

## Vibrational Kondo Effect in Pure Organic Charge-Transfer Assemblies

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A Kondo resonance has been observed using a scanning tunneling microscope on a single molecular layer of a purely organic charge-transfer salt grown on a metal surface. Analysis of the Kondo anomaly reveals that the electron acceptor of the film possesses a spin- $\frac{1}{2}$  ground state due to the localization of an unpaired electron in the conjugated lowest unoccupied molecular orbital. Because of the  $\pi$  character of this molecular state the unpaired electron is strongly coupled to molecular vibrations, leading to the split of the Kondo resonance in vibrational sidebands.

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The localization of unpaired electrons in an organic molecule is an essential requirement to accomplish molecular magnetic materials [1]. Traditionally, this has been advanced through the synthesis of organic coordination compounds, where unpaired electrons in the paramagnetic transition metal atoms provide the molecule with a net magnetic moment [2]. Molecular-based magnetism has been successfully achieved in metal-organic charge-transfer (CT) materials, typically metal-cyanide-based compounds. Here, an electron transfer from the metallic centers into a molecular state leads to the formation of stable organic radicals. Magnetic ordering in these solids is usually associated to exchange interactions between the metal cations and the organic species [3].

The synthesis of metal-free magnetic materials, where unpaired electrons reside in  $\pi$  molecular orbitals, remains as a difficult challenge to achieve.  $\Pi$ -orbital radicals are expected to exhibit enhanced magnetic order due to the more extended character of their spin polarized shells. However, overlapping and broadening of their extended  $\pi$  molecular states in a crystal hinders, at the same time, the localization of a single electron. In particular, the pure-organic CT complex TTF-TCNQ [4,5] (where TTF, which denotes tetrathiafulvalene, and TCNQ, which denotes tetracyanoquinodimethane, are the molecular donor and acceptor, respectively) has only a fractional charge transfer ( $0.6e$ ) in the solid crystal, which is delocalized in extended electron bands along molecular  $\pi$  stacks [4].

Here, we show that a single molecular layer of the TTF-TCNQ complex grown on a Au(111) surface exhibits a spin- $\frac{1}{2}$  degenerate ground state. We demonstrate its free-radical state by the observation of the Kondo effect in transport experiments using a low temperature scanning tunneling microscope (STM). We find that an unpaired electron is localized in a  $\pi$  orbital of the TCNQ molecule, which interacts very weakly with the underlying metal surface. Because of its  $\pi$  character, the unpaired electron appears strongly coupled to molecular vibrations, leading to the split of the Kondo resonance in various vibrational sidebands.

The experiments were carried out in a custom-built scanning tunneling microscope (STM), in ultrahigh vacuum and at a temperature of 4.8 K. On the Au(111) surface, TTF-TCNQ layers with 1:1 stoichiometry are formed spontaneously by codeposition of both species at room temperature [5]. Scanning tunneling microscopy (STM) images [Figs. 1(a) and 1(b)] resolve that, contrary to the bulk structure of the CT compound, molecules in the layer lie parallel to the gold surface, forming extended molecular rows. Density functional theory calculations for this layer structure [5] predict the single occupation of the TCNQ lowest unoccupied molecular orbital (LUMO) by yielding its alignment close to the metal Fermi level ( $E_F$ ). In our experiment, this is confirmed by scanning tunneling microscopy (STM) images around the zero-bias value, picturing TCNQ molecules with the distinctive shape of its unperturbed LUMO, i.e., a nodal plane at the center and two maxima at each of the  $C(CN)_2$  terminations [Fig. 1(b)].

To probe their electronic configuration close to  $E_F$ , we investigate electron transport characteristics through an individual TCNQ molecule at low temperatures (4.8 K) using the tip of our STM as a source or drain of tunneling electrons. Differential conductance ( $dI/dV$ ) spectra measured on top of a TCNQ molecule show an unusually narrow ( $8 \pm 1$  mV FWHM at 4.8 K) zero-bias peak (ZBP) [Fig. 1(c)]. The peak is completely absent on the TTF molecules [Fig. 1(d)], neither can it be observed on pure TCNQ domains, showing that its origin lies in the particular charge state of TCNQ interacting with TTF molecules in the CT layer. The ZBP cannot be directly ascribed to a molecular resonance, because a state with such sharp linewidth at  $E_F$  should rather appear split in the spectra as a consequence of Coulomb blockade [6,7]. As we shall demonstrate in the following, the ZBP is a manifestation of the Kondo effect.

The Kondo effect appears in the tunneling spectra as a resonance at zero bias, with linewidth  $2k_B T_K$  at zero temperature ( $k_B$  is the Boltzmann constant and  $T_K$  the Kondo temperature) [7]. To prove the Kondo origin of the ZBP we analyze the dependence of its line shape with temperature

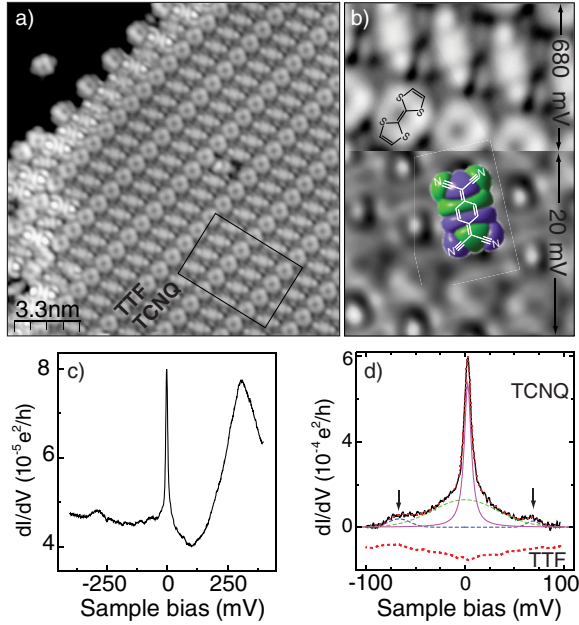


FIG. 1 (color online). (a) STM image of an ordered TTF-TCNQ island on Au(111) ( $V = 680$  mV,  $T = 4.8$  K). (b) Enlarged images [as the rectangle shown in (a)] obtained with two different bias values, indicated in the figure. At the lowest bias, TCNQ shows the characteristic intramolecular structure of the free-molecule LUMO (shown in the figure). Data analysis is performed using the freeware WSXM [26]. (c)  $dI/dV$  spectrum measured on the CN sites of TCNQ molecules in the mixed layer shows a sharp zero-bias peak associated here to the Kondo effect ( $V_{ac} = 1$  mV rms). The broader feature at 300 mV corresponds to a hybrid (TTF-Au) interface state [5,27]. (d) Comparison of  $dI/dV$  spectrum on TCNQ and on TTF (dashed line, shifted down). A linear background has been subtracted. A good fit to the spectrum on TCNQ is obtained when including two Gaussian side peaks (marked with arrows), associated here to the singly occupied LUMO resonance, at  $\varepsilon = -67$  mV, and its corresponding Coulomb-charging peak, at  $\varepsilon + U = 67$  mV. The fit includes a broad Gaussian background centered at 0 V.

[8,9]. Figure 2 shows the ZBP measured on top of the CN side groups of a TCNQ molecule as the substrate is warmed up from 4.8 K, its base temperature, to 13 K. In agreement with the expected behavior for a Kondo resonance, the ZBP broadens and reduces its intensity appreciably as a response to the increase of temperature ( $T$ ). The linewidth broadening with  $T$  can be fitted using an approximated expression developed in the framework of Fermi-liquid theory [9] to determine a Kondo temperature of  $26 \pm 2$  K. The suppression of the peak height (i.e., the linear response conductance  $G_0$ ) with  $T$  is also a characteristic of the Kondo effect. Fitting the gradual decrease of the peak height  $G$  with the empirical expression  $G = G_0((T/T_K^*)^2 + 1)^{-s}$ , which reproduces numerical renormalization group results for spin- $\frac{1}{2}$  systems [8] with the parameter  $s = 0.22$  and with  $T_K^* = T_K/(2^{1/s} - 1)^{1/2}$ , al-

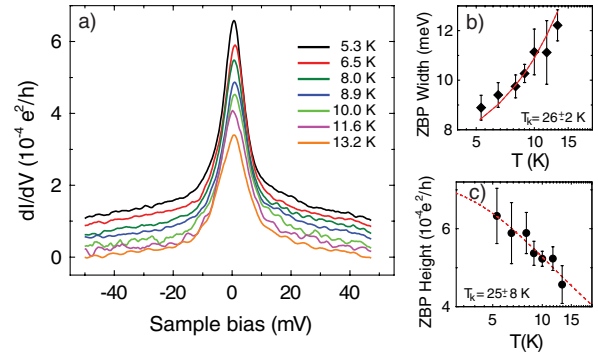


FIG. 2 (color online). Temperature dependence of the zero-bias peak. (a) Set of spectra (shifted upwards for clarity) measured on the CN sites of TCNQ molecules for various temperatures ( $V_{ac} = 1$  mV rms). The effect of vertical thermal drift has been corrected by a factor obtained from the removed background linear slope. (b) Temperature dependence of the peaks' linewidth. The corresponding fit (see text) includes the finite temperature and bias modulation broadening. The fitted Kondo temperature agrees with the temperature dependence of the peaks' intensity shown in (c), where the experimental broadening has also been corrected.

low us to obtain a similar value for the Kondo temperature ( $T_K = 25 \pm 8$  K). The temperature dependence of the ZBP is thus consistent with the predicted behavior for a spin- $\frac{1}{2}$  Kondo effect.

The spin-Kondo effect has been often found in magnetic systems adsorbed on metal surfaces [10–14]. It describes the condensation of a spin doublet into a singlet ground state at low temperatures due to the exchange interaction of a localized spin with the underlying sea of delocalized electrons. However, a Kondo resonance on the TTF-TCNQ layer cannot be directly ascribed to the magnetic properties of the individual molecular components, as none of them has a spin degenerate ground state [15]. A spin-Kondo fingerprint is here still possible if charge reorganization in the molecular layer leads to a single electron in a fairly localized molecular orbital (i.e., with linewidth  $\Gamma$  smaller than the electronic Coulomb repulsion  $U$ ).

Coulomb effects determine that a singly occupied molecular orbital (SOMO) (i.e., at an energy  $\varepsilon < U$  below the Fermi level) should appear as two resonances in the tunneling spectra [6]. They correspond to either tunneling through the SOMO, for negative sample bias ( $V_s < 0$ ), or through the doubly occupied state at  $\varepsilon + U$ , for  $V_s > 0$ . In all the spectra on TCNQ, the ZBP is accompanied by two broader and weaker features at  $\pm 67$  mV around zero bias [arrows in Fig. 1(d)], which we identify as the two Coulomb blockade peaks associated with the SOMO. Their separation ( $U = 134$  meV) is larger than their linewidth ( $\Gamma \sim 22$  mV and 12 mV for the states  $\varepsilon$  and  $\varepsilon + U$ , respectively) and they are symmetric with respect to zero bias (the so-called particle-hole symmetry point). This confirms that the origin of the Kondo resonance on

TCNQ molecules is the singly occupation of their LUMO, i.e., the formation of an  $\text{TCNQ}^-$  anion, due to charge rearrangement in the TTF-TCNQ/Au(111) system.

A crucial property of this ensemble of organic radicals is that the unpaired electron resides localized in a  $\pi$  molecular orbital (i.e., the LUMO), which is more extended than, for example,  $d$  or  $f$  orbitals of transition metal atoms. The localization of this molecular state is achieved because  $\text{TCNQ}^-$  anions are maintained sufficiently decoupled from the underlying metal surface by lateral interactions with the TTF neighbors [5]. As we show next, the molecular character of the unpaired electron leads to interesting phenomena in the Kondo state, related to the intrinsic coupling of molecular orbitals with molecular vibrations.

The Kondo ZBP shows a strong dependence of its line shape on the internal position within the TCNQ molecule where it is measured [Fig. 3(a)]. A strong peak like in Fig. 1(c) is only found on the  $\text{C}(\text{CN})_2$  terminations, as can be observed by representing the ZBP height in a differential conductance map [Fig. 3(b)]. At the center of the molecule, the ZBP appears smaller and it is accompanied by two characteristic side peaks at  $\pm 41$  meV, emerging with a comparable size. For a Kondo system, coupling of electrons with molecular phonons is expected to lead to the splitting of the ZBP in various (vibrational) sidebands [16–

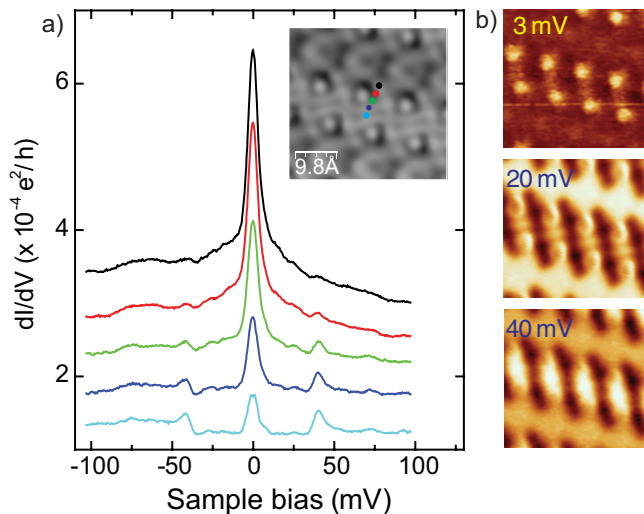


FIG. 3 (color online). Spatial dependence of the zero-bias peak. (a) Shows a set of spectra (shifted upwards for clarity) measured at different locations within a TCNQ molecule, as indicated in the inset ( $V_s = 20$  mV). The sharp Kondo resonance vanishes gradually as the spectra are taken towards the center of the TCNQ molecule and two side peaks appear. (b)  $dI/dV$  maps measured simultaneously to a STM topography at the indicated bias values ( $V_{ac} = 2$  mVrms at 720 Hz). The maps at 3 and 40 mV confirm the localization of the Kondo ZBP and side peaks at the CN sites and center ring of the TCNQ molecule, respectively. At other bias values (here at 20 mV),  $dI/dV$  maps reproduce the orbital structure of the TCNQ LUMO (here inverted due to convolution with STM feedback).

20]. The symmetric position of the peaks around zero bias and their narrow line shape, similar to the ZBP [Fig. 4(a)], thus constitute a key fingerprint of vibronic tunneling through the center of the molecule, involving a spin-flip plus the excitation of a molecular vibration [label 2 in Fig. 4(b)]. As a resonant process, the emergence of the sidebands is compensated by a decrease of the ZBP intensity [18].

A second clear feature observed in the spectra is a stepped increase of the  $dI/dV$  signal for bias values larger than the side peaks [label 4 and dashed lines in Fig. 4]. Such steps are characteristic of an inelastic electron transfer process (in contrast to the resonant character of the Kondo side peaks) assisted by the excitation of vibrations during tunneling through a vacuum barrier [19,21]. The steps correspond to an increase in the junction conductance

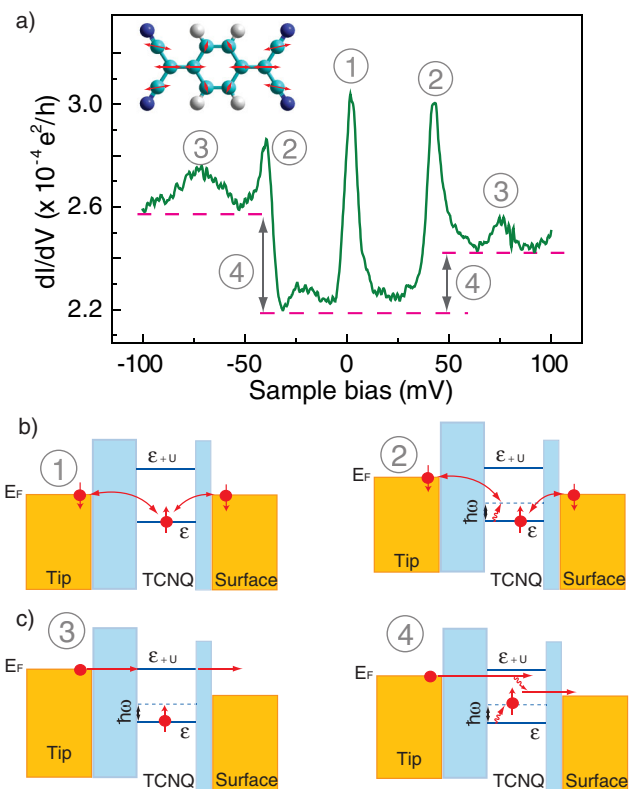


FIG. 4 (color online). (a) A  $dI/dV$  spectrum obtained on the center of a TCNQ molecule shows a rich structure (indicated by numbers) revealing various elastic and inelastic processes during electron tunneling through the TCNQ molecule. The inset shows the motion of TCNQ carbon atoms for the  $\nu^9$  vibrational mode. The arrows are proportional to the amplitude of motion. (b) Energy scheme of Kondo (1) and phonon-assisted Kondo (2) tunneling, observed as sharp peaks in the spectrum (a). (c) Energy diagram of resonant tunneling through the doubly occupied LUMO state (3) and inelastic (off-resonance) tunneling (4), observed as broad peaks and steps in the spectrum (a), respectively. Similar diagrams can be constructed for negative sample bias.



of  $\sim 15\%$  (10%) at negative (positive) bias, a large value that supports the strong electron-phonon coupling in this system. Furthermore, the spectra at the center of the TCNQ<sup>-</sup> anion show also a ubiquitous asymmetry with the polarity. At negative bias the effect of inelastic tunneling (4) is larger, whereas at positive bias the phonon-assisted Kondo resonance (2) becomes stronger. Since inelastic tunneling is enhanced by molecular resonances close to the Fermi level [22], this asymmetry seems to be related to the larger area of the SOMO peak (3, at  $V_s < 0$ ), with respect to the corresponding peak for the double occupied state, at  $\varepsilon + U$  (3, at  $V_s > 0$ ). It thus confirms that two different phonon-assisted electron transfer processes apparently compete here, one involving a spin flip (i.e., vibrational Kondo) and, the other, an inelastic tunneling event.

The origin of the strong coupling of electrons tunneling around the central carbon ring with the 41 meV vibrational mode can be rationalized by inspecting its corresponding atomic motion. This vibration corresponds to the  $\nu^9$  mode, with  $a_g$  symmetry, of the TCNQ<sup>-</sup> anion (the free-molecule eigenvalue, 41.6 meV, persists in TTF-TCNQ films [23,24]), which essentially consists in an in-plane ring deformation, accompanied by the stretching of the C=C(CN)<sub>2</sub> double bonds [inset of Fig. 4(a)]. The  $a_g$  modes of TCNQ are known to lead to a shift in the LUMO position, thus driving charge out (into) the molecule [24]. In particular, the  $\nu^9$  mode found here exhibits a large electron-vibration coupling [23] because it fits with the structural distortions undergone by the TCNQ<sup>-</sup> anion upon electron attachment (detachment), namely, an increase (decrease) in the aromatization of the central ring and the decrease (increase) of the external C=C bond order [25]. The effect of other vibrational modes, including external vibrations, can be also detected (albeit weaker) at other sites of the molecular backbone, thus suggesting that  $\pi$ -orbital magnetism is inherently associated to intramolecular motion.

In summary, the observation of the spin-Kondo effect on pure organic charge-transfer films has been used to demonstrate the free-radical state of individual acceptor molecules on a metal surface. Since the unpaired electron resides localized in a  $\pi$ -molecular orbital it appears strongly coupled to molecular vibrations, leading to the split of the Kondo resonance in various vibrational sidebands. Organic donor-acceptor interactions thus steer a promising route towards the self-assembly of free molecular radicals. Further strategies to achieve their magnetic ordering may reveal that the  $\pi$ -orbital character of unpaired electrons provides new phenomenology in comparison with traditional heavy atom-based magnetism.

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- [1] O. Kahn, *Molecular Magnetism* (Wiley-VCH, New York, 1993).
  - [2] J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed.* **33**, 385 (1994).
  - [3] J. M. Manriquez *et al.*, *Science* **252**, 1415 (1991).
  - [4] J. Fraxedas, *Molecular Organic Materials: From Molecules to Crystalline Solids* (Cambridge University Press, Cambridge, UK, 2006).
  - [5] N. Gonzalez-Lakunza *et al.*, *Phys. Rev. Lett.* **100**, 156805 (2008).
  - [6] P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).
  - [7] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, UK, 1993).
  - [8] D. Goldhaber-Gordon *et al.*, *Phys. Rev. Lett.* **81**, 5225 (1998).
  - [9] K. Nagaoka *et al.*, *Phys. Rev. Lett.* **88**, 077205 (2002).
  - [10] J. T. Li *et al.*, *Phys. Rev. Lett.* **80**, 2893 (1998).
  - [11] V. Madhavan *et al.*, *Science* **280**, 567 (1998).
  - [12] P. Wahl *et al.*, *Phys. Rev. Lett.* **93**, 176603 (2004).
  - [13] A. D. Zhao *et al.*, *Science* **309**, 1542 (2005).
  - [14] V. Iancu, A. Deshpande, and S. W. Hla, *Phys. Rev. Lett.* **97**, 266603 (2006).
  - [15] Other types of exotic Kondo effects, like those due to charge [A. W. Holleitner *et al.*, *Phys. Rev. B* **70**, 075204 (2004)] or orbital [O. Y. Kolesnychenko *et al.*, *Nature (London)* **415**, 507 (2002); P. Jarillo-Herrero *et al.*, *Nature (London)* **434**, 484 (2005)] degenerate ground states, can be here excluded as the TCNQ frontier molecular orbitals are nondegenerate.
  - [16] J. König, H. Schoeller, and G. Schön, *Phys. Rev. Lett.* **76**, 1715 (1996).
  - [17] J. Paaske and K. Flensberg, *Phys. Rev. Lett.* **94**, 176801 (2005).
  - [18] Z. Z. Chen *et al.*, *J. Phys. Condens. Matter* **18**, 5435 (2006).
  - [19] L. H. Yu *et al.*, *Phys. Rev. Lett.* **93**, 266802 (2004).
  - [20] J. J. Parks *et al.*, *Phys. Rev. Lett.* **99**, 026601 (2007).
  - [21] B. C. Stipe, M. A. Rezaei, and W. Ho, *Science* **280**, 1732 (1998).
  - [22] B. N. J. Persson and A. Baratoff, *Phys. Rev. Lett.* **59**, 339 (1987).
  - [23] N. O. Lipari *et al.*, *Chem. Phys. Lett.* **44**, 236 (1976).
  - [24] J. R. Cooper, T. Ivezic, and I. Zoric, *J. Phys. C* **15**, L397 (1982).
  - [25] W. Kaim and M. Moscherosch, *Coord. Chem. Rev.* **129**, 157 (1994).
  - [26] I. Horcas *et al.*, *Rev. Sci. Instrum.* **78**, 013705 (2007).
  - [27] The zero-bias peak reported here did not appear in the data shown in Fig. 2 in Ref. [5] because of the different intramolecular site and the larger bias modulation amplitude ( $V_{ac} = 15$  mV rms) used in that work.