle and transmission spectra, respectively) were mostly insensitive to the thickness. If such small spectral shifts are not crucial for material identification, the phase signal may be used to identify the chemical composition of samples with varying thicknesses. In contrast, although the peak intensities of absorption spectra are a non-monotonic function of thickness, their peak positions match well with the bulk transmission spectra for thick (174 nm) samples or with the grazing angle spectra for thin (10 nm) samples, allowing for direct comparison with far-field measurements. Although for intermediate or unknown sample thicknesses, modeling is necessary for comparing the s-SNOM absorption spectra with FTIR absorbance spectra, these recent findings bring the application of multivariate analysis at the nanoscale a step closer.

5. Photothermal Induced Resonance (PTIR)

In PTIR (28-30), the AFM cantilever serves the function of near-field detector to measure the absorption of IR light in the sample. PTIR characterization has been applied to investigate a wide array of samples including bacteria (28, 29, 103–106), cells (107–110), lipids (111), proteins (112), polymers (30, 113-121), drugs (122, 123), quantum dots (124), plasmonic nanostructures (97, 125–127), metal-organic frameworks (MOFs) (128), and organo-trihalide perovskites (129). PTIR setups require a pulsed, spectrally narrow, wavelength-tunable laser source; an AFM tip operating in contact mode; and far-field optics to focus light under the tip. PTIR was implemented initially with a free electron laser offering wavelength tunability over the whole mid- and far-IR (28, 103). Today, PTIR more commonly relies on tabletop sources based on optical parametric oscillators (30, 114, 130) or difference frequency generation (118, 128), covering a range as large as $625 - 20,000 \text{ cm}^{-1}$ (0.5–16.0 µm) (130) and reaching the visible range. Most commonly, total internal reflection (30, 115, 118) is used to illuminate a sample placed on top of an optically transparent prism (i.e., zinc selenide) (Figure 6a). In total internal reflection, the evanescent field excites the sample and minimizes the direct light-tip interaction, resulting in better SNR. Setups using top illumination (40, 41, 113) or transmission (109) through a transparent substrate have also been reported.



Figure 6: (a) PTIR schematic: When the sample absorbs an IR laser pulse, it rapidly expands, deflecting the AFM cantilever, which is monitored by a 4-Q detector. (b) The maximum peak to peak deflection during the cantilever ring down is proportional to the absorbed energy. (c) Cantilever's contact resonance modes excited by the sample expansion and obtained by Fourier transformation of the ring-down signal. (d) AFM topography image of a sample made of PMMA and PS particles in epoxy matrix. (e) PTIR spectra recorded at the locations marked with + symbols in panel *d*. (f) PTIR image recorded at 1,142 cm⁻¹ corresponding to PMMA. (g) PTIR image recorded at 825 cm⁻¹ corresponding to epoxy. (h) PTIR image recorded at 694 cm⁻¹ corresponding to PS. All scale bars are 1 μ m. Figure adapted with permission from Reference 118. Copyright 2013 American Chemical Society. Abbreviations: 4-Q, four-quadrant; AFM, atomic force microscopy; PMMA, poly(methyl methacrylate); PS, polystyrene; PTIR, photothermal-induced resonance.

Although the laser spot is large ($\approx 30 \ \mu$ m), the sharp AFM tip serves as a near-field detector by locally transducing the small thermal expansion resulting from light absorption in the sample into large cantilever oscillations, thus conferring high lateral resolution on the measurement. Such oscillations are monitored by reflecting the AFM laser beam from the cantilever onto a fourquadrant photodetector (**Figure 6**). The theory of PTIR signal generation was developed in detail by Dazzi and coworkers (131, 132) and was recently corroborated with experimental observations (30, 118). Briefly, the PTIR signal is obtained by transducing optical energy into heat, heat into thermal expansion, thermal expansion into cantilever oscillation, and cantilever motion into photodetector signal (118, 131). The sample thermal expansion is much faster than the AFM feedback (impulsive loading), fast enough to induce a ring down in the photodetector signal (**Figure 6b**) and to excite several mechanical modes in the cantilever (**Figure 6c**). The laser repetition rate (typically 1 kHz) allows sufficient time for completing the ring down before the arrival of a new pulse and enables synchronous signal averaging. Spectroscopic information is extracted either by determining the deflection maximum in the time domain (**Figure 6b**) or by determining the amplitude of one of the cantilever normal modes in the frequency domain obtained by Fourier transforming the ring-down signal (**Figure 6c**). Location-specific IR spectra are obtained by plotting the signal, normalized by the laser power, as a function of λ (**Figure 6e**). Chemical maps (see, for example, **Figure 6f–h**) are obtained by illuminating the sample at constant wavelength and plotting the signal as a function of location. Typically, several pulses are averaged at each point to increase the SNR.



Figure 7: Photothermal-induced resonance spectra of an 800-nm-thick ethylene acrylic acid polymer film obtained with commercial rectangular Si cantilever (bottom, black), paddle probe (middle, blue), and modified paddle probe (top, red). The spectra obtained with the paddle and the modified paddle probes have amplitudes three and six times larger than the rectangular probe, respectively. Figure adapted with permission from Reference 114. Copyright Institute of Physics. All rights reserved.

Methods for achieving a higher SNR are of great interest because, by reducing the acquisition time, they can increase the typically low throughput of scanning probe experiments. Because the PTIR signal varies in both time and frequency (**Figure 6**), noise can be reduced by applying a time-frequency signal transformation (such as the Morlet wavelet transform) and by filtering the signal for times longer than the cantilever ring down and for frequencies not corresponding to the

cantilever bending modes (119, 120). By virtue of reduced noise, this method yields a 32-fold reduction in the need for pulse averaging (120), resulting in a corresponding throughput increase. The SNR can also be increased by using cantilevers with higher sensitivity, which provide a stronger signal. For example, modified Si cantilevers with an internal resonator paddle (**Figure 7**) resulted in a 6-fold SNR increase with respect to unmodified cantilevers (114). Such modification reduces the cantilever stiffness, providing higher sensitivity, and reduces the cantilever dumping, prolonging the ring down, thus reducing the relative noise. Because the SNR is a square root function of the number of averages, a 6-fold-better SNR leads to a 36-fold-higher throughput (114).

According to theory (131, 132), the PTIR signal (S) is proportional to the absorbed energy per unit area (U_{abs}), to the cube of the sample thickness (z), and to the sample thermal expansion coefficient (α_{exp}). It is also inversely proportional to the sample thermal conductivity (η):

$$S \sim \frac{\alpha_{exp}}{\eta} \cdot U_{abs} \cdot z^3$$
. (14)

This expression was confirmed experimentally in a total internal reflection configuration by analyzing the spectra of a poly(methyl methacrylate) (PMMA) wedge patterned with e-beam lithography (30) (**Figure 8**). The PTIR signal increases linearly with thickness up to $\approx 1 \mu m$; it then reaches a (λ -dependent) maximum and decreases for larger *z* (**Figure 8a**), because of the exponentially decaying field amplitude in the sample. In a total internal reflection configuration, U_{abs} is not proportional to the sample thickness and does not have a simple analytical expression. Instead, it depends on how steeply the evanescent field intensity decays inside the sample (30). In total internal reflection, the field amplitude in the sample (*E*) is usually expressed as a function of the penetration depth (d_p) (133, 134):

$$E = E_0 \cdot e^{-z/d_p}, \quad (15)$$

where E_0 is the electric field amplitude at the prism-sample interface and d_p is the distance where E is reduced by a factor of e and it is given by (135):

1 /2

$$d_p = \frac{\lambda}{2 \cdot \pi} \cdot \left[\frac{\sqrt{\left(n_1^2 \cdot \sin^2\theta - n_2^2 + \kappa_2^2\right)^2 + \left(2 \cdot n_2 \cdot \kappa_2\right)^2} + \left(n_1^2 \cdot \sin^2\theta - n_2^2 + \kappa_2^2\right)}{2} \right]^{-1/2}, \quad (16)$$

where (ϑ) in the light incident angle, $\mathcal{N}_1(\lambda) = n_1(\lambda)$ and $\mathcal{N}_2(\lambda) = n_2(\lambda) + i\kappa_2(\lambda)$ are the refractive index of the nonabsorbing prism and of the sample, respectively (30). U_{abs} is a non-monotonic function of z (**Figure 8c**) and can be calculated (30) as the difference between the evanescent fields intensities for a non-absorbing medium ($\kappa = 0$) and for a sample with extinction coefficient κ_2 :

$$U_{abs} \sim E_{\kappa=0}^2 - E_{\kappa=\kappa2}^2$$
. (17)



Figure 8: (a) Photothermal-induced resonance (PTIR) intensity of the 1,720 cm⁻¹ poly(methyl methacrylate) (PMMA) peak as a function of thickness; experimental data are interpolated by the function $\mathbf{a} \cdot \mathbf{z}^3 \cdot \mathbf{e}^{-2 \cdot \frac{1}{d_P}}$ with correlation coefficient (R^2) of 0.963 and $d_P = 1,070$ nm. (b) PTIR intensity of 1,720 cm⁻¹ PMMA peak as a function of thickness (up to 1,200 nm). In this region, the data can be interpolated linearly with an $R^2 = 0.993$. (c) Calculated absorbed energy per unit area as a function of thickness according to Equation 17 ($\lambda = 1,720$ cm⁻¹, $\theta = 45^\circ$, $n_{ZnSe} = 2.438$, $n_{PMMA} = 1.54$, and $\kappa_{PMMA} = 0.2$). (d) PTIR spectra as a function of PMMA thickness. Copyright Wiley-VCH Verlag GmbH & Co., KGaA. Figure adapted with permission from Reference 30.

By using λ -dependent optical constants (47), the data in **Figure 8** (30) fit well with the theory prediction (131, 132) (Equation 14), demonstrating the proportionality between the PTIR signal and the absorbed energy. Additionally, for thin (z < 1 µm) samples, the PTIR signal increases approximately linearly with thickness (**Figure 8b**), a necessary condition for enabling quantitative IR analysis. For a mixture of two components (A, B), the thermal conductivity can be expressed as the concentration-weighted average of the component's thermal conductivities (η^A , η^B):

$$\eta^{mix} = c_A \cdot \eta^A + (1 - c_A) \cdot \eta^B.$$
(18)

Because the PTIR signal is proportional to the absorbed energy and, in first approximation, the absorbance is proportional to the molar concentration (Equation 7), the concentration of A (c_A) affects both the absorbed energy (Equation 14) and the thermomechanical properties of the mixture (Equation 18). Consequently, the PTIR signal is strictly linearly proportional to the concentration only for components with the same thermomechanical properties and will deviate from linearity if α/η is substantially different for the two components. However, for mixtures with similar thermomechanical properties such as some biological samples (136), polymer blends, and diluted mixtures, the deviation is small (30).

The application of PTIR in biology and polymer science was reviewed recently (85, 137) and is not discussed here extensively. A short list of those applications includes the localization of viruses inside bacteria and the identification of viral infection stages (103), the localization and quantification of biopolymer (105) and biofuel (106) production in bacteria cultures, the imaging of phase-separated drug-polymer blends (122), and the characterization of drug nanocrystals in solid matrixes (123). A few examples of PTIR characterization in materials science are reported below.

Plasmonic nanostructures attract interest in energy (138), sensing (139), and therapeutic (14, 140) applications because of their ability to enhance light-matter interactions at the nanoscale. Surface-enhanced infrared absorption (SEIRA) spectroscopy (66, 97, 141, 142) exploits this effect to increase the sensitivity of IR spectroscopy. Until recently, SEIRA hot-spot engineering relied only on theoretical calculations (143) because of the low resolution of IR microscopy. Furthermore, high SEIRA sensitivity is typically accompanied by Fano spectral distortions (144), which can complicate chemical identification. PTIR broke those paradigms by enabling direct observation and quantification of SEIRA near-field hot spots with nanoscale resolution (97). For

example, PTIR maps and spectra on gold asymmetric split ring resonators coated with PMMA revealed local absorption enhancement factors up to ≈ 30 at 100-nm lateral resolution (**Figure 9**) (97). Because the PTIR signal is a function of κ and independent of *n* (scattering) (30), PTIR spectra are proportional to the local field intensity times the sample absorption coefficient and are free of Fano distortions [which derive from $n(\lambda)$] (97). For the same reason, PTIR maps of PMMA absorption in **Figure 9** are a direct image of the near-field absorption enhancement.



Figure 9: (a) AFM height image of gold resonators with 1,700-nm diameter coated with a 200nm PMMA film. The white arrow indicates the direction of the electric field polarization in the PTIR experiments. (b) PTIR image of the PMMA CH₃ antisymmetric deformation mode at 1,455 cm⁻¹. (c) PTIR image of PMMA C–O stretching vibrational mode at 1,263 cm⁻¹. The intensity scale of the PTIR images was normalized by the incident laser power; the scale bars are 500 nm. (d) PTIR spectra (in common scale) for 200-nm-thick PMMA, either away from the array (*red*) or on the hot spot of a resonator with 2,000-nm diameter (*black*). (e) Surface-enhanced IR absorption enhancement factor is defined as the ratio of the PTIR spectral intensity of PMMA in the hot spot to the spectral intensity of PMMA away from the resonator. Figure adapted with permission from Reference 97. Copyright 2013 American Chemical Society. Abbreviations: AFM, atomic force microscopy; ASRR, asymmetric split ring resonators; PMMA, poly(methyl methacrylate); PTIR, photothermal-induced resonance.

PTIR has also been used to obtain near-field absorption spectra of plasmonic resonators and to image their plasmonic modes (**Figure 10**) (126). Again, the PTIR spectra of the resonators are not complicated by Fano resonances, typically observed in s-SNOM and far-field spectroscopies. Although probed locally, the PTIR spectra are characteristic of the resonator's collective plasmonic modes, not of the constituent isolated arcs. The PTIR images in **Figure 10** display the energy dissipated in the arcs due to the plasmonic excitation (126, 145), and provide evidence of the interference between the bright and dark modes in these structures. One limitation of PTIR images is that they do not provide phase information, making theoretical calculations necessary to assign bright- or dark-mode excitations (97).



Figure 10: (a) Photothermal-induced resonance (PTIR) spectra of a gold asymmetric split ring resonator collected at locations identified by a color-coded plus symbol in the inset height image. (b–d) PTIR maps (each displayed with its own unique full scale) emphasize the contribution of each arc to the collective resonator's modes at wavelengths corresponding to the dotted color-coded vertical lines in panel a. All scale bars are 500 nm. White arrow in the inset in panel a indicates the direction of the electric field polarization. Copyright Wiley-VCH Verlag GmbH & Co., KGaA. Figure reproduced with permission from Reference 126.

Another challenge that PTIR has addressed is the determination of the linkers' distribution within MOF single crystals (128). MOFs are nanoporous functional materials consisting of inorganic clusters interconnected by organic linkers whose structure and properties can be tailored by chemical design (146–148). MOFs find applications in catalysis (149), separation (150), sensing (151), etc. Synthesis of MOFs with multiple linkers (mix-MOFs) raised the question pertaining to the linkers' spatial distribution within MOF crystals (148), which is hardly determinable with conventional techniques because of the low spatial resolution. PTIR data on individual mix-MOF crystals isoreticular to In-MIL-68 (152) determined that those crystals are homogeneous at the \approx 100-nm scale (128). Additionally, such characterization enabled the development of a new synthesis method for engineering anisotropic domains in MOF single crystals with linker composition gradients occurring over ≈ 600 nm (128).

In contrast with FTIR, the lateral resolution of PTIR does not depend on λ (118, 130, 132), but instead depends on the tip size and on the sample thermomechanical properties (132). For thin samples with η^{sample} significantly smaller than $\eta^{substrate}$, the resolution is determined by the tip size rather than by the sample properties (105, 130). For thicker samples, the lateral resolution may also depend on the sample properties, but it is not easily predictable because the thermal properties at the nanoscale often differ from bulk values (153) and because the thermal diffusion at the materials' interfaces is not well understood. In fact, mismatches in phonon energy and density of states across different materials can cause phonon scattering instead of transmission, resulting in interfacial thermal resistance (154, 155). Even if not completely understood, these effects favor high lateral resolution in PTIR, which is typically 100 nm or better (30, 104, 107, 114, 116). Recently, the PTIR spectra range was extended to the visible range, enabling the acquisition of correlated vibrational (chemical) and electronic property maps and spectra with a wavelength-independent resolution as high as ≈ 20 nm (130). As in the case of s-SNOM, the lateral resolution is reduced for buried objects (97, 103).

A major challenge of PTIR in the total internal reflection configuration is the sample preparation on the prism. However, the linear dependence of the PTIR signal with sample thickness (for $z < 1 \mu$ m), its proportionality to the absorption coefficient, and its independence of scattering (30) allow materials to be identified at the nanoscale using FTIR spectral libraries. Newly commercially available setups employing top sample illumination remove the challenge of sample preparation, but they require gold-coated cantilevers to avoid direct light absorption in the tip. The dependence of the signal intensity on the sample thickness has not yet been determined for the top sample illumination configuration.

6. Resonance Enhanced AFM-IR (RE-AFMIR)

RE-AFM-IR is a novel technique combining some aspects of PTIR and s-SNOM measurements and has been used to characterize polymers (40) and self-assembled monolayers (41). RE-AFM- IR setups require a pulsed, spectrally narrow laser source tunable both in wavelength and in repetition rate, an AFM tip operating in contact mode, far-field optics to focus light under the tip, and a lock-in amplifier (**Figure 11**). A gold reference spectrum is typically used to account for the instrument spectral response (41). The sample is illuminated either through a transparent substrate (40) or from the top (41). Quantum cascade lasers have characteristics suitable for RE-AFM-IR. RE-AFM-IR exploits both the *Q*-factor of the cantilever and the sample thermal expansion to measure IR absorption spectra and maps, by matching the laser repetition rate to the frequency of one of the cantilever oscillations. This way, subsequent laser pulses induce sample expansion and transfer energy to the cantilever synchronously with the cantilever oscillation (i.e., on resonance), resulting in *Q*-fold amplification of the signal ($Q \approx 100$ for commercially available cantilevers).

Lu et al. (41) showed that by exploiting the large electromagnetic field enhancement ($\approx 10^5$) found in the nanogap between a sharp gold-coated tip and a gold substrate, RE-AFM-IR can achieve monolayer sensitivity (see **Figure 11**). In this case, the field confinement at the tip provided lateral resolution comparable to the tip size (≈ 25 nm). RE-AFM-IR induces very small temperature changes in the sample, which is important for studying biological samples. While scanning, the cantilever resonances typically vary in frequency, intensity, and *Q*-factor because of, for example, changes in the sample mechanical properties. Consequently, for general applicability, measurement schemes that spatially maintain or track the cantilever resonance should be employed to ensure measurement stability.



Figure 11: (a) Schematic of resonance-enhanced AFM-IR (RE-AFM-IR) setup: Light pulses from a quantum cascade laser (p-polarized) are focused on a sample. The signal of the cantilever deflection is sent to a lock-in amplifier referenced to the laser repetition rate. The amplifier output is a measure of the cantilever oscillation amplitude at the lock-in reference frequency. (b) Topography of poly(ethylene glycol)-methyl-ether-thiol monolayer islands; (c) corresponding RE-AFM-IR absorption image at 1,342 cm⁻¹ (CH₂ wagging mode). Bright regions are the sample, and dark regions are gold. (d) Topographic line scan along the blue arrow in panel *b*: Square symbols mark positions where the RE-AFM-IR spectra were recorded. (e) RE-AFM-IR spectra (with offset) corresponding to the color-coded positions in panel *d*. Figure adapted with permission from Macmillan Publishers Ltd., *Nature Photonics*, Reference 41, copyright 2014.

7. Concluding Remarks and Perspective

Although driven by a common goal, by measuring absorbed and scattered light, respectively, PTIR and s-SNOM are largely complementary techniques. For example, bright and dark plas- monic modes behave differently: The bright-mode excitation results mainly in scattered light and little absorption, whereas the dark mode exhibits strong absorption and weak scattering (126). Consequently, PTIR is typically more sensitive to dark modes, whereas s-SNOM is more sensi- tive to bright modes. Additionally, s-SNOM is mostly sensitive to a thin portion of the sample in proximity to the tip, whereas, in the total internal reflection configuration, PTIR probes sam- ple thicknesses comparable to the field penetration depth (30). Finally, materials with large α_{exp} and small η are generally easy to measure with PTIR, whereas materials with very small α_{exp} are challenging (118). However, the latter do not present additional challenges for s-SNOM. Consequently, the nature of the material and its thickness play important roles when choosing an appropriate measurement method. Furthermore, the two methods are not entirely equivalent: s-SNOM can provide phase information and potentially provides information about the sam- ple complex refractive index; PTIR provides spectra that depend on absorption and are directly comparable with IR spectral databases.

The three nanoscale techniques described here produce chemical maps at selected wavelengths or spectra at selected locations, but the acquisition of full IR spectra at each pixel, and within a reasonably fast timeframe, has not yet been achieved. It is expected that research will focus on increasing the SNR by increasing the sensitivity and by reducing noise, thus increasing throughput. To this end, improvements to laser sources will certainly be beneficial. Another important area to be addressed for both s-SNOM and PTIR is the interpretation of the signal intensity for samples presenting material heterogeneity through the sample thickness. The availability of commercial s-SNOM, PTIR, and RE-AFM-IR setups, combined with the general utility of IR analysis and the growing breadth of nanomaterials and biological applications, suggests that the field of nanoscale IR imaging and spectroscopy is poised for rapid growth in both academic and industrial settings.

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Literature Cited

- 1. Gates BD, Xu Q, Stewart M, Ryan D, Willson CG, Whitesides GM. 2005. New approaches to nanofabrication: molding, printing, and other techniques. *Chem. Rev.* 105:1171–96
- 2. Henzie J, Lee MH, Hasan W, Odom TW. 2009. Nanofabrication of plasmonic structures. *Annu. Rev. Phys. Chem.* 60:147–65
- 3. Murray CB, Norris DJ, Bawendi MG. 1993. Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. J. Am. Chem. Soc. 115:8706–15
- 4. Perez-Juste J, Pastoriza-Santos I, Liz-Marzan LM, Mulvaney P. 2005. Gold nanorods: synthesis, characterization and applications. *Coord. Chem. Rev.* 249:1870–901
- 5. Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J. 2003. Reticular synthesis and the design of new materials. *Nature* 423:705–14
- 6. Lee C, Wei XD, Kysar JW, Hone J. 2008. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* 321:385–88
- 7. Cahill DG, Ford WK, Goodson KE, Mahan GD, Majumdar A, et al. 2003. Nanoscale thermal transport. J. Appl. Phys. 93:793-818
- 8. Zhang LJ, Webster TJ. 2009. Nanotechnology and nanomaterials: promises for improved tissue regeneration. *Nano Today* 4:66–80
- 9. Centrone A, Penzo E, Sharma M, Myerson JW, Jackson AM, et al. 2008. The role of nanostructure in the wetting behavior of mixed-monolayer-protected metal nanoparticles. *PNAS* 105:9886–91
- 10. El-Sayed MA. 2001. Some interesting properties of metals confined in time and nanometer space of different shapes. *Acc. Chem. Res.* 34:257–64
- 11. Huber AJ, Wittborn J, Hillenbrand R. 2010. Infrared spectroscopic near-field mapping of single nanotransistors. *Nanotechnology* 21:235702
- 12. Nicholson PG, Castro FA. 2010. Organic photovoltaics: principles and techniques for nanometre scale characterization. *Nanotechnology* 21:492001
- 13. Fernandez DC, Bhargava R, Hewitt SM, Levin IW. 2005. Infrared spectroscopic imaging for histopathologic recognition. *Nat. Biotechnol.* 23:469–74
- 14. Park JH, von Maltzahn G, Ong LL, Centrone A, Hatton TA, et al. 2010. Cooperative nanoparticles for tumor detection and photothermally triggered drug delivery. *Adv. Mater.* 22:880–85
- 15. Centrone A, Hu Y, Jackson AM, Zerbi G, Stellacci F. 2007. Phase separation on mixed-monolayer- protected metal nanoparticles: a study by infrared spectroscopy and scanning tunneling microscopy. *Small* 3:814–17
- 16. Centrone A, Brambilla L, Renouard T, Gherghel L, Mathis C, et al. 2005. Structure of new carbonaceous materials: the role of vibrational spectroscopy. *Carbon* 43:1593–609
- 17. Petibois C, Piccinini M, Guidi MC, Marcelli A. 2010. Facing the challenge of biosample imaging by FTIR with a synchrotron radiation source. J. Synchrotron Radiat. 17:1–11
- Nasse MJ, Walsh MJ, Mattson EC, Reininger R, Kajdacsy-Balla A, et al. 2011. High-resolution Fourier- transform infrared chemical imaging with multiple synchrotron beams. *Nat. Methods* 8:413–16
- 19. Binnig G, Quate CF, Gerber C. 1986. Atomic force microscope. Phys. Rev. Lett. 56:930-33
- 20. Sahin O, Magonov S, Su C, Quate CF, Solgaard O. 2007. An atomic force microscope tip designed to measure timevarying nanomechanical forces. *Nat. Nanotechnol.* 2:507–14
- 21. Hurley DC, Shen K, Jennett NM, Turner JA. 2003. Atomic force acoustic microscopy methods to determine thin-film elastic properties. J. Appl. Phys. 94:2347–54
- 22. Herruzo ET, Perrino AP, Garcia R. 2014. Fast nanomechanical spectroscopy of soft matter. Nat. Commun. 5:3126

- 23. Oliver RA. 2008. Advances in AFM for the electrical characterization of semiconductors. Rep. Prog. Phys. 71:076501
- 24. Majumdar A. 1999. Scanning thermal microscopy. Annu. Rev. Mater. Sci. 29:505-85
- 25. Buzin AI, Kamasa P, Pyda M, Wunderlich B. 2002. Application of a Wollaston wired probe for quantitative thermal analysis. *Thermochim. Acta* 381:9–18
- 26. Knoll B, Keilmann F. 1999. Near-field probing of vibrational absorption for chemical microscopy. Nature 399:134-37
- 27. Knoll B, Keilmann F. 2000. Enhanced dielectric contrast in scattering-type scanning near-field optical microscopy. *Opt. Commun.* 182:321–28
- 28. Dazzi A, Prazeres R, Glotin E, Ortega JM. 2005. Local infrared microspectroscopy with subwavelength spatial resolution with an atomic force microscope tip used as a photothermal sensor. *Opt. Lett.* 30:2388–90
- 29. Dazzi A, Prazeres R, Glotin F, Ortega JM. 2007. Analysis of nano-chemical mapping performed by an AFM-based ("AFMIR") acousto-optic technique. *Ultramicroscopy* 107:1194–200
- 30. Lahiri B, Holland G, Centrone A. 2013. Chemical imaging beyond the diffraction limit: experimental validation of the PTIR technique. *Small* 9:439–45
- 31. Zhang M, Andreev GO, Fei Z, McLeod AS, Dominguez G, et al. 2012. Near-field spectroscopy of silicon dioxide thin films. *Phys. Rev. B* 85:075419
- 32. Xu XJG, Tanur AE, Walker GC. 2013. Phase controlled homodyne infrared near-field microscopy and spectroscopy reveal inhomogeneity within and among individual boron nitride nanotubes. J. Phys. Chem. A 117:3348–54
- 33. Craig IM, Taubman MS, Lea AS, Phillips MC, Josberger EE, Raschke MB. 2013. Infrared near-field spectroscopy of trace explosives using an external cavity quantum cascade laser. *Opt. Express* 21:30401–14
- 34. Huth F, Govyadinov A, Amarie S, Nuansing W, Keilmann F, Hillenbrand R. 2012. Nano-FTIR ab-sorption spectroscopy of molecular fingerprints at 20 nm spatial resolution. *Nano Lett.* 12:3973–78
- 35. Govyadinov AA, Amenabar I, Huth F, Carney PS, Hillenbrand R. 2013. Quantitative measurement of local infrared absorption and dielectric function with tip-enhanced near-field microscopy. J. Phys. Chem. Lett. 4:1526–31
- 36. Amarie S, Zaslansky P, Kajihara Y, Griesshaber E, Schmahl WW, Keilmann F. 2012. Nano-FTIR chemical mapping of minerals in biological materials. *Beilstein J. Nanotechnol.* 3:312–23
- Bechtel HA, Muller EA, Olmon RL, Martin MC, Raschke MB. 2014. Ultrabroadband infrared nanospec- troscopic imaging. PNAS 111:7191–96
- 38. Hermann P, Hoehl A, Patoka P, Huth F, Ruhl E, Ulm G. 2013. Near-field imaging and nano-Fourier- transform infrared spectroscopy using broadband synchrotron radiation. *Opt. Express* 21:2913–19
- 39. Hermann P, Hoehl A, Ulrich G, Fleischmann C, Hermelink A, et al. 2014. Characterization of semi- conductor materials using synchrotron radiation-based near-field infrared microscopy and nano-FTIR spectroscopy. *Opt. Express* 22:17948–58
- 40. Lu F, Belkin MA. 2011. Infrared absorption nano-spectroscopy using sample photoexpansion induced by tunable quantum cascade lasers. *Opt. Express* 19:19942–47
- 41. Lu F, Jin MZ, Belkin MA. 2014. Tip-enhanced infrared nanospectroscopy via molecular expansion force detection. *Nat. Photonics* 8:307–12
- 42. Wilson EB, Decius JC, Cross PC. 1955. Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra. New York: Dover
- 43. Centrone A, Brambilla L, Zerbi G. 2005. Adsorption of H₂ on carbon-based materials: a Raman spec- troscopy study. *Phys. Rev. B* 71:245406
- 44. Agosti E, Rivola M, Hernandez V, Del Zoppo M, Zerbi G. 1999. Electronic and dynamical effects from the unusual features of the Raman spectra of oligo and polythiophenes. *Synth. Met.* 100:101–12
- 45. Laibinis PE, Nuzzo RG, Whitesides GM. 1992. Structure of monolayers formed by coadsorption of 2 normal-alkanethiols of different chain lengths on gold and its relation to wetting. J. Phys. Chem. 96:5097–105
- 46. Porter MD, Bright TB, Allara DL, Chidsey CED. 1987. Spontaneously organized molecular assemblies. 4. Structural characterization of *n*-alkyl thiol monolayers on gold by optical ellipsometry, infrared- spectroscopy, and electrochemistry. *J. Am. Chem. Soc.* 109:3559–68
- 47. Graf RT, Koenig JL, Ishida H. 1985. Optical-constant determination of thin polymer films in the infrared. *Appl. Spectrosc.* 39:405–8
- 48. Levin IW, Bhargava R. 2005. Fourier transform infrared vibrational spectroscopic imaging: integrating microscopy and molecular recognition. *Annu. Rev. Phys. Chem.* 56:429–74
- 49. Kazarian SG, Chan KLA. 2010. Micro- and macro-attenuated total reflection Fourier transform infrared spectroscopic imaging. *Appl. Spectrosc.* 64:135A–52A
- 50. Bhargava R. 2012. Infrared spectroscopic imaging: the next generation. Appl. Spectrosc. 66:1091-120

- 51. Bellisola G, Sorio C. 2012. Infrared spectroscopy and microscopy in cancer research and diagnosis. Am. J. Cancer Res. 2:1–21
- 52. Reddy RK, Walsh MJ, Schulmerich MV, Carney PS, Bhargava R. 2013. High-definition infrared spectroscopic imaging. *Appl. Spectrosc.* 67:93–105
- 53. Phillips MC, Ho N. 2008. Infrared hyperspectral imaging using a broadly tunable external cavity quantum cascade laser and microbolometer focal plane array. *Opt. Express* 16:1836–45
- 54. Bassan P, Weida MJ, Rowlette J, Gardner P. 2014. Large scale infrared imaging of tissue micro arrays (TMAS) using a tunable quantum cascade laser (QCL) based microscope. *Analyst* 139:3856–59
- 55. Martin MC, Dabat-Blondeau C, Unger M, Sedlmair J, Parkinson DY, et al. 2013. 3D spectral imaging with synchrotron Fourier transform infrared spectro-microtomography. *Nat. Methods* 10:861–64
- 56. Davis BJ, Carney PS, Bhargava R. 2010. Theory of mid-infrared absorption microspectroscopy: II. Heterogeneous samples. *Anal. Chem.* 82:3487–99
- 57. Pohl DW, Denk W, Lanz M. 1984. Optical stethoscopy: image recording with resolution λ/20. Appl. Phys. Lett. 44:651– 53
- 58. Lewis A, Isaacson M, Harootunian A, Muray A. 1984. Development of a 500-Å spatial-resolution light- microscope: I. Light is efficiently transmitted through $\lambda/16$ diameter apertures. *Ultramicroscopy* 13:227–31
- 59. Michaels CA, Stranick SJ, Richter LJ, Cavanagh RR. 2000. Scanning near-field infrared microscopy and spectroscopy with a broadband laser source. *J. Appl. Phys.* 88:4832–39
- 60. Bethe HA. 1944. Theory of diffraction by small holes. Phys. Rev. 66:163-82
- 61. Olmon RL, Krenz PM, Jones AC, Boreman GD, Raschke MB. 2008. Near-field imaging of optical antenna modes in the mid-infrared. *Opt. Express* 16:20295–305
- 62. Alonso-Gonzalez P, Schnell M, Sarriugarte P, Sobhani H, Wu CH, et al. 2011. Real-space mapping of Fano interference in plasmonic metamolecules. *Nano Lett.* 11:3922–26
- 63. Yoxall E, Navarro-Cia M, Rahmani M, Maier SA, Phillips CC. 2013. Widely tunable scattering-type scanning near-field optical microscopy using pulsed quantum cascade lasers. *Appl. Phys. Lett.* 103:213110
- 64. Grefe SE, Leiva D, Mastel S, Dhuey SD, Cabrini S, et al. 2013. Near-field spatial mapping of strongly interacting multiple plasmonic infrared antennas. *Phys. Chem. Chem. Phys.* 15:18944–50
- 65. Awad E, Abdel-Rahman M, Zia MF. 2014. Checkerboard nanoplasmonic gold structure for long-wave infrared absorption enhancement. *Photonics J. IEEE* 6:1–7
- 66. Neubrech F, Pucci A, Cornelius TW, Karim S, Garcia-Etxarri A, Aizpurua J. 2008. Resonant plasmonic and vibrational coupling in a tailored nanoantenna for infrared detection. *Phys. Rev. Lett.* 101:157403
- 67. Zentgraf T, Dorfmuller J, Rockstuhl C, Etrich C, Vogelgesang R, et al. 2008. Amplitude- and phase- resolved optical near fields of split-ring-resonatur-based metamaterials. *Opt. Lett.* 33:848–50
- 68. Stiegler JM, Tena-Zaera R, Idigoras O, Chuvilin A, Hillenbrand R. 2012. Correlative infrared-electron nanoscopy reveals the local structure-conductivity relationship in zinc oxide nanowires. *Nat. Commun.*3:1131
- 69. Stiegler JM, Huber AJ, Diedenhofen SL, Rivas JG, Algra RE, et al. 2010. Nanoscale free-carrier profiling of individual semiconductor nanowires by infrared near-field nanoscopy. *Nano Lett.* 10:1387–92
- 70. Xu XG, Ghamsari BG, Jiang J-H, Gilburd L, Andreev GO, et al. 2014. One-dimensional surface phonon polaritons in boron nitride nanotubes. *Nat. Commun.* 5:4782
- Xu XJG, Raschke MB. 2013. Near-field infrared vibrational dynamics and tip-enhanced decoherence. *Nano Lett.* 13:1588– 95
- 72. Westermeier C, Cernescu A, Amarie S, Liewald C, Keilmann F, Nickel B. 2014. Sub-micron phase coexistence in small-molecule organic thin films revealed by infrared nano-imaging. *Nat. Commun.* 5:4101
- 73. Deleted in proof
- 74. Dominguez G, McLeod AS, Gainsforth Z, Kelly P, Bechtel HA, et al. 2014. Nanoscale infrared spec- troscopy as a nondestructive probe of extraterrestrial samples. *Nat. Commun.* 5:5445
- 75. Fei Z, Rodin AS, Gannett W, Dai S, Regan W, et al. 2013. Electronic and plasmonic phenomena atgraphene grain boundaries. *Nat. Nanotechnol.* 8:821–25
- 76. Chen JN, Nesterov ML, Nikitin AY, Thongrattanasiri S, Alonso-Gonzalez P, et al. 2013. Strong plasmon reflection at nanometer-size gaps in monolayer graphene on SiC. *Nano Lett.* 13:6210–15

77. Chen J, Badioli M, Alonso-Gonzalez P, Thongrattanasiri S, Huth F, et al. 2012. Optical nano-imaging of gate-tunable graphene plasmons. *Nature* 487:77–81

- 78. Dai S, Fei Z, Ma Q, Rodin AS, Wagner M, et al. 2014. Tunable phonon polaritons in atomically thin van der Waals crystals of boron nitride. *Science* 343:1125–29
- 79. Brehm M, Taubner T, Hillenbrand R, Keilmann F. 2006. Infrared spectroscopic mapping of single nanoparticles and viruses at nanoscale resolution. *Nano Lett.* 6:1307–10
- Berweger S, Nguyen DM, Muller EA, Bechtel HA, Perkins TT, Raschke MB. 2013. Nano-chemical infrared imaging of membrane proteins in lipid bilayers. J. Am. Chem. Soc. 135:18292–95
- Amenabar I, Poly S, Nuansing W, Hubrich EH, Govyadinov AA, et al. 2013. Structural analysis and mapping of individual protein complexes by infrared nanospectroscopy. *Nat. Commun.* 4:2890

- 82. Keilmann F, Hillenbrand R. 2004. Near-field microscopy by elastic light scattering from a tip. *Philos.Trans. R. Soc. Lond.* A 362:787–805
- Atkin JM, Berweger S, Jones AC, Raschke MB. 2012. Nano-optical imaging and spectroscopy of order, phases, and domains in complex solids. Adv. Phys. 61:745–842
- 84. Schmidt DA, Kopf I, Brundermann E. 2012. A matter of scale: from far-field microscopy to near-field nanoscopy. *Laser Photonics Rev.* 6:296–332
- 85. Griffiths PR, Miseo EV. 2014. Infrared mapping below the diffraction limit. In *Infrared and Raman Spectroscopic Imaging*, ed. R Salzer, HW Siesler, pp. 513–40. Weinheim: Wiley-VCH. 2nd ed.
- Cvitkovic A, Ocelic N, Hillenbrand R. 2007. Analytical model for quantitative prediction of material contrasts in scattering-type near-field optical microscopy. *Opt. Express* 15:8550–65
- 87. Xu XJG, Rang M, Craig IM, Raschke MB. 2012. Pushing the sample-size limit of infrared vibrational nanospectroscopy: from monolayer toward single molecule sensitivity. *J. Phys. Chem. Lett.* 3:1836–41
- 88. Huth F, Chuvilin A, Schnell M, Amenabar I, Krutokhvostov R, et al. 2013. Resonant antenna probes for tip-enhanced infrared near-field microscopy. *Nano Lett.* 13:1065–72
- 89. Aizpurua J, Taubner T, Garcia de Abajo FJ, Brehm M, Hillenbrand R. 2008. Substrate-enhanced infrared near-field spectroscopy. *Opt. Express* 16:1529–45
- 90. De Angelis F, Das G, Candeloro P, Patrini M, Galli M, et al. 2010. Nanoscale chemical mapping using three-dimensional adiabatic compression of surface plasmon polaritons. *Nat. Nanotechnol.* 5:67–72
- 91. Ropers C, Neacsu CC, Elsaesser T, Albrecht M, Raschke MB, Lienau C. 2007. Grating-coupling of surface plasmons onto metallic tips: a nanoconfined light source. *Nano Lett.* 7:2784–88
- 92. Neacsu CC, Berweger S, Olmon RL, Saraf LV, Ropers C, Raschke MB. 2010. Near-field localization in plasmonic superfocusing: a nanoemitter on a tip. *Nano Lett.* 10:592–96
- 93. Gomez L, Bachelot R, Bouhelier A, Wiederrecht GP, Chang SH, et al. 2006. Apertureless scanning near-field optical microscopy: a comparison between homodyne and heterodyne approaches. J. Opt. Soc. Am. B 23:823–33
- 94. Ocelic N, Huber A, Hillenbrand R. 2006. Pseudoheterodyne detection for background-free near-field spectroscopy. *Appl. Phys. Lett.* 89:101124
- 95. Vogelgesang R, Dmitriev A. 2010. Real-space imaging of nanoplasmonic resonances. Analyst 135:1175-81
- Lal S, Grady NK, Kundu J, Levin CS, Lassiter JB, Halas NJ. 2008. Tailoring plasmonic substrates for surface enhanced spectroscopies. *Chem. Soc. Rev.* 37:898–911
- 97. Lahiri B, Holland G, Aksyuk V, Centrone A. 2013. Nanoscale imaging of plasmonic hot spots and dark modes with the photothermal-induced resonance technique. *Nano Lett.* 13:3218–24
- 98. Huth F, Schnell M, Wittborn J, Ocelic N, Hillenbrand R. 2011. Infrared-spectroscopic nanoimaging with a thermal source. *Nat. Mater.* 10:352–56
- Taubner T, Keilmann F, Hillenbrand R. 2005. Nanoscale-resolved subsurface imaging by scattering- type near-field optical microscopy. Opt. Express 13:8893–99
- 100. Engelhardt AP, Hauer B, Taubner T. 2013. Visibility of weak contrasts in subsurface scattering near-field microscopy. *Ultramicroscopy* 126:40–43
- 101. Zhang LM, Andreev GO, Fei Z, McLeod AS, Dominguez G, et al. 2012. Near-field spectroscopy of silicon dioxide thin films. *Phys. Rev. B* 85:075419
- 102. Mastel S, Govyadinov AA, de Oliveira TVAG, Amenabar I, Hillenbrand R. 2015. Nanoscale-resolved chemical identification of thin organic films using infrared near-field spectroscopy and standard Fourier transform infrared references. *Appl. Phys. Lett.* 106:023113
- 103. Dazzi A, Prazeres R, Glotin F, Ortega JM, Al-Sawaftah M, de Frutos M. 2008. Chemical mapping of the distribution of viruses into infected bacteria with a photothermal method. *Ultramicroscopy* 108:635–41
- 104. Mayet C, Dazzi A, Prazeres R, Ortega JM, Jaillard D. 2010. In situ identification and imaging of bacterial polymer nanogranules by infrared nanospectroscopy. *Analyst* 135:2540–45
- 105. Mayet C, Deniset-Besseau A, Prazeres R, Ortega JM, Dazzi A. 2013. Analysis of bacterial polyhydroxy-butyrate production by multimodal nanoimaging. *Biotechnol. Adv.* 31:369–74
- 106. Deniset-Besseau A, Prater CB, Virolle MJ, Dazzi A. 2014. Monitoring TriAcylGlycerols accumulation by atomic force microscopy based infrared spectroscopy in *Streptomyces* species for biodiesel applications. *J. Phys. Chem. Lett.* 5:654–58
- 107. Mayet C, Dazzi A, Prazeres R, Allot E, Glotin E, Ortega JM. 2008. Sub-100 nm IR spectromicroscopy of living cells.

Opt. Lett. 33:1611–13

- 108. Policar C, Waern JB, Plamont MA, Clede S, Mayet C, et al. 2011. Subcellular IR imaging of a metal- carbonyl moiety using photothermally induced resonance. *Angew. Chem. Int. Ed.* 50:860–64
- 109. Kennedy E, Al-Majmaie R, Al-Rubeai M, Zerulla D, Rice JH. 2013. Nanoscale infrared absorption imaging permits non-destructive intracellular photosensitizer localization for subcellular uptake analysis. *RSC Adv.* 3:13789–95
- 110. Kennedy E, Al-Majmaie R, Al-Rubeai M, Zerulla D, Rice JH. 2013. Quantifying nanoscale biochemical heterogeneity in human epithelial cancer cells using combined AFM and PTIR absorption nanoimaging. J. Biophotonics 8:133–41
- 111. Marcott C, Lo M, Kjoller K, Fiat F, Baghdadli N, et al. 2014. Localization of human hair structural lipids using nanoscale infrared spectroscopy and imaging. *Appl. Spectrosc.* 68:564–69
- 112. Muller T, Ruggeri FS, Kulik AJ, Shimanovich U, Mason TO, et al. 2014. Nanoscale spatially resolved infrared spectra from single microdroplets. *Lab Chip* 14:1315–19
- 113. Hill GA, Rice JH, Meech SR, Craig DQM, Kuo P, et al. 2009. Submicrometer infrared surface imaging using a scanningprobe microscope and an optical parametric oscillator laser. *Opt. Lett.* 34:431–33
- 114. Kjoller K, Felts JR, Cook D, Prater CB, King WP. 2010. High-sensitivity nanometer-scale infrared spectroscopy using a contact mode microcantilever with an internal resonator paddle. *Nanotechnology*21:185705
- 115. Marcott C, Lo M, Kjoller K, Prater C, Noda I. 2011. Spatial differentiation of sub-micrometer domains in a poly(hydroxyalkanoate) copolymer using instrumentation that combines atomic force microscopy (AFM) and infrared (IR) spectroscopy. *Appl. Spectrosc.* 65:1145–50
- 116. Felts JR, Kjoller K, Lo M, Prater CB, King WP. 2012. Nanometer-scale infrared spectroscopy of heterogeneous polymer nanostructures fabricated by tip-based nanofabrication. ACS Nano 6:8015–21
- 117. Van Eerdenbrugh B, Lo M, Kjoller K, Marcott C, Taylor LS. 2012. Nanoscale mid-infrared evaluation of the miscibility behavior of blends of dextran or maltodextrin with poly(vinylpyrrolidone). *Mol. Pharm.* 9:1459–69
- 118. Katzenmeyer AM, Aksyuk V, Centrone A. 2013. Nanoscale infrared spectroscopy: improving the spectral range of the photothermal induced resonance technique. *Anal. Chem.* 85:1972–79
- 119. Felts JR, Cho H, Yu MF, Bergman LA, Vakakis AF, King WP. 2013. Atomic force microscope infrared spectroscopy on 15 nm scale polymer nanostructures. *Rev. Sci. Instrum.* 84:023709
- 120. Cho H, Felts JR, Yu MF, Bergman LA, Vakakis AF, King WP. 2013. Improved atomic force microscope infrared spectroscopy for rapid nanometer-scale chemical identification. *Nanotechnology* 24:444007
- 121. Ghosh S, Remita H, Ramos L, Dazzi A, Deniset-Besseau A, et al. 2014. Pedot nanostructures synthesized in hexagonal mesophases. New J. Chem. 38:1106–15
- 122. Van Eerdenbrugh B, Lo M, Kjoller K, Marcott C, Taylor LS. 2012. Nanoscale mid-infrared imaging of phase separation in a drug-polymer blend. *J. Pharm. Sci.* 101:2066–73
- 123. Harrison AJ, Bilgili EA, Beaudoin SP, Taylor LS. 2013. Atomic force microscope infrared spectroscopy of griseofulvin nanocrystals. *Anal. Chem.* 85:11449–55
- 124. Sauvage S, Driss A, Reveret F, Boucaud P, Dazzi A, et al. 2011. Homogeneous broadening of the *S* to *P* transition in InGaAs/GaAs quantum dots measured by infrared absorption imaging with nanoscale resolution. *Phys. Rev. B* 83:035302
- 125. Felts JR, Law S, Roberts CM, Podolskiy V, Wasserman DM, King WP. 2013. Near-field infrared absorption of plasmonic semiconductor microparticles studied using atomic force microscope infrared spectroscopy. *Appl. Phys. Lett.* 102:152110
- 126. Katzenmeyer AM, Chae J, Kasica R, Holland G, Lahiri B, Centrone A. 2014. Nanoscale imaging and spectroscopy of plasmonic modes with the PTIR technique. *Adv. Opt. Mater.* 2:718–22
- 127. Aksyuk V, Lahiri B, Holland G, Centrone A. 2015. Near-field asymmetries in plasmonic resonators. *Nanoscale* 7:3634–44
- 128. Katzenmeyer AM, Canivet J, Holland G, Farrusseng D, Centrone A. 2014. Assessing chemical hetero- geneity at the nanoscale in mixed-ligand metal-organic frameworks with the PTIR technique. *Angew. Chem. Int. Ed.* 53:2852–56
- 129. Dong R, Fang Y, Chae J, Dai J, Xiao Z, et al. 2015. High gain and low driving-voltage photodetectors enabled by organolead triiodide perovskites. *Adv. Mater.* 27:1912–18
- 130. Katzenmeyer AM, Holland G, Kjoller K, Centrone A. 2015. Visible through mid-infrared absorption spectroscopy with 20 nm spatial resolution. *Anal. Chem.* 87:3154–59
- 131. Dazzi A, Glotin F, Carminati R. 2010. Theory of infrared nanospectroscopy by photothermal induced resonance. J. Appl. Phys. 107:124519
- 132. Dazzi A. 2009. Photothermal induced resonance. Application to infrared spectromicroscopy. In Thermal Nanosystems and

Nanomaterials, ed. S Volz, pp. 469-503. Berlin: Springer

- 133. Harrick NJ. 1967. Internal Reflection Spectroscopy. New York: Interscience
- 134. Hosono H. 1991. Fourier-transform infrared attenuated total reflection spectra of ion-implanted silica glasses. J. Appl. Phys. 69:8079–82
- 135. Lahiri B, Holland G, Centrone A. 2013. Chemical imaging beyond the diffraction limit: experimental validation of the PTIR technique. *Small* 9:1876–76
- 136. Valvano JW, Cochran JR, Diller KR. 1985. Thermal-conductivity and diffusivity of biomaterials measured with selfheated thermistors. *Int. J. Thermophys.* 6:301–11
- 137. Dazzi A, Prater CB, Hu QC, Chase DB, Rabolt JF, Marcott C. 2012. AFMIR: combining atomic force microscopy and infrared spectroscopy for nanoscale chemical characterization. *Appl. Spectrosc.* 66:1365–84
- 138. Atwater HA, Polman A. 2010. Plasmonics for improved photovoltaic devices. Nat. Mater. 9:205-13
- 139. Stewart ME, Anderton CR, Thompson LB, Maria J, Gray SK, et al. 2008. Nanostructured plasmonic sensors. *Chem. Rev.* 108:494–521
- 140. Hirsch LR, Stafford RJ, Bankson JA, Sershen SR, Rivera B, et al. 2003. Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance. *PNAS* 100:13549–54
- 141. Adato R, Yanik AA, Amsden JJ, Kaplan DL, Omenetto FG, et al. 2009. Ultra-sensitive vibrational spectroscopy of protein monolayers with plasmonic nanoantenna arrays. *PNAS* 106:19227–32
- 142. Wu CH, Khanikaev AB, Adato R, Arju N, Yanik AA, et al. 2012. Fano-resonant asymmetric metamaterials for ultrasensitive spectroscopy and identification of molecular monolayers. *Nat. Mater.* 11:69–75
- 143. Fedotov VA, Rose M, Prosvirnin SL, Papasimakis N, Zheludev NI. 2007. Sharp trapped-mode resonances in planar metamaterials with a broken structural symmetry. *Phys. Rev. Lett.* 99:147401
- 144. Luk'yanchuk B, Zheludev NI, Maier SA, Halas NJ, Nordlander P, et al. 2010. The Fano resonance in plasmonic nanostructures and metamaterials. *Nat. Mater.* 9:707–15
- 145. Lahiri B, Khokhar AZ, De La Rue RM, McMeekin SG, Johnson NP. 2009. Asymmetric split ring resonators for optical sensing of organic materials. *Opt. Express* 17:1107–15
- 146. Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, et al. 2002. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science* 295:469–72
- 147. Centrone A, Harada T, Speakman S, Hatton TA. 2010. Facile synthesis of vanadium metal-organic frameworks and their magnetic properties. *Small* 6:1598–602
- 148. Deng H, Doonan CJ, Furukawa H, Ferreira RB, Towne J, et al. 2010. Multiple functional groups of varying ratios in metalorganic frameworks. *Science* 327:846–50
- 149. Lee J, Farha OK, Roberts J, Scheidt KA, Nguyen ST, Hupp JT. 2009. Metal-organic framework materials as catalysts. *Chem. Soc. Rev.* 38:1450–59
- 150. Alaerts L, Maes M, Giebeler L, Jacobs PA, Martens JA, et al. 2008. Selective adsorption and separation of *ortho*-substituted alkylaromatics with the microporous aluminum terephthalate MIL-53. *J. Am. Chem. Soc.* 130:14170–78
- 151. Talin AA, Centrone A, Ford AC, Foster ME, Stavila V, et al. 2014. Tunable electrical conductivity in metal-organic framework thin-film devices. *Science* 343:66–69
- 152. Volkringer C, Meddouri M, Loiseau T, Guillou N, Marrot J, et al. 2008. The Kagomé topology of the gallium and indium metal-organic framework types with a MIL-68 structure: synthesis, XRD, solid-state NMR characterizations, and hydrogen adsorption. *Inorg. Chem.* 47:11892–901
- 153. Toprak MS, Stiewe C, Platzek D, Williams S, Bertini L, et al. 2004. The impact of nanostructuring on the thermal conductivity of thermoelectric CoSb3 . *Adv. Funct. Mater.* 14:1189–96
- 154. Nan CW, Birringer R, Clarke DR, Gleiter H. 1997. Effective thermal conductivity of particulate coposites with interfacial thermal resistance. J. Appl. Phys. 81:6692–99
- 155. Pollack GL. 1969. Kapitza resistance. Rev. Mod. Phys. 41:48