APPLICATIONS OF ATOMIC FORCE MICROSCOPY TO ORGANIC MOLECULES

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BACKGROUND

Basic Principles Behind AFM

Although atomic force microscopy (AFM) was established in 1986 to image the topography of non-conductive surfaces,[1] recent advances in instrument design and acquisition methods have resulted in its use to image and characterize organic molecules.[2] Furthermore, combination of the atomic manipulation capabilities of scanning tunneling microscopy (STM) with the atomic resolution given by AFM allows for the direct visualization of reaction intermediates.[3]

In general, AFM operates by measuring the force (F_{ts}) between the sharp cantilever tip and the sample (Figure 1). For imaging of organic molecules, AFM is operated in non-contact, dynamic mode. Dynamic mode uses an oscillating cantilever that is scanned across the surface of the sample. The basic operation of the microscope starts with the excitation of the cantilever near its resonance frequency. As the cantilever scans over the sample, interactions between the tip and sample cause deviations in the oscillation frequency. In basic AFM designs, the change in oscillation frequency can be detected by using a laser beam which is reflected from the cantilever into a split photodiode. A feedback loop enables the instrument to be operated at either constant height (z) or constant frequency. Adjustments to the height or frequency at certain x,y positions ultimately results in the generation of an AFM image.

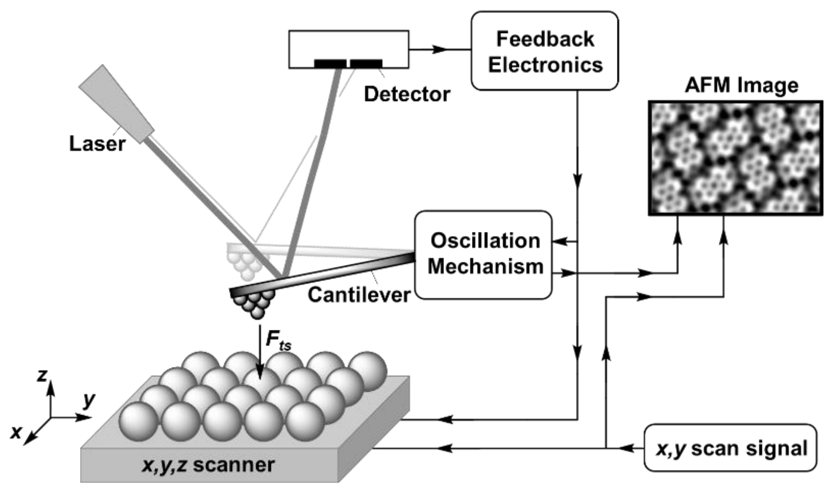

Figure 1. General Schematic of AFM Design

Advancements in AFM to Achieve Atomic Resolution

The first advancement toward atomic resolution was the implementation of qPlus sensors.[4] Both the excitation and detection of the oscillation frequency of the cantilever could be done electrically. Moreover, the qPlus sensor could be used to make hybrid STM/AFM instruments, opening the door for atomic manipulation. Further, by functionalizing the cantilever tip apex with a single molecule or atom, the exact geometry of the tip could be determined, and the first organic molecule, pentacene, was resolved using a carbon monoxide functionalized tip.[5]

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Molecular Structure Elucidation and Characterization

Following the imaging of pentacene, AFM has become a useful technique for the determination of organic structures, and while AFM has been used to assign the structure of natural products,[6] the advantage of AFM compared to other spectroscopic techniques is its additional characterization capabilities. AFM can determine the absorption geometry and electronic charge distribution of molecules.[2] Both features provide insight into the use of single molecules to function as molecular switches and transistors in the nanotechnology field.

Atomic Manipulation by Hybrid STM/AFM

Using hybrid STM/AFM instruments, on-surface chemical reactions can be induced and imaged. STM uses quantum tunneling to create a current between the metallic tip and sample using an applied voltage. A voltage pulse can be applied to the molecule, resulting in a bond dissociation event. The hybrid STM/AFM instrument can provide insight into reaction mechanisms.[7] Further, STM/AFM can generate and characterize highly reactive intermediates[8] and novel molecules incapable of being generated by traditional solution chemistry.[9]

SUMMARY AND OUTLOOK

AFM provides an exciting new method to image and characterize organic molecules. Moreover, hybrid STM/AFM instruments allow for the promotion of surface chemical reactions, characterization of reaction intermediates, and analysis of product distribution. These results provide insight into reaction mechanisms, catalysis and catalyst design, and molecular electronics. Although much progress has been made in the resolution of organic molecules, imaging non-planar and topologically complex molecules is still a great challenge. Further, atomic manipulations have been largely limited to bond dissociation events, and molecular fusion by STM/AFM remains difficult. Although fairly new in the realm of imaging organic molecules, AFM will undoubtedly continue to change rapidly within the next decade and provide new insights in the field of organic chemistry.

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