

# Nanoscale Infrared Spectroscopy of Materials by Atomic Force Microscopy

Craig Prater,<sup>1</sup> Kevin Kjoller,<sup>1</sup> Debra Cook,<sup>1</sup> Roshan Shetty,<sup>1</sup> Gregory Meyers,<sup>2</sup> Carl Reinhardt,<sup>2</sup> Jonathan Felts,<sup>3</sup> William King,<sup>3</sup> Konstantin Vodopyanov<sup>4</sup> and Alexandre Dazzi.<sup>5</sup> 1. Anasys Instruments, Santa Barbara, CA, USA. 2. The Dow Chemical Company, Midland, MI, USA. 3. University of Illinois, Urbana-Champaign, IL, USA. 4. Stanford University, Stanford, CA, USA. 5. Université Paris-Sud, Orsay, France.

## BIOGRAPHY

Dr Craig Prater received a BS from Texas A&M in 1987 and a PhD from the University of California Santa Barbara in 1992. Between 1992 and 2007 Craig served in many technology development and management roles at Digital Instruments/Veeco. In 2007 he became the CTO at Anasys Instruments. Craig and his colleagues have been focused on advancing nanoscale measurements of material properties with atomic force microscopy.



## ABSTRACT

The ability to identify material under the tip of an AFM has been identified as one of the 'Holy Grails' of scanning probe microscopy. While AFM can measure mechanical, electrical, magnetic and thermal properties of materials, it has lacked the robust ability to chemically characterize unknown materials. Infrared spectroscopy is a benchmark technique used in a broad range of sciences and industry to characterize and identify materials via vibrational resonances of chemical bonds. We have successfully integrated AFM with IR spectroscopy to allow measurement of high quality IR spectra at arbitrary points in an AFM image, thus providing nanoscale chemical characterization.

## KEYWORDS

atomic force microscopy, infrared spectroscopy, polymer, photothermal induced resonance, contact resonance, nanothermal analysis

## ACKNOWLEDGEMENTS

This work was supported in part by NIST-ATP 70NANB7H7025 and NSF-SBIR 0750512.

## AUTHOR DETAILS

Dr Craig B. Prater  
121 Gray Avenue  
Santa Barbara, CA 93101, USA  
craig@anasysinstruments.com

**Microscopy and Analysis** 24 (3):5-8 (SPM), 2010

## INTRODUCTION

Atomic force microscopy (AFM) has been enormously successful addressing problems in basic nanoscale research as well as applied problems in materials science and engineering. A clear gap in AFM capabilities, however is the ability to chemically characterize regions of the sample. This is especially important in the study of heterogeneous materials like polymer blends, multilayer films, nanocomposites and many other areas.

Several AFM probe-based techniques have been used to exceed the diffraction limit of conventional infrared (IR) measurements. Traditional IR microscopy has a resolution limit roughly three times the incident wavelength [1], on the scale of several to tens of micrometers. Various optical scattering methods attempt to relate spectral optical properties of materials to their chemical composition [2,3]. However, in general, nearfield approaches are single or narrow band and do not produce rich spectra that can be used to characterize a broad range of vibrational resonances associated with different chemical species. Other IR techniques are based on measuring local tem-

perature rise from spectral absorption through the use of AFM cantilevers integrated with conventional Fourier transform IR (FTIR) spectrometers [4,5]. These approaches allow broader spectrum measurement than near-field approaches, but the spatial resolution is typically limited due to thermal diffusion to the scale of many micrometers.

We have developed and implemented a novel lab-based instrument that combines atomic force microscopy and infrared spectroscopy to enable chemical characterization of polymer and other samples at scales below the diffraction limit. The instrument employs photothermal induced resonance (PTIR) that uses an AFM probe to measure local thermal expansion from IR light incident upon a sample. The PTIR technique was originally developed by Dazzi et al. [6-9] using the CLIO free electron source facility at Université Paris-Sud. To make this capability more broadly available, we have developed an instrument based on a lab-scale IR source.

As shown in Figure 1, the sample is illuminated with the pulsed tunable IR laser light source. When IR radiation is absorbed by the

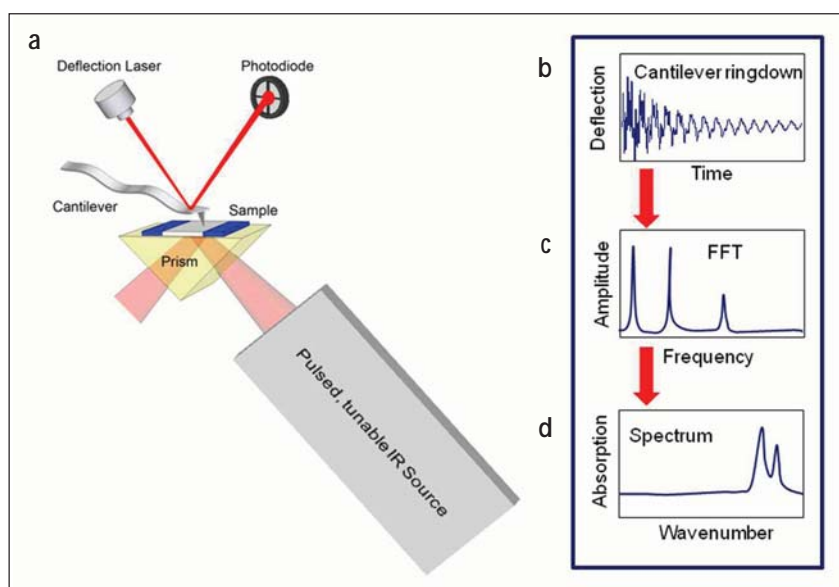


Figure 1:

The instrument (a) uses a pulsed, tunable IR source to excite molecular resonances in the sample. Absorption of IR radiation by the sample leads to a rapid thermal expansion that excites resonant oscillations of the cantilever. These oscillations decay in a characteristic ring-down (b). The ring-downs can be analyzed by Fourier techniques (c) to extract the amplitude and frequency of oscillations. Measuring the amplitude of the cantilever oscillation as a function of the source wavelength creates local absorption spectra (d). The oscillation frequencies of the ring-down are also related to mechanical stiffness of the sample.

sample, it creates a rapid thermal expansion wave that excites resonant oscillations of the AFM cantilever. By measuring the amplitude of the cantilever vibrations as a function of the IR source wavelength, a local IR absorption spectrum can be created.

## MATERIALS AND METHODS

### Materials

Several polymer materials were used in these experiments, including a polymer blend, a multilayer film and a dropcast film. The polymer blend is a 50/50 blend of polycarbonate/acrylonitrile butadiene-styrene (PC/ABS) that was developed for automotive applications. The multilayer film of the type A-B-A and nominal layer composition and thickness are given in Table 1. The polystyrene was drop cast from solution at a concentration of 5 mg ml<sup>-1</sup>.

### Sample Preparation

Samples are prepared on ZnSe prisms in one of two ways. For many samples we employ ultramicrotomy to cut sections with thicknesses between 100 nm and 1000 nm and then we transfer the sections to a prism surface. In other sample preparations we cast thin films from solvent directly on the prism.

### Atomic Force Microscopy

Measurements were performed on a custom built AFM/IR spectroscopy platform using contact mode AFM and contact resonance imaging modes. We have used both standard silicon contact mode cantilevers (nominal spring constants ~0.2 N m<sup>-1</sup>) and Anasys ThermoLever self-heating probes. We also employed novel enhanced resonance probes [11].

### Infrared Instrumentation

The new compact IR source is based on a cascaded optical parametric oscillator [10], pumped by a nanosecond diode-pumped 1- $\mu$ m Nd:YAG laser, and is continuously tunable from 2.5  $\mu$ m to 10  $\mu$ m (4000 to 1000 cm<sup>-1</sup>). This covers a major portion of the mid-IR including important CH, NH and CO bands, as well as carbonyl and amide I and II bands. The spectral width of the IR source is less than 16 cm<sup>-1</sup> over the range between 1200 and 3600 cm<sup>-1</sup>. The sample is mounted (Figure 1) on a zinc selenide (ZnSe) prism and the IR beam is arranged to illuminate the sample by total internal reflection similar to the attenuated total reflection (ATR) technique employed in IR spectroscopy. This arrangement reduces stray light that could cause background absorption in the probe if illuminated from above.

The cantilever deflection is recorded with a traditional AFM optical lever system with a detection bandwidth of roughly 2 MHz. A high speed data acquisition system records each cantilever ring-down event. The IR source is pulsed at ~1 kHz repetition rate and we typically synchronously average multiple ring-downs (e.g. 256) to improve the measurement sensitivity. With measurement and tuning time, each spectrum currently takes roughly one minute. The IR source can also be tuned to

Layer	Composition	Nominal Thickness ( $\mu$ m)
A	EAA	5.1
B	Nylon	10.2
A	EAA	5.1

Table 1:  
Multilayer film structure.

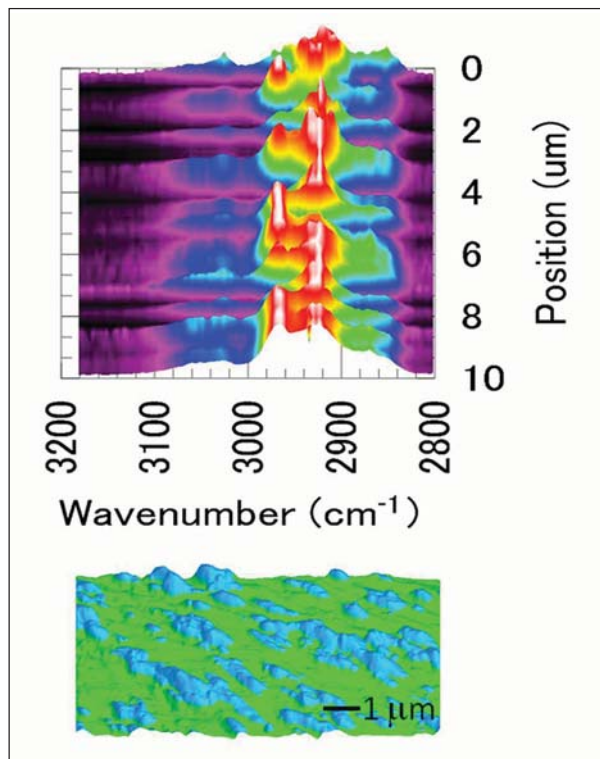


Figure 2:  
(Top) Line spectral map of blend of polycarbonate (PC) and acrylonitrile butadiene styrene (ABS). Note the shift in the position of the highest CH peak from ~2920 to ~2970 cm<sup>-1</sup> as the AFM tip moves from regions of ABS to regions of PC, respectively. (Bottom) AFM image of the polymer blend showing PC and ABS domains.

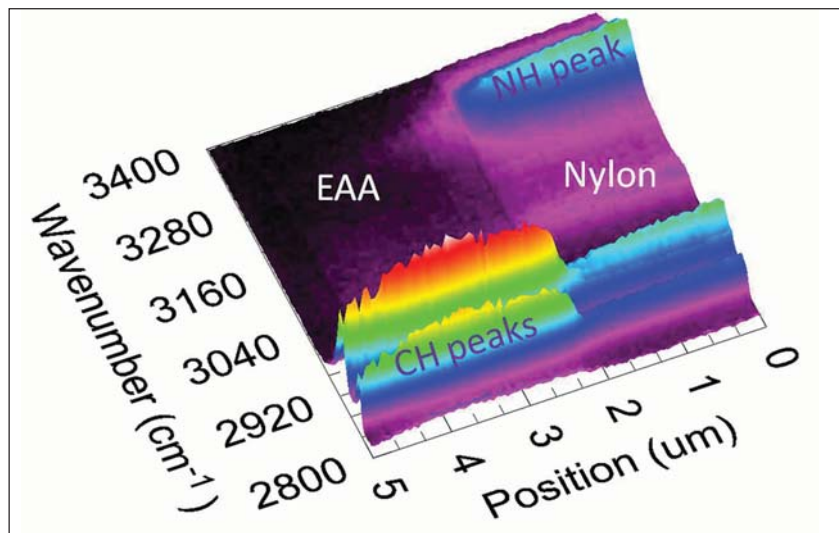


Figure 3:  
High resolution line spectral map across boundary between EAA and Nylon layers in a laminated multilayer film. Across the boundary the transition between the CH and NH absorption peaks is resolved far below the diffraction limit of conventional IR spectroscopy.

a single wavelength and the absorption at that wavelength can be spatially mapped over the sample.

The co-averaged ring-down events are analyzed to extract both IR absorption and mechanical properties. The ring-down events typically include one or more 'contact resonances', i.e. modes of oscillation that couple the cantilever's resonant properties with the

mechanical stiffness and damping of the sample area in contact with the AFM tip. The peak amplitude of the ring-down and/or the amplitude of one or more contact resonance modes is extracted for each wavelength to construct an absorption spectrum. The contact resonant frequencies can be used to extract relative stiffness and sample viscosity.

RESULTS

Polymer Samples

We have used PTIR to measure and map a variety of polymer samples. Figure 2 shows measurements performed on a blend of polycarbonate (PC) and acrylonitrile butadiene styrene (ABS). These materials are employed commercially for properties including high flow for molding, heat resistance and toughness. Polymer blends like these are used in many applications including automotive and consumer electronics. We used PTIR to measure a series of spectra in the CH stretch region while moving the AFM tip 333 nm between each spectrum. The resulting line spectral map shows the spatially resolved IR absorption as a function of the excitation IR frequency (in wavenumbers) and position on the sample. Local chemical variations in this sample are clearly resolved via the change in the position of the CH peak between 2920 and 2970  $\text{cm}^{-1}$  as the tip moves from PC to ABS domains.

The PTIR technique was also used to create a chemical map across the interface of a laminated multilayer film. Multilayer polymer films are becoming widely used in many commercial applications including food and beverage packaging, adhesive layers, surface coatings, electronic displays and organic photovoltaics. High resolution PTIR analysis was performed on an interface of a laminated film of ethylene acrylic acid (EAA) copolymer and Nylon (a polyamide material), as shown in Figure 3. For the wavelengths used in this measurement ( $\sim 3 \mu\text{m}$ ), the diffraction limit of IR microscopy would be around  $10 \mu\text{m}$ , roughly the entire width of the Nylon layer and twice the field of view of Figure 3. Using the PTIR technique with spectra measured every 50 nm, this line spectral map in Figure 3 clearly resolves the interface on a scale well below the diffraction limit of conventional IR microscopy.

Comparison with Bulk FTIR Analysis

We have compared measurements with the PTIR technique to bulk FTIR measurements. Figure 4 shows example measurements that have been performed on a variety of polymer films with both FTIR and PTIR. Despite the fact that the PTIR measurements are performed on length scales orders of magnitude smaller than bulk FTIR, the measurements exhibited generally good correlation between FTIR and PTIR.

Mechanical and Thermal Analysis

The PTIR technique can also provide simultaneous mechanical and thermal property mapping along with chemical analysis. When an IR pulse is absorbed by the sample, the rapid thermal expansion induces resonant oscillation of the cantilever. The frequencies of oscillation, called contact resonances [12,13], are dependent on the contact stiffness of the sample directly under the AFM tip. As illustrated in Figure 5, contact resonances shift to higher frequencies on harder materials and vice versa. Recent progress has been made in extracting quantitative measurements of elastic and viscous properties of materials by analyzing these cantilever contact resonances [14].

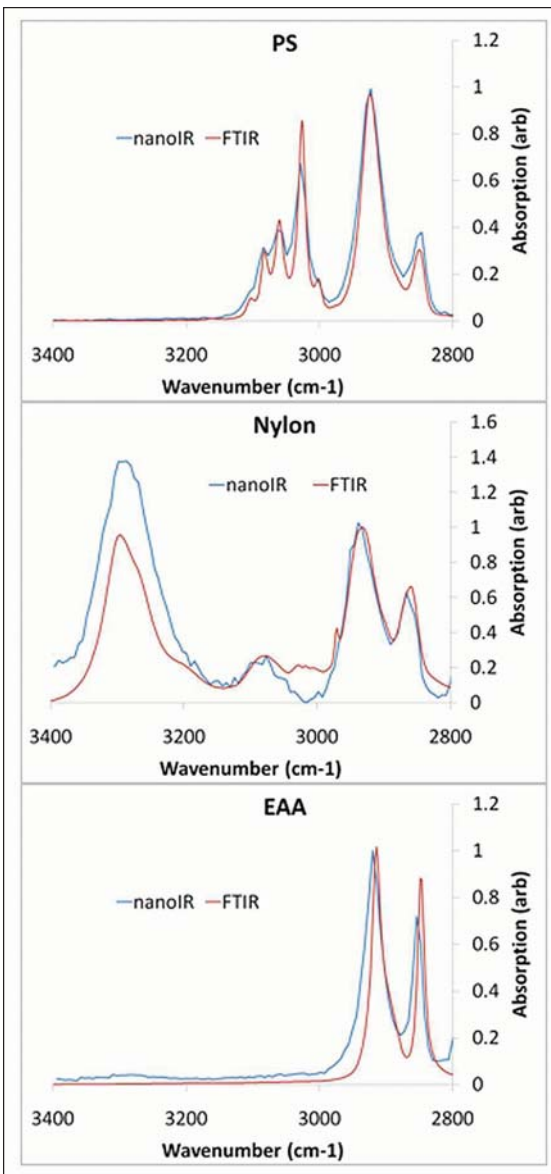


Figure 4: The PTIR technique provides spectra of nanoscale areas that are rich and interpretable with good correlation to FTIR measurements on bulk samples. These plots show comparisons of PTIR spectra of polystyrene (top), Nylon (middle) and ethylene acrylic copolymer (bottom) with reference spectra measured by FTIR.

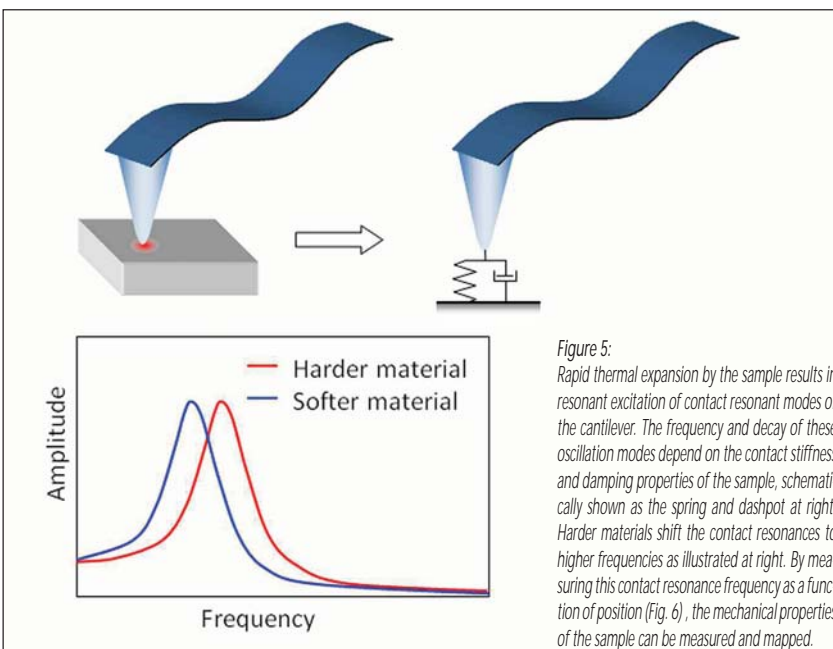
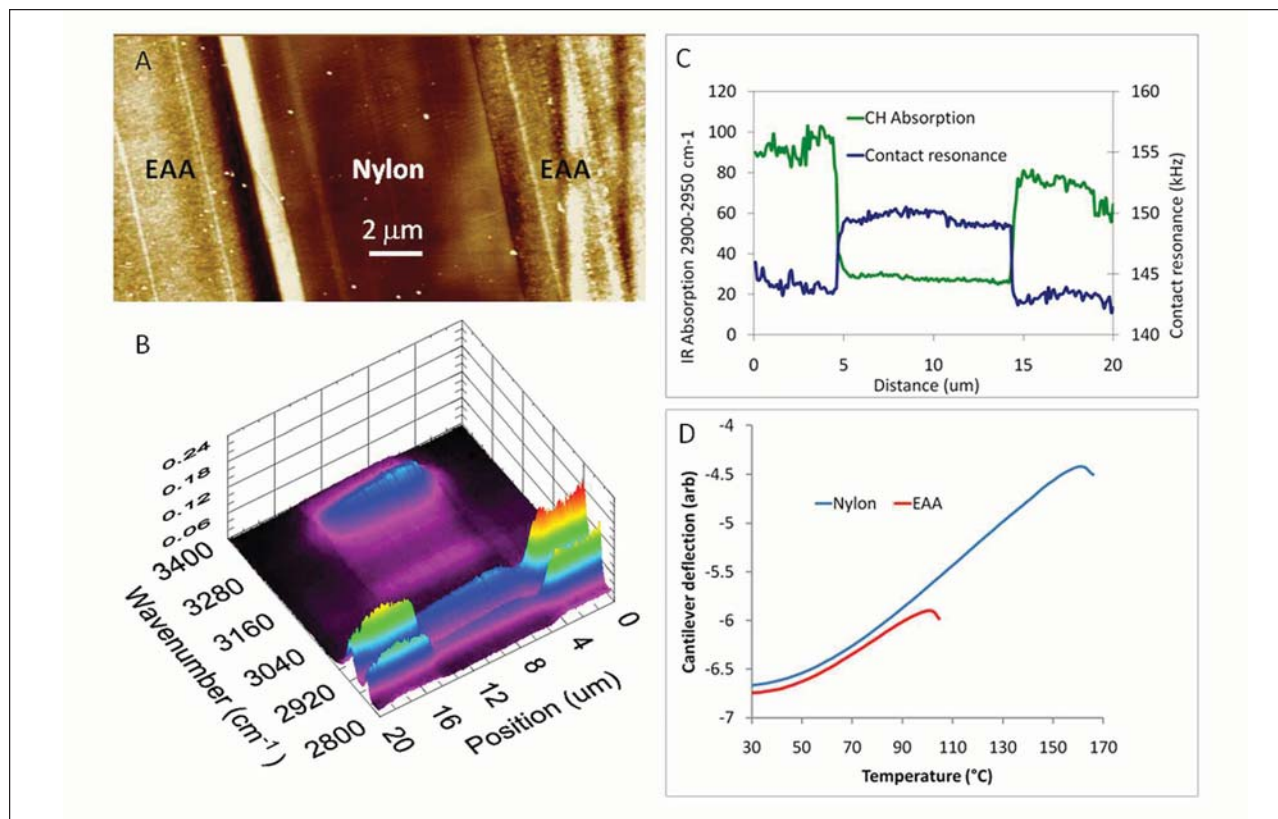


Figure 5: Rapid thermal expansion by the sample results in resonant excitation of contact resonant modes of the cantilever. The frequency and decay of these oscillation modes depend on the contact stiffness and damping properties of the sample, schematically shown as the spring and dashpot at right. Harder materials shift the contact resonances to higher frequencies as illustrated at right. By measuring this contact resonance frequency as a function of position (Fig. 6), the mechanical properties of the sample can be measured and mapped.



**Figure 6:** PTIR can be used to provide integrated measurements of topographic, chemical, mechanical and thermal properties on the same sample. (A) AFM image of a laminated polymer multilayer comprising EAA and Nylon layers. (B) Line spectral map across the interfaces showing CH and NH absorption peaks. (C) Simultaneous chemical and mechanical characterization. The green curve shows the strength of the CH absorption between 2900 and 2950  $\text{cm}^{-1}$  while the blue curve shows the relative mechanical stiffness across the interfaces. (D) Nanothermal analysis measurements performed on the Nylon and EAA layers showing material softening at different temperatures.

Figure 6 shows measurements of topographic, chemical, mechanical and thermal properties performed on the multilayer sample shown in Figure 3. The mechanical and spectroscopic data were obtained simultaneously, thus allowing direct correlation of mechanical stiffness information with chemical composition data. Note that the transitions in contact stiffness correlates extremely well with the strength of the CH absorption. Nanothermal analysis [15] was also performed on the same sample clearly identifying softening at different temperatures for the Nylon and EAA layers.

## DISCUSSION

The correlation of structure and function is of critical importance to materials science and engineering at the nanoscale. With the PTIR technique, we have demonstrated the ability to measure spatially resolved topographic, chemical, mechanical and thermal properties. The nanoscale resolution of these measurements operates well below the diffraction limits of conventional IR spectroscopy. Further these measurements can be performed either simultaneously and/or with the same probes on the same samples. As a result, it is possible to measure and study materials with greater richness and spatial resolution than previously available. Because of the high correlation to FTIR spectra, the PTIR technique can leverage the enormous existing materials databases of IR absorption reference spectra. We have

exported PTIR spectra into Bio-Rad's KnowItAll spectral analysis and successfully identified unknown materials via correlation with IR absorption databases.

## CONCLUSION

We have demonstrated the application of PTIR that combines infrared spectroscopy and atomic force microscopy to provide high resolution topographic, chemical, mechanical and thermal mapping. This combination provides spatial resolution at length scales well below the diffraction limit of conventional IR spectroscopy and adds chemical spectroscopy to the field of atomic force microscopy.

## REFERENCES

1. See for example: [www.thermo.com/eThermo/CMA/PDFs/Articles/articlesFile\\_7208.pdf](http://www.thermo.com/eThermo/CMA/PDFs/Articles/articlesFile_7208.pdf)
2. Martin, Y. et al. Scattering spectroscopy of molecules at nanometer resolution. *Applied Physics Letters* 68(18):2475-2477, 1996.
3. Knoll, B., Keilmann, F. Near-field probing of vibrational absorption for chemical microscopy. *Nature* 399(6732):134-137, 1999.
4. Anderson, M. S. Locally enhanced Raman spectroscopy with an atomic force microscope. *Applied Physics Letters* 76(21):3130-3132, 2000.
5. Hammiche, A. et al. Mid-infrared microspectroscopy of difficult samples using near-field photothermal microspectroscopy. *Spectroscopy* 19(2):20-42, 2004.
6. Dazzi, A. et al. Local infrared microspectroscopy with subwavelength spatial resolution with an atomic force microscope tip used as a photothermal sensor. *Optics Letters*

30(18): 2388-2390, 2005.

7. Dazzi, A. et al. Analysis of nano-chemical mapping performed by an AFM-based (AFMIR) acousto-optic technique. *Ultramicroscopy* 107(12):1194-1200, 2007.
8. Dazzi, A. et al. Chemical mapping of the distribution of viruses into infected bacteria with a photothermal method. *Ultramicroscopy* 108(7):635-641, 2008.
9. Dazzi, A. Sub-100-nanometer infrared spectroscopy and imaging based on a near-field photothermal technique (PTIR). In: *Biomedical Vibrational Spectroscopy*, Eds: Kneipp, J. and Lasch, P. Wiley Hoboken, NJ, USA. pp 291-312, 2008.
10. Vodopyanov, K. L., Schunemann, P. G. Broadly tunable noncritically phase-matched ZnGeP<sub>2</sub> optical parametric oscillator with a 2- $\mu\text{m}$  pump threshold. *Optics Letters* 28:441-443, 2003.
11. Felts, J. R. et al. Nanometer-scale infrared spectroscopy using a contact mode microcantilever with an internal resonator paddle. *Proceedings of IEEE 23rd International Conference on Micro Electro Mechanical Systems*, 2010, In Press.
12. Yamanaka, K., Nakano, S. Quantitative elasticity evaluation by contact resonance in an atomic force microscope. *Applied Physics A: Materials Science & Processing* 66:S313-S317, 1998.
13. Rabe, U. et al. Analysis of the high-frequency response of atomic force microscope cantilevers. *Applied Physics A: Materials Science & Processing* 66:S277-S282, 1998.
14. Yuya, P. A. et al. Contact-resonance atomic force microscopy for viscoelasticity. *Journal of Applied Physics* 104(7):074916-074917, 2008.
15. Nelson, B. A., King, W. P. Measuring material softening with nanoscale spatial resolution using heated silicon probes. *Review of Scientific Instruments* 78(2):023702-023708, 2007.

©2010 John Wiley & Sons, Ltd