Absorption Spectroscopy and Imaging from the Visible through Mid-IR with 20 nm Resolution Using AFM probes
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Correlated nanoscale composition and optical property maps are important to engineer nanomaterials in applications ranging from photovoltaics to sensing and therapeutics. Wavelengths (λs) from the visible to near-IR probe electronic transitions in materials, providing information regarding band gap and defects while light in mid-IR probes vibrational transitions and provide chemical composition. However, light diffraction limits the lateral resolution of conventional micro-spectroscopic techniques to approximately λ/2, which is insufficient to image nanomaterials. Additionally, the λ-dependent resolution impedes direct comparison of spectral maps from different spectral ranges. Photo Thermal Induced Resonance (PTIR) is a novel technique that circumvents light diffraction by employing an AFM tip as a local detector for measuring light absorption with λ-independent nanoscale resolution. Our PTIR setup combines an AFM microscope with three lasers providing λ-tunability from 500 nm to 16000 nm continuously. The AFM tip transduces locally the sample thermal expansion induced by light absorption into large cantilever oscillations. Local absorption spectra (electronic or vibrational) and maps are obtained recording the amplitude of the tip deflection as a function of λ and position, respectively. The working principles of the PTIR technique will be described first, and nano-patterned polymer samples will be used to evaluate its lateral resolution, sensitivity and linearity. Results show that the PTIR signal intensity is proportional to the local absorbed energy suggesting applicability of this technique for quantitative chemical analysis at nanoscale, at least for thin (less than 1000 nm thick) samples. Additionally, a λ-independent resolution as high as 20 nm is demonstrated across the whole spectral range. In the second part of the talk, PTIR will be applied to image the dark plasmonic resonance of gold Asymmetric Split Ring Resonators (A-SRRs) in the mid-IR. Additionally, the chemically-specific PTIR signal will be used to map the near-field absorption enhancement of PMMA coated A-SRRs, revealing hot-spots with enhancement factors up to ≈ 30. PTIR has broad applicability; recent examples from my lab include the characterization of chemically heterogeneous domains in metal-organic frameworks crystals and solar cells materials.