Kondo Effect of Molecular Complexes at Surfaces: Ligand Control of the Local Spin Coupling

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The spin state of single magnetic atoms and molecules at surfaces is of fundamental interest and may play an important role in future atomic-scale technologies. We demonstrate the ability to tune the coupling between the spin of individual cobalt adatoms with their surroundings by controlled attachment of molecular ligands. The strength of the coupling is determined via the Kondo resonance by low-temperature scanning tunneling spectroscopy. Spatial Kondo resonance mapping is introduced as a novel imaging tool to localize spin centers in magnetic molecules with atomic precision.

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The ability to control and manipulate individual spins and the coupling of single spins to their environment is at the basis of prospective quantum technologies, where miniaturization reaches the atomic level [1]. The detailed understanding of the interactions of a spin with its surroundings and the possibility to tune this coupling are therefore essential in nanotechnology. It is only recently that the detection of single spins which are decoupled from a substrate has been demonstrated [2,3]. In this Letter, we exploit the Kondo effect to investigate the coupling of individual spins to a metallic substrate. The Kondo effect is a many-body effect which leads, at sufficiently low temperatures, to a pronounced resonance in the local density of states (LDOS) [4]. This Kondo resonance can be detected by low-temperature scanning tunneling spectroscopy (STS) [5–9] and thus can be used to characterize the magnetic properties of single spin impurities. Up to now, STS studies concentrated on characterizing the spin of single adatoms and the influence of the substrate on the magnetic properties of the adatoms [9]. In this Letter we demonstrate how the coupling of the spin of a single magnetic adatom to the substrate can be controlled by changing its local environment through ligand attachment. The Kondo resonance is exploited to study the magnetic interactions between the spin of the molecules and the substrate. Furthermore, we demonstrate how the Kondo resonance can be used to spatially localize a spin center within a single molecule.

In STS, the Kondo peak is observed as a resonance that can be described by a Fano function [10]. This is due to the hybridization of the Kondo state with the conduction band electrons [11,12]. From the fit of a Fano function to the measured spectra, width, energy, and a line shape parameter of the resonance can be extracted. The width is proportional to the characteristic Kondo temperature T_K of the system under consideration. T_K is a direct measure of the coupling between the spin and the surrounding electron sea.

The experiments have been performed using a Cu(100) single crystal surface, prepared carefully by sputtering and annealing cycles in ultra high vacuum (base pressure 1×10^{-10} mbar). Cobalt atoms were evaporated from an electron-beam heated cobalt rod onto the sample at a surface temperature of ~150 K, where diffusion, and hence island formation, is inhibited. After evaporation of minute amounts of cobalt (~0.001 ML), the sample was exposed to 0.1 to 0.5 L ($1\mathrm{L} = 1 \times 10^{-6}$ mbar · s) carbon monoxide and subsequently annealed to 200–300 K, which results in the formation of cobalt carbonyls. The final annealing also ensures the desorption of extraneous CO from clean areas of the substrate [13]. Thereafter, the sample was transferred *in situ* into a home-built low-temperature STM operating at 6 K. The bias voltage is applied to the sample. Spectroscopic measurements were performed with open feedback loop using a lock-in technique with a modulation of the sample voltage of 1–3 $\mathrm{mV_{RMS}}$ at a frequency of 4.5 kHz to record the dI/dV signal. For bias voltages close to the Fermi energy this signal is proportional to the LDOS of the sample. The spectra shown are background subtracted [14], i.e., the spectrum of the clean Cu(100)-surface has been subtracted from the spectra taken on atoms or molecules with the same tip in order to remove tip-related features.

After preparation, the surface is covered predominantly with cobalt tetracarbonyl complexes. Occasionally, other species are found on the surface, especially binuclear cobalt carbonyls, which consist of two cobalt atoms plus a number of carbonyl groups and at lower post-annealing temperatures cobalt tricarbonyls. Cobalt dicarbonyl molecules have been prepared by controlled tip-induced dissociation of cobalt tetracarbonyl by injecting tunneling electrons at a bias voltage of about 2–3 V into the complex.

The composition of the molecules can be proven by complete dissociation by the injection of tunneling electrons. The remainders, a single cobalt adatom and CO molecules, can be identified by tunneling spectroscopy. The spectrum acquired on a cobalt adatom shows a pronounced resonance at the Fermi level due to the Kondo effect [8], while spectra acquired on the CO molecules exhibit distinct vibrational features due to inelastic tunneling processes [15].

STM images of the carbonyl species together with that of a cobalt adatom are summarized in Figs. 1(a)–1(d) with the spectra acquired on the molecules. Carbonyls are identified by comparison of the STM images to simulated images from density-functional theory (DFT) calculations [16] and by tip-induced disassembly. A single cobalt adatom [Fig. 1(a)] is imaged as a spherical bump. The STM image of the dicarbonyl molecule [Fig. 1(b)] exhibits a fourfold symmetry—as the image of the tetracarbonyl molecule. In the case of the dicarbonyl molecule, the fourfold symmetry is due to a continuous flipping of the two CO molecules between the two equivalent configurations [as indicated in the model in Fig. 1(b)]. If impurities or defects are close to a dicarbonyl molecule, the two CO molecules are locked in one of the two possible directions and the STM image shows only the expected twofold symmetry. The tricarbonyl molecule shows three lobes. Two CO molecules point towards the nearest neighbor Cu atom in the substrate while the third is directed towards a bridge site [Fig. 1(c)]. For the $Co(CO)_4$ molecule, all four CO molecules point in the direction of the next on-top sites [Fig. 1(d)].

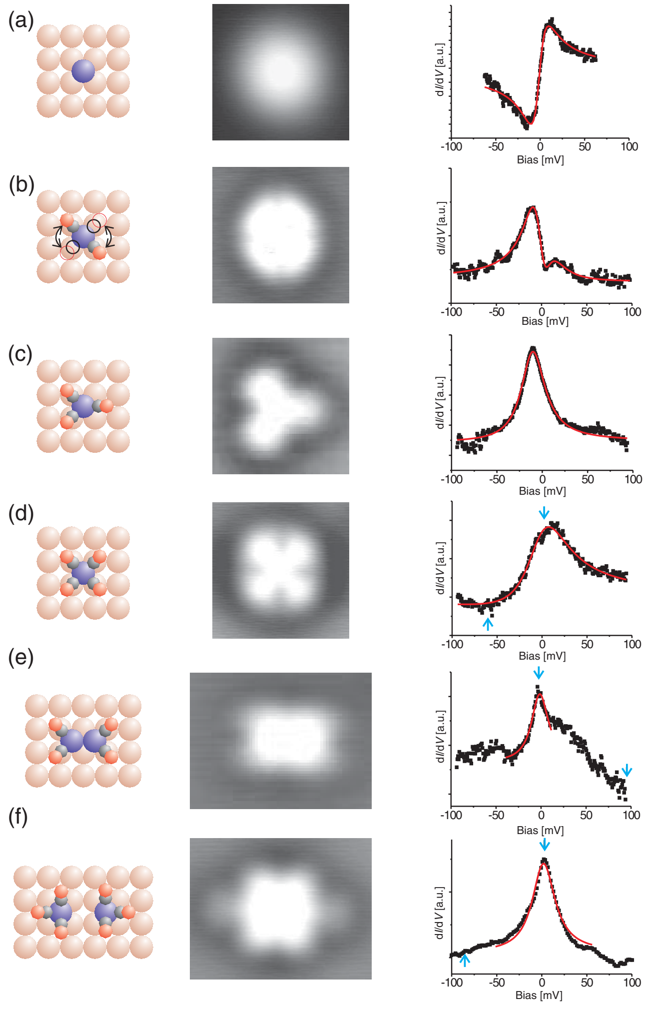

FIG. 1 (color online). Models, STM topographies, and STS spectra in the center of the Co adatoms and complexes under investigation: (a) Cobalt adatom, (b) $Co(CO)_2$ (constantly flipping; from the spectrum a linear background has been removed), (c) $Co(CO)_3$, (d) $Co(CO)_4$, (e) $(Co(CO)_2)_2$, (f) $(Co(CO)_3)_2$. Models and topographies in (a)–(f) drawn to the same scale. The solid lines in the spectra are fits of a Fano function.

Tunneling spectra acquired in the center of the molecules show a pronounced feature near the Fermi energy in all cases. From the fit of a Fano function we can extract the widths of the resonances. On cobalt dicarbonyl [Fig. 1(b)], the feature at the Fermi level is more complicated than for the other species. It is superimposed to a linear background and vibrational features from the CO molecules. However, when the linear background is subtracted, the feature is more clearly visible as can be seen in Fig. 1(b). The widths of the resonance observed on individual cobalt adatoms and the cobalt carbonyls are listed in Table I, where they have been converted to temperatures ($k_B T_K = \Gamma$, where Γ is the half width of the resonance). The values are averaged for several molecules and tips. The Kondo temperature is found to increase with the number of ligands attached to the impurity from 88 K for the single cobalt adatom to about 280 K for the cobalt tetracarbonyl complex. On binuclear carbonyl complexes, which are shown in Figs. 1(e) and 1(f) similar features can be observed at the Fermi level, revealing a consistent trend of increasing resonance width with increasing effective number of ligands per cobalt atom.

The resonance in the spectrum acquired on a single cobalt adatom has previously been assigned to be the Kondo resonance due to the interaction of the spin of the adatom with the conduction electrons of the host [5–8]. By adding carbon monoxide molecules, not only the electronic properties of the cobalt atom are modified—which leads to a drastic change in the apparent height of the complex compared to a single cobalt adatom and probably also induces the change in the line shape, but also its magnetic properties are affected. Carbon monoxide is a strong-field ligand and thus increases the splitting between the molecular orbitals—especially those derived from the cobalt *d* orbitals. The pairing of electrons is facilitated and the molecule is presumably in a low-spin state. It is known that free cobalt carbonyl molecules have an odd number of valence electrons with one unpaired electron. Thus the narrow feature at the Fermi energy can be rationalized as

TABLE I. Parameters determined from the fit of a Fano function for the various cobalt carbonyl complexes.

Molecule	T_K [K]	ϵ_K [meV]
Cobalt	88 ± 4	-1.3 ± 0.4
$Co(CO)_2$	165 ± 21	-1.8 ± 4.2
$Co(CO)_3$	170 ± 16	-13.2 ± 1.5
$Co(CO)_4$	283 ± 36	-5 ± 10
$(Co(CO)_2)_2$	138 ± 21	-3.8 ± 5.9
$(Co(CO)_3)_2$	176 ± 13	-1 ± 15

the Kondo resonance of the spin of the unpaired electron in the cobalt $3d$ orbital which is coupled to a bath of conduction electrons. Similar features at the Fermi energy have previously been observed by Lee and Ho on iron mono- and dicarbonyls on Ag(110) but no assignment was reported [17]. We have also observed a similar resonance on iron tetracarbonyl molecules adsorbed on the Cu(100) surface. To verify the magnetic origin of the resonance, we have changed the metal center to copper. Following a similar preparation as for the cobalt tetracarbonyl molecules, $Cu(CO)_2$ molecules are formed on the surface. Copper carbonyl complexes did not show any resonance peak at the Fermi energy, but clearly exhibit the signatures of vibrational excitation of the hindered rotation of CO at 35 meV [17]. In the case of cobalt carbonyls, the vibrational features are buried by the dominating Kondo resonance. The fact that the resonance observed on the transition metal carbonyl complexes stays pinned to the Fermi level either when changing the central atom to iron or the number of ligands—while it disappears for copper carbonyls—is further evidence for the Kondo effect.

Since the Kondo resonance is a signature of the spin of the molecule it can be exploited as a sensor for its magnetic properties. The behavior of the Kondo temperature of the complexes as a function of the number of ligands can be understood in the Kondo model [18]. The Hamiltonian of this model describes the interaction between a localized spin in an impurity orbital with a surrounding sea of conduction electrons. The interaction is described by the exchange coupling J between the spin of the impurity and that of the host electrons. While an increased hybridization between the orbital which carries the spin and the conduction band of the host leads to an increased exchange coupling, an increased on-site Coulomb repulsion results in a reduction in J [19]. The bond between the CO molecules and the cobalt adatom consists of a donation of electrons from the σ orbital to the transition metal adatom and a backdonation from the d orbitals to the $2\pi^*$ orbital of the CO molecules [20]. This backdonation leads to a delocalization of the d electrons and therefore reduces the Coulomb repulsion and eventually increases the coupling to the substrates conduction band electrons. Both lead to an increased exchange coupling J.

Within a simple model, we assume that the product of exchange coupling and density of states at the Fermi energy $J\rho_0$ scales linearly (apart from an additive constant J_0) with the number n of CO molecules attached to the cobalt atom

$$J\rho_0 = J_0 + c_J n, \tag{1}$$

where c_J is the proportionality constant. The characteristic Kondo temperature T_K and hence the width of the Kondo resonance can now be calculated within the Kondo model [4] from

$$k_B T_K \sim D e^{-1/J\rho_0}, \tag{2}$$

where D is the width of the conduction band. In addition to the increased hybridization, geometric effects, especially for the carbonyls with two and three ligands might come into play; these are neglected within our simple model. Describing the coupling as discussed above, we treat D, J_0, and c_J as fitting parameters. Figure 2 shows a fit of Eq. (2) to the experimental data. Within the errors, the agreement between the model and our data is very good. From the fit we obtain $D = 1.83$ eV, $J_0 = 0.182$, and $c_J = 0.01$. The value for D is of the order of magnitude which is typically assumed for the bandwidth of metals (see, e.g., [11]), that for J_0 compares reasonably with a similar fit for cobalt impurities [8]. It should be noted that while the Kondo effect describes only spin fluctuations, with increasing hybridization, also the contribution of charge fluctuations to the resonance at the Fermi energy will increase, bringing the system closer to the mixed valence regime for an increasing number of ligands. We find a comparable increase in the Kondo temperature for iron adatoms and iron tetracarbonyl molecules: for an iron adatom the Kondo temperature is smaller than 60 K on the Cu(100) surface, while the Kondo resonance of a $Fe(CO)_4$ complex yields a T_K of about 140 ± 23 K. We therefore have two handles to control the coupling of a spin to its surroundings: on one hand by changing the substrate and thus the occupation of the d orbital as shown recently [9], and on the other hand by tuning the exchange coupling between the electrons in the d level and the substrate by attaching ligands. By carefully choosing the ligand, it should also be possible to stabilize the spin of the metal center and decouple it from its environment resulting in a reduced Kondo temperature.

The STM is able to go a step beyond spectroscopically characterizing the Kondo resonance by exploiting its spatial resolution. In Fig. 3 we show the spatial mapping of the amplitude of the resonance for a cobalt tetracarbonyl

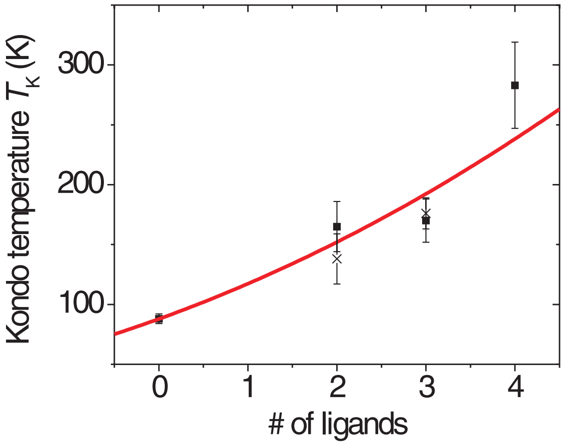

FIG. 2 (color online). Scaling behavior of a cobalt impurity with n CO molecules attached to it. Data for dicobalt carbonyls are shown as crosses, the number of ligands refers to the number of CO molecules per cobalt atom. The solid curve shows a fit of Eq. (2) to the data.

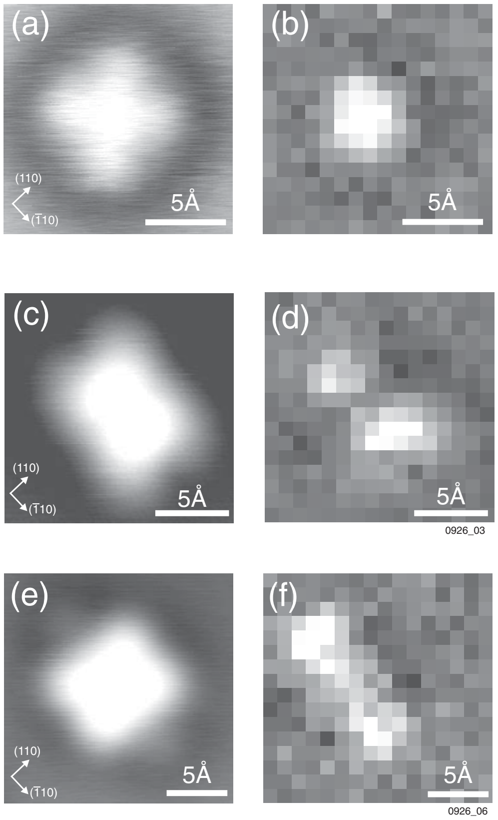

FIG. 3. (a) Topography and (b) simultaneously acquired Kondo map of a cobalt tetracarbonyl molecule. (c) and (d) show topography and Kondo map for $(\mathrm{Co(CO)_2})_2$, (e) and (f) for $(\mathrm{Co(CO)_3})_2$.

molecule. The difference between the dI/dV signal at the voltages marked by the arrows in Fig. 1(d) is a measure of the height of the resonance shown as intensity in Fig. 3(b), while Fig. 3(a) shows the simultaneously acquired topography. The spectroscopic image does not reflect the fourfold symmetry of the molecule showing only a spherically symmetric maximum in the center of the molecule—localized within a radius of ≈ 2.5 Å. It is at this position, where the cobalt adatom is located in the complex and accordingly where the spin of the complex originates from. Thus, we can detect the spin by STS via the Kondo resonance and localize it within the molecule.

The spatial mapping of the Kondo resonance can be easily applied to more complicated species with more than one cobalt atom. In Figs. 3(c)–3(f), similar measurements as for the $\mathrm{Co(CO)_4}$-molecule are shown for binuclear cobalt carbonyl complexes, namely $(\mathrm{Co(CO)_2})_2$ and $(\mathrm{Co(CO)_3})_2$. Figs. 3(c) and 3(e) display the topographies of the two species. The spatial mapping [Figs. 3(d) and 3(f)] of the resonance found on these species allows for a localization of the cobalt atoms and the corresponding spin centers on the complex with atomic precision. In conclusion, we have characterized the coupling of magnetic complexes at surfaces by exploiting the Kondo effect. We have shown how the coupling of an individual spin to the substrate can be tuned by attaching ligands to a cobalt adatom thereby increasing the coupling of the spin to the substrates conduction electrons. Thus it becomes possible to control the balance between magnetic coupling between neighboring spins and screening of the spin by the substrates conduction electrons. Moreover, the combination of spectral and spatial resolution of STM enables to localize the spin center at an unprecedented resolution. This method can serve as a powerful technique to study the coupling of spin centers in magnetic molecules in contact to metallic substrates and even interactions between magnetic molecules.

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