INTRODUCTION

The nanoscale world is exciting because it is governed by rules different than those in the macroscopic, or even microscopic, realm. It is a world where quantum mechanics dominates the scene and events on the single molecule, or even single atom, scale are critical. What we know about the behavior of material on our scale is no longer true on the nanometer scale and our formularies must be rewritten. In order to study this quantum world, a quantum mechanical probe is essential. Electron tunneling provides that quantum mechanical tool.

In the Newtonian world, a particle can never be in a region where its potential energy is greater than its total energy. To do so would require a negative kinetic energy -- a clear impossibility since \( mv^2/2 \geq 0 \). As the scale shrinks to molecular dimensions, of the order of 1 nanometer, classical concepts fail and the correct mechanics is quantum mechanics. Thus, it is possible for a particle to move from one classically allowed region to another through a region where its potential energy is greater than its total energy -- this is the phenomenon of tunneling. While it can occur for relatively heavy particles such as protons, it is far more probable for light particles such as electrons. Electron tunneling is a particularly useful probe because it is easy to control the flow and energy of electrons and to set up precisely controlled regions through which the electron must tunnel. An early example of an electron-tunneling device was the metal-insulator-metal (M-I-M) tunnel diode, Figure 1. [1-7] Also shown in Figure 1 are the corresponding features of a scanning tunneling microscope (STM). [8-11] Both devices rely on exactly the same physics. Within the conductors (metal electrodes in the M-I-M' case, substrate and atomically sharp tip in the STM case) the electrons are in classically allowed regions I and III. Within these regions, their total energy \( E \) is greater than their potential energy. In the gap between conductors (the insulator in the M-I-M' case, the vacuum or solvent gap in the STM case) however, the potential is greater than \( E \), region II. This region is classically forbidden but quantum mechanically allowed. A simple quantum mechanical calculation quickly demonstrates that the probability of transmission through the barrier decreases exponentially with the thickness of the barrier and the square root of the potential (barrier height) relative to the electron energy. If distance, \( d \), is measured in Angstroms (0.1 nm) and energies (\( E \) and \( U \)) are measured in electron volts, then the constant \( A \) in Figure 1 is approximately 1. [6,8] If one assumes that the bias voltage is small compared to the barrier height, \( U-E \) is approximately equal to the work function, \( \Phi \), and the tunneling current is roughly given by:

\[
I = cV \exp(-d\sqrt{\Phi})
\]

A more sophisticated treatment of the tunneling problem based on WKB method can be used and one then finds that the tunneling current is given by the expression [10]:
\[
I = \int_0^{eV} \rho_t(r, E) \rho_s(r + eV - E) T(E, eV, r) dE
\]

where the density of states of the tip and sample as a function of position along the surface plane must be considered along with the exponential transmission probability.

The exponential dependence of tunneling current on electrode separation is the essential element of the STM, a device that can produce exquisitely well resolved images of molecules and atoms. Modern scanning tunneling microscopes are capable of resolving single atoms at temperatures ranging from near 0 K to above 600 K. STM images have been acquired in ultra high vacuum (UHV), in air, even in electrochemical cells. The STM has allowed us to visualize the nanoscale world in a way that is essential for understanding processes on that scale. But there is more information in the tunneling current than just the surface geometry. If a structured barrier is considered, one in which there is a non-uniform distribution of states, the tunneling current can also reflect this energetic variation. Changes in current with applied bias voltage at constant electrode separation provide spectroscopic information about the surface of the electrodes and any material located in the barrier region. Moreover, there are several different types of interactions that can lead to distinctly different spectroscopic methods. These electron tunneling spectroscopies can be generally classed as based upon either inelastic or elastic electron tunneling processes. Our primary interest in this article is on the spectroscopic information that can be obtained with the STM. This encompasses both inelastic and elastic processes. On the other hand, some understanding of the experimental requirements and limitations on the imaging technique are essential for a real appreciation of the range of applications of the spectroscopic methods. Thus, we will begin this

**Figure 1:** Schematic drawings of a tunnel diode, an STM, and the electronic energy diagram appropriate for both. U is the height of the potential barrier, E is the energy of the incident electron, d is the thickness of the barrier, A is approximately 1.02 Angstrom/(eV)^{1/2} if U and E are in electron volts and d is in angstroms, \( \psi_0 \) is the wavefunction of the incident electron and \( \psi_d \) is the wavefunction after transmission through the barrier. I is the measured tunneling current, V is the applied bias, and M and M’ are the electrode metals.
article with an overview of STM imaging and then proceed to an introduction of the basic spectroscopic methods. Along the way, we will provide examples from the literature of applications of tunneling spectroscopy. Because STM imaging has been extensively reviewed, we will limit our presentation on this topic to a few basic points and refer the reader to the literature for a deeper understanding of the method. [8-19] We will also only give a cursory treatment of STM based spectroscopy of semiconductors and metals. Understanding of the spectra of these crystalline surfaces has been well documented in a number of outstanding reviews and books, [8,12,13,18] with my personal favorite being the chapter by Hamers. [9]

THE SCANNING TUNNELING MICROSCOPE (STM)

The forefather of the STM was the topographiner. The topographiner was a device demonstrated in the early 1970's that utilizing field emission rather than tunneling as the surface sensing technique. [20] Like the modern STM, the device consisted of a sharp metallic tip mounted on a piezoelectric element for positioning and an electronic feedback system that maintained the tip-sample spacing during a raster scan of the surface. The resolution was limited to about 3 nm in the vertical direction and 400 nm in the horizontal due to the weak distance dependence of the field emission current. In the early 1980's, Gerd Binnig and Heinrich Rohrer began investigating the possibility of using tunneling electrons to probe the surface of conductors and semiconductors. [21-23]. In 1983, Binnig and Rohrer succeeded in producing an atomic resolution image of two unit cells of the 7x7 reconstruction surface of Silicon (111). It was this image that captured the attention of the surface science world and resulted in their receiving the Nobel Prize in 1986. [23]

Figure 2: Schematic representation of a scanning probe microscope. The critical element in differentiating the different probe techniques and their relative resolutions is the tip-surface interaction and the method of sensing that interaction. In STM it is the tunneling current that is sensed.
From the STM has evolved an entire menagerie of scanning probe microscopy (SPM) techniques. While this chapter is solely concerned with STM, it is useful to introduce it by way of the more general SPM approach. A schematic representation of the essential elements for any scanning probe microscope is presented in Figure 2. The tip-sample interaction defines the type of SPM and controls the spatial resolution possible with the particular technique. For example, if mechanical forces are measured by physical contact between tip and sample, then the radius of curvature of the tip and the elastic compliance of the substrate limit the possible spatial resolution in the x-y plane. In STM it is the tunneling current that is probed. The exponential dependence of the current on tip-sample separation results in the possibility single atom resolution. This is generally explained by considering a tip formed from a single atom sitting in a 3 fold hollow site. For conditions normally used in high resolution STM (1 nA set point and 300 mV bias), about 90% of the current is carried by the apical atom because of the difference in distance between it and the atoms at its base. For the general SPM technique, the finer one can make the tip, the higher the x-y spatial resolution. Good STM tips are generally atomically sharp and methods for fabricating them will be discussed later. The z (or normal direction) resolution depends solely upon the z dependence of the interaction between tip and sample. Because of its exponential form, STM is the most sensitive SPM technique, easily achieving 0.005 nm sensitivity.

Another essential feature of all SPMs is the feedback control loop. This electronic system maintains the tip-sample interaction at a preset value by controlling the z position (or deflection) of the tip relative to the surface (or to an undeflected position). In the case of the STM, the absolute distance of the tip from the surface is difficult to impossible to determine, and the relative height is controlled through setting fixed values of current and voltage (I~exp(-dΦ)). Typical current values range from picoamps to nanoamps, while the bias voltage can vary from millivolts to volts. Commercial feedback loops generally incorporate both integral and proportional gain stages. As in all feedback loop applications, it is desirable to set the gain as high as possible but not so high as to drive the system into oscillation. Oscillation of the
feedback loop is especially bad in STM where repeated contacts between tip and surface (called crashes) can destroy the usefulness of the tip.

The SPM image is generated by performing a raster scan of the tip over the surface while recording the z deflection required to maintain the setpoint. Almost all commercial instruments use one or more piezoelectric elements to perform the fine motion required to generate images with sub angstrom data intervals. Instruments designed for high resolution are usually limited to piezoelectric elements having 1 to 10 micron maximum scan widths, while 100 micron scan widths are available for lower resolution SPM studies. It is important to note that in the feedback controlled scan regime, one is almost never measuring a true height. In STM, for example, the changes in tip height with position under feedback control reflect both the tip-sample separation and the spatial variation of the local density of surface states (LDOS) of the sample (Φ(x,y) in the simple model). Thus, the constant current image only reflects true height changes if the LDOS of the surface (the local work function) is constant across the surface. This would be the case for atomic steps on clean metal surfaces, but would NOT be the case for adsorbates on surfaces.

The range of z motion possible for the fine position control is generally only a few microns. Thus, some method of bringing the tip within a few microns of the surface without crashing it is required. This is identified as the coarse approach mechanism in the cartoon. Often, this coarse approach is accomplished by a fine pitch screw (as in the Veeco electrochemical STM [24]) or a piezoelectric driven slip-stick (inertial approach) mechanism (as in the McAllister [25]). Some designs incorporate x,y coarse motion into their coarse approach mechanism, as does the RHK design [26].

The computer control system does more than integrate the feedback loop with the scanning mechanism while saving piezo position coordinates. Another essential feature is in displaying the data in a manner easily interpreted by the human eye. The left hand image of figure 3 shows the STM constant current height versus position of a large area of a Au(111) surface. While the data was actually acquired with a 512x512 grid, only a small portion of the grid is shown for clarity. The change in tip height relative to the initial setpoint at each grid crossing is mapped both as a 3D projection and by brightness. The lighter the area, the higher the feature. While these 3D projection images are lovely, a real appreciation of the data requires the ability to rotate and tilt the image interactively relative to the observer. Almost all modern SPM software is capable of doing this real time, but this interactive image is not something that can be placed in a publication. Instead, a top view, sometimes called bird's eye view, is most frequently published. The right hand image is a standard top view of the same area as shown in the left image. Here, all the height information is contained in the color scale which is displayed to the far right.

While virtually any commercial STM will do a good job of taking pictures of surfaces, spectroscopic applications place extra requirements on the instrumentation that must be met if even low quality data is desired.

1) The control and data acquisition system must be able to ramp the bias voltage or the tip sample separation while acquiring the tunneling current or some other voltage signal supplied by an external device. The rate at which data is acquired must be variable over a wide range in time (from about 5 microseconds to about 10 milliseconds per data point), in voltage (from about ±0.5 volts to ±10.0 volts, with the ability to set asymmetrical limits being highly desirable), or in z span (from about -2 nm to +5 nm, where negative distance moves the tip closer to the substrate than at the setpoint. The most commonly used auxiliary input is the output of a lock-in amplifier that detects a modulated signal in the tip current.

2) It must be possible to add modulation (typically sine or square wave) to the bias or tip position voltage. An old version of the Digital Instruments (now Veeco) software, version 3.2x, had built in square wave modulation and the software directly could display dl/dV determined from the resulting modulation in the current. This system worked very well, but was dropped from, or incorrectly implemented in, later versions of the software. To our knowledge, none of today's manufacturers offer such complete 'built in' spectroscopic capability.
3) The control system must be able to shut off the feedback loop during data acquisition, when desired.

4) The drift (both x, y and z) must be low. The extent of acceptable x, y drift is determined by the amount of spatial resolution desired for the spectroscopic data. If one is acquiring spatially averaged molecular spectra from a dense monolayer with a large curvature tip, drifts of the order of 1 nm/sec can be tolerated. On the other hand, if one is trying to locate particular atoms through their vibrational signature in STM based IETS, drifts of less than 0.1 nm/min are required. The amount of acceptable drift in the z direction is determined by the intensity of the spectral feature to be studied relative to the background tunneling current in the absence of that feature. Since this background increases (approximately) as \( I = CV \exp(-A(z+d)\sqrt{\Phi}) \), a small change in z, dz, results in an increase in relative current \( \frac{dI}{I} \) of \(-A\sqrt{\Phi}dz\). Or, using z in nm and \( \Phi \) in volts, the background change in relative current with a small z drift of dz is given by, \( \frac{dI}{I} \approx -0.1 \text{ dz} \). For true vibrational IETS (with no resonance enhancements), \( \frac{dI}{I} \) for the spectral transition, \( \frac{dI}{I_s} \approx 0.002 \). Thus, less than \( 1 \times 10^{-2} \) nm of z drift is allowed during the time required to scan a particular spectral band. For STM-OMTS, on the other hand, \( \frac{dI}{I_s} \approx 0.1 \), and 100 times as much z drift is allowed. Moreover, because the OMTS signal is so much stronger than that of IETS, equal signal to noise can be obtained about \((0.1/0.002)^{1/2} \approx 7\) times faster. Overall, STM-OMTS is expected to be about 1000 times less z drift sensitive than STM-IETS of non-resonance enhanced transitions.

5) Sample and tip geometry and shielding. Because of the drift constraints discussed above, one needs to take spectra as fast as the electronic bandwidth allows. With the feedback loop turned off, the limiting term is the capacitance in the tip-sample assembly and the wires leading to the preamplifier circuit. Thus, the preamplifier needs to be close to the tip, and the tip and sample need to be electrically isolated and as small as possible.

6) An essential requirement for STM-IETS is that the working parts of the STM be at or below 10K. Otherwise, the thermal line width destroys the information inherent in identifying vibrational peak positions. It is not enough to cool the sample, the sample, tip, and all parts physically close must be cooled to this temperature. In the case of STM based OMTS or spectroscopic studies of density of states in metals or semiconductors, room temperature measurements are usually satisfactory, and many measurements can be made at significantly elevated temperatures.

Commercial Instruments

There are currently available a wide range of SPM instruments which incorporate all of the features discussed above (except for tips which we will discuss later). I will list a number of commercial suppliers, many of whom currently only provide AFM instruments and not STM. Please note, however, that this is a rapidly evolving business and companies may broaden or narrow their offerings on short notice. This list is not exhaustive and the absence of a manufacturer from the list does not indicate any preference. In the US, Veeco Metrology [24] is the major supplier of ambient and solution phase SPM's, followed by Molecular Imaging Corporation [27]. Asylum Research is an offshoot of the original Digital Instruments (now owned by Veeco) and specializes in atomic force microscopy (AFM) and pico-force measurements [28]. Novascan provides ambient scanning force microscopes, AFM tips, and chemically modified tips and samples. [29] Quesant, in partnership with Novascan, provides a full range of ambient and liquid scanning probe microscopes. [30] For UHV systems made in the United States, one must turn either to McAllister Technical [25] or RHK Technology [26]. The McAllister system is very inexpensive and has provided very high resolution images in the hands of a number of research groups, but it is a room temperature only STM. RHK now offers both STM and AFM in UHV with variable temperature achieved by cooling the sample (only). Note, as indicated in a previous section, that for the purposes of measuring vibrational inelastic spectroscopy the entire microscope (sample and tip) must be cooled. To
our knowledge there are currently no US suppliers of such microscopes. While commenting on spectroscopy, it is useful to note that STM heads where the sample and tip are electrically isolated from the rest of the microscope (including the sample holder) are especially desirable for spectroscopic purposes. These designs (like that of the RHK) minimize the capacitive coupling that can limit the sampling speed.

The best known UHV STM and AFM system provider is the German company, Omicron [31]. Omicron offers a range of UHV systems with cooled sample STM and AFM capability, and the multiprobe LT which is a dedicated low temperature STM wherein both the tip and sample are cooled. Witech is another German company that makes commercial AFM and SNOM equipment, but appears to have dropped their STM line [32]. Nanosurf is a Swiss company that manufactures extremely compact and inexpensive STM and AFM systems suitable for use in undergraduate laboratories [33]. Both Witech and Nanosurf are represented in the US by Nanoscient Instruments. Nanotech Electronica is a Spanish company specializing in scanning force microscopy and distributing a free SPM (including STM) data analysis program WSxM [35]. In Russia, NT-MDT is a comprehensive supplier of STM, and AFM instruments and supplies, and also offers a small education oriented multi-purpose scanning probe microscope [36]. Other SPM manufacturers include Danish Micro Engineering [37], JPK [38] and attocube [39] instruments specializing in AFM and SNOM, PSIA in Korea specializing in AFM [40]; SIS ambient AFM systems [41] and Triple-O offering AFM and SNOM systems [42].

Tips

Once an appropriate SPM has been purchased or built from scratch, one must obtain appropriate tips and samples. Since the emphasis here is on STM, suffice it to say that there are a number of commercial sources for silicon, silicon nitride, and variously coated tips appropriate for scanning force microscopy [24,29,34,36,43]. While research grade AFM tips are commercially available at reasonable prices, this is not the situation for STM. While a few companies offer etched STM tips, they are expensive and generally unsuitable for spectroscopic applications because of their long exposure to various ambient environments. Thus, the STM practitioner almost always makes his own tips. These fall generally into two classes, mechanically formed and etched tips.

The first STM tips were mechanically formed by Binnig et al. [44,45]. These were formed by mechanical grinding (at 90°!) 1 mm diameter tungsten wire. To day, by far the most common mechanically formed tips are cut wire tips. While Au, Pt0.9Ir0.1, Pt1-xRh_x, and similar metal wires have been used, the most popular cut tip is made from 0.25 mm diameter Pt0.8Ir0.2 wire. Almost every laboratory has their own preferred cutting method. Some anneal the wire before cutting with dull scissors using a pulling motion. Others prefer to use very sharp dykes. Some suggest that a 60° angle cut is best, while others prefer larger or smaller angles. Since the 'tip' is really an atomic asperity at the end of a rather rough mass of metal, it is not too surprising that the macroscopic and microscopic (as in microns) morphology have little relevance to the quality of the tip. In fact, the tips that give the best images do not always appear sharp under an optical microscope (200 to 400 power). In fact, there are almost always a number of 'tips' like fingers of a hand extending towards the surface. See for example figure 6.4a in reference 46. Because of the strong exponential dependence of the tunneling current, only the longest 'finger' is important when measuring flat surfaces. When imaging rough surfaces, or intermediate to large features (a nm or more tall) on a flat surface, one may see 'ghost images' resulting from tunneling through secondary tips of nearly the same length as the longest. The offset between the ghost and the primary image is related to the offset between the longest and second longest asperity. The cure for ghost images is to re-cut the tip until they disappear. Cut Pt0.8Ir0.2 tips are inexpensive, quickly made, and have a fairly good yield (usually 1 in 3 will show atomic reconstruction lines on Au).

Electrochemically etched tips offer a well defined geometry near the atomic asperity that functions as the tip. Methods for preparing atomically sharp tips from a number of different metals were first developed primarily for field ion microscopy [47,48]. Etched tips are commonly made from Pt, Ir, Au, W, Pd, Ni, and Ag. Prescriptions for a number of these metals were given by Nam et al. [49].
solution, and especially electrochemical applications, etched Pt$_{0.8}$Ir$_{0.2}$ tips are preferred. Various methods for making these are described in the literature [49-52], including descriptions of how to limit Faradaic currents through tip coating [53,54]. Au tips, both etched [55,56] and coated [57] have been reported in the literature, as have etched silver tips [58]. For spin polarized tunneling studies, Cavallini reports that etched nickel tips work well and have better oxidation resistance than tungsten tips. [59] By far the most commonly used tip material for UHV studies is tungsten, and these tips are almost always etched tips.

One has a great variety of methods to choose from when etching W tips. [49,60,61,62] One may either follow the prescriptions and designs in the literature, or purchase commercial tip etching stands such as those offered by W-tech (through Omicron) or Shrodinger's Sharpener from Obbligato Objectives [63]. Electrochemically etched W tips have an oxide layer on the surface. This oxide layer can be up to 20 nm thick. [64] Dipping the W tips in 47% HF prior to loading in the UHV chamber has been reported to improve tips, [65-67] but an insulating layer is still apparently left on the tip surface. [65,67] For simple imaging, the oxide layer on freshly prepared tips is usually not a problem. For spectroscopic studies, however, it is a major impediment since the spectrum can be dominated by the density of states of the oxide layer. The stable form of the oxide is WO$_3$, and can be removed by heating above 800°C. [68] At this temperature WO$_3$ reacts with W to form WO$_2$ which then sublimes. W melts at 3410°C, so a wide window exists to remove the oxide without deforming the tip. A convenient method of heating the tip to remove contaminants is to use electron bombardment. However care still needs to be taken since the local temperature at the tip can easily reach the melting point -- even to the extent of forming an obvious round ball at the end of the tip wire.

Some crude but effective in situ methods for tip cleaning have also been successful. In the earliest days of STM, it was found that applying a 10 kHz 2 nm peak to peak (vertical) oscillation to a tip initially in contact with a platinum plate could produce clean sharp tips. [44] Binnig thought that this procedure might clean the tip through some type of ultrasonic interaction. The application of a large voltage pulse (from 3 volts to hundreds of volts) has also been used for tip cleaning. Field emission cleaning is proposed to account for why application of about 100 V between tip and sample at a distance suitable to produce nA to mA currents can result in clean tips. In the above two cases, one had best use either a clean portion of the sample (that is sacrificed), or another clean metal sample. Another common method for eliminating the oxide involves 'controlled' crashiong of the tip on a clean gold surface. This method does work on occasion, but it can also lead to dull (poor resolution) or even bent (unrealistic surface images) tips. An extreme example of this is to simply let the tip scan over a large area of the surface for an extended time. For all the methods of this paragraph, it is not clear whether one cleans the W, or coats the tip with the metal counter surface.

SCANNING TUNNELING SPECTROSCOPY OF SEMICONDUCTORS & METALS

The scanning tunneling spectroscopy of metals and semiconductors primarily focus on elastic tunneling current changes associated with the local density of states (LDOS), $\rho_s(r,E)$, that appears in equation 2. To a good approximation, $\rho_s(r,E)$ is proportional to $dI/dV$ when the tip is far from the substrate and the density of states of the tip is reasonably smooth. These are elastic tunneling spectra, as will be described in a later section.

Jacklevic and co-workers first demonstrated imaging of metal surface states when they identified the Au(111) surface state in its $dI/dV$ spectrum. [69,70] They found that the surface state peak was centered just above -500 mV sample bias with a full width at half height of about 300 mV. They observed changes in the peak intensity and position that correlated with surface features. The surface state intensity was found to be substantially reduced at step edges as compared to values observed for large terraces. A change in the intensity by a factor of 2 over the $23 \times \sqrt{3}$ reconstruction unit cell was also observed. These effects were attributed to a spatial variation of the surface state intensity with the local potential. Upward shifts of the surface state energy were also observed on narrow terraces. Kuk and Silverman performed tunneling spectroscopy of Au(100)-(5 $\times$ 20) and Fe on Au(100) surfaces. [71] Using a well-defined tunneling tip, I-d, I-V, and dlnI/dlnV-V spectra were obtained (d is the tip-Au separation). The results
confirmed that the characteristics of the spectra resemble those of previously reported semiconductors. From I-d relations, they found that the tunneling barrier decreased abruptly when the tunneling gap was <0.6 nm. Later, Kuk reviewed the elastic scanning tunneling spectroscopy of a number of clean metal surfaces. [72] In this chapter he presented the operating principles of the scanning tunneling microscope as applicable to the problem of the small corrugations seen on metallic samples. Various spectroscopies were described and compared with theory. Some examples of past accomplishments on metal surfaces were given.

Fonden and coworkers investigated unoccupied surface resonances seen in a plot of dI/dV versus V. [73] The authors extend and detail a previously developed model for formation of electronic resonances at free-electron-like metal surfaces, to calculate scanning tunneling spectra. The effect of the tip is mimicked by inclusion of an external field, self-consistently, in a jellium description of the surface potential. The lattice-induced corrugation of the potential is included perturbatively via a pseudopotential. The authors compare the calculated spectra for Al(111) with experimental results conclude that a peak occurring below the metal vacuum level is a 'crystal-derived' resonance, in the sense that lattice effects are crucial for its manifestation. Hoermandinger [74] and Doyen and Drakova [75] also investigated the theoretical underpinnings for the observation of metallic surface states by dI/dV spectroscopy.

Bischoff and coworkers examined the role of impurities on the surface state of V(001). [76] They reported the first scanning tunneling spectroscopy measurements on V(001). A strong surface state was detected that was very sensitive to the presence of segregated carbon impurities. This surface state energy shifted from 0.03 eV below the Fermi level in clean regions, up to as much as +0.2 eV above the Fermi level in contaminated areas. Because of the negative dispersion of this state, the upward shift could not be described in a simple confinement picture. Rather, Bischoff concluded that the surface state energy was governed by vanadium surface s-d interactions which are altered by carbon coverage. Differences in the tunneling spectrum of metals has been used to provide chemical selectivity for one metal on another. [77,78] Himpsel and coworkers studied the growth of copper stripes on stepped W(110) and Mo(110) surfaces. Contrast between copper and the substrate metal was achieved by resonant tunneling via surface states and image states. These states are characterized independently by inverse photoemission. Image states provide elemental identification via the work function, since their energy is correlated with the local work function. Element-specific surface states produce contrast at higher spatial resolution, but the contrast is smaller than that for image states. [77] Weisendanger and coworkers studied the topography and chemical surface structure of a submonolayer Fe film on a W (110) substrate by combined STM and spectroscopy. [78] Local tunneling spectra revealed a pronounced difference in the electronic structure between nanometer-scale Fe islands of monolayer height and the bare W (110) substrate. In particular, a pronounced empty-state peak at 0.2 eV above the Fermi level was identified for the Fe islands. Based on the pronounced difference in the local tunneling spectra measured above the Fe islands and the W substrate, element specific imaging was achieved. Scanning tunneling spectroscopy has also permitted real-space observation of one-dimensional electronic states on a Fe(100) surface alloyed with Si. [79] These states are localized along chains of Fe atoms in domain boundaries of the Fe(100) c(2x2)Si surface alloy. The calculated spin charge densities illustrate the d-like orbital character of the one-dimensional state and show its relationship to a two-dimensional state existing on the pure Fe(100) surface.

Scanning tunneling spectroscopy can also be used to study small metallic structures on surfaces. Scanning tunneling spectroscopy and microscopy show that the empty states of linear Au clusters supported on a metal surface behave as if they are the states of an electron in an empty one-dimensional box. [80] It was suggested that certain difficulties of this description are removed by a particle-in-a-cylinder model. Their interpretation was supported by density functional calculations. Crommie et al. [81] have studied the local properties of low-dimensional electrons (such as standing wave patterns in the surface local density of states due to the quantum mechanical interference of surface state electrons scattering off of step edges and adsorbates). The authors found that Fe adatoms strongly scatter the surface state and, as a result, are good building blocks for constructing atomic-scale barriers ("quantum
corrals") to confine the surface state electrons. Tunneling spectroscopy performed inside of the corrals reveals discrete resonances, consistent with size quantization. [81]

The potential of spin-polarized scanning tunneling microscopy and spectroscopy (SP-STM/S) was by demonstrated Wiesendanger and coworkers [82,83] on antiferromagnetic and ferromagnetic transition metals and on rare-earth metals. Data measured on the antiferromagnetic Cr(001) surface revealed that screw dislocations cause topology induced spin frustrations leading to the formation of domain walls with a width of about 120 nm. [82] On another antiferromagnetic surface a pseudomorphic monolayer film of chemically identical manganese atoms on W(110), they showed that SP-STM provides the surface magnetic structure with atomic resolution. SP-STS also allows the imaging of the domain structure of self-organized Fe nanostructures which are antiferromagnetically coupled due to dipolar interaction. Using spin-polarized scanning tunneling microscopy in an external magnetic field, the Wiesendanger's group observed magnetic hysteresis on a nm scale in an ultrathin ferromagnetic film. [83] The film was an array of Fe nanowires two atomic layers thick was grown on a stepped W (110) substrate. The microscopic sources of hysteresis in this system (domain wall motion, domain creation, and domain annihilation) were observed with nm spatial resolution. [83] A saturation field stable residual domain was found that measures 6.5 nm by 5 nm. Its stability was ascribed to the consequences of a 360° spin rotation.

In the early days of STM it was noted (first with dismay, but then with excitement) that the image obtained from a semiconductor surface depended significantly on the polarity and magnitude of the applied bias. [6,7,10,12-15] A wonderful example of this is provided by the Si(001) reconstructed surface. Figure 4 shows the constant current image at –2 V bias while B was taken at +2 V sample bias. [8] As will be discussed in detail in subsequent sections, the negative bias image reflects occupied regions of the LDOS while the positive bias image probes unoccupied regions. In the case of this reconstructed surface, two Si atoms form strong and relatively localized double bonds. These pairs of atoms have occupied π and unoccupied π* orbitals near the Fermi surface. All the other occupied states lay deeper than the π and the other unoccupied states lie above the π*. When the bias voltage is near –2 V most of the tunneling is going through the localized π orbital (the max in the LDOS at that bias), and the image is essentially a picture of the π bonding orbitals of the Si-Si dimers (Figure 4A). If the bias is set to +2 volts, most of the tunneling current is carried through the π* like unoccupied portion of the LDOS.

![Figure 4: A) Negative bias, and B) positive bias constant current STM images of the Si(001)-(2x1) reconstructed surface. The cartoons at the bottom depict side views of the surface dimer structure giving rise to filled and empty π and π* type orbitals. Reprinted with permission from reference 8. Copyright 1996 The American Chemical Society.](image-url)
Because there is a node in the spatial distribution of the antibonding dimer wavefunction, the tip must push in close to the surface to maintain constant current. Similarly, the tip can pull back as it moves over the regions where the antibonding wavefunction (and therefore available electron density) is large.

There are several extremely important general messages here. First, the images seen in constant current STM reflect the density of states at the bias energy and tip position \((p_s(r,E))\), and are generally not what one identifies as the ‘structure’. The ‘structure’ is generally derived from scattering experiments in which all the electrons contribute. Second, the STM is actually providing a surface site dependent spectroscopy. In the example above the occupied \(\pi\) states were proved when the bias was near \(-2\) V and the unoccupied \(\pi^*\) were probed with the bias set at \(+2\) V. Moreover, we only ‘saw’ them when the tip was in a region of high electron density for that particular state. Finally, the data in Figure 4 suggests that there should be a way to literally measure the surface state spectra as a function of position.

The first site resolved STM based elastic tunneling spectrum was reported by Hamers, Tromp, and DeMuth [84] and is partially reproduced in Figure 5. I/V and dI/dV curves were taken at fixed sample-tip height at a different points in the 7x7 unit cell. The unit cell contains 12 adatoms and 6 rest atoms (positions indicated by squares and dots in Figure 5). The I/V curves show that the adatom sites contribute significantly to the LDOS near +0.7 volts, while the rest atom sites do not. On the other hand, the occupied states near -1 volt bias are predominantly located on the rest atom sites. Ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPS) are techniques that provide the spatially averaged occupied and empty (respectively) state densities, and these spectral results are shown in the middle portion of Figure 5. Finally, the spatially averaged tunneling spectrum (reported as a normalized intensity \(-\frac{dI}{dV}/(I/V)\)) is presented in the lower third of Figure 5. As stated above, the dI/dV plot is expected to be proportional to the local density of states, and the spatially averaged spectrum should approximate the Figure 5: First atomically resolved tunneling spectrum obtained on Si(111)-(7x7). Conductance as a function of position (a), ultraviolet photoelectron spectrum and inverse photoemission spectrum (b), and area averaged normalized tunneling spectrum of the reconstructed surface. Reprinted with permission from 8. Copyright 1996 the American Chemical Society.
density of states for the entire surface. It is gratifying, therefore, to see that the UPS, IPS, and tunneling spectra are all in close agreement.

ELECTRON TUNNELING SPECTROSCOPY OF ADSORBED MOLECULES

Instead of the quantum mechanical conceptual structure depicted in Figure 1, let us now consider a real tunneling device -- either a metal-insulator-metal (M-I-M) tunnel diode, or a substrate and STM tip. In a real device, there are many electrons and the Pauli principle plays a key role. A simple and useful model for the conduction electrons in a metal assumes that the one begins by removing the valence electrons, then spreads the remaining positive charge into a uniform distribution (jelly) producing a simple constant potential box. Into this box the valence electrons are returned, 2 at a time into each energy level, until the metal is just neutrally charged. The energy of the last electron to go in is the Fermi energy, $E_F$, and the energy required to just remove it from the metal is the work function, $\Phi$. If there are no molecules in the barrier region (tunneling gap), the current is approximately proportional to the voltage difference between the two metals (called the bias) and $\exp(-Ad\sqrt{\Phi})$. This current is said to be due to elastic tunneling since the electron loose no energy to the barrier.

Figure 6: Inelastic tunneling process and associated spectral peaks. $h\nu$ is the molecular energy level spacing, $\phi$ is the barrier height in eV (approximately the metal work function for a symmetrical vacuum barrier), $d$ is the barrier width in Angstroms, $I$ is the tunneling current, and $V$ is the applied bias voltage. The reader is encouraged to consult references 5 and 27 for a detailed description of this diagram and its interpretation. Reprinted with permission from reference 85. Copyright (2005) the Journal of Chemical Education.

If the gap (barrier) between the electrodes is not a vacuum, equation 1 must be modified in several ways. The simplest effect is a reduction in the effective barrier height. For an insulator or semiconductor, it may only require a volt or two of energy above $E_F$ for the electron to reach the conduction band in the barrier, while the work function may be 4 to 6 volts. In these cases, the work function in equation 1 is replaced by barrier height, $\Phi_b$, where $\Phi_b$ is approximately the difference in energy between the bottom of the conduction band (in the insulator) and the Fermi energy in the electrodes at zero applied bias. If individual molecules are present in the barrier, several new interaction mechanisms can affect the tunneling current. The best known of these is inelastic electron tunneling and is the basis for inelastic electron tunneling spectroscopy (IETS). [4-7] In IETS the moving electronic charge interacts with the time varying molecular dipoles (electronic or vibrational) to induce excitation of the molecule in the barrier with concomitant loss of energy by the electron. This process is similar to a Raman photon process. Consider a vibrational motion with frequency $\nu$ and energy spacing $h\nu$. This is shown in Figure 6 as an excitation from the ground vibrational state to the first excited vibrational state with a corresponding loss of energy by the tunneling electron. If the applied voltage is less than $h\nu/e$, the inelastic channel is closed because the final states for the tunneling electron, the electronic levels in the metal electrode of the appropriate
energy, are already filled. At $V=\hbar\nu/e$ the inelastic channel opens. Further increases in $V$ result in additional possible final states with an associated increase in current due to this channel. As is depicted in Figure 6, this opening of an inelastic conductance channel results in a break in the $I(V)$ curve at $V=\hbar\nu/e$. Note that the size of the break is exaggerated. In the conductance, $dI/dV$, the opening of the inelastic channel is signaled by a step -- typically 0.1% of the tunneling electrons utilize a vibrational inelastic channel and 5% utilize electronic inelastic channels. To obtain an IETS spectrum we can plot $d^2I/dV^2$ versus $V$ and expect to see peaks whenever the energy difference between the ground and excited state (electronic or vibrational) just matches the applied bias voltage. The width of IETS bands depends upon the sharpness of the thermal distribution of electron energies. Thus, the IETS line width (full width at half height) is $5.4kT$ ($3.5T$ cm$^{-1}$ or about 0.5T mV, where $T$ is in Kelvin) [86] and vibrational IETS is most often performed below 10 K. As the bias voltage, $V_{bias}$ or $V_b$, increases (in either sign!) higher vibrational excitation (as seen in Figure 7) or even inelastic electronic excitation can occur. As shown in Figure 7 for a tunnel diode containing a sub-monolayer of VOPc, both electronic and vibrational inelastic transition can be seen. [87] It is important to note that IETS bands appear at the same bias magnitude independent of sign, although the intensities may differ. [5-7] This is a diagnostic feature for non-resonant IETS. For many electronic transitions, the intensity and band width are orders of magnitude greater than for vibrational IETS and cooling to 100 K, or even greater temperatures, is sufficient.

**Figure 7:** Schematic diagram of inelastic and resonant elastic tunneling processes (left). Tunneling spectroscopy data obtained from an Al-Al$_2$O$_3$-VOPc-Pb tunnel junction at 4K with 10 mV rms modulation (VOPc is vanadyl phthalocyanine). Vertical lines guide the eye to the inelastic excitations which occur in both bias directions. The OMTS band associated with transient reduction of the Pc ring, on the other hand, appears only on the Pb+ bias side. Reproduced by permission from reference 87. Copyright (2000) the American Chemical Society.

In its simplest form, an IET spectrum is a plot of $d^2I/dV^2$ versus $V$. It turns out that using $d^2I/dV^2/(dI/dV)$ as the $y$ axis provides spectra having flatter baselines and is most appropriate for high bias work. [6,7,88-90] These are called normalized tunneling intensities (NTI) or constant modulation spectroscopy. Simple tunneling spectra are measured by applying both a variable bias, $V$, and a small modulation component, $V_f$, at frequency, $f$. A lock-in amplifier is used to detect the $2f$ signal which is proportional to $d^2I/dV^2$. The instrumentation required for obtaining normalized intensities, NTI, is a bit more complex. [88-90] In general, the bias voltage may be converted to the more conventional
wavenumbers through the factor of 8066 cm\(^{-1}\)/volt. The amplitude of the modulation affects both the observed signal strength and resolution. The signal increases as \(V_f^2\) but the experimental line width is proportional to \(V_f\). \([5,7,86]\)

Until about 1988 essentially all of tunneling spectroscopy was carried out in tunnel diodes and almost all of it was IETS. In 1989 Hipps and Mazur began observing strange vibrational line shapes and huge new signals that were as big or greater in intensity than electronic IETS but that could not be explained by a simple molecular excitation process. \([91]\) These new transitions produce peaks in \(dI/dV\) (rather than \(d^2I/dV^2\)) and are due to direct tunneling via either unoccupied or occupied molecular orbitals. The very intense but weirdly shaped band seen only in positive bias (near +0.3 volts) in Figure 7 is an example of one of these bands. These transitions are due to what is (approximately) an elastic tunneling mechanism in that the energy of the tunneling electron that causes the excitation as the absolute energy (not an energy difference) of a molecular state. The temperature dependence of a delta function line is only 3.5kT (0.3T mV) and amounts to 90 mV at 300K. In fact, the OMT bands are usually not temperature dependent until well in excess of 500 K. This is due to the large intrinsic width of OMT bands (usually more than 0.25 V).

The exact mechanism of the OMT process can vary from case to case. It might be true resonance tunneling where the effective residence time of the tunneling electron on the molecule is negligible compared to nuclear motion. It might be a real oxidation or reduction of the molecule followed by thermally induced return to the original charge state (electron hopping), or it might be a redox that occurs too rapidly for thermal relaxation, such as in ultra-violet photoelectron spectroscopy (UPS) or inverse photoemission spectroscopy (IPS). Because there are a number of different physical processes that can give rise to these bands, the spectroscopy associated with measuring these transitions is called orbital mediated tunneling spectroscopy (OMTS). \([92-94]\) Because the time scales are usually unknown, we often refer to transient redox processes. The technique might equally well be called ionization and affinity level spectroscopy. Ionization spectroscopy is the measurement of the energy required to remove electrons from a filled (or partially filled) orbital. Affinity level spectroscopy measures the energy
released when an electron is captured by an atom or molecule. Since there are generally several vacant orbitals that may be occupied, there is a spectrum of affinity levels associated with the addition of a single electron.

A qualitative understanding of OMTS may be obtained with reference to Figure 8. When the sample is biased positively ($V_{bias} > 0$) with respect to the tip, and assuming that the molecular potential is essentially that of the substrate [95], only the normal elastic current flows at low bias ($\leq 1.0$ V). As the bias increases electrons at the Fermi surface of the tip approach, and eventually surpass, the absolute energy of an unoccupied molecular orbital (the LUMO at +1.7 V). OMT through the LUMO at $\Phi - 1.7$ V below the vacuum level produces a peak in $dI/dV$ seen in the actual STM based OMTS data for cobalt(II) tetraphenylporphyrin (CoTPP). If the bias is increased further, higher unoccupied orbitals produce additional peaks in the OMTS. Thus, the positive sample bias portion of the OMTS is associated with electron affinity levels (transient reductions). In reverse (opposite) bias as in the lower part of Figure 8, the LUMO never comes into resonance with the Fermi energy and no peak due to unoccupied orbitals is seen. However, occupied orbitals are probed in reverse bias. In the CoTPP case, there are two occupied orbitals near the Fermi Energy. The half filled $d_{x^2}$ orbital lies only -0.1 volts below the Fermi energy while the highest occupied porpyrin ring orbital is found at -1.20 V bias. The fully occupied ring MO, therefore, is located at $\Phi + 1.20$ V below the vacuum level and produces a peak in $dI/dV$ at -1.20 V sample bias. [96,97] It is also clear from the figure that there are other occupied MOs, with one near -1.2 V giving a well-defined shoulder.

Note that peaks are observed in $dI/dV$ (and not I). This is because once current starts to flow through orbital mediated channels, increasing bias doesn't turn it off. On the other hand, the probability of tunneling is greatest for electrons near the Fermi surface; so, as the Fermi surface passes the appropriate orbitals, $dI/dV$ is maximized. Another way of seeing this is through differentiation of equation 2. This derivative is given to good approximation by the formula for $dI/dV$ shown in Figure 8. Note that the density of states of the tip contributes equally with that of the sample. Thus, any contamination (including surface molecules picked up during scanning) of the tip will lead to contributions in the OMTS. It is very important, therefore, to ensure that the tip and substrate density of states peaks are not confused with those of the adsorbate. Figure 9 provides an example of how the tip and substrate density of states contribute to the overall OMTS in the case of two different tetraphenylporphyrin complexes. In the case of the data presented in Figure 9, the surface coverage was about 0.7 of a monolayer and regions of clean gold separated well defined islands of either CoTPP or NiTPP. [96,97] By alternately acquiring

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**Figure 9:** Elastic tunneling spectra of a Au substrate, CoTPP on Au, and of NiTPP on Au taken with a clean tungsten tip in UHV at room temperature. The orbital mediated tunneling peaks obtained from the metalorganic adlayers are clearly distinguished from the contributions of tip (W) and substrate (Au). Data obtained by K.W. Hips, D. E. Barlow, L. Scudieo, and U. Mazur during the study reported in references [96,97].
spectra over the molecular islands and the clean substrate regions, it is possible to precisely identify the OMTS of the adsorbate.

PRACTICAL CONSIDERATIONS RELATING TO STM-IETS AND STM-OMTS

The first molecular excitations seen in the STM were vibrational IET bands,[98-100] followed closely by OMT spectra. [87,96,101] One might think that vibrational IETS in the STM should be the holy grail of surface analysis. It offers the exquisite selectivity of vibrational spectroscopy combined with the possibility of sub-molecular spatial resolution. However, in actual practice, it has proven to be less valuable than expected.

Consider, for example, the STM based IETS obtained from C\textsubscript{60} on Ag(110) at 4.5 K by Pascual and co workers (Figure 10). [102] This is an interesting case because both the tunnel junction and STM based IETS are available. Pascual's data are as clean as any STM-IETS reported, and his paper provides the STM-OMTS as well as the STM-IETS. Thus, he could correlated the active vibration with the change in geometry induced by the electronic excitation. As in tunnel diode IETS, one expects that inelastic transitions should appear symmetrically in either bias direction. This is observed. The number and intensity of bands, is not as expected from junction based IETS.

C\textsubscript{60} has 176 possible vibrational eigenvalues, but the high symmetry and associated degeneracy reduce the number of unique frequencies to 46. These modes have one, three, four and five fold degeneracy. Four of these modes (the F\textsubscript{1u}) are IR active, and 10 are Raman active (2A\textsubscript{g} + 8H\textsubscript{g}). While conventional M-I-M spin-doped tunnel junctions provided only 24 of the 46 modes, these were only partially overlapped the 24 modes seen in inelastic neutron scattering and the 4 IR and 10 Raman modes.

\textbf{Figure 10:} Comparison of consecutive STM-IETS obtained from two neighboring C\textsubscript{60} molecules adsorbed on Ag(110). The dashed spectra were taken over bare silver. The normalized intensity for the 54 mV peaks in spectrum a is about 9%. Setpoint (I=1.6 nA, V=0.5 V), modulation = 5 mV, temperature = 4.5 K, modulation frequency = 341 Hz. Reprinted with permission from reference 102. Copyright 2002 American Institute of Physics.
Thus, all but 9 of the 46 fundamental bands could be assigned through a combination of all four data sets. Very recently, Nolen and Ruggiero have used an interesting composite barrier design to make tunnel junctions that provided IETS wherein 26 of the silent modes of $C_{60}$ were identified. [104] Thus, all but 6 of the 46 fundamentals have been directly observed through the concerted use of IR, Raman, INS, and M-I-M based IETS. In the tunnel junction IETS, more than 14 vibrational bands are observed in the same region (0 to 100 mV) where only one is clearly seen in STM-IETS (Figure 10). Moreover, the one band seen in Figure 10a is about 100 times the intensity of the bands observed in tunnel junction experiments [102-104].

Observing vibrational IETS in an STM is experimentally demanding and interpretation of the data is challenging. The 5kT line width associated with IETS bands requires that STM-IETS experiments be performed at cryogenic temperature (usually near or below 10 K) and in ultra-high vacuum (UHV). The signals are generally weak and require extremely stable instruments. [98-100,102,105] Unlike M-I-M diode IETS where data is easily correlated with IR and Raman peak positions and line shapes, [5,6,7] surprisingly few vibrational modes are seen in STM-IETS and their line shapes are generally not easy to predict. [99,105,106,107] The STM-IETS bands are often derivatives or even inverted relative to diode-IETS bands. This behavior is reminiscent of the vibrational peaks seen in diode-IETS when there are OMT bands near the vibrational bands. [108] It is very likely that a resonance mechanism is essential for producing sufficient vibrational IETS intensity in the STM environment. [102,106] While M-I-M diode spectroscopist has long taken advantage of the 'finger print' bands familiar to the IR chemical analyst, they are not accessible in STM-IETS because the resolution required (~0.5 mV) is beyond the current sensitivity limit for STM-IETS.

STM-OMTS can be performed at room temperature and most commercial UHV scanning tunneling microscopes have sufficient mechanical and electronic stability to allow spectra to be acquired. Moreover, the location and nature of bands observed can be easily interpreted in terms of the electronic orbitals (both occupied and unoccupied) of the molecular system of interest. This latter strength is also its weakness, since molecular systems having large band gaps (> 5 eV) have OMTS bands that can only be observed at very large applied voltages. At large bias voltage the elastic tunneling current and the potential for current induced instabilities in the tip and substrate can effectively mask the OMTS. Fortunately, a very large percentage of all molecules have either occupied or unoccupied states within a few volts of the Fermi energy of a typical metal substrate, and many have both occupied and unoccupied states within this range. The large background elastic currents at high bias can be reduced in significance by reporting the normalized OMTS, $\frac{dI}{dV} / \frac{I}{V}$ (vide infra), thereby canceling out much of the exponential dependence of $T(E, eV, r)$ on $V$. We will place our primary focus on STM-OMTS in the examples that follow.

### STM Based Orbital Mediated Tunneling Spectra and Electrochemistry

One view of the OMT process is that the molecule, M, is reduced, M-, or oxidized, M+, during the tunneling process. [92,93,96,101,109-112,115] In this picture a fully relaxed ion is formed in the barrier. The absorption of a phonon (the creation of a vibrational excitation) then induces the ion to decay back to the neutral molecule with emission of the electron -- which then completes tunneling through the barrier. For simplicity, the reduction case will be discussed in detail; but, the oxidation arguments are similar. A transition of the type $M + e^- \rightarrow M^-$ is conventionally described as formation of an electron affinity level. The most commonly used measure of condensed phase electron affinity is the half-wave reduction potential measured in non-aqueous solvents, $E_{1/2}$. Often these values are tabulated relative to the saturated calomel electrode (sce). In order to correlate OMTS data with electrochemical potentials, we need them referenced to an electron in the vacuum state. That is, we need the potential for the half reaction

$$M(\text{solution}) + e^- (\text{vac}) \rightarrow M^-(\text{solution})$$
These values can be closely approximated from those referenced to sce by adding 4.70 V to $E_{1/2}(\text{sce})$. [111-114] That is, $E_{1/2}(\text{vacuum}) = E_{1/2}(\text{sce})+ 4.71\, \text{V}$. This connection between solution phase electrochemical potentials and vacuum level based spectroscopic values such as OMTS and UPS is extremely useful but the derivation is rather complex. For example, the difference in electron affinity in the gas phase and in solution is primarily due to solvation stabilizing the reduced form. The reader wishing to better understand its origins is encouraged to consult references 113 and 114. The various energy conventions are depicted in Figure 11, where the connection between OMTS bands and electron affinities is made within the context of the model. This diagram is based on one presented by Loutfy et al. [113] and expanded to OMTS by Mazur and Hipps. [7,92,93,96,101,115-118] By using the measured value of $E_F$ (from UPS), the OMTS bands can be located both relative to the vacuum level and also to electrochemical potentials. The details of the procedure for locating the vacuum level will be presented in a later section.

*Figure 11:* Electrochemical energy level model for orbital mediated tunneling. $A_g$ and $A_c$ are the gas and crystalline phase electron affinities. $E_{1/2}(\text{sce})$ is the electrochemical potential referenced to the saturated calomel electrode, and provides the solution phase electron affinity. $E_F$ is the Fermi level of the substrate (Au here). The corresponding positions in the OMT spectrum are shown by $\Delta_r$ and $\Delta_o$ and correspond to the electron affinity and ionization potential of the adsorbate film modified by interaction with the supporting metal, $A_c$. The spectrum is that of nickel(II) tetraphenylporphyrin on Au (111). Reprinted with permission from reference 85. Copyright (2005) the Journal of Chemical Education.

Because the dielectric constant of most organic solids is less than for common solvents, redox potentials in the solid state are expected to differ from those in solution as shown (qualitatively) in Figure 11. [113] There will also be shifts associated with intermolecular interaction that are very difficult to predict and that vary considerably in different types of molecules that are not depicted. Moreover, there will be shifts in the potentials of a thin film relative to that of a solid due to interactions with the metal support and counter electrode, including image charge effects. These all tend to stabilize ion formation. Thus, they are act to return the ionization and reduction potentials for the species adsorbed on a metal surface to those for the species in solution, as shown in Figure 11. There also may be an opposite signed shift due to the absence of a covering layer of solvent or adsorbed molecules in the case of a monolayer (or less) in UHV. [116] Another complication is the fact that electrochemical potentials are equilibrium values and therefore reflect the energy associated with the formation of an ion in its equilibrium state. OMTS transitions, as discussed in the next section, may occur so rapidly that the ion is formed in an excited state -- a vertical transition in the Frank-Condon sense. For a wide range of materials and film thickness (sub-monolayer to about 0.5 nm) studied to date, a fortuitous cancellation of
polarization terms and differences between vertical and equilibrium affinities has resulted in many OMTS bands laying close to the positions predicted from electrochemistry (see Figure 12). This correlation is especially good for unoccupied orbitals. Unfortunately, OMTS bands associated with occupied orbitals generally lay deeper than predicted by solution phase electrochemical oxidation potentials. The transferability of electrochemical values to thin film band positions for affinity levels but not ionization levels indicates that the polarization energy terms differ for these processes. This is a failure in the simple model used to generate Figure 11, where it was assumed that only the sign of the polarization energy changed. [101] This failure is particularly large for porphyrins. Given the trends in stabilization of ion energies by the surrounding molecules and image charges induced in the metal substrate, we would expect the ionization potential of thin film NiOEP to be about 0.5 to 1.0 eV less than for the gas phase. Instead, the ionization energies measured from a thin film are nearly identical to those reported from the gas phase. [101,119] As we shall see in the next section, these discrepancies are also consistent with UPS observations, suggesting that the problem is in the model, not the technique.

**Figure 12:** Correlation between electrochemical potentials and OMTS bands for more than 10 compounds including polyacenes, phthalocyanines, and porphyrins. OMTS data were acquired both from tunnel junctions and STM measurements and individual points have been reported in references 92-94,96,101,115,117,118. The potential on the left is that associated with the half reaction \( \text{M(solute)} + e^-(\text{vac}) \rightarrow \text{M}^+(\text{solute}) \).

Molecular models of a metal tetraphenylporphyrin (MTPP) and of a metal phthalocyanine (MPC). Metal ions are in the +2 oxidation state while the rings are in the -2 state. Ball and stick models based on the solid state crystal structures of the nickel(II) complexes.
While the first electrochemical reduction potential provides an estimate for $A_c$ (assuming it is a reversible non-reaction process), the second and higher reduction potentials do not provide the spectrum of single electron affinity levels. Rather, they provide information about 2-electron, 3-electron, and higher electron reduction processes and, therefore, depend on electron pairing energy. Thus, the utility of solution phase reduction potentials for estimating solid state affinity levels is limited to the lowest affinity level. The same argument applies to oxidation potentials beyond the first. OMTS, on the other hand, probes the single electron reduction energies for the spectrum of states of the negative ion, and the single electron ionization energies for the spectrum of states of the positive ion. Thus, OMTS can be used to determine ionization spectra and affinity levels beyond the first transitions of each type. [7,115]

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**Figure 13:** Schematic of significant parameters in the UPS of a clean metal (left) and a molecular coating on a metal (right). The work function of the metal is given by $\Phi_m$ and can be calculated from the relationship $h\nu = W_m + \Phi_m$, where $W_m$ is the width of the photoelectron spectrum in eV. Ionization energies of the highest occupied and second highest occupied molecular orbitals relative to the vacuum level are given by $\varepsilon_{HOMO}$ and $\varepsilon_{SOMO}$. The corresponding quantities measured relative to the Fermi level are given with a superscript F. $\Delta$ is a measure of the interface dipole moment and is shown in the case where it has a negative sign. $E_{F}^m$ and $E_{vac}^m$ are the energies of the Fermi and vacuum levels of the clean metal substrate, respectively. $E_{vac}$ is the vacuum level energy over the adsorbate covered metal surface. Note that these are cartoons. In real cases, one sometimes sees the Fermi edge of the metal superimposed on that of the adlayer (high KE end of the spectrum). Reprinted with permission from reference 85. Copyright (2005) the Journal of Chemical Education.

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**STM Based OMTS and Ultraviolet Photoemission Spectroscopy**

An alternative mechanism for OMTS is one in which the electron residence time is long enough to cause electronic excitation of the molecule, but not so long as to allow vibrational relaxation to occur. Thus, the electron capture or emission is a vertical process in the Frank-Condon sense. For the reverse bias region of the OMTS, this is essentially the condition for ultraviolet photoemission. In general, ultraviolet photoemission spectroscopy (UPS) is described by the following expression:

$$M_0 + h\nu \rightarrow M_j^+ + e^-$$

The ionization energy to produce state $j$ of the positive ion, $M^+$, is expressed by: $\varepsilon_j^F = h\nu - KE_j$. Where $\varepsilon_j^F$ is the ionization energy measured relative to the Fermi Energy ($E_F$), KE is the kinetic energy of the ejected photoelectron, and $h\nu$ is the energy of the photon. KE and $\gamma$ are the directly measured quantities. $M_0$ is the ground state molecule of interest and $M_j^+$ is the ionized molecule in its $j^{th}$ excited electronic and vibrational state reflecting a vertical Frank-Condon transition.

To acquire an UPS spectrum, one irradiates the sample with UV light causing electrons to be ejected from the higher bands. The kinetic energy of these ejected electrons is then measured. UPS is an extremely surface sensitive tool, probing only about 1 nm into the surface of the sample. Because of the
photoionization cross section differences at the relatively low energies typically used for UPS, the technique is much more sensitive to p-type valence orbitals than d-type. Thus, valence shell UPS is the technique of choice for studying the highest energy π orbitals of a molecular system. Figure 13 shows schematic band diagrams for a metal, and for a molecular film coated on a metal, that illustrates the important energetic parameters derivable from UPS data. [117,120-122] The energy of the vacuum level over the molecular coating relative to that of the clean metal is given by the quantity Δ (shown for the case where Δ is a negative quantity: This is NOT Δ or Δ). The work function of the clean metal is given by Φ, and can be calculated from the relationship hν = Wm + Φ, where Wm is the width of the photoelectron spectrum of the clean metal expressed in eV. In order to compare ionization energies to other quantities, one needs the ionization energy of an occupied orbital relative to the vacuum level. This is given by:

\[ ε_j = ε_j^F + Φ + Δ \]  

where \( ε_j \) is the energy of the \( j^{th} \) occupied state relative to the vacuum level and \( ε_j^F \) is the energy of the \( j^{th} \) occupied state relative to the Fermi level of the metal contact.

\[ \text{Figure 14: Constant current STM image, OMTS, and UPS of a monolayer of nickel(II) octaethylporphyrine (NiOEP) on Au(111). The absolute energy scale was derived by taking } \Phi = 5.20 \text{ V and } Δ = -0.2 \text{ V. The STM image was acquired at a sample bias of -0.6 V and a setpoint voltage of 0.30 nA. The STM image is reprinted with permission from reference 101. Copyright (2002) American Chemical Society.} \]

Both the UPS and the STM-OMTS obtained from a nickel(II) octaethylporphyrin film on Au(111) are depicted in Figure 14. The UPS sample was about 1 monolayer (~10^{12} molecules) while the STM-OMTS was taken from a single molecule. In order to place both spectra on the same scale, one correction and one assumption was required. The assumption was that the potential at the molecule was essentially the same potential as the substrate (gold electrode). We will address this assumption in more detail later. The correction required first that the vacuum level over the NiOEP film on gold be correctly located. This was done using equation 3, above, where \( Φ_m \) and Δ were obtained form clean gold and NiOEP covered gold spectra. The OMTS band energies were also referenced to the vacuum level through the measured work function. The vacuum level referenced OMTS energy, \( ε_{\text{OMTS}} \), is then calculated from the bias voltage of the transition peak, \( V_{\text{peak}} \), using equation 4:

\[ ε_{\text{OMTS}} = -eV_{\text{peak}} + Φ + Δ \]
The values of $\Phi_m$ and $\Delta$ were the same as used for the UPS spectrum. The derived values of energy relative to the vacuum level are shown in the right panel of Figure 14 as the top scale.

In some cases the UPS spectrum is taken with the adsorbate on a different crystal face or metal than is used for the OMTS. In these cases caution is required. Different values of $\Phi_m$ must be used to for UPS and OMTS and the values of $\Delta$ may also vary.

Thus, it is possible to make a direct comparison of occupied orbital energies as derived from UPS and those observed by OMTS. We have made these measurements for a number of phthalocyanines and porphyrins [85, 96, 101, 118] and find good agreement between the UPS positions of the occupied $\pi$ type orbitals and the band positions seen in OMTS. In cases where there are occupied d orbitals near the Fermi surface, the OMTS spectrum is richer than that of the UPS. Because of the difference in cross section for electron emission by tunneling and electron ejection by photon absorption, d type orbitals are seen with much greater intensity in OMTS than in UPS. For example, the UPS spectra of nickel(II) tetraphenylporphyrine (NiTPP) and cobalt(II) tetraphenylporphyrine (CoTPP) near $E_F$ are almost the same, but the STM-OMTS of CoTPP has a well defined band due to the partially occupied d$_z^2$ orbital that is absent in the OMTS of NiTPP (see Figure 9). [96]

Because of the relatively relaxed selection rules associated with near resonant elastic electron scattering, OMTS provides more information about occupied orbitals near $E_F$ than does UPS. But OMTS offers much more than that. The ability to observe unoccupied orbitals (affinity levels) gives OMTS the capabilities normally associated with inverse photoemission without the problems created when organic molecules are subjected to the intense electron beams essential to the inverse photoemission (IPS) process. The practical resolution of IPS when studying organic adlayers is generally of the order of 0.5 volts [123]. OMTS, on the other hand, has significantly greater resolution capabilities. Even at room temperature, an instrumental resolution of less than 0.1 volts is easily obtained. By cooling the sample to 100 K, the resolution can be improved below 0.03 volts (240 cm$^{-1}$). While this has little effect on the overall band intensity (as discussed above), it does provide sufficient resolving power to make possible the observation of vibronic structuring on the OMTS bands.

Figure 15: Schematic potential energy surfaces for a parent molecule, M, and its most stable positive ion, M$^+$. 
In the previous section we stated that the agreement between occupied orbital positions as predicted by oxidation potentials did not compare well with the OMTS band positions for the ring oxidations of metal porphyrins. Armstrong and co-workers have also noticed this difficulty in reconciling solution phase oxidation potentials with thin film UPS data. [97,124] Rather than using the simple formula that results from Figure 11, \( I_1 = 4.71 \text{ eV} + E_{\text{OX}}^{\text{cse}} \frac{1}{2} \), they find that multiplication of the oxidation potential by a factor of about 1.7 is necessary to bring UPS HOMO peaks and solution phase electrochemical first oxidation potentials into agreement. The close agreement between UPS and OMTS positions, and the disagreement with electrochemical predictions, suggests that the OMT process is a vertical process in the Frank-Condon sense. As shown in Figure 15, the center of the UPS band is the vertical transition labeled \( \Delta E_p \). The width of the band arises from vibrational (molecular and lattice) vibrations associated with the change in geometry inherent in the \( M \rightarrow M^+ \) transition. The electrochemical potential, on the other hand, is given by \( \Delta E_0 \). The larger the difference in geometry between the parent and the ion, the greater the difference between \( \Delta E_0 \) and \( \Delta E_p \). If the OMTS in the porphyrins case is a vertical excitation process then the OMTS energy should agree well with that from UPS. Based on our results, it would appear that the two processes are very similar. This conclusion should be drawn with care. First the band widths seen in both UPS and OMTS of thin films are of the order of 0.5 eV, or 4000 cm\(^{-1}\). Since a typical C-C stretch or C-H bend is less than half this value there could be some significant vibronic differences in the transition types that are hidden within the room temperature peak shapes. Low temperature measurements are essential in resolving this issue. The second caution is that each molecular type will interact in a complex way with the tunneling environment. There is no single mechanism that describes OMTS for all molecules.

Why, one might ask, is it only the porphyrins that show the large disparity? One likely answer within the context of Figure 15 is that the porphyrin ring is smaller and less rigid than that of the phthalocyanine. Moreover, all of the porphyrins studied have peripheral substituents that are subject to low frequency vibrational modes. Thus, one would expect a larger geometry change upon removing an electron from a porphyrin relative to a phthalocyanine. A larger geometry change translates into a greater difference between \( \Delta E_0 \) and \( \Delta E_p \). If this argument is accepted, one must then ask why the other OMTS bands of the porphyrins agree with the electrochemical model. The answer here is more complex and ultimately will require detailed quantum mechanical calculations. Consider the cobalt ion. The molecular geometry change most likely to play a role is the change in force constant between cobalt and nitrogen -- not a change in position since the entire.

Figure 16: STM-OMTS spectra of four compounds on Au(111) at room temperature. Zero bias ~ 5 eV. Reprinted with permission from reference 85. Copyright (2005) American Chemical Society.
ring tends to restrict the possibilities. A force constant change with no change in equilibrium geometry leads to no difference in $\Delta E_0$ and $\Delta E_p$.

Tsiper, Soos, Gao, and Kahn have performed STM-OMTS, UPS, and IPS measurements of PTCDA (perylene-tetracarboxylic acid dianhydride) films as a function of thickness. [125] They also find good agreement between the three techniques. In this context it is interesting to note that PTCDA is a large rigid planar molecule and that the first ionization and affinity levels involve electrons delocalized over much of the molecule.

OMTS as a Chemical Analysis Tool: direct spectral characterization

Based upon its ability to determine the location of HOMOs and LUMOs, OMTS offers at least as much chemical selectivity as does electrochemistry. The limiting factor in the selectivity of OMTS is the thermal line width -- of the order of 3 kT or about 0.09 eV at room temperature. Because typical UV-Vis bands observed in molecular species are of the order of 0.25 eV, the thermal broadening is not significant until about 700 $^\circ$C. Thus the selectivity of OMTS is better than or of the order of that afforded by UV-Vis spectra. To quantify these ideas, consider Figure 16.

The room temperature STM-OMTS obtained from single molecules of four chemically similar species are shown in Figure 16. All have a central +2 transition metal ion, all have four coordinating nitrogens, and all have large $\pi$ systems. Nevertheless, each is clearly distinguishable from the others by its OMTS spectrum in a 4 eV window centered about the Fermi energy of gold (the substrate used). In the cases where the $\pi$ systems are different, the positions of the $\pi$ HOMO and LUMO distinguish the compounds. For those complexes having the same ligand but different metals, the metal d orbital occupancy provides clear selectivity.

What about other types of molecules? Are the porphyrin and phthalocyanine cases really representative, or do they constitute some kind of special (best) case? To answer that question we have prepared Table I. Table I is a selection of electrochemical potentials for the first reduction or oxidation of a wide range of molecules. Polyacenes, hetero-organics, metalorganics, and transition metal complex inorganics all appear on the list. We have then used the correlation between first reduction and oxidation potentials discussed in a previous section, and exemplified in Figure 12, to estimate the position of the corresponding first ionization and affinity levels in OMTS. We used the formula,

$$E_{\text{OMTS}} \approx E_{1/2(\text{sce})} + 4.71 \, \text{V}$$

to produce the values in the far right column of Table I. Note first that these values span a range of about 5 volts and that including second ionizations and or affinity levels would expand this range even farther. Thus, even with a line width (determined by the intrinsic width) of 0.25 volts, there is enough spread in values to make identification from even a single ionization or affinity level possible in a suitable mixture of molecular species. When one takes the pair of energies formed by the first ionization and affinity levels, it is clear that almost any pair of molecular species can be identified at a particular site on a surface using STM based OMTS. In fact, the situation here is nearly ideal for the analytical chemist wishing to identify individual molecules on a surface even if there are a large number of components. This is NOT like conventional spectroscopic analysis of mixtures where the individual spectra must be sufficiently unique to allow their presence to be identified in the complex spectrum that results from a multicomponent mixture. Because STM-OMTS provides the spectra of one molecule at a time, it is only necessary to match that pure spectrum to that of the suspected component. Thus, not only is the sensitivity of STM-OMTS exceptional (one molecule at a time) its selectivity is also significantly better than conventional UV-Vis absorption and fluorescence techniques.

Another interesting issue to the analyst, is the range of energies that can be measured in any one experiment. At very high (positive or negative) bias, field emission will occur and OMTS will no longer be available in the current-voltage curve. If we take this range (some what arbitrarily) as $\pm 2$ volts, we will have a 4 volt span over which to measure spectral bands of interest. The central location of that span
will be determined by the Fermi energy of the substrate-adsorbate system. For gold, values near 5 eV are expected so one has a 3 to 7 volt ‘window’ for spectral observation. If silver is used instead, the window is shifted up by about 0.5 volts, while choosing a platinum substrate shifts the window down by about 0.4 volts. This assumes, of course, that the adsorption mechanism is physisorption. By judicious choice of substrate(s), the entire range of affinity and ionization levels shown in Table I is accessible by STM-OMTS. In fact, OMTS transitions beyond the 2-7 volt range are accessible.

In this section we have assumed that the potential at the molecule is essentially that of the substrate. One can (and should) question the validity of this assumption. [95,109,112,126-133] Consider, for example, the case of STM based spectroscopy of quantum dots. [132] Bakkers and coworkers found that by varying the tip–dot distance they could change the relative rate of tunneling into, versus tunneling out of, the dot. If the tip is retracted relatively far from the dot, tunneling into the dot was much slower than tunneling out of the dot resulting in single electrons tunnel through the dot. This is similar to OMTS where the resonances in the conductance spectrum corresponded to the single-particle energy levels of the CdSe quantum dot. When the tip was brought closer to the dot, tunneling into the dot became as fast as tunneling out of it. In this regime they found that up to three (extra) electrons could be present in the particle. The resulting electron–electron Coulomb interactions lead to a much more complex conductance spectrum. This is Coulomb blockade behavior. In order to see this, Bakkers et al had to electronically isolate the nanoparticle from the substrate by using a self-assembled monolayer (SAM) as a spacer. Katz and coworkers performed a similar experiment with InAs nanocrystals. [133] While they were never able to enter the Coulomb blockade regime, they did see the positions of the resonant tunneling bands shift with dot-tip distance. They attributed this change as due to the local potential at the dot being intermediate between that of the substrate and tip, with the SAM and tip-dot gaps acting as two parts of a voltage divider. As the size of adsorbed molecules increases, especially in cases like proteins which have an electroactive portion buried inside a relatively electronically inert sheath, the molecule might become indistinguishable from a small quantum dot. In this case one would expect that the potential at which oxidation or reduction occurred would begin to depend on tip-molecule separation and not be simply related to spectroscopic or electrochemical values. Lindsey and coworkers attempted to measure experimentally the ratio of the local potential (at a molecule experiencing OMTS) to the applied potential (between tip and substrate) in the case of porphyrins, but were unable to demonstrate a significant dependence. [112]

Deng and Hipps set out to test the tip-molecule dependence of the OMTS in the case of nickel(II) tetraphenylporphyrin (NiTPP) adsorbed on Au(111) under UHV conditions. [95] Adjusting the set-point prior to spectral measurement allowed for the control of the tip-sample distance. A sequence of dI/dV(V), I(V), and I(z) curves were acquired over a wide range of setpoint currents and bias voltages. The I(z) data was measured to provide a means of converting set-point values to relative tip displacements. Determining the peak positions and peak shapes from the dI/dV curves was difficult because of the strong variation in both the resonant and elastic (background) intensities with tip-sample separation. Stroscio and Feenstra [134-136] considered this problem several years ago and determined that this difficulty could often be eliminated by using the logarithmic derivative, dlnI/dlnV(V), as the spectral intensity function. Ukrainstev discussed some problems with this method [137], but they were not relevant in the NiTPP case. The results obtained by Deng and Hipps are presented in Figure 17.

Deng and Hipps found that changes in tip-sample distance over several Angstroms and a factor of 20 in set-point current produce no measurable changes in orbital energy splitting. [95] This means that ionization and affinity level spectra obtained by STM-OMTS for molecules of the order of the size of porphyrins can be used reliably. It was suggested that it may be possible to reliably measure STM-OMTS on molecules larger than tetraphenylporphyrin without concern about the tip-molecule separation distance provided that the effective gap impedance (between electroactive moiety in the molecule and the substrate) does not drop below about 500 MΩ. An unexpected result of this study was the small but persistent shift of all OMTS bands to energies deeper than the vacuum level. In the case of NiTPPP, this shift is of the order of 50 mV and may be associated with the electronic and structural properties of NiTPP rather than some universal phenomena.
Table I: Energy estimate for LUMO and HOMO OMTS energies (relative to the vacuum level) based on electrochemical potentials.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E_{1/2}^{\circ}$ (sce)</th>
<th>$E_{OMTS}$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>REDUCTION (M$^{+}$ electron $\rightarrow$ M$^{-}$)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pyridine</td>
<td>-2.72&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.99</td>
</tr>
<tr>
<td>biphenyl</td>
<td>-2.55&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.16</td>
</tr>
<tr>
<td>pyrimidene</td>
<td>-2.34&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.37</td>
</tr>
<tr>
<td>Ni(acac)$_2$</td>
<td>-2.24&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.47</td>
</tr>
<tr>
<td>quinoline</td>
<td>-2.12&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.59</td>
</tr>
<tr>
<td>s-triazine</td>
<td>-2.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.66</td>
</tr>
<tr>
<td>anthracene</td>
<td>-1.91&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.80</td>
</tr>
<tr>
<td>perylene</td>
<td>-1.70&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.00</td>
</tr>
<tr>
<td>tetracene</td>
<td>-1.59&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.12</td>
</tr>
<tr>
<td>zinc(II) tetrabenzoophorhine</td>
<td>-1.47&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.24</td>
</tr>
<tr>
<td>indene</td>
<td>-1.45&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.26</td>
</tr>
<tr>
<td>pentacene</td>
<td>-1.31&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.40</td>
</tr>
<tr>
<td>Co(acac)$_2$</td>
<td>-1.24&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.47</td>
</tr>
<tr>
<td>cobalt(II) etioporphyrin I</td>
<td>-1.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.67</td>
</tr>
<tr>
<td>Cr(C$_6$H$_6$)$_2$&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>-0.88&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.83</td>
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<tr>
<td>copper(II) tetraselphidotalcocyamine</td>
<td>-0.73&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.98</td>
</tr>
<tr>
<td>Ru(acac)$_2$</td>
<td>-0.54</td>
<td>4.16</td>
</tr>
<tr>
<td>cobalt(III) ethylenedimine cation</td>
<td>-0.43&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.28</td>
</tr>
<tr>
<td>itc-TPP-FeCl</td>
<td>-0.34&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.37</td>
</tr>
<tr>
<td>itc-TPP-MnBr</td>
<td>-0.26&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.45</td>
</tr>
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<td>tetracyanoethylen</td>
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<td>4.50</td>
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<tr>
<td>tetracyanodimethane</td>
<td>-0.15&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.56</td>
</tr>
<tr>
<td>Ferricyanide</td>
<td>+0.09</td>
<td>4.80</td>
</tr>
<tr>
<td><strong>OXIDATION (M $\rightarrow$ M$^{+}$ + electron)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cobalt(II) tetraselphidotalcocyamine</td>
<td>+0.45&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.16</td>
</tr>
<tr>
<td>chlorophyll b</td>
<td>+0.65&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.36</td>
</tr>
<tr>
<td>diphenylypcrilhydrazyl</td>
<td>+0.73&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.44</td>
</tr>
<tr>
<td>perylene</td>
<td>+0.85&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.56</td>
</tr>
<tr>
<td>Tetraethylthiohydrazyl</td>
<td>+0.90&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.61</td>
</tr>
<tr>
<td>2,4,6-tri-t-butylnitrosobenzene</td>
<td>+1.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.71</td>
</tr>
<tr>
<td>anthracene</td>
<td>+1.09&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.80</td>
</tr>
<tr>
<td>coronene</td>
<td>+1.23&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.94</td>
</tr>
<tr>
<td>dibenzylthiophene</td>
<td>+1.35&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.06</td>
</tr>
<tr>
<td>1-nitronaphthalene</td>
<td>+1.62&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.36</td>
</tr>
<tr>
<td>propylene sulfide</td>
<td>+1.69&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.40</td>
</tr>
<tr>
<td>methoxybenzene</td>
<td>+1.76&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.47</td>
</tr>
<tr>
<td>thiophene</td>
<td>+1.84&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.55</td>
</tr>
<tr>
<td>biphenyl</td>
<td>+1.91&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.62</td>
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<tr>
<td>nitrosobenzene</td>
<td>+2.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.71</td>
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<tr>
<td>purine</td>
<td>+2.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.81</td>
</tr>
<tr>
<td>Methylciodide</td>
<td>+2.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>6.83</td>
</tr>
<tr>
<td>benzene</td>
<td>+2.30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.01</td>
</tr>
</tbody>
</table>

a) Referene 138; b) reference 112. c) Reference 139; d) reference 140. All measurements in non-aqueous solvents.
OMTS as a Chemical Analysis Tool: bias dependent imaging

While the selectivity offered by measuring the full OMTS for each molecule on the surface is extremely good, it can be experimentally demanding in terms of data acquisition time, the need for very low drift rates, and if large areas of a sample must be considered. It is possible to use this high selectivity to do a much faster and easily visualized chemical map of the surface. If one monitors \( \frac{dI}{dV} \) (with a lock-in amplifier) at the peak bias voltage for a particular band as a function of position on the sample surface, a spatial distribution of that species can be obtained. The downside of this method is that we forgo the excellent selectivity inherent in collecting one full spectrum per molecule, and return to the equivalent of the mixed sample problem. Since spectral data is collected at only one energy (bias voltage) per component to be identified, that component must have a strong feature in OMTS that is absent or weak for all the other components. Consideration of Figure 16, for example, suggests that setting the bias at about -0.7 volts (near 5.7 relative to the vacuum level) would allow the CoPc complex to be easily distinguished from the nickel complexes, and would even allow discrimination between the two cobalt complexes (CoPc and CoTPP).

The difference in the cobalt and nickel centered porphyrins and phthalocyanines is so large, in fact, that an even simpler method of chemical mapping is possible. Namely, one need only take two constant current images with the bias set at appropriate values. Figure 17 provides two such constant current STM images of a mixed layer of NiTPP and CoTPP on Au(111) at room temperature. These were taken within minutes of each other on the same area of the same sample. The only difference was the bias voltage setting. In the −1.4 V image, the NiTPP and CoTPP molecules cannot be distinguished. In the −1.0 V image, however, the CoTPP molecules become very apparent by ‘lighting up’. At −1.0 V a significant fraction of the tunneling current is orbitally mediated through the half filled \( d_z^2 \) orbital on the cobalt(II) center, a current pathway not available to the nickel(II) ion. Thus, by adjusting the bias at which the constant current images are taken, one can often rapidly map out chemical composition.

Some points to note about Figure 18. Note first that this is a very large area scan and it would be possible (by counting bright and dark molecules) to arrive at a statistically significant estimate of the relative concentrations of the two species. Second, while there may be some drift (a change in origin of the image with scan time), it has no significant effect on the molecular identification because the pictures are so big that reference points can be tracked from one picture to the next. Finally, note that there appears to be more CoTPP near the edges of the islands than in the centers. This is in fact the case since the NiTPP was deposited first and then followed by the CoTPP. The fact that we do not see a core of NiTPP surrounded by a shell of CoTPP allows us to learn about surface diffusion.

---

**Figure 17**: Logarithmic derivative, \( \frac{d\ln I}{d\ln V} \), orbital mediated tunneling spectra of NiTPP on Au(111) in UHV at room temperature. Relative tip-molecule distances are given on the far right. A different constant was added to each data set to allow them to be better distinguished. Reprinted with permission from reference 95. Copyright (2002) American Chemical Society
OMTS as a Sub-Molecular Electron Transport Mapping Tool

We can use spectroscopic mapping to image the electron transport pathways on a sub-molecular scale. Since the resolution of STM-OMTS can be 0.1 nm, it is conceivable that one may map electron transport at the single atom level within a given molecule. A tantalizing first look at how this might be done is provided in Figure 19. [85] Shown are three points of a map that should eventually include a number of different ionization and affinity levels. A map of the electron transport path from the molecule to the tip via the HOMO is provided by the image taken at –1.0 volt bias (6.3 eV below the vacuum level). Clearly, most of the current is flowing through the carbon $p_z$ orbitals of the porphyrin ring. The ethyl groups, central nitrogen atoms, and the nickel(II) ion are not conducting at this bias. In the intermediate bias region the tunneling pathway is not strongly affected by any particular orbital and an
image similar to the actual molecular structure is observed. Note the eight individual ethyl groups per molecule are clearly seen (at about 5.7 eV below the vacuum level). Compare the space filling CPK model of NiOEP (shown to the center right) with the actual STM image (center). As the bias is increased positively and approaches the first affinity level, a new image appears. This image is a map of the electron accepting regions of the NiOEP molecule. At 4 eV below the vacuum level most of the current from the tip to the molecule flows through the central portion of the molecule. The central area is so bright that it seems likely that there are contributions from all the atoms in the porphyrin ring, with the greatest current being carried through the nitrogen and nickel(II) orbitals.

**Figure 19**: Bias dependent constant current STM imaging of a mixed composition adlayer of NiTPP and CoTPP. The bright spots in the right hand image (bias = -1.0 V) are due to enhanced tunneling through the cobalt(II) d_{z^2} orbital in CoTPP. Reprinted with permission from reference 85. Copyright 2005, the American Chemical Society

**SOME CONCLUDING POINTS**

The future of STM based spectroscopy is a bright one. The advantages offered are great and can be grouped into those based on the particular physical advantages inherent in STM based spectroscopy:

1) As a single molecule spectroscopy:
   a) Locate and identify species at particular sites on surfaces.
b) Perform highly selective surface analysis even where there are several different components present.
c) Map electron transport through different portions of a particular molecule or nanostructure.
d) Map molecular force fields (through local vibrational frequencies) on an atomic level.

2) As an elastic electron tunneling spectroscopy:
   a) Locate both electron affinity levels and ionization states simultaneously and without utilizing energy probes that can decompose the molecule.
   b) The selection rules are more relaxed than for UPS or IPS, thereby allowing a more complete description of the electronic states.
   c) Can be applied to samples over a range of temperature (0 to $\geq 700$K).
   d) Conduction pathways both in space and in energy can be mapped and used in the design of complex molecular electronic devices.

3) As an inelastic tunneling spectroscopy:
   a) Utilize the higher intensity and wider acceptable temperature range of inelastic electronic state tunneling as a surface analytical tool when OMTS is not appropriate.
   b) In resonant IETS, knowing which vibrational mode is activated by excitation through a particular resonant electronic state can lead to better assignments of the nature of the electronic states involved (similar to resonance Raman analysis).
   c) [For non-resonance enhanced IETS] The selection rules are more relaxed than for infrared or Raman spectroscopy, thereby allowing a more complete description of the vibrational states.

4) Combining advantages:
   a) Identify chemical species formed through surface or in situ manipulation by the tip or tip current.
   b) Utilize the voltage dependence of resonant tunneling induced structural and physical changes (either through inelastic or quasi-elastic processes) to understand the mechanism of molecular change.
   c) By comparing the electronic spectra of single molecules on surfaces to those of aggregates (multiples of the same molecules or different geometry configurations of different molecules) we can make precise measurements of the role of intermolecular interaction on electronic states.

Some of these advantages will only be realized when we have improved the stability of the STM to the point were non-resonance enhanced IETS can be observed. This is a point we have not yet reached, but that should be attainable. STM-IETS on electronic states has not yet been demonstrated only because the materials studied to date have stronger OMTS bands masking them. They will be seen once the appropriate materials are examined. Most of the advantages enumerated above, however, have been demonstrated and only require that they be applied to a wider range of problems.

ACKNOWLEDGEMENT

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