

## Shifting the Voltage Drop in Electron Transport Through a Single Molecule

Sujoy Karan,<sup>1,\*</sup> David Jacob,<sup>2</sup> Michael Karolak,<sup>3</sup> Christian Hamann,<sup>1</sup> Yongfeng Wang,<sup>1,†</sup> Alexander Weismann,<sup>1,‡</sup> Alexander I. Lichtenstein,<sup>4</sup> and Richard Berndt<sup>1</sup>

<sup>1</sup>*Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany*

<sup>2</sup>*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany*

<sup>3</sup>*Institut für Theoretische Physik und Astrophysik, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

<sup>4</sup>*I. Institut für Theoretische Physik, Universität Hamburg, 20355 Hamburg, Germany*

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A Mn-porphyrin was contacted on Au(111) in a low-temperature scanning tunneling microscope (STM). Differential conductance spectra show a zero-bias resonance that is due to an underscreened Kondo effect according to many-body calculations. When the Mn center is contacted by the STM tip, the spectrum appears to invert along the voltage axis. A drastic change in the electrostatic potential of the molecule involving a small geometric relaxation is found to cause this observation.

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The spin states of molecules at surfaces are intriguing because of the interaction of localized molecular orbitals with delocalized substrate states. When a molecular spin is screened by delocalized electrons, the Kondo effect may be observed, which gives rise to a characteristic anomaly in the excitation spectrum close to the Fermi energy [1–6]. Several approaches are being explored to control molecular Kondo systems at surfaces. These include the application of electric fields [7], mechanical deformation [8], chemical modification of the ligand shell [9–12], and electronic excitation followed by spin state trapping [13,14].

In purely metallic systems, the proximity of a metal tip in a scanning tunneling microscope (STM) has been shown to modify the Kondo effect through changes of the Co *d* band and exchange interaction [15–17]. It seems natural to extend this method to the spin states of metal complexes using the tip as an additional ligand. By moving the tip, the ligand strength may be continuously modified with the subsequent changes in the local environment of the molecule, making this approach particularly appealing. The concomitant forces were observed to lead, in extreme cases, to the transfer of an atom or molecule from the sample to the tip [18,19].

Moreover, the electrostatic potential at the molecule may be modified. Although the electrical field in a nanoscopic junction is fundamentally interesting and drives current through the molecule little is known about it from experiments. Usually, it is assumed that the states of an adsorbed molecule are pinned with respect to the Fermi level of the substrate. A voltage drop between molecules and their substrate has been reported in cases where the molecules or parts of them were decoupled from a metal substrate by insulating layers [20–22] or by a particular geometric arrangement such as rod-shaped molecules adsorbed vertically [23] or molecular double deckers [24]. The question of the voltage drop within a molecular junction has been addressed by nonequilibrium *ab initio* quantum transport

calculations. These calculations show that most of the voltage drops at the weakest bond of the junction [25,26]. Calculations also indicate that a voltage drop between molecule and substrate may lead to negative differential resistance [27] and two-level fluctuations [28] of C<sub>60</sub> junctions as well as rectification in a molecular wire [29].

Here we present STM data and results of *ab initio* calculations for a metal complex on Au(111). In the limit of weak interaction with the STM tip the complex exhibits an underscreened high-spin Kondo effect. When the tip is moved closer to the metal ion, the differential conductance spectrum changes drastically. It turns out, however, that this change is due to sub-Angstrom structural relaxations. Similar to a mechanically operated switch, the voltage drop over the junction moves from the tip-molecule gap to the molecule-substrate bond.

Purified 5, 10, 15, 20-tetrakis(4-sulfonatophenyl)-21H, 23H-porphine manganese(III) chloride (MnTPS-Cl) was dissolved in aqueous methanol in the presence of 1 vol % acetic acid. Mass-selected singly charged MnTPS cations originating from the dissolution of Cl ions were electro-sprayed onto clean Au(111) surfaces in ultrahigh vacuum (UHV) [30]. Thus prepared samples were cooled to 77 K and subsequently transferred into a STM, which was operated at ~5 K in UHV. Tips were electrochemically etched from tungsten wire and further prepared *in situ* by indentation into the substrate. A sinusoidal modulation (2 mV<sub>rms</sub>, 1.2 kHz) was added to the bias to record spectra of the differential conductance.

Figure 1(a) schematically shows MnTPS, which hosts a Mn ion at the center of a tetraphenylporphyrin with four sulfonyl hydroxide (–SO<sub>3</sub>H) groups occupying *para* positions of the phenyl rings. When adsorbed on Au(111), the molecules appear quatrefoil shaped in STM topographs at positive sample voltage *V* [Fig. 1(b)], as typically observed for porphyrins and phthalocyanines [3,4,11]. One of the

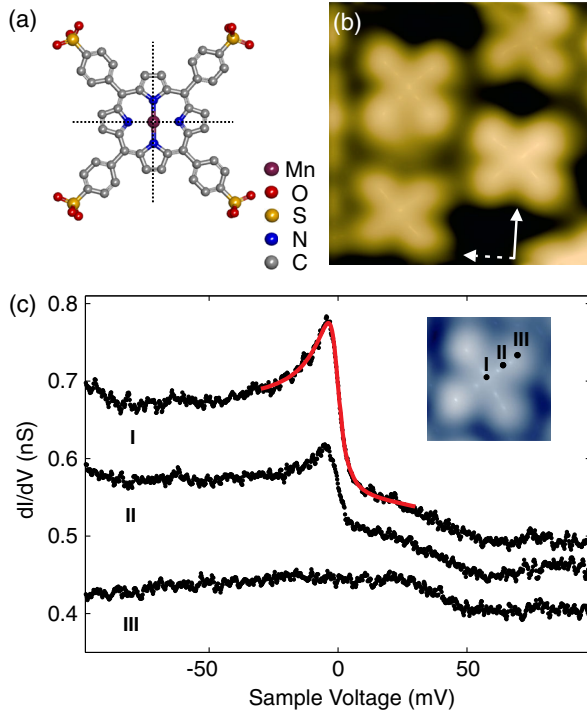


FIG. 1 (color online). (a) Structure of MnTPS (H atoms not shown). Dotted lines through pairs of opposite pyrrole units indicate  $C_2$  axes. (b) STM topograph ( $4 \times 4$  nm<sup>2</sup>, sample voltage  $V = 2.65$  V, current  $I = 50$  pA) of MnTPS agglomerated into an island on Au(111). The data are displayed in a pseudo-three-dimensional fashion. The apparent height of the molecular lobes is  $\approx 0.28$  nm. Solid and dashed vectors indicate the  $[0\bar{1}1]$  and  $[\bar{2}11]$  directions of Au(111), respectively. (c) Spatial evolution of  $dI/dV$  spectra of MnTPS. Dots in the inset indicate the positions of the measurements (spectrum I above the molecular center, spectrum III at the center of a lobe). For clarity, spectra II and III are shifted by  $-0.05$  and  $-0.1$  nS, respectively. The solid red line depicts a Frota fit to spectrum I.

molecular  $C_2$  axes preferably aligns along a  $\langle 0\bar{1}1 \rangle$  direction of Au(111) within the agglomerates. However, deviations of  $\approx \pm 5^\circ$  from this orientation were observed. Slight variations in apparent heights among the lobes of a particular as well as of different molecules are likely due to incommensurability with the substrate lattice. This structural variability may indicate a fairly weak molecule-substrate interaction as expected for Au.

$dI/dV$  spectra measured over various positions of the molecules are shown in Fig. 1(c). Above the Mn center (spectrum I) a resonance is observed close to zero bias, which continuously vanishes as the tip is moved sideways onto a lobe (spectra II and III). Following previous reports from metals [31] and metal porphyrins [2,32], we attribute the resonance as a signature of the Kondo effect. The spectrum of the Mn center may be described well by a Frota line [33,34] (solid red line) leading to an estimated Kondo temperature  $T_K \sim 100$  K [35].  $T_K$  measured from different molecules scattered in the range 100(7) K. No systematic

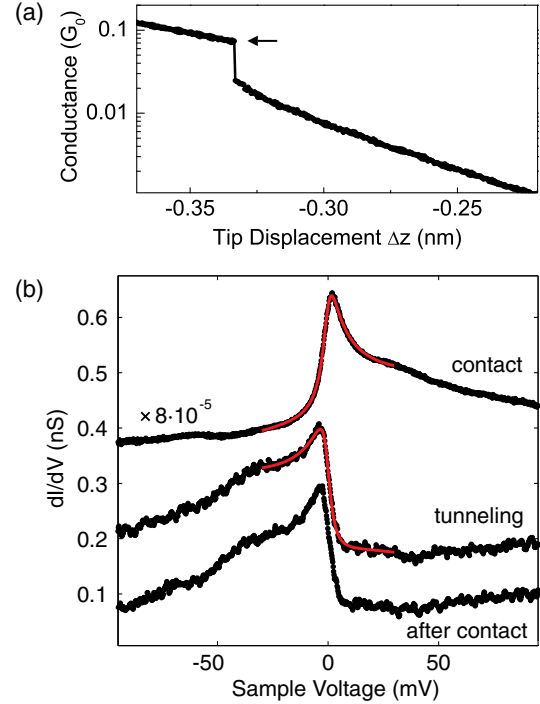


FIG. 2 (color online). (a) Conductance vs displacement  $\Delta z$  of the tip from the tunneling condition ( $\Delta z = 0$  at  $V = 100$  mV and  $I = 0.05$  nA) towards contact at the center of a MnTPS molecule. At contact formation (arrow) the conductance is  $0.074 G_0$  with  $G_0 = 2e^2/h$  being the conductance quantum. The conductance measured from different molecules scattered in the range of  $0.07 \pm 0.03 G_0$ . (b)  $dI/dV$  spectra acquired at  $\Delta z = 0$  (tunneling) and  $0.33$  nm (contact) at the center of a molecule. The bottom two curves are shifted by  $-0.45$  and  $-0.35$  nS, respectively, for clarity. Solid red lines show fits of Frota functions in the range of  $\pm 30$  mV.

effect of the position of a molecule in the agglomerates on the line shape was observed.

Next, the tip was brought closer to the center of a molecule until contact was reached. Data recorded for a molecule in a fcc region of the Au(111) reconstruction are shown in Fig. 2(a).  $\Delta z$  is the displacement of the tip from its initial height defined by  $V = 100$  mV and  $I = 0.05$  nA. The abrupt rise of the conductance at  $\Delta z = 0.33$  nm signals the transition to contact.

$dI/dV$  spectra were acquired by holding the tip at pre-determined heights over the molecular center [Fig. 2(b)]. Spectra recorded in the tunneling range exhibit similar line shapes (only spectra corresponding to  $\Delta z = 0$  are shown). At contact, a resonance near zero bias is still observed but surprisingly the line shape appears to be inverted on the voltage axis. Further approach of the tip from the point of contact does not change the shape of the spectrum. Approach of the tip beyond  $\sim 0.03$  nm from the point of contact usually led to the destruction of the junction. Very similar Kondo temperatures ( $\sim 100$  K) are obtained from the fits of Frota line shapes to both the tunneling and contact spectra. Tunneling spectra ( $\Delta z = 0$ ) recorded after the contact experiment were unaltered [bottom

curve in Fig. 2(b)], excluding the possibility that an irreversible change of the tip or the molecule occurred at contact. Isolated molecules, which were prepared by manipulation with the tip, exhibited tunneling characteristics virtually identical to that of the molecules in the agglomerates [Fig. 2(b)]. However, at contact isolated molecules were usually unstable.

At first glance, it may seem natural to attribute a changed Kondo line to a modified molecular spin state. On the other hand, it appears difficult to interpret the observed inversion of the line in such a scenario. We therefore performed density functional theory (DFT) based *ab initio* electronic structure and transport calculations to investigate to what extent the Kondo physics is modified by the proximity of the tip. The calculation explicitly takes into account the strong dynamic correlations originating from the Mn 3*d*-shell that give rise to the Kondo effect [36–38]. First, the MnTPS molecule was relaxed in the junction between the Au(111) substrate and the STM tip, modeled by a small Au pyramid built in the [111] direction, using VASP [39,40] with the exchange correlation functional by Perdew, Burke, and Ernzerhof (PBE) functional [41] and the dispersion correction due to Grimme [42] (see details in the Supplemental Material [43]). Figures 3(a) and 3(b) show the resulting structures in the tunneling regime and at contact, respectively. Without the tip, the Mn center is found to be at a height of 2.77 Å above the surface. When the tip is brought closer to the Mn center, the molecule is lifted from the surface. At contact (tip at a height of 6 Å above the surface), the displacement of Mn center is  $\approx 0.7$  Å [46].

In order to determine the dynamic single-particle broadening  $\Gamma_d(\omega)$  of the Mn 3*d*-levels due to the coupling to the organic framework of the molecule, the substrate, and the tip, DFT-based transport calculations were performed using the ANT.G code [47]. To make the calculations computationally feasible we replaced the sulfonatophenyl groups of the molecule by hydrogen atoms, which leaves the local environment of the Mn center unchanged. Figure 3(c) shows  $\Gamma_d(\omega)$  of the 3*d*<sub>z<sup>2</sup></sub> orbital, which is the only orbital that couples directly to the *s*-type conduction electrons of the substrate (similar to MnPc [38,48]) and effectively binds to the *s* level of the Au tip atom (details in the Supplemental Material [43]). Hence, the 3*d*<sub>z<sup>2</sup></sub> orbital is essentially the only *d* orbital that responds to the lifting of the molecule from the substrate. In the tunneling regime the broadening is featureless around the Fermi energy  $E_F$  [Fig. 3(c), solid red line], while the coupling to the *s* level of the tip at contact leads to a broad feature at  $\approx 1.2$  eV above  $E_F$  [Fig. 3(c), dashed blue line]. The concomitant increased broadening at  $E_F$  is partially compensated by reduced coupling to the substrate.

To capture correlation effects beyond the mean-field approximation, the Mn 3*d* shell was augmented by a Hubbard interaction term that takes into account density-density interactions and Hund's rule coupling. We assume

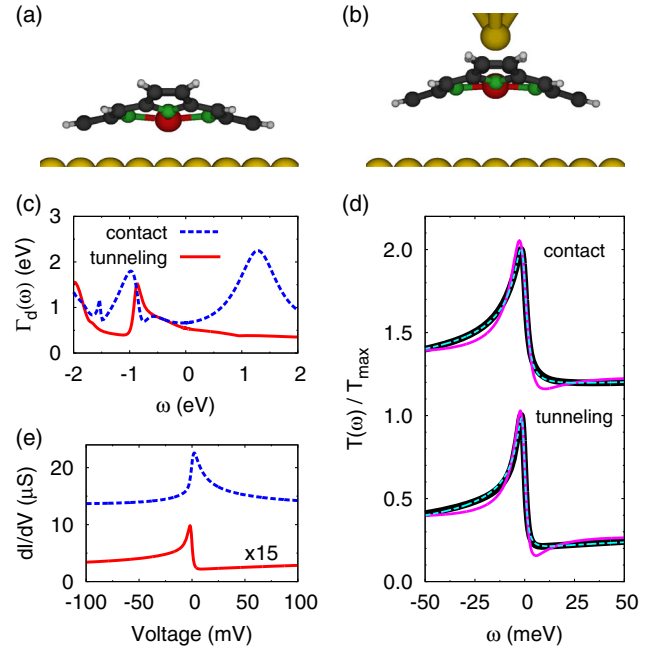


FIG. 3 (color online). (a),(b) Schematics of relaxed structures in tunneling and contact regimes. At contact, which corresponds to a tip height of 6 Å above the substrate, the Mn center is lifted from the surface by 0.7 Å with respect to the tunneling regime. This vertical displacement is exaggerated in the figure for better perceptibility. (c) Broadening of 3*d*<sub>z<sup>2</sup></sub> orbital in the tunneling (solid red line) and contact (dashed blue line) regimes. (d) Calculated transmission functions  $T(\omega)$  normalized to the maximum transmission  $T_{\max}$  in the tunneling and contact (solid black lines) regimes along with fits using Frota (dashed cyan lines) and Fano (solid magenta lines) line shapes. Fits minimize the mean-square deviation over the interval of 100 to 100 meV. For clarity, a narrower range is shown. The transmission curve at contact is shifted by 1. (e) Calculated  $dI/dV$  curves in the tunneling (solid red line) and in the contact regime (dashed blue line).  $\alpha$  is 0.02 and 0.8 in the tunneling and contact regimes, respectively. The contact spectrum is shifted by 10  $\mu$ S.

an intraorbital repulsion  $U = 4.5$  eV, an interorbital repulsion  $U' = 3.1$  eV, and a Hund's coupling  $J_H = 0.7$  eV [49]. The one-crossing approximation (OCA) [50] was used to solve the multiorbital Anderson impurity model of the Mn 3*d*-shell coupled to the rest of the system. The solution yields the spectral function of the Mn 3*d* shell  $A_d(\omega)$  (see Supplemental Material [43]). Only the 3*d*<sub>z<sup>2</sup></sub> orbital couples to the conduction electrons near  $E_F$  and thus shows a Kondo resonance. While the width of the resonance is comparable to that of the  $dI/dV$  spectra recorded in the tunneling regime, a slightly broader resonance appears at contact due to a small increase of  $\Gamma_d(E_F)$  and charge fluctuations of the 3*d*<sub>z<sup>2</sup></sub> orbital (see Supplemental Material [43]). The total spin of the Mn 3*d* shell is found to be approximately 1.7, i.e., halfway between spin-3/2 and spin-2 systems. Hence MnTPS displays an underscreened high-spin Kondo effect.

To obtain the low-bias transport properties of the system we calculated the transmission function  $T(\omega) =$



$\text{Tr}[\hat{\Gamma}_T(\omega)\hat{G}_M^\dagger(\omega)\hat{\Gamma}_S(\omega)\hat{G}_M(\omega)]$ , where  $\hat{G}_M(\omega)$  is the correlated Green's function of the extended molecule that contains the Kondo resonance.  $\hat{\Gamma}_T$  and  $\hat{\Gamma}_S$  are operators describing the coupling to the tip and the substrate, respectively. Figure 3(d) shows the calculated transmission curves (for both the tunneling and contact regimes) that exhibit asymmetric resonances similar in shape to those of the  $dI/dV$  spectra measured in the tunneling regime [Fig. 2(b)]. However, in contrast to the experiment no line shape inversion occurs at contact. Figure 3(d) also shows fits of Fano (solid magenta lines) and Frota (dotted cyan) functions to the calculated transmissions for both tunneling and contact. Interestingly, the fit of the Frota line to our results, which are based on the OCA, is superior. Similar observations were previously made for spectral functions calculated using numerical renormalization group [51,52] and quantum Monte Carlo [53] approaches. Second order perturbation theory, on the other hand, results in a Fano line shape [54].

The difference in line shape between the calculated transmission functions and the measured  $dI/dV$  is understood by considering the voltage drop across the junction. The current through the molecule can be written in terms of the transmission function as  $I(V) = (2e/h) \int_{\mu}^{\mu+eV} d\omega T(\omega - \alpha eV)$ , where  $\mu$  is the chemical potential of the substrate and  $\alpha$  is a dimensionless parameter determining the local chemical potential at the position of the molecule [23,55]. Similar to a voltage divider,  $\alpha$  can be obtained from the broadenings  $\Gamma_t$  ( $\Gamma_s$ ) due to the tip (substrate) as  $\alpha = (\Gamma_t/\Gamma_t + \Gamma_s)$ . Since the transport through MnTPS is dominated by transmission through the  $3d_{z^2}$  orbital, for  $\Gamma_t$  and  $\Gamma_s$  we use the couplings of the Mn  $3d_{z^2}$  orbital to the tip and substrate, respectively. We estimate  $\alpha = 0.02$  with  $\Gamma_t \sim 0.01$  eV and  $\Gamma_s \sim 0.54$  eV in the tunneling regime, and  $\alpha = 0.7$  at contact (tip 6 Å above the surface) with  $\Gamma_t \sim 0.47$  eV and  $\Gamma_s \sim 0.2$  eV. As expected, e.g., from nonequilibrium quantum transport calculations [26],  $\Gamma_t \ll \Gamma_s$  in the tunneling range,  $\alpha$  is small, the potential at the molecule is pinned to  $\mu$ , and the applied bias drops over the vacuum gap between the tip and the molecule.

Figure 3(e) shows the calculated  $dI/dV$  spectra for  $\alpha = 0.02$  (tunneling) and  $\alpha = 0.8$  (contact). The latter value is chosen because the estimated  $\alpha = 0.7$  gives a rather symmetric resonance (also see Supplemental Material [43]). Like in the experiments, the line shape of the spectrum at contact (dashed blue line) is inverted with respect to the tunneling regime (solid red line). Since no such inversion occurs in the underlying transmission curves [Fig. 3(d)], the observed inversion is solely due to the modified local potential of the molecule. In other words, the voltage drop has shifted to the molecule-substrate spacing [56]. This shift is not only due to an increased molecule-tip coupling but also to a sub-Angstrom displacement of the molecule, which reduces  $\Gamma_s$ . Moreover, since  $\alpha \geq 0.8$  is required to produce an asymmetry

comparable to that of the experimental data, we conclude that at least 80% of the voltage drops between molecule and substrate in the contact regime.

A second, less obvious difference between tunneling and contact is that the Kondo screening of the molecular spin is mainly mediated by the electron systems of the substrate and the tip, respectively. In the present experiments, the tip was covered with Au, the material of the substrate and the Kondo temperature happens to be hardly changed. Occasionally, with some tips, the Kondo resonance disappeared in the contact range, possibly because the material at the apex of those tips did not provide the required screening.

The model of the voltage drop used above has been very useful in interpreting data from double-barrier situations like tunneling to a molecule on a thin insulator. The data presented here for a flat molecule between two metal electrodes, shows that the voltage drop can be very relevant ( $\geq 80\%$  between substrate and molecule) in a case that is less expected. While for MnTPS ( $\alpha$  close to one) an inversion of the line shape is observed, a more symmetric coupling ( $\alpha \approx 0.5$ ) would cause an artificial broadening of the measured resonance. In summary, the electrical potential in molecular and atomic junctions apparently deserves more attention.

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\*karan@physik.uni-kiel.de

†Present address: Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, P. R. China.

‡weismann@physik.uni-kiel.de

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