Spin-coupled double-quantum-dot behavior inside a single-molecule transistor

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We report on the observation of Kondo and split Kondo peaks in single-molecule transistors containing a single spin transition molecule with a Fe$^{2+}$ ion. Coulomb blockade characteristics reveal a double quantum dot behavior in a parallel configuration, making our system a molecular equivalent to a semiconducting double-quantum-dot system. As the gate voltage is increased the charging of the second dot by an additional electron induces a splitting of the Kondo peak. We discuss possible origins of this effect including a spin transition into a high-spin state.

The Kondo effect, originally observed in diluted magnetic alloys is induced by the interaction between a local spin and conduction electrons [1]. In a quantum dot (QD), this effect gives rise to a zero-bias conductance peak (ZBP) for charge states with a total spin S=1/2 [2,3]. When a magnetic field is applied, the degeneracy of the spin state is lifted by the Zeeman effect and a splitting of the ZBP is observed [4]. In the absence of a magnetic filed, a split ZBP corresponding to a bias-induced transition from singlet to triplet state can also be observed for charge states with an integer spin [5–7]. Another system where the Kondo effect has been investigated is the two impurities system originally described by Jones et al. [8]. For example, split ZBPs have been observed in double QD systems where two dots interact via a conducting region or via direct tunneling [8,10]. The exchange interaction between the spin of the two dots lifts the degeneracy of the ground state. Besides semiconducting double QDs, this effect has been observed in only a few other systems: in metallic dots containing magnetic impurities [11] and in scanning tunnelling microscopy experiments with two interacting magnetic atoms [12]. In addition to the fundamental interest in studying the Kondo effect on single impurities, some of those works have been motivated by the general goal of addressing and manipulating single spins with possible application in quantum information processing [13]. Particularly promising systems towards this direction are magnetic molecules in which the exchange coupling between the spins can be manipulated by charging the molecule with an electric field [14].

In this letter, the Kondo effect is used to characterize the exchange interaction inside a single-molecule transistor (SMT) containing a spin transition (ST) molecule. This type of compound supports a transition between a low-spin (LS) and a high-spin (HS) state, which can be induced by a change in temperature, pressure, magnetic field or by light irradiation [15]. We have studied a ST molecule containing a Fe$^{2+}$ metal ion connected to two ligands : [Fe-(L)$_2$]$^{2+}$[L=4′-(4′′-pyridyl)-1,2′:6′:1″-bis-(pyrazolyl)pyridine] (referred to as [Fe-(L)$_2$]$^{2+}$) (see Fig. 1(a)). This molecule shows a reversible thermally driven spin transition at 286 K in its bulk crystalline form [2,3]. This type of ST molecule is particularly suited for studies in a SMT geometry since the charge state of the molecule can be modified by applying a potential on the gate electrode. According to recent ab-initio calculations [16,17], this charging may drive the ST from LS to HS in analogy to charge transfer ST compounds [18].

To connect the molecule, we fabricate nanometer sized gaps by a controlled electromigration process on a thin Au wire deposited on top of an oxidized Al gate [19]. Electromigration and the subsequent self breaking of the wire is carried out at room temperature in a solution containing the molecule; the solvent is subsequently evaporated. If a molecule is trapped in the gap a three terminal device is formed in which the molecule connects via tunnel barriers to source and drain electrodes and couples electrostatically to an external gate (see Fig. 1(b)).

We present in Figs. 2(a) and 3(a) the differential conductance over bias and gate voltage obtained at $T = 1.5$ K for two samples, A and B. The data exhibits classical behavior of single-electron transport through a nano-object with a single relevant energy level. The extracted addition energies $E_{add}$ >100 meV and gate couplings $\beta = C_g/C_{tot} \approx 0.02$ ($C_g$: gate-dot capacitance; $C_{tot}$: total capacitance of the dot) are typical of transport through a single molecule [19]. The tunnel couplings for samples A and B can be estimated from the Lorentzian

![FIG. 1: Schematic representation of: (a) the molecule [Fe-(L)$_2$]$^{2+}$[L=4′-(4′′-pyridyl)-1,2′:6′:1″-bis-(pyrazolyl)pyridine] and (b) the the transistor geometry.](image-url)
broadening $\Gamma$ of the Coulomb peaks: $\Gamma_A \approx 60$ meV and $\Gamma_B \approx 10$ meV. A ZBP, characteristic of the Kondo effect, is observed for both samples in a pronounced regime of gate voltages. For sample A, the Kondo temperature extracted from the temperature dependence of the zero-bias conductance of the Kondo peak [20] presented in Fig. 5 is $T_{K,A} \approx 70$ K. For sample B, a temperature $T_{K,B} \approx 25$ K is deduced from its full width at half height.

FIG. 2: (a) Differential conductance of sample A versus source-drain ($V_b$) and gate ($V_g$) voltages. (b) Zoom of the differential conductance plot. (c) Differential conductance traces (from top to bottom) versus $V_b$ taken at gates voltages of respectively 2, 2.4, 2.9 and 3.3 V. The black (red) traces correspond to gates voltages on the right (left) hand side of the diagonal line.

In addition to this typical SMT behavior we observe a particular feature visible as a diagonal line (indicated by a red arrow) in the differential conductance plots of Figs. 2(a,b) and 3(a,b). In Fig. 3(a) on the right hand side of this line, a shift $\Delta V_g$ of the Coulomb diamond edges in gate voltage is present, which finds a natural interpretation as a response to a modification of the electrostatic environment. This feature can be reproduced by a Coulomb blockade model which is based on a scenario with two parallel dots: current flows through one QD, the ”transfer dot” in the presence of a second dot, the ”spectator dot” (see Fig. 4(a)). This second dot is electrostatically coupled to the first dot and as its tunnel coupling to one of the electrodes is very weak; there is no net current through it. However when the gate voltage is increased this dot can be charged by an additional electron, thereby, modifying the electrostatic environment of the other dot via their mutual capacitance $C_M$. This charging induces an horizontal shift of the Coulomb diamond edges by $\Delta V_g$. Fig. 4(b) shows the result of a rate equation calculation of two single-level QDs capacitively-coupled (see supplementary information for more details), which mimics the situation for sample B.

We first focus on the low-bias regime. A zoom of this region is shown in Fig. 2(b) and 3(b). For sample A the ZBP is clearly split on the right hand side of the diagonal line and two peaks appear at $\pm eV_b = \pm \Delta_A = \pm 2.75$ meV (see Fig. 2(c)). The temperature dependence of the ZBP and split ZBP are presented in Fig. 5(a,b). In case of the split ZBP, the zero-bias conductance $G(0)$ exhibits a nonmonotonic temperature dependence (Fig. 5(c)). For sample B the splitting is less pronounced and is visible as a reduction of the zero bias conductance (Fig. 3(c)). When the gate voltage is further increased the splitting becomes more pronounced due to the decrease of the Kondo temperature as we go away from the degeneracy point [21]. For the trace indicated as ”e” in Fig. 3(c) we extract a splitting $\Delta_B \approx 0.5$ meV for sample B. Split ZBP as well as nonmonotonic temperature dependence of $G(0)$ are reminiscent of spin-spin interactions competing with Kondo screening, as observed in coupled QDs systems [9, 10] and described theoretically in Refs. [22, 23]. With this in mind one might expect that the split ZBP is induced by interactions between the two spins of the double dot also in our case. This explanation would be consistent with the observed transport
charactersitics in Fig. 2(a) and 3(a), if we assume the occupation of the dots to be as represented schematically in Fig. 4(b). On the left hand side (region I), the transfer dot (1) has an even occupancy (as confirmed by the absence of Kondo peak in this region in Fig. 3(a)). When the gate voltage is increased (region II), the transfer dot is charged by an additional electron, leading to an odd occupancy, \( S_t=1/2 \) and the observation of a Kondo peak (Fig. 2(a) and 3(a)). In region III the spectator dot is in turn charged leading to an odd occupancy \( S_s=1/2 \) of both dots, if an even occupancy is assumed for the spectator dot on the left hand side of the diagram. A sizable spin interaction between the transfer and the spectator dot could then explain the experimentally observed peak splitting. However, as we will argue below the estimated exchange interaction between the two dots is typically too small in order to account for the experimentally observed value \( \Delta_{AB}=0.5-3 \text{ meV} \). Here the spin transition will come in.

Two possible physical realizations of the double-dot scenario, \( R_t \) and \( R_s \), are conceivable (see Fig. 4(c) and 4(d)). In the first realization, \( R_t \), we make explicit reference to the internal molecular structure of our \( \text{Fe-(L)}_2^{2+} \) molecule. To support this scenario, we have carried out ab-inito density functional theory (DFT) calculations \cite{17} (see also supplementary information) on the molecule. The two bi-pyrazolyl-pyridine ligands support \( \pi \)-systems, which are oriented perpendicularly to each other by the octahedral coordination around the \( \text{Fe}^{2+} \) metal ion. Therefore, left and right ligand states hybridize only weakly with each other. In particular, for the situation of double reduction (i.e., when two excess electrons are added) our calculations confirm that each electron is localized on one ligand only, with very little excess charge penetrating the region connecting the two ligands near the \( \text{Fe}^{2+} \) ion. In the asymmetric situation where one ligand is connected with two electrodes via \( \pi \)-ligand metal-electrode half-sandwich type binding interactions \cite{24}, and the other one only to a single electrode (as represented in Fig. 4(c)), the double dot system sketched in Fig. 4(a) is indeed realized. In the alternative way to produce a double dot system, \( R_s \), one could imagine an extrinsic spectator dot, that does not form a chemical bond with the original molecule, e.g. a second molecule or a small metallic grain (see Fig. 4(d)).

We start the discussion with the scenario \( R_t \) as illustrated in Fig. 4(c). A first estimate for the ligand-ligand exchange coupling (with the molecule being in the LS state) may be obtained using \( J_{t-L}^L \sim \gamma^2 U \) (\( \gamma=\text{t}/\text{E}_{\text{HOMO}} \)): relative energy splitting between symmetric/anti-symmetric combinations of ligand orbitals; \( U \): effective interaction energy in the near ion region of wavefunction overlap, roughly approximated by the \( e_g-t_{2g} \)-splitting: \( U \lesssim \Delta_{\text{orb}} \). We have typically \( \gamma \approx 0.1-1 \text{ eV}, \) and \( J_t \lesssim 0.01-1 \text{ meV} \). This rough estimate is fully supported by our \textit{ab initio} calculations \cite{17} (CASSCF level, see supplementary information) that predict for the LS state a weak ligand-ligand ferromagnetic exchange coupling \( J_{t-L}^L \approx 0.095 \text{ meV} \). Essentially, this low value is due to the suppression of the tunneling matrix elements, \( t \), between the two ligand systems. It is only weakly modified if a small variation of the 90° angle between the ligands is taken into account (0.15meV change at 20°). To further support the theoretical arguments, we can compare these values with observed exchange splittings for LS transition metal complexes \cite{25}, which are in the \( \mu \text{eV} \) range. In conclusion, according
to our calculations, the scenario $R_1$ when assuming a LS state leads to an exchange coupling too small to explain the observed splitting $\Delta_{A,B}$.

Now, in the second case involving an extrinsic dot, $R_e$, the direct tunneling between the spectator and the transfer dot $[9, 20]$ should be expected to be even smaller than in the scenario $R_i$ since they are not connected via a chemical bond. Hence, also the associated exchange coupling will be very small. Of course, in principle there is an additional indirect interaction due to the RKKY coupling via the leads $[10]$. An accurate estimation of this splitting is difficult to obtain as it depends strongly on the spatial configuration and geometry of the dots and electrodes. However, we argue that the associated exchange coupling should anyways be very weak. This is because coherent tunneling processes connecting the two dots have to take electrons across two barriers: from the spectator dot into the leads and then from the leads into the transfer dot (and the same way back to establish coherence). The parametrical estimate ("golden rule" type) for the associated coupling is $J_{eRKKY} \approx \Gamma_i \Gamma_s / \Delta_{sz}^2 (r_{sl}s) F_k$ electrode induced broadening of the molecular levels of the transfer and spectator dot; $\Delta_{sz}$: mismatch of the two coupled energy levels; $r_{sl}s$: spatial distance of the two contact points of the two dots with the electrodes measured in units of the Fermi-wavelength). Assuming $\Gamma_i \approx 10$ meV, $\Delta_{sz} \approx 100$ meV and $r_{sl}s F_k \approx 3 - 10$ typical values of $J_{eRKKY}$ lie between 0.01-0.1 meV. Hence we conclude: an explanation of the observed split ZBP, which would be based on a conventional spin-spin interaction inside a double-dot seems hardly consistent with the values of the observed splittings $\Delta_{A,B}$.

So far, our analysis was based on the assumption that the molecule is in the LS state. However, a detailed theoretical analysis suggests that the LS state may give way against a HS state when the $[Fe-(L)_2]^{2+}$ molecule is doubly charged $[17]$. Accordingly, the molecule could be in its LS state in region I and II, while it would be in the HS state in region III. In HS the Fe$^{2+}$ core possesses a spin $S = 2$ which is antiferromagnetically coupled to the spins on the ligands. The ground state is thus a spin triplet $[17]$. Due to the spin-orbit interaction the triplet splits into a Kramer’s doublet and a singlet state. In the optimized high-spin geometry of our molecule, we find that this zero field splitting, $\Delta E$, is about 0.16 meV. This value will be larger if distortions due to incorporation in the planar device geometry are present and our preliminary calculations suggests that it can reach values of several meV. We thus expect that among all the possible scenarios, $R_1^{HS}$ gives rise to the strongest splittings which approach the experimental values of a few meV.

In summary we have observed a double-quantum-dot behavior in combination with a split Kondo peak. We suggest that the split ZBP indicates a charged-induced spin-transition inside the molecule. To reach a definitive conclusion in favor of this high-spin scenario, further experiments, which could involve, e.g., a detailed measurement of the Kondo splitting in magnetic fields, would be needed. The observation of such a spin-transition would be an important step towards the development of molecular spintronics, as it demonstrates the possibility of addressing and controlling with an electric field individual spin states engineered at the molecular scale.

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[1] J. Kondo, Prog. Theor. Phys. 32, 37 (1964).
[2] D. Goldhaber-Gordon et al., Nature(London) 391, 156 (1998).
[3] S. M. Cronenwett et al., Science 281, 540 (1998).
[4] T. A. Costi, Phys. Rev. Lett. 85, 1504 (2000).
[5] S. Sasaki et al., Nature (London) 405, 764 (2000).
[6] J. Nygård et al., Nature (London) 408, 342 (2000).
[7] E. A. Osorio et al., Nanoletters 7, 3336 (2007).
[8] B. A. Jones, C. M. Varma, and J. W. Wilkins, Phys. Rev. Lett. 61, 125 (1988).
[9] H. Jeong et al., Science 293, 2221 (2001).
[10] N. J. Craig et al., Science 304, 565 (2004).
[11] H. B. Heersche, et al., Phys. Rev. Lett. 96, 017205 (2006).
[12] A. F. Otte et al., Phys. Rev. Lett. 103, 107203 (2009).
[13] D. Loss and D. P. DiVincenzo, Phys. Rev. A 57, 120 (1998).
[14] J. Lehmann et al., Nat. Nanotech. 2, 312 (2007).
[15] P. Gülich and H. A. Goodwin, eds., Spin Crossover in Transition Metal Compounds in Topics in Current Chemistry, vol. 233 (Springer: Berlin, 2004).
[16] C. Rajadurai et al., Inorg. Chem. 45, 10019 (2006).
[17] V. Meded et al., to be published, preprint (2010).
[18] D. M. Adams et al., J. Am. Chem. Soc. 116, 6221 (1993).
[19] E. A. Osorio et al., J. Phys.: Condens. Matter 20, 374121 (2008).
[20] T. A. Costi et al., J. Phys.: Condens. Matter 6, 2519 (1994).
[21] D. Goldhaber-Gordon et al., Phys. Rev. Lett. 81, 5225 (1998).
[22] M. G. Vavilov and L. I. Glazman, Phys. Rev. Lett. 94, 086805 (2005).
[23] P. Simon, R. Lopez, and Y. Oreg, Phys. Rev. Lett. 94, 086602 (2005).
[24] C. Eschenbroich and A. Salzer, Organometallics (Wiley-VCH, Weinheim, 1989).
[25] C. Stroh et al., Inorg. Chem. 40, 5334 (2001).
[26] J. C. Chen, A. M. Chang, and M. R. Melloch, Phys. Rev. Lett. 92, 176801 (2004).
[27] E. A. Osorio et al., Nanoletters 10, 105 (2010).
[28] Our CASSCF result indicates that the splitting between ground state triplet and the consecutive quintet is at least 53.2 meV corresponding to a metal ion-ligand exchange interaction $t^{Fe-L}_{ex} \approx 13.3$ meV, in the same range as the one experimentaly observed in similar transition metal complex $[25, 27]$. 