Photothermal spectroscopy for nanoscale chemical imaging

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Diffraction limits in mid-IR microscopy – Technological progress over the last decade has in large part been contingent of understanding, designing and controlling materials and devices at ever smaller length scales. As theses length scales keeping going down established analytical chemistry tools end up not being able to resolve them anymore. For example, while mid-IR spectroscopy coupled to an optical microscope is a great tool for rapid chemical imaging at the millimetre and micrometre scale, it relies on the interaction of micron range (2 µm to 20 µm) electromagnetic radiation with the specimen. Hence, the diffraction limit prevents us from building mid-IR optical microscopes that can resolve structures on the nanoscale.

Chemical imaging below the diffraction limit – We can circumvent the diffraction limit by building a nearfield imaging system, i.e., by moving the detector and/or the light source as close to our specimen as possible. One approach to move the "detector" closer that has found wide acceptance for mid-IR spectroscopy is to use photothermal expansion induced by a tuneable pulsed laser for detection of local absorption. This PTIR (photothermal induced resonance) or AFM-IR (atomic force microscopy induced resonance) technique reads the local thermal expansion using an AFM tip to enable nanometre scale spatial resolution chemical imaging. AFM-IR can be used to collect mid-IR absorption spectra from nanoscale samples that resemble conventional bulk spectra and it can be used to image the chemical makeup of the sample at nanoscale lateral resolution without the need for labelling or staining [1].

Within the last decade AFM-IR has found applications across fields and disciplines, from microbiology [2] and medicine [3] to polymer science [4] and material science [5]. AFM-IR has been used to study the secondary structure of peptides in water [6] and to detect a chemotherapeutic at the zeptomole level inside a nanoscale drug carrier [7]. AFM-IR can also be used to determine thermal conductivity and interfacial thermal resistance at the nanoscale [8].

Nanoscale chemical imaging – One of the most exciting aspects of AFM-IR is that it can be used to apply multivariate chemical imaging techniques that are well established for IR microscopy at the nanoscale. These enable to combine information from multiple spectra or multiple single wavelength images into actual maps of chemical composition (see fig. 1) – if we are doing it right. "Doing it right" requires an understanding of the signal transduction chain in AFM-IR and the peculiarities of scanning probe microscopy. It also requires to understand optical effects that limit the linear range of AFM-IR [9].

This presentation will discuss the AFM-IR signal transduction chain and which of its parameters can (need to be) controlled to achieve reproducible AFM-IR measurements and what the particular challenges are in applying chemometric algorithms to AFM-IR datasets.

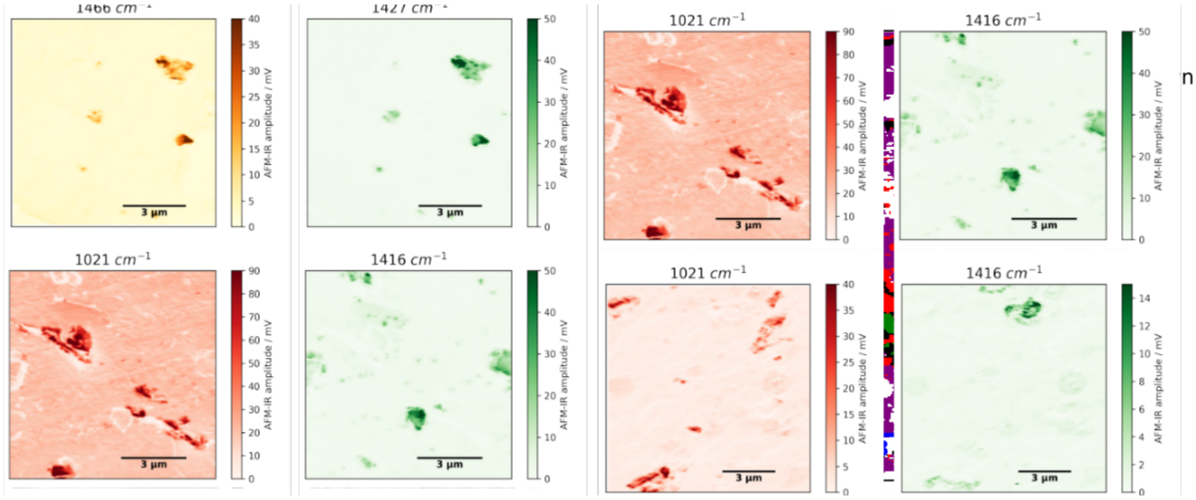

Fig. 1. Left: Topography and single wavelength images of a polymer material. Right: Chemical image calculated via Gaussian unmixing (reproduced from [10]).

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