Vibrational Spectroscopy on the Nanoscale

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The spatial resolution of optical spectroscopy, including vibrational spectroscopy, is generally diffraction limited, meaning that one cannot resolve features that are separated by less than $\lambda/2$, with λ being the wavelength of the light. For infrared spectroscopy (λ = 2.5 … 20 µm) the diffraction limit is in the µm range, for Raman spectroscopy (λ = 400 … 800 nm) it is in the range of 200 nm or more. However, there is an urgent need to resolve and spectroscopically identify true nanoscale features that have dimensions of only 10s of nm or even below.

There are several recent developments that allow one to circumvent the optical diffraction limit, both for IR and for Raman spectroscopy. These methods are: scattering-Scanning Near-field Optical Microscopy (s-SNOM), nanoscale Fourier-transform Infrared Spectroscopy (Nano-FTIR), Photothermal AFM-IR (also known as Photothermal Induced Resonance, PTIR), and Tip-Enhanced Raman Spectroscopy (TERS). All of them involve a scanning probe microscopy method such as atomic force microscopy (AFM) or scanning tunneling microscopy (STM), which when coupled with the spectroscopic method in a clever fashion provides the nanoscale spatial resolution. The working principles of these methods as well as typical applications will be discussed.