Description/Abstract

The focus of this project is on understanding the nature of intramolecular chemical bonds and intermolecular interactions using a unique technique developed in 2014 under DOE support: the inelastic tunneling probe (itProbe) with the scanning tunneling microscope (STM). By operating the STM at ~0.6 K, high energy resolution of ~0.6 meV is achieved, in combination with the inherent atomic scale spatial resolution of the STM. High energy and spatial resolutions of inelastic electron tunneling spectroscopy (IETS) with the STM enables itProbe to monitor energy shifts in the CO hindered translational vibration as the CO-tip is scanned over an adsorbed molecule. Images are obtained that relate to the two-dimensional slices of the potential energy surface for different heights above the substrate, rendering a tomography of the molecule. Comparison of experimental results to density functional theory (DFT) calculations relates itProbe images to the potential energy surface of the CO-tip probing the potential of the adsorbed molecule. Results from this project provide information on the electronic, vibrational, and structural properties of single molecules, as well as how these properties relate to the reactivity, chemical sensing, self-assembly, and other chemical interactions of higher complexity. This research leads to new insights into the fundamental principles of chemistry that can be applied to the understanding of a broad range of phenomena, such as surface chemistry and catalysis, environmental processes and energy generation, electronic processing and electron transport through molecules as in molecular electronics.

STI Product

This project relies on spectroscopic imaging of the molecular structure to understand its relation to molecular functions. During this grant period, we focused on probing the nature of intermolecular interactions responsible for self-assembly. The arrangement of atoms in a molecule implicates its physical and chemical properties. The scanning tunneling microscope (STM) previously has provided spatially resolved electronic and vibrational signatures of single molecules. However, the spatial distributions of these signatures do not relate directly to the geometric structures of the molecules. When a carbon monoxide terminated tip (CO-tip) is scanned over an adsorbed molecule, the energy, intensity, and line shape of the lowest energy, hindered translational vibration of CO vary over each atom, bond, and any lone electron pair in the molecule. These variations in the CO vibration are detected by inelastic electron tunneling spectroscopy (IETS) with the STM. Spatial imaging of the hindered translational vibration of the CO-terminated tip yields direct visualization of the skeletal structure of the molecule. This new imaging capability, the inelastic tunneling probe (itProbe) has contributed greatly in the description of molecules and chemical interactions. The combined capabilities of the STM suggest the possibility of relating the electronic, vibrational, and geometric structure to function in chemistry at the single molecule level.

Demonstration of the Inelastic Tunneling Probe (itProbe)

One of the highlights during this grant period lies in the demonstration that molecular skeletal structures can be imaged by the STM. Specifically individual atoms and bonds, as well as lone electron pairs are resolved. We have developed a new approach with the STM by transferring a CO molecule to the tip and monitor its low energy, hindered translational vibration

as the CO-terminated tip is scanned over another molecule adsorbed on the surface. We show that the energy, intensity, and line shape of the CO vibration are sensitive to the atoms, bonds, and lone electron pairs in the adsorbed molecule, for example in resolving the 57 atoms, 68 bonds, and 4 lone pairs of electrons in a single cobalt phthalocyanine (CoPc) molecule. The CO vibration senses the skeletal structure of the molecule.

The ability of the STM to image molecular structure is an important addition to its previously shown capabilities for manipulation and spectroscopy of the electronic and vibrational states. The arrangement of atoms in a molecule implicates its physical and chemical properties. The results obtained by the itProbe suggest new opportunities to relate structure and function in chemistry at the single molecule level.

Imaging the Halogen Bond and the Hydrogen Bond: Fluorobenzenes

Following the work on Co-phthalocyanine, the itProbe was used to image 1,3-difluorobenzene ($C_6H_4F_2$), 1,3,5-trifluorobenzene ($C_6H_3F_3$), hexafluorobenzene (C_6F_6), and benzene (C_6H_6) on the Ag(110) surface. These results visualize halogen bonding that leads to intermolecular interactions responsible for self-assembly of ordered two-dimensional islands. The number and location of the fluorine atoms influence the nature of the intermolecular interactions that cause differences in the translational and rotational orders of the molecules within the self-assembly. An example of a self-assembled island of 1,3-difluorobenzene shows clearly the locations of the two C-F bonds, imaged as two “ears” in each molecule. These “ears” facilitate the determination of the partners involved in the intermolecular interactions that drive the self-assembly. The island shows translational order but orientation disorder due to the locations of the two C-F bonds. The intermolecular interactions are mainly hydrogen bonding between the F and the H and the less frequent halogen bonding between two F atoms due to the 1:2 ratio of F:H in each molecule. The itProbe images show the presence of multiple center bonds. A F atom can interact with one, two, or three neighboring atoms of either H or F. Similarly, a H atom can interact with one or two neighboring F atoms.

When all the H atoms are replaced by F atoms, the self-assembly of C_6F_6 would not be expected because the electronegative F atoms around the molecule would suggest a repulsive interaction between the molecules. However, islands of C_6F_6 are formed with translational and rotational orderings of the molecules in each island. Indeed, a rich network of intermolecular interactions is revealed by the itProbe images. In addition, all six C-F bonds in each molecule are clearly revealed. Side bonding between two C-F bonds is seen in the itProbe image, creating the rich intermolecular network that leads to translational and rotational orders for molecules in the self-assembled islands. The molecules are all tilted with an experimental value of $21.2 \pm 1.3°$.

The electrostatic interactions between C_6F_6 molecules are responsible for their orientation by minimizing the repulsive interactions between C_6F_6 molecules. DFT calculations show that the stabilization of the assembly, however, is due predominantly to van der Waals interactions. Results from DFT calculations imply two conclusions: 1. van der Waals interactions are responsible for the formation energy of the self-assembly, and 2. the molecular orientation angle is due to the minimization of electrostatic interaction and independent of the van der Waals attraction. The origin of the “lines” in the itProbe bond image is revealed by DFT calculations of

the potential energy surface (PES) for the CO-tip interacting with the potential of the C_6F_6 self-assembled monolayer. A comparison of the itProbe image with the PES shows that the "lines" in itProbe correspond to ridges in the PES. These ridges are regions of negative curvature, or negative second derivative of the PES that is proportional to the electron density.

itProbe Images of Single Molecules

Significant differences separate C_6H_6 from C_6F_6 (or $C_6H_4F_2$ and $C_6H_3F_3$). Self-assembly of C_6H_6 does not occur and benzene molecules adsorb in isolation for similar coverages as the fluorinated benzene molecules. The lack of island formation suggests that the intermolecular interactions between C_6H_6 molecules are weak, and weaker than the interaction of each molecule with the Ag(110) surface. The C_6H_6 molecules preferentially adsorb at step edges due to the higher adsorption energy. Structural images of C_6H_6 molecules obtained by itProbe provide new insights into the concept of the size and shape of molecules. For C_6H_6 adsorbed on the flat terrace of Ag(110) compared to the known molecular geometry, the skeletal structure shows a larger size and has the rectangular symmetry of the substrate surface. In contrast, a molecule at the step edge has a size close to the known structure of C_6H_6 and the expected hexagonal symmetry. The CO-tip maps out the spatial variations in the potential energy surface above the C_6H_6 that change the CO vibrational energy. The potential energy surface is defined primarily by the C_6H_6 electron density and the associated electrostatic potential that CO interacts with. The itProbe images reveal that a benzene molecule has variable size and shape as seen by a CO molecule at a certain height above it. The itProbe senses changes in the CO hindered translational vibration that depends on the spatial variations in the potential energy surface defined predominantly by the adsorbed C_6H_6.

The fact that molecules self-assemble into ordered structures that differ in symmetry from the substrate points to dominance of intermolecular bonding. Thus features between molecules revealed in itProbe images can be attributed to intermolecular bonding that drives the self-assembly. For isolated single molecules, itProbe images provide visual verification of expected skeletal structures. However, new features have also been discovered for some of these molecules. Intramolecular interactions are revealed in cobalt(II) phthalocyanine among the two hydrogens in C-H bonds and the lone pair of electrons of the nearest N atom. When adsorbed on the surface, cyclooctatetraene assumes a planar structure even though DFT calculations do not show the required two-electrons charge transfer to the ring to achieve aromaticity. In the case of hexabromobenzene, a ring is present around the molecule, suggesting a potential energy barrier surrounding the molecule. In all these molecules, an outer ring is consistently imaged, suggesting the Van der Waals radius for each molecule.

Probing Further Halogen Bonding

The self-assembly of 1,3,5-trifluorobenzene ($C_6H_3F_3$) poses two interesting questions: 1. How do the molecules self-assemble? 2. How do the hydrogen bond and the halogen bond compete and coordinate to produce the lowest energy state for the self-assembly? For hexafluorobenzene (C_6F_6), the halogen bond prevails since it is the only type of bonding that is possible. In 1,3,5-trifluorobenzene, the molecule has more "knobs". It is not obvious a priori on how the molecules are coupled to each other. This network could not be revealed by topography

alone, either with the bare metal tip or a CO-terminated metal tip. Using itProbe, the intermolecular interactions are fully resolved and in hindsight, the pattern of intermolecular interactions makes sense but difficult to predict. In 1,3-diflurobenzene ($C_6H_4F_2$), the lower molecular symmetry leads to dominant hydrogen bond between H and F and to a lesser degree halogen bond between F's because the molecule has less number of F atoms. While there is translational order, the rotational order is missing in the self-assembly of $C_6H_4F_2$.

The intermolecular interactions have also been imaged in the self-assembly of hexabromobenzene (C_6Br_6). Distinct from fluorobenzenes, the larger polarizability, C-Br bond length, and the distinct ring around the molecule provide a deeper understanding into the nature of halogen bonding, intermolecular interactions, and the properties of molecules.

Imaging van der Waals Interaction

The itProbe was used to visualize the van der Waals (vdW) interaction through imaging and analyses by density functional theory calculations. Self-assembly of Xe atoms on a metal surface presents an ideal vdW system for fundamental studies. The vdW interaction is imaged by the itProbe that detects changes in the hindered translational vibration of a CO molecule attached to the tip as it senses the spatial variations of the potential over the Xe layer adsorbed on the surface. The spatial variations in the potential reflect the vdW interactions between the Xe atoms.

Traditionally, vdW interaction has been associated with charge fluctuations that lead to attractive interactions between the instantaneous dipole with its induced counterpart in an adjacent entity. On the other hand, when atoms are in the vicinity of each other, electron redistribution is bound to occur, which is captured by the itProbe and DFT calculations.

Our study reports real-space imaging of vdW interaction between adjacent Xe atoms, and DFT calculations (with vdW correction) reveal tiny shift of electron density toward the region between adjacent Xe atoms. Directionality is observed in the itProbe images and can be correlated with the ridges of the potential energy surface associated with the charge density. Comparison of experiment and theory concludes that ridges of the charge density (and the corresponding potential energy surface) in the two-dimensional plane above the Xe layer reflect the vdW interaction. These results add an understanding for the formation of weak chemical bonds and provide insights into chemical interactions as charge rearrangement between atoms and the associated potential perturbation in space. Unlike covalent interactions formed by carbon, the angle between two adjacent vdW interactions is not constrained and can take on continuous values depending on the positions of the adjacent atoms. The vdW interaction in simple systems as the Xe monolayer is directed along a line connecting the centers of the two interacting atoms.