STM Contrast, Electron-Transfer Chemistry, and Conduction in Molecules

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We have used a series of metalloporphyrin compounds to test for a relationship between the contrast of STM images and the electrochemical properties of the molecules. Molecules were tethered to a gold (111) surface by means of an isothiocyano linkage and both images and current-voltage (I-V) curves were obtained with the sample submerged in oxygen-free mesitylene. The contrast of the reducible molecules changed strongly with bias, and the corresponding I-V curves were highly asymmetric. The derivative of these curves (dI/dV) had a Gaussian-shaped peak at a voltage characteristic of the compound, although local measurements showed that there was considerable variation in this value from molecule to molecules, so the STM is capable of distinguishing electroactive molecules from non-electroactive molecules as we demonstrate with images of mixed films. We discuss one- and two-step electron-transfer mechanisms which are consistent with these observations.

Introduction

The mechanism of electronic conduction in and between molecules is a question of fundamental importance in molecular electronics, electrochemistry, and biochemistry. It is now possible to examine the conductivity of single molecules by means of the scanning probe microscope, and one might expect mechanisms quite different from metallic conduction because electronic charge is usually localized in molecules.¹ To date, however, most scanning tunneling microscope (STM) images of atoms² and molecules^{3,4} have been successfully interpreted in terms of modification of metallic states at the Fermi energy caused by the interaction of the atom or molecule with the metal surface. The electrons are assumed to be passed through the molecule by tunnel transport,⁵ and charge does not accumulate on the molecule. Current-voltage, I(V), characteristics are linear (for small voltages), reflecting the slowly varying electronic transmission of the tails of broadened molecular orbitals in the HOMO-LUMO gap.5

At higher bias, however, the molecular states can be probed, and there is evidence of their contributions in the voltage dependence of images of benzene on graphite and MoS₂.⁶ In a condensed environment, it is more appropriate to consider the relaxed states of the HOMO and LUMO. Schmickler^{7,8} has suggested that the relaxed LUMO distribution (or density of oxidized states) can be probed by an STM. In this context, the "density of oxidized states" means the electron affinity levels as broadened and shifted by coupling to the environment and fluctuations. A similar use of tunneling at macroscopic electrodes was proposed by Bennett9 and demonstrated by Morisaki et al.¹⁰ Tao¹¹ has studied the potential dependence of STM images of protoporphyrin molecules adsorbed onto a graphite electrode and kept under potential control by means of a supporting aqueous electrolyte which covered the sample during the STM imaging. He found that images of reducible

molecules (protoporphyrins containing iron) showed a strong potential dependence, the STM contrast increasing approximately 10-fold when the substrate potential was adjusted to the half-wave potential, E_0 , for the Fe^{III} to Fe^{II} reduction. (The relatively small difference between half-wave and formal potentials¹² will be ignored in this paper.) No such effect was observed in the protoporphyrins that did not contain iron. Mazur and Hipps¹³ have noted that the position of a peak in the derivative of the current-voltage characteristics of a number of metal-insulator-molecule-metal tunnel junctions coincides approximately with the first reduction potential of the molecules. They made this connection by assuming that the electrons were injected at the Fermi energy of the electrode plus the applied bias, and they used the work function of the normal hydrogen electrode (NHE) to relate this energy to reduction potentials measured relative to a standard reference. Further evidence for such a correlation is found in the data of Burghard et al.¹⁴ Snyder and White¹⁵ measured enhanced tunnel current in films of iron protoporphyrin on graphite. However, they found an enhancement that was identical for both signs of the tip bias, a result different from the data of Tao¹¹ and Mazur and Hipps.¹³ Bumm et al.¹⁶ have used both STM and alternating-current STM to show that a "molecular wire" (an ethyl-substituted 4,4'-di-(phenyleneethynylene)benzothioacetate) is more conductive than a surrounding "inert" matrix, but current-voltage characteristics were not reported.

At first glance, a connection between a maximum in the derivative of a tunneling current I(V) characteristic and a half-wave potential is rather surprising. The half-wave potential does not correspond to any molecular eigenstate energy but rather to the equilibrium potential established when reduction and oxidation currents are balanced at an electrode.¹⁷ In Schmickler's model, a maximum in the derivative curve occurs when electrons are aligned with the peak in the "density of oxidized states" (the occupied states do not contribute to the current). Thus, in this model, the peak current is shifted away from the half-wave potential (which lies between the peak in the reduced and the peak in the oxidized state densities) by the amount of the reorganization energy (λ in the terminology of Marcus^{18,17}).

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Figure 1. Structure of the molecules used in this study.

This is often a substantial fraction of an electronvolt.¹⁷ Both Tao's data and the experiments of Mazur and Hipps,¹³ on the other hand, indicate that the maximum molecular contribution to the current occurs quite close to the half-wave potential.

Tao's experimental approach has the considerable advantage that the potential of at the molecular adlayer is well established. However, the experiments are difficult to carry out because the adlayer must remain stable over a wide range of potential in the supporting aqueous electrolyte. The limited available range of tip potential further restricts conventional spectroscopic measurements. An alternative is to attach a molecule firmly to a substrate with a tether and carry out two-electrode spectroscopic measurements in an electrochemically inert environment. We have developed a chemical tether¹⁹ which we have used to attach a number of molecules to a gold electrode. The sample is submerged in a dielectric fluid to permit spectroscopic, I(V), measurements but with consequent loss of potential control. While this introduces uncertainties, we believe that these are on the order of a fraction of an electronvolt and are comparable to other uncertainties, as we will discuss.

The molecules we have used are tetraphenylporphyrin derivatives (TPP) into which various metals (TPP-M) have been substituted. One of the porphyrin meso aryl rings bears an isothiocyano group (itc-TPP-M) which tethers the molecule to a gold substrate.¹⁹ The other three rings have methyl substituents in the para positions. The structures of these molecules are shown schematically in Figure 1. We studied the free base (M = 2H), iron(III), manganese(III), and zinc(II) porphyrins. The iron and manganese atoms bear formal charges and are bound to a halide ion ligand (itc-TPP-FeCl, itc-TPP-FeBr, and itc-TPP-MnBr). This series of molecules is easily reduced, while the free base and zinc porphyrins are not. We report the results of STM imaging and spectroscopic measurements of these molecules on Au(111) in this paper.

Experimental Section

Samples. Itc-TPP was prepared by methods previously reported.^{20,19} The composition of all samples was verified by mass spectrometry (MS), and measured mass/charge ratios (m/z) are listed for each compound.

Itc-TPP-FeCl. A portion of acetonitrile (20 mL) was heated at reflux for 30 min with vigorous stirring under a stream of nitrogen. Ferrous chloride (133 mg, 1.05 mmol) was added and completely dissolved by stirring the mixture for several minutes at reflux. The solution was cooled to 50 °C, and a solution of 30 mg (0.042 mmol) of itc-TPP in nitrogen-purged chloroform (8 mL) was added. The mixture was stirred for 15 min under nitrogen, exposed to air, diluted with 100 mL of dichloromethane, and stirred with 1 M hydrochloric acid saturated with sodium chloride (100 mL). The organic phase

TABLE 1: Measured First Reduction (E_0^{-1}) and First Oxidation Potentials (E_0^{+1}) for the Compounds Used in This Work. Data for itc-TPP-Zn Are Estimated As Outlined in the Text

compound	$E_0^{-1}(SCE)$ (V)	$E_0^{+1}(SCE)$ (V)
itc-TPP-H ₂	-1.23	+0.96
itc-TPP-Zn	-1.30	+0.77
itc-TPP-FeCl	-0.34	+1.13
itc-TPP-FeBr	-0.24	+1.13
itc-TPP-MnBr	-0.26	+1.14

was washed with 100 mL of water and separated from the water phase, and the solvent was evaporated under vacuum. Flash chromatography on silica gel (dichloromethane-methanol) afforded 30 mg (89%) of itc-TPP-FeCl. MS m/z: 802 (M⁺) (802 calculated for C₄₈H₃₃N₅SFeCl), 767 (M⁺-Cl).

Itc-TPP-FeBr was prepared as described for itc-TPP-FeCl using 12 mL of acetonitrile, 108 mg (0.501 mmol) of ferrous bromide, and 22 mg (0.031 mmol) of itc-TPP in 6 mL of chloroform. The solution was diluted with 100 mL of dichloromethane and stirred with 1 M hydrobromic acid saturated with potassium bromide (100 mL). Flash chromatography on silica gel (dichloromethane–methanol) yielded 23 mg (88%) of itc-TPP-FeBr. MS m/z: 846 (M⁺) (846 calculated for C₄₈H₃₃N₅-SfeBr), 767 (M⁺-Br).

Itc-TPP-MnBr was synthesized by refluxing 30 mg (0.042 mmol) of itc-TPP and 218 mg (1.26 mmol) of manganese(II) acetate in 30 mL of glacial acetic acid and 20 mL of chloroform for 4 h. After cooling, the solution was stirred with 1 M hydrobromic acid saturated with potassium bromide (100 mL). The organic phase was washed with 100 mL of water and separated from the water phase, and the solvent was evaporated under vacuum. Flash chromatography on silica gel (chloroform— methanol) afforded the product, 33 mg (93%). MS m/z: 845 (M⁺) (845 calculated for C₄₈H₃₃N₅SMnBr), 766 (M⁺-Br).

Itc-TPP-Zn was prepared by dissolving 17 mg (0.024 mmol) of itc-TPP in 5 mL of dichloromethane and adding a saturated solution of zinc(II) acetate in methanol. The mixture was stirred for 30 min. The product, 18 mg (96%), was isolated by column chromatography on silica gel (dichloromethane). MS m/z: 775 (M⁺) (775 calculated for C₄₈H₃₃N₅SZn).

Freshly distilled mesitylene was used as a solvent in all STM experiments reported (but see below).

Cyclic Voltammetry. Cyclic voltammograms of itc-TPP-FeCl, -FeBr, and -MnBr were recorded at a glassy C electrode in benzonitrile solutions with 0.1 M tetrabutylammonium hexafluorophosphate electrolyte. Ag/0.01 M AgNO3 served as a provisional reference electrode, but ferrocene ($E_0 = 0.46$ V vs the saturated calomel electrode (SCE) in benzonitrile) was used as an internal reference for correlating potentials. The voltammograms, which covered approximately the range -2.0V to ± 1.6 V vs Ag/Ag⁺, showed a reversible first oxidation wave, an irreversible second oxidation wave, and two or more reduction waves with various degrees of reversibility. Since ligating anions dissociated to some extent upon reduction of the trivalent metal ions, reversibility was improved by adding some quaternary Cl⁻ or Br⁻ salt, and in these cases only halfwave potentials recorded in the presence of excess anions are reported in Table 1.

Voltammograms of itc-TPPH₂ were recorded in CH_2Cl_2 with the same electrolyte and glassy C electrode but were referred directly to the SCE. Ferrocene (0.52V vs SCE in CH_2Cl_2) was used to correct the values in CH_2Cl_2 to benzonitrile in Table 1. Values for itc-TPPZn were not measured, but were estimated, with good expectation of reliability, from values for itc-TPPH₂, for tetraphenylporphyrin²¹ and for its Zn complex²² in CH_2Cl_2 . STM Contrast in Molecules

Scanning Probe Microscopy and Spectroscopy. We used a PicoSPM (Molecular Imaging Corp., Tempe, AZ) which employs a single-piece Teflon fluid cell. It was necessary to clean the cell thoroughly prior to each experiment by washing it in a Soxhlet extractor containing a mixture of dichloromethane (20%) and methanol (80%) for at least 4 days. We prepared gold (111) substrates on mica as described elsewhere²³ and annealed them in a hydrogen flame immediately prior to use. A 10-20 μ M solution of the itc-TPP-M in freshly distilled mesitylene was placed onto the gold immediately after the liquid cell was assembled (resulting in 5-10 min of exposure to ambient conditions in a laminar flow hood). The sample stage was mounted on the PicoSPM and sealed into the environmental chamber. The chamber was flushed continuously with ultrapure nitrogen gas. The instrument was left to stabilize (1-10 h)after which time images and spectra were collected. We used etched Pt_{0.8}Ir_{0.2} tips that had been thoroughly rinsed in ultrapure water and dried in a stream of clean nitrogen. Images were collected as described in the figure captions.

Current-voltage spectra were obtained starting at a set point of 80 mV bias and 50 pA tunneling current. The sample bias was swept over ± 1 V, and 256 sample points of 25 μ s dwell time were collected. Thirty consecutive sweeps were integrated for each spectrum accumulated. On the order of 100 such integrated spectra were obtained from randomly chosen sites on a given sample, and the experiment was repeated several times. The total number of integrated spectra were 672 (gold under clean mesitylene), 848 (itc-TPP-FeCl), 598 (itc-TPP-FeBr), 473 (itc-TPP-MnBr), 508 (itc-TPP-Zn), and 588 (itc-TPP-H₂).

Results

The images of the various molecules did not show submolecular resolution, the molecules appearing as blobs with a characteristic size of around 2nm. For that reason, it was not possible to distinguish images of the molecules we prepared from some forms of contamination. Thus, scrupulous attention to cleanliness was required. In addition, failure to purge oxygen from the samples led to complicated and generally nonreversible current—voltage characteristics. The cleaning procedures described were developed to yield images in which the density of features scaled with the concentration of the molecules in the solution. These clean conditions generally yielded reproducible tunneling spectra. Examples of images obtained under these conditions are shown in Figure 2.

Despite thorough cleaning of the mesitylene by repeated distillation in clean glass, we found a low level of background features on clean gold under mesitylene (around 10 features in an area 100 nm by 100 nm). These features were not found when toluene was used. However, toluene evaporated too quickly to permit experiments of adequate duration reliably. We repeated our measurements on itc-TPP-FeCl in toluene, finding no difference from results obtained in mesitylene. For that reason, we used mesitylene for all the work reported here.

Figure 2 shows that there is a strong bias dependence in the contrast of the images of the three reducible molecules (itc-TPP-FeCl, itc-TPP-FeBr, and itc-TPP-MnBr). There appears to be a threshold for the onset of enhanced image contrast (of around 0.5V), and the effect was only observed when the substrate was biased negative with respect to the tip. Images taken at positive sample bias are similar to the low-bias images in Figure 2. In contrast, the less electroactive molecules, itc-TPP-Zn and itc-TPP-H₂, show no effect of bias in the range of ± 1 V.

Lowering the bias applied to the STM tip results in the tip being positioned closer to the metal surface, so it is conceivable



Figure 2. Typical STM images of the Au(111) surface under mesitylene after adsorption of itc-TPP-FeBr (A), itc-TPP-FeCl (B), itc-TPP-MnBr (C), itc-TPP-Zn (D), and itc-TPP-H₂ (E). Data are shown for low (left) and high (right) substrate bias as marked. Contrast changes were not observed with the substrate bias positive (data not shown). Images were acquired at a line scan rate of 3 Hz with a tunnel current of 50 pA. A scale bar for all images is shown on the lower right of E.

that a mechanical interaction between the tip and the molecules could play a role in the bias dependence of the images. We show that this is unlikely to be the case with images of a mixed film (20% itc-TPP-FeCl, 80% itc-TPP-H₂) in Figure 3. The large white spot near the middle of the image is one of the mesitylene-induced features described earlier, but the other features in Figure 3A are owing to the presence of porphyrin molecules on the surface. When the negative sample bias was increased (Figure 3B), additional features were observed on the



Figure 3. Series of successive scans over a mixed adlayer of itc-TPP- H_2 and itc-TPP-FeCl with the bias of the substrate switched as shown by the inset in the upper right of each image. A cluster of molecules (pointed to by the arrow) lights up at high bias (B) but becomes invisible again at low bias (C), returning again whenever the bias is high (D, E). Tunneling conditions were as in Figure 2.

surface (one example is indicated by the arrow). These were much brighter, having a contrast similar to the itc-TPP-FeCl images at high negative bias (Figure 2A). When the bias was returned to a small value, these additional features disappeared (Figure 3C). On returning the bias to a large negative value, the additional features were restored (Figure 3D). The cycle is repeated in subsequent images (Figures 3E,F). The reversibility of the effect argues against a simple mechanical interaction, such as the tip sweeping some molecules away at low bias. Averaged over a number of images like those shown in Figure 3, the population of molecules with bias-dependent contrast was close to 20%, showing that these are the iron-containing porphyrins.

Inspection of Figure 3 reveals an unexpected phenomenon which is not evident in the images shown in Figure 2, where the contrast has been adjusted to make all the images exhibit approximately the same contrast at low bias. Compared to the free base porphyrins, the iron-containing porphyrins are almost invisible at low bias. This effect emphasizes the electronic (as opposed to topographic) nature of the contrast.

Rather than attempt to extract quantitative data from the images, we chose to accumulate tunneling spectra. In this mode, the scan was disabled and the tip set to tunnel at a fixed resistance (50 pA at 180 mV bias). The STM servo was then transiently opened and the bias scanned from -1000 to +1000 mV over 6 ms and servo control then restored. The shape of the spectra depends critically on the exact location of the tip in relation to a molecule on the substrate. However, for bare gold in mesitylene, the curves are symmetrical and the currents small, so the integrated data taken from many scans correspond to an average over all tip positions with respect to the molecule.

The integrated sum of all our data is shown for all the molecules studied in Figure 4. We also include data for the gold substrate under clean mesitylene. The gold data are quite symmetrical in the range of ± 1 V. The molecular adlayers show some sign of additional current at the highest positive biases, but the differences are most pronounced for high negative substrate bias, consistent with the images (Figure 2). Note that because the gap resistance was a set to a common value before the acquisition of spectra, relative variations at low bias, such as the anomalous contrast for the itc-TPP-FeCl discussed above, are not evident in these curves.

Most noticeable is the marked increase in tunnel current at high negative substrate bias for the three reducible molecules, itc-TP-FeCl, itc-TPP-FeBr, and itc-TPP-MnBr. Interpreting this



Figure 4. Current-voltage curves averaged for many molecules obtained over several runs as described in the text. Curves for the reducible molecules (itc-TPP-FeCl, itc-TPP-FeBr, and itc-TPP-MnBr) show significantly enhanced current at large negative substrate bias. The curve for gold in mesitylene is symmetrical about the origin, while the curves for itc-TPP-Zn and itc-TPP-H₂ show some enhancement at large positive bias.



Figure 5. (A) Derivatives (dI/dV) of the current—voltage curves shown in Figure 4. Data for the three reducible molecules (itc-TPP-FeCl, itc-TPP-FeBr, and itc-TPP-MnBr) are fitted by Gaussians of the form given in eq 1 (solid lines). (B) Series of local scans (30 sweeps) over itc-TPP-FeCl. Within the noise, each curve is well described by a Gaussian, but the peak position is quite variable and the width is less than that of the curves fitted to the full data set.

data according to the theory of Schmickler⁸ suggests that this extra current results from tunneling via oxidized states on the molecule. The extra current is integrated into the total as the bias voltage is made more negative, but the derivative, dI/dV, should show evidence of the peak in the molecular density of states. We show the numerical derivatives of these spectra in Figure 5(A). There are distinct peaks for the iron-containing molecules and evidence of the onset of a maximum in the data for itc-TPP-MnBr. We fitted the peaks with Gaussians of the form

$$\frac{dI}{dV} = A \exp\left[\frac{(V - V_{\rm p})^2}{B^2}\right] + C \tag{1}$$

where V_p is the peak voltage and B is related to the half-width



Figure 6. (A) Distribution of peak potentials and (B) width parameters obtained from fits to local scans over itc-TPP-FeCl of the sort shown in Figure 5B.

TABLE 2: Measured Peak Positions (V_p) and Width Parameters (*B*) for the Maxima in dI/dV. The Middle Row Is an Estimate of V_p Based on Eq 2 Using the Measured Reduction Potentials (Table 1)

	itc-TPP-FeCl	Itc-TPP-MnBr	Itc-TPP-FeBr
$V_{\rm p}\left({ m V} ight)$	-0.89 ± 0.004	-1.05 ± 0.018	-0.89 ± 0.002
$V_{\rm p}$ predicted, λ ,	$-0.968/\alpha$	$-0.892/\alpha$	$-0.873/\alpha$
$\delta = 0$	0.00	0.04.1.0.04.0	0.04.1.0.000
B(V)	0.28 ± 0.006	0.26 ± 0.012	0.26 ± 0.002

at half-height, ΔV , by $\Delta V = B \sqrt{-\ln 0.05} = 0.8333B$. The constant *C* accounts for the ohmic part of the background tunnel current. Fitted values for *B* and V_p are listed in Table 2.

The data discussed above were obtained from many runs taken over several different experiments, and it is of interest to know what information can be extracted from spectra obtained over one point. Such data show considerable run-to-run variation. However, most runs (of 30 sweeps) over the electroactive molecules have in common the peak in dI/dV. This is illustrated in Figure 5B, where we have selected three such runs which illustrate peaks with low, typical, and high values for $V_{\rm p}$. The signals are noisy, but are well fitted by Gaussian curves of the form of eq 1. These data suggest a significant variable contribution to the tunneling process from the local environment. We show histograms of the values of V_p and width parameters B obtained from each of the individual runs in Figure 6. The solid curve is a Gaussian fit to these distributions, giving $V_p = -0.855 \pm 0.1$ V (Figure 6A) and B = 0.18 ± 0.07 (Figure 6B). The width parameters are smaller than those fitted to the full data set (Table 2), indicating a significant inhomogeneous broadening of the distribution owing to environmental fluctuations. The intrinsic width for the itc-TPP-FeCl is about 0.15 V (0.833 \times 0.18 V), while the width of the averaged data (Table 2) is 0.23 V (0.833 \times 0.28 V). This shows that the averaged data set is broadened considerably by spatial heterogeniety. One might expect that the average value of the peak voltage, V_p , would be the same for the two sets of measurements. This is not the case because our fitting program essentially ignores the tails corresponding to high values of V_p (see Figure 6A). When the combined data set is averaged, these runs pull the averaged data to a slightly higher value (Table 1). These data are useful in as much as they show that a characteristic peak value can be determined to within about ± 0.1 V from local measurements, indicating the extent to which these measurements might be used as quantitative nanoscale probes.

Discussion

Our results demonstrate the link between tunneling and redox properties first proposed by Schmickler⁷ on theoretical grounds and Mazur and Hipps¹³ on experimental grounds. The three reducible compounds show a bias dependence in STM contrast, while the less electroactive compounds do not. It is not just a question of whether or not a metal is present, as demonstrated by the behavior of the itc-TPP-Zn. Neither is the chemical identity of the counterion of importance, a result that may reflect a much slower dissociation in the STM experiment (where an ionic solvent is not used) than in the electrochemical experiment (where it is). The ring is reduced in the free base and itc-TPP-Zn, and counterions are not involved in the same way.

The connection between bias dependence and redox properties is consistent with Tao's earlier experiment.¹¹ These results extend the work to more compounds and demonstrate the effect in a different experiment. In our view, however, the most important aspects of the present results lie in the degree to which they allow us to characterize the ability of the simple twoelectrode scanning probe microscope to analyze individual molecules. We have demonstrated that there are large local fluctuations in the derivative peak position. In this section we turn our attention to the theoretical basis of these phenomena.

We note that, in contrast to the earlier work of Snyder and White,¹⁵ our results show that the current–voltage characteristics for these porphyrin molecules are characteristically asymmetric. However, Snyder and White worked with mobile adlayers which adsorbed on both tip and substrate, thereby allowing electron transfer to occur at either electrode. Here, with the molecule bound to the substrate in a submonolayer, we expect that the predominant interaction is with the substrate, the tip acting to control the local field.

The problem has been treated thoroughly by Schmickler and Widrig,⁸ whose notation we shall use. To attempt some quantitative analysis, it is necessary to fix values for some of the parameters used in that theory. Perhaps the most vexing is the local energy of a molecular level, $\epsilon_m + \alpha V$, where ϵ_m is the potential of the maximum in the density of unoccupied states and αV is the energy shift caused by the tip-substrate bias, V. Here, α is a parameter that describes the fraction of the total potential drop that occurs across the region between substrate and molecule. In the Marcus theory, ϵ_m for the unoccupied (oxidized) states is related to the formal potential, E_0 , by $\epsilon_m =$ $E_0 + \lambda$, where λ is the reorganization energy (typically on the order of 1 eV in relatively polar solvents).¹⁷ The quantities E_0 and αV are calibrated under three-electrode potential control but have to be related to the applied bias here. We use the convention that when quantities such as V and E_0 appear in expressions for energies, units of electronvolts are implied. When referring to measured potentials, units of volts are implied.

Electrochemical potential scales and work functions are related by the work function of the normal hydrogen electrode (NHE), $\Phi_{\text{NHE}} = 4.43 \text{ V},^{24}$ or for the SCE values used here $\Phi_{\text{SCE}} = 4.67 \text{ V}$ since zero on the SCE scale lies 0.24 V positive (i.e., further from the vacuum) of zero on the NHE scale. With this information, a potential on an electrochemical scale may be



Figure 7. Relationship between reduction potentials measured on the SCE scale (right side) and the position of the Fermi energy of the metal substrate (left side). More negative potentials on the SCE scale are closer to the vacuum. The lack of potential control at the surface results in uncertainty $(\pm \delta)$, on the order of 1 eV or less) in the potential at the molecule. The potential difference between electrons at the Fermi energy and a point E^0 on the SCE scale, ΔV , could take on a range of values as indicated.

related to a potential (such as a Fermi energy) that is expressed with respect to the vacuum. The situation is more complex here. An electron is removed from the Fermi surface (at an energy $E_{\rm F}$) of a metal to a molecule, located not outside the metal in a vacuum, but rather in a region near the surface where the electric field is still varying rapidly. We refer to this interfacial region as the double layer, in accordance with surface science convention. Thus, the electric potential at the molecule differs from that in the vacuum by some amount, which can be positive or negative, depending upon the orientation of local dipoles. We call this difference between the vacuum and the potential on the edge of the double layer $\pm \delta$, and we expect it to be small in the case of dense metals where most of the work function arises from electron-electron interactions intrinsic to the metal.²⁵ (Experimental support for this approximation is to be found in the emersion experiments of Kötz et al.²⁶) These relationships are illustrated schematically in Figure 7. Thus, the potential difference needed to bring an electron from the Fermi energy to a potential E_0 is

$$\Delta V = \alpha V = \Phi_{\rm M} - \Phi_{\rm SCE} - E_0 \pm \delta \tag{2}$$

where $\Phi_{\rm M}$ is the work function of the metal (5.3 V for the Au-(111) surface²⁷) and δ is expected to be small (less than 1 eV). Evaluation of the local potential shift is complicated, involving polarization of the surrounding medium and transitions within the molecule which may not be strictly proportional to the applied voltage. Nonetheless, we expect $0 < \alpha < 1$. We note in passing that Snyder and White have proposed that the electrode may float to an equilibrium potential controlled by the molecular adsorbate.¹⁵ This cannot be the case here where the electrodes are connected by low-impedance circuitry.

The electron-transfer process may be described in one of two ways which involve the states of the molecule explicitly. In one model due to Schmickler^{8,28} electrons tunnel from tip to substrate (or vice versa) by a resonant transition through the unoccupied (oxidized) states. The molecule itself does not acquire a charge over a time scale comparable to or longer than the phonon relaxation time in the process. In another process, discussed by Kuznetsov,²⁹ the electron transfers to the molecule where it is trapped by relaxation (i.e., it reduces the molecule). A second thermal fluctuation then allows the molecule to transfer the electron to the other electrode, returning the molecule to its oxidized state.

Schmickler⁸ has evaluated some representative cases showing that a Gaussian peak occurs in the quantity dI/dV as observed in these experiments. The second case has not been analyzed in the same manner, so we present a discussion below.

A simple derivation of the theory of the first process from quantum mechanical principles has been presented by Schmick-ler.^{8,17} The calculated current density, j, is

$$j = -e \frac{\pi}{\hbar} \int_0^{\nu} \frac{\rho_{\rm s}(\epsilon) |V_{\rm sm}|^2 \rho_{\rm t}(\epsilon) |V_{\rm mt}|^2}{\rho_{\rm s}(\epsilon) |V_{\rm sm}|^2 + \rho_{\rm t}(\epsilon) |V_{\rm mt}|^2} D_{\rm ox}(\epsilon) \,\mathrm{d}\epsilon \qquad (3)$$

where $\rho_s(\epsilon)$, $\rho_t(\epsilon)$ are the densities of states of the tip and substrate, respectively, V_{sm} and V_{mt} are the matrix elements for tunneling from substrate to molecule and molecule to tip, and $D_{ox}(\epsilon)$ is the density of oxidized states given by

$$D_{\rm ox}(\epsilon) = \sqrt{\frac{\pi}{k_{\rm B}T\lambda}} \exp\left[-\frac{(\epsilon - E_0 - \lambda + \alpha V)^2}{4\lambda k_{\rm B}T}\right]$$
(4)

The derivative of the current with respect to voltage between tip and substrate shows a maximum at potential corresponding to ϵ_m , the energy level of the oxidized state.⁸ Schmickler also shows that the current from this process is probably larger than that due to direct tunneling without interaction with the oxidized states.

There is also the possibility that the tunneling electron stays on the electroactive molecule long enough for the molecule to relax into its "reduced" state. This two-step process has been considered by Kuznetsov et al.²⁹ Clearly, this implies that the time for electron transfer is much longer than the vibration time of the molecule, which is on the order 10^{-14} s. Neglecting backward flowing current from tip to substrate, the observed current would be proportional to

$$\left(\frac{\pi}{k_{\rm B}T\lambda}\right)\frac{R_{\rm sm}R_{\rm mt}}{R_{\rm sm}+R_{\rm mt}}$$
(5)

where

$$R_{\rm sm} = \int_{-\infty}^{\infty} \rho_{\rm s}(\epsilon) |V_{\rm sm}|^2 f_{\rm s}(\epsilon) \exp\left[-\frac{(\epsilon - E_0 - \lambda + \alpha V)^2}{4\lambda k_{\rm B}T}\right] \quad (6)$$

$$R_{\rm mt} = \int_{-\infty}^{\infty} \rho_{\rm s}(\epsilon + eV) |V_{\rm mt}|^2 (1 - f_{\rm t}(\epsilon + eV) \times \exp\left[-\frac{(\epsilon - E_0 - \lambda + \alpha V)^2}{4\lambda k_{\rm B}T}\right]$$
(7)

and $f_{\rm s}(\epsilon)$, $f_{\rm t}(\epsilon)$ are the Fermi functions for the substrate and tip, respectively. The functions are, of course, identical, but are labeled here in order to clarify the direction of tunneling.

We have evaluated dI/dV for the two models (model I, eqs 3 and 4; model II, eqs 5, 6, and 7) and the following parameter values: $E_0 = 0.6$ V, $\lambda = 0.5$ V, and $\alpha = 0.5$. Here, E_0 is taken to be a negative voltage referenced to the metal Fermi energy (taken as zero). We also used the broad-band approximation, taking the matrix elements and the densities of states of the metals to be constant over the energy range of interest. The results of the calculations are shown in Figure 8 (crosses for model I, dots for model II). As expected, model I shows a maximum in dI/dV at $(E_0 + \lambda)/\alpha$, and the points are well fitted by a Gaussian of the form of eq 1 (solid line).



Figure 8. Calculated dI/dV for the one-step tunneling process (eqs 3 and 4) shown by the crosses and the two-step process (eqs 5, 6, and 7) shown by the dots. Parameters were $E_0 = -0.6$ V, $\lambda = 0.5$ V, and $\alpha = 0.5$. The solid lines are fits to Gaussians of the form of eq 1.

Model II is more complicated, containing the product of two molecular densities of states separated by 2λ . The corresponding maximum is not centered between these peaks but is pulled to somewhat higher voltages by the rapid increase in current at high bias. For these parameters, dI/dV is a maximum at about 0.2 V lower bias than for model I. The form of dI/dV is clearly not Gaussian, but the data are still fitted quite well by a simple Gaussian (solid line). Thus, within experimental error, we cannot distinguish these two processes on the basis of our data.

We can use eq 2 and the measured reduction potentials (Table 1) to estimate to position of the peaks in dI/dV as referenced to the gold Fermi energy. For simplicity, we have used model I and taken λ to be zero. The results are expressed in terms of α in Table 2.

The agreement with the measured values is good if α is taken to be unity and λ very small. This result is unexpected, but significant, since departure from the assumptions used here would push the peak to higher voltages, not lower. We note that Mazur and Hipps¹³ analyzed their data as though the full potential difference were applied across the molecule ($\alpha = 1$). This phenomenon requires further investigation. It should be pointed out, however, that a value of α close to unity is required for the observation of asymmetric tunnel-current characteristics (0.5 would give symmetric curves and zero would give no effect).

A small value for λ is also consistent with the results of Tao.¹¹ In general, electron transfer according to model II (the twostep process) would be consistent with a small effective value for λ , but our data do not discriminate between the models.

Finally, we note that we have not considered the effects of the matrix elements between the electrodes and the molecules. These can make large differences, particularly when internal molecular structure is resolved. This has been demonstrated beautifully in a series of experiments by Lu et al.,^{30,31} who show that, for metallophthalocyanines with states close to the Fermi energy, the metal is visible only if d_z states interact with the gold substrate.

Conclusions

We have shown that the bias dependence of the current through individual molecules can be used to discriminate between electroactive and non-electroactive molecules imaged in a scanning probe microscope. Local fluctuations and lack of a strict correlation with macroscopic electrochemistry preclude the use of the microscope as a precise analytical probe. Nonetheless, certain rather characteristic signals are observed which could aid identification of molecules among a limited range of candidate species. In addition, the ability to discrimi-

nate among electroactive and non-electroactive molecules could have applications in the design of molecular-scale electronic devices. The nature of the electron transfer through the molecules is not clear. Both one-step (resonant tunneling) and two-step (reduction/oxidation) processes are consistent with our observations, and further experiments, such as measurement of the temperature dependence of the currents, are required to elucidate this point. One might expect the resonant tunneling contribution to be larger (because it is a first-order process), but electron interactions and thermal fluctuations may favor the two-step process. We note that the relative contrast of electroactive molecules far from the reduction potential appears to be less than that of similar but non-electroactive molecules. Furthermore, the molecules appear to behave as though all of the applied potential is dropped across them. Further work is required to understand these observations.

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