

Submicrometer infrared surface imaging using a scanning-probe microscope and an optical parametric oscillator laser

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Submicrometer IR surface imaging was performed with a resolution better than the diffraction limit. The apparatus was based on an IR optical parametric oscillator laser and a commercial atomic force microscope and used, as the detection mechanism, induced resonant oscillations in an atomic force microscopy (AFM) cantilever. For the first time to our knowledge this was achieved with top-down illumination and a benchtop IR source, thus extending the range of potential applications of this technique. IR absorption and AFM topography images of polystyrene beads were recorded simultaneously with an image resolution of 200 nm.

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IR spectroscopy is a well-developed method for characterizing chemical composition. IR spectroscopy utilizes radiation in the region of 2–20 μm to determine absorption as a function of wavelength [1]. IR spectra of large molecules are frequently complex, so it is possible to use them in an analogous way to “fingerprints,” characterizing even chemically similar compounds. Imaging materials using IR spectroscopy is extremely valuable, where sample heterogeneity presents particular challenges to analysis using topographical imaging alone, such as pharmaceuticals or cell biology. Optical imaging using far-field methods is limited by diffraction to length scales at approximately equal to $\lambda/2$ [2,3], thus of the order of 1–5 μm for IR microscopy.

Scanning-probe methods such as atomic force microscopy (AFM) have a high spatial resolution, i.e., <1 nm [4]. Combining IR spectroscopy with AFM potentially allows for a method that can chemically map materials with nanometer spatial resolution. Hammiche *et al.* demonstrated that IR spectra of a wide variety of samples can be recorded by combining Fourier-transform IR spectroscopy (FTIR) with a scanning thermal microscope [5,6]. This approach utilizes a miniature temperature sensor to detect the temperature fluctuation caused by absorbing IR radiation. The same group also demonstrated the first thermal expansion spectrum [7]. In both cases illumination was provided by directing the IR radiation downward onto the sample surface by means of a custom-designed interface [8].

An alternative photothermal approach has been demonstrated by Dazzi *et al.* [9–12] based on detecting the resonant oscillations of the cantilever induced by the rapid transient deformation caused by thermal expansion following excitation with a laser pulse. This enables the generation of IR spectra and IR imaging. Dazzi *et al.* have applied this method to image

E. coli bacteria at the N–H absorption bands, InAs/GaAs self-assembled quantum dots (in resonance with intrasubband transitions) and live *Candida albicans* fungi cells (monitoring the glycogen absorption band) with sub-diffraction-limited image resolution of >60 nm [10–12]. This approach uses an attenuated total internal reflection (ATR) arrangement in combination with IR cyclotron radiation. ATR removes direct interaction of the AFM tip with the laser beam and was reported to strongly reduce the signal background. In addition, a thin gold layer was added to the AFM tip to avoid residual absorption. ATR limits the scope of the samples that can be studied to thin films or small isolated objects.

Brehm *et al.* have described a scanning-probe-microscopy technique with top-down illumination using a benchtop laser source capable of very high spatial resolution [13]. However, it is an optical-scattering-based method and as such represents a completely different approach to the one adopted here. The scattering experiment provides less direct access to the IR absorption spectra of materials, as the measured response is a convolution of this and the local dielectric properties. In this Letter we present what we believe to be the first photothermal submicrometer IR images and spectra based on a top-down excitation arrangement using a benchtop IR laser source.

We have developed and applied a novel instrument based on the induced resonant motion phenomena to enable IR imaging with a resolution beyond the diffraction limit. Our experimental setup was based on an in-house-built IR laser source and a commercial AFM. The IR source followed the design of Vodopyanov and Schuneman [14] and was constructed from an optical parametric oscillator (OPO) emitting tuneable IR laser radiation over 3.13 to 3.57 μm . This was constructed using a periodically poled lithium

niobate (PPLN) crystal (Super Optronics, Inc.) and a 1 kHz repetition rate nanosecond Nd:YAG pump laser (model NL202, EKSPILA). The PPLN crystal had a fanned-out (variable across the sample width) domain reversal period of between 29.0 and 30.6 μm and was kept at a constant temperature of 90°C using a crystal oven heater (temperature controller, model TC038 and model III crystal heater, HC Photonics Corp). Selective filtering of IR output laser radiation was achieved using a long-pass filter (LP-2500 nm, Spectrogon). The AFM (Veeco Explorer system) was used with a scanner with lateral and vertical scans of 100 μm \times 100 μm and 10 μm , respectively. A Stanford SR650 was used to amplify and filter the signal from the AFM, which was routed to the input of an Agilent DSO5012A oscilloscope, where it was retrieved and analyzed with the WSxM program [15]. Tips were silicon nitride V-shaped cantilever tips (used as received from Veeco). Samples were prepared by dispersing 3 μm polystyrene beads (PSBs) onto a freshly cleaved mica surface and then heating the sample above the polystyrene glass transition so they adhered to the mica. The PSB were purchased from Aldrich. An IR spectrum of polystyrene was recorded using a commercial spectrometer (Perkin-Elmer, Spectrum BX, FTIR system).

The IR output of the OPO is directed and focused onto the surface (see Fig. 1) using a concave silver mirror. Samples were probed with an average power density of 0.2 W/cm². This method extends the method of Dazzi *et al.* to enable the probing of the surface of samples of any thickness via top-down excitation. Here we use the term photothermally induced resonance (PTIR) to describe our technique.

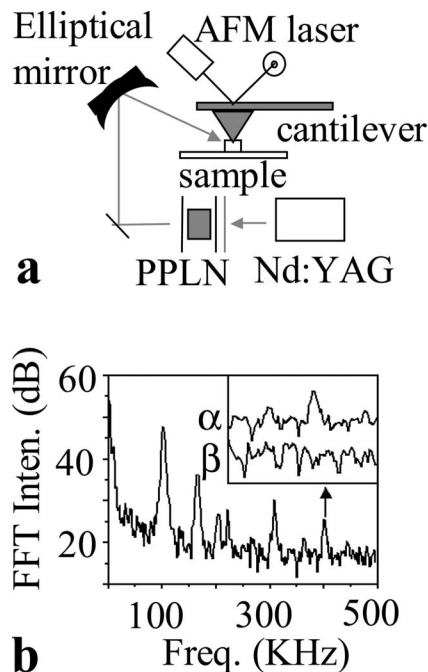


Fig. 1. a, Schematic drawing of experimental setup. b, FFT of the deflection signal at α (signal recorded at resonance with C–H stretch) with an inset showing the difference between α and β (signal recorded off resonance with C–H stretch) at 400 kHz.

PTIR imaging of individual PSBs was undertaken. A PSB, 3.5 μm in diameter and 750 nm in height, was located. The AFM cantilever tip was positioned over the PSB with the tip in contact with the sample. The transient deformation in the PSB caused by thermal expansion following excitation with a laser pulse was monitored via measurement of the resonant oscillations of the cantilever. In the FFT of the resonant oscillations of the cantilever, there exist peaks that are characteristic of the absorption spectrum of the sample and are not dependent on the absorption of IR by the tip. These are discovered by searching for peaks that change in intensity as the wavelength is varied, but only when the tip is on a PSB. By concentrating on these peaks and ignoring those exhibiting a behavior indicative only of the tip, it is possible to measure the IR absorption spectrum of the sample only [9–12].

The IR laser source was tuned to the C–H stretch absorption band of polystyrene at 2920 cm^{-1} (position α in Figs. 1 and 2). The fast Fourier transform (FFT) of the AFM tip response is shown in Fig. 1. The FFT of the signal shows the presence of peaks corresponding to the resonant vibrational modes of the AFM tip. By monitoring the intensity of the FFT peaks it is possible to track the resonant response of the cantilever that is influenced by the absorption behavior of the sample. In Fig. 1 this response, indicated by the arrow, is absent when the laser is tuned away from an absorption peak and when the tip is not in contact with the sample but is present both when the tip is on the sample and when the laser is tuned to an absorption peak; by induction this is the response of the sample to the IR. By monitoring the intensity of this FFT peak while scanning the excitation laser wavelength, an IR spectrum can be constructed (Fig. 2). The PTIR spectrum closely resembles that obtained

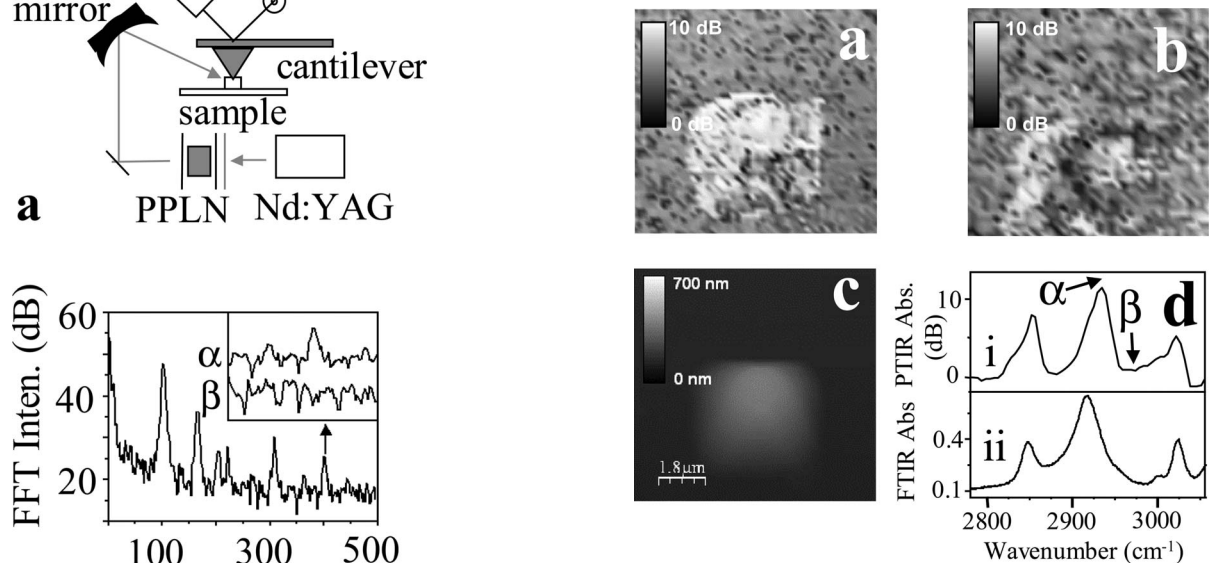


Fig. 2. a, Topography AFM image, photothermal induced resonance images. b, On-resonance absorption image. c, Off-resonance absorption image. d, Spectrum showing the (i) PTIR response (ii) and FTIR response of polystyrene to IR. The vertical scale in both cases is proportional to absorption of infrared by the sample and hence to the IR spectrum of the sample.

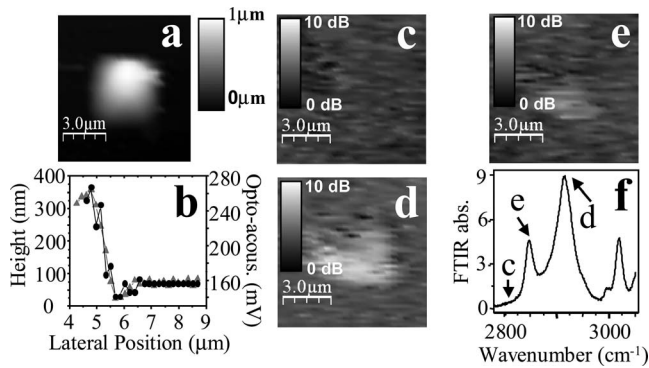


Fig. 3. a, Topographic image for a polystyrene sphere on mica. b, Plot of PTIR (black curve) and AFM topographic (gray curve) data from a single PSB. c–e, PTIR images recorded at three different excitation energies. f, Corresponding positions of the three different excitation energies on the FTIR spectrum.

using a commercial FTIR instrument in ATR mode (also shown in Fig. 2). Good agreement is seen between spectra; however, there are differences in relative peak intensity between photothermal and ATR spectra owing to, for example, photothermal saturation effects that are expected [16].

AFM topography and IR absorption images of a single PSB were recorded simultaneously. This was done by recording the response of the FFT peak at ca. 400 kHz (see Fig. 1) at each image point, thus building an IR absorption image at a fixed wavelength. Figure 2 shows also the IR absorption image recorded at the C–H vibration frequency (position α) and away from it (position β), plus the topographic image. The IR absorption image recorded on the absorption peak shows an object that absorbs intensely (light coloring) present on a nonabsorbing (dark) background. The position and extent of the IR absorbing object matches the AFM topography image. We can conclude that the pattern arises from IR absorption by the PSB, an absorption that is absent for the mica substrate. The IR absorption image recorded after moving the excitation wavelength away from a strong absorption at position α shows the presence of a much weaker absorption pattern due to the much reduced residual absorption at position β .

The image resolution of the system was measured by recording a linescan across the edge of a PSB and comparing the resolution with an AFM topography scan recorded at the same time. Figure 3 shows a graph of the AFM topography response plus an on-resonance IR signal recovered from an IR image scan. An excellent agreement is seen with an estimated edge resolution of 200 nm. This demonstrates most importantly that the image resolution of our system is subdiffraction limited. Figure 3 also shows how the PTIR image varies as the IR wavelength is scanned across the C–H absorption bands. It can be seen that the presence of the PSB in the PTIR image correlates with the absorption in the polystyrene IR spectrum.

In conclusion, nanoscale IR surface imaging was performed with a subdiffraction resolution. Our experimental setup was based on a benchtop IR laser source and a commercial AFM utilizing top-down illumination and photothermally induced resonant motion as the means of detection. IR absorption and AFM topography images of polystyrene beads were recorded simultaneously with an image resolution of approximately 200 nm.

The high intensity source used in this study provides the means for solving the problem of imaging using the temperature detection technique mentioned above. We are currently exploring the use of newly developed high-spatial-resolution thermal probes for IR imaging in conjunction with an OPO laser source.

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