MOLECULAR ANALYSIS ON THE NANOMETER SCALE

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This lecture will present novel near-field methods for spectroscopic investigations with nanometer scale spatial resolution. Two basic principles will be presented: (i) laser ablation through scanning near-field optical microscopy (SNOM) aperture probes with mass spectrometric detection of the ablation products [1], and (ii) and apertureless methodology called tip-enhanced Raman spectroscopy (TERS) [2]. The SNOM-MS approach is extremely challenging for standard MS instrumentation in terms of detection sensitivity. A novel instrument for SNOM-MS has been designed and built in our laboratory for near-field laser ablation at atmospheric pressure with ion-trap/time-of-flight mass spectrometric detection [3]. The current performance, figures of merits, and limitations will be discussed. In the second part, ongoing efforts to develop TERS into a generally applicable analytical method, in terms of data acquisition speed, imaging capabilities, spatial resolution, limit of detection, and robustness, will be presented. For nanoscale analysis by Raman spectroscopy/TERS, the suitability of the tip to provide large local enhancement is crucial. We have found how an optimum combination of the laser illumination wavelength, the tip substrate material [4], the properties of the enhancing metal nanoparticle at the tip apex, and the design of the microscope optics leads to much improved signal-to background ratios. An alternative is to purposely create a "hot" site, by studying molecules in the gap formed between a metallic surface and a very sharp STM tip, using reflection mode optics. Very large enhancement factors can be achieved in this fashion, and it has become possible to achieve single-molecule sensitivity [5]. A range of applications will be shown, in the areas of polymer science, semiconductor nanostructures, and bacterial biofilms.

References

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