Identifying Charge States of Molecules with Spin-Flip Spectroscopy

Ying-Shuang Fu,[1,2] Tong Zhang,[1,2] Shuai-Hua Ji,[1,2] Xi Chen,[1,*] Xu-Cun Ma,[2] Jin-Feng Jia,[1] and Qi-Kun Xue[1,2,†]

[1]*Key Laboratory for Atomic and Molecular Nanoscience, Department of Physics, Tsinghua University, Beijing 100084, China*
[2]*Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*
(Received 8 October 2009; published 17 December 2009)

The charge states of single molecular magnetic chains were manipulated with a scanning tunneling microscope and identified by spin-flip inelastic tunneling spectroscopy. We show that the charged and neutral states have different spin structures and therefore exhibit different features associated with the spin-flip processes in tunneling spectra. The experiment demonstrates a general approach for detecting the charge states at the nanometer scale in a more straightforward manner than using indirect information.

Single-electron charging is one of the most fundamental physics phenomena in molecular electronic systems that involves charge transfer [1–7]. The capability to manipulate and control the charge states is essential for molecule-based electronic applications and has been extensively investigated. Recent progress in scanning tunneling microscopy (STM) and spectroscopy (STS) experiments has made it possible to charge individual atoms or molecules on surfaces with an STM tip [8–10]. To date, the occurrence of charging in these studies is, however, only deduced from less direct information, such as the sombrero shape around an adsorbate in the STM images [8,10,11], the formation of ordered arrays [11,12] or the pattern of molecular orbitals that can be discriminated by the STM images [9]. Thus, it is indispensable to develop a reliable approach to detecting the charge state of single atoms or molecules in a more straightforward manner.

In this work, we demonstrate the ability to identify the charge states at the single molecular level by spin-flip inelastic electron tunneling spectroscopy (IETS) with STM, where the tunneling electrons transfer energy to the spin degree of freedom of an adsorbate via the spin-flip process [13–17]. The inelastic tunneling channels are opened after the bias voltage between the STM sample and tip reaches thresholds at $\pm\Delta/e$ (where Δ is the spin excitation energy and $-e$ is the charge on an electron). The threshold can be visualized by a steplike increase in dI/dV at bias voltages of $\pm\Delta/e$. Spin-flip IETS provides direct information of the spin states and spin coupling at the nanometer scale [13–17]. In addition, it is also sensitive to the charge states, which are closely related to the magnetic moment of an adsorbate. Therefore, we are able to characterize single-electron charging by spin-flip IETS. The work expands the application scope of STS to charge detection.

The experiments were conducted with a Unisoku ^{3}He-STM that reaches a base temperature of 0.4 K by means of a single shot ^{3}He cryostat [16,18,19]. Magnetic field up to 11 Tesla can be applied perpendicular to the sample surface. We prepared the multilayer structures of

cobalt phthalocyanine (CoPc) molecules [Figs. 1(a)–1(c)] on the Pb island in ultrahigh vacuum. The procedure of the sample preparation has been reported in previous studies in detail [16,18].

The Co^{2+} ion in a free CoPc molecule has a spin of $S = 1/2$, resulting from the singly occupied d_{z^2} orbital. If a CoPc is charged with an electron, the extra charge will preferentially occupy the lowest unoccupied molecular orbital (LUMO) of CoPc, which is still the d_{z^2} orbital according to the first principles calculation. The additional electron will experience the Coulomb repulsion from the other electron on the same d_{z^2} orbital. Upon adsorption on the Pb island, the spin of a molecule remains to be 1/2, except those in the first layer whose magnetic moment is completely quenched by the substrate [16]. The molecules from the second layer and above form chainlike stacks [Fig. 1(b)]. In a chain the molecules are antiferromagnetically coupled through the superexchange interaction, as shown recently [16]. In the current experiment, we focus on the charging phenomena and their influence on the spin excitation spectrum of CoPc molecules. The experiment demonstrates the capability to charge a single spin chain and detect the charging by the spin excitation spectrum.

Figure 1(d) shows the typical tunneling spectra measured on molecules in the third monolayer [Fig. 1(c)]. A magnetic field of 1.5 T was applied to completely quench the superconductive state of Pb. A CoPc in the third layer and the one right below it in the second layer form a spin chain of length $N = 2$. The chain has a spin singlet ground state. The spectra of different molecules share some common features but vary periodically due to the lattice mismatch between the molecular superstructure and Pb(111) − (1 × 1). The opening of inelastic tunneling channel is clearly noted on molecules 2, 3, and 4. The steps at both positive and negative bias in Fig. 1(d) correspond to the transition from the singlet ground state to the triplet excited state [Fig. 1(e)] [16]. On molecules 1 and 5, a step is still clearly seen at the negative bias. However, more electronic features are superimposed on the inelastic signal at the positive bias. These equidistant peaks (mole-
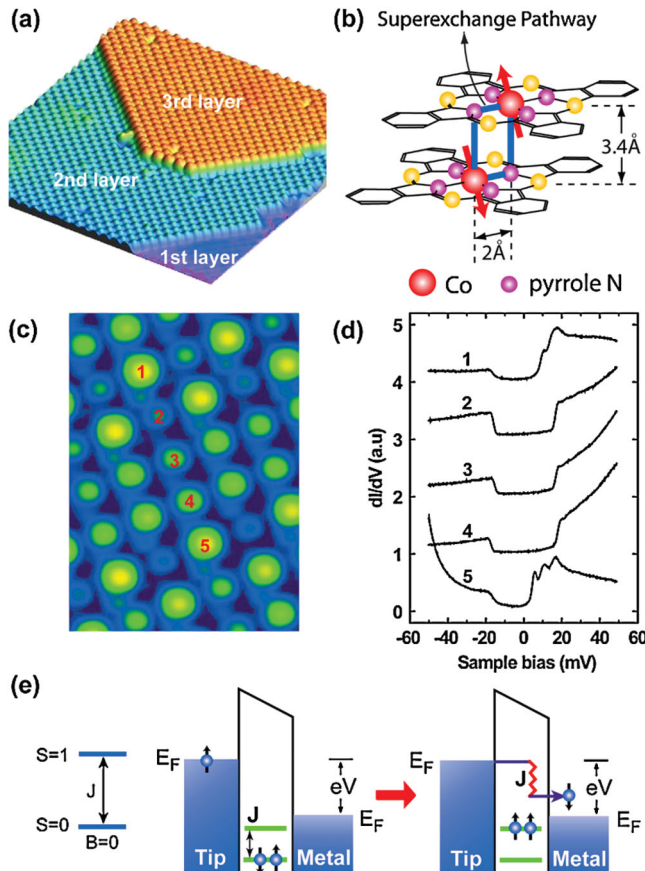
FIG. 1 (color). CoPc multilayers and spin-flip IETS. (a) STM image ($V = 1$ V, $I = 0.1$ nA) of the self-assembled multilayers of CoPc molecules on the Pb(111) island. (b) The superexchange interaction between a molecule in the second layer and the molecule right above it in the third layer. The superexchange pathway is indicated. (c) Topographic image ($V = 50$ mV, $I = 0.05$ nA) of CoPc molecules on the third layer. (d) Spectra acquired with the STM tip positioned on the center of the five molecules indicated in (c). The spectra indicate a transition from the singlet to the triplet states of a pair of antiferromagnetically coupled spins with an exchange parameter of $J \sim 18$ meV [16]. The spectra are offset for clarity. The tunneling gap was set at $V = 50$ mV, $I = 0.2$ nA. The bias modulation was 1 mV (rms) at 799 Hz. The steps in the spectra indicate the threshold of inelastic tunneling. Vibronic peaks are clearly noted on molecules 1 and 5. (e) Schematic showing the singlet to triplet transition.

cule 5, in particular) are attributed to the vibronic states of LUMO [20]. The first peak represents the vibrational ground state. Different from IETS, the excitation of molecular vibrations in molecule 5 is due to the resonant tunneling and becomes possible when energy of tunneling electrons are higher than that of the negatively charged molecule in its ground vibrational state. The vibrational energy, which is 45 ± 2 cm^{-1}, can be ascribed to the skeletal doming mode of CoPc [21].

The chain can be considered as embedded in a double-barrier tunnel junction (DBTJ), formed by the vacuum barrier between the tip and the molecules and the first

molecular layer above substrate. In a DBTJ, the energy of LUMO varies for different gap separation (z offset) between tip and sample [22]. This variation is simply due to the electrostatic effect, in particular, the image potential [6] in the present study. Because the first vibronic peak of molecule 5 in Fig. 1(d) is very close to zero bias, it is relatively easy to move it below the Fermi level by tuning the tunneling gap, and therefore charge the molecule right below the tip. The charge states are stabilized by the presence of the tip at a given tip-sample distance. Figure 2(a) shows the hysteresis loops for charging and discharging molecules when changing the bias voltage (so the tunneling gap) with feedback on. The detailed mechanism of charging will be discussed elsewhere. From A to B, the pair of molecules is kept neutral with decreased bias. At point B, the molecules are charged and the tip suddenly moves closer to the sample. When increasing the bias, the molecules become neutral again at point F. Similar loops can also be observed at negative bias. At certain bias voltage and tunneling current [0.4 nA in Fig. 2(a)], the molecules below the tip can be either neutral or negatively charged, depending on the history of voltage ramping. Thus, the STS of both neutral (spin 0) and singly charged (spin 1/2) states of an $N = 2$ spin chain can be recorded by setting the tunneling condition with the appropriate se-
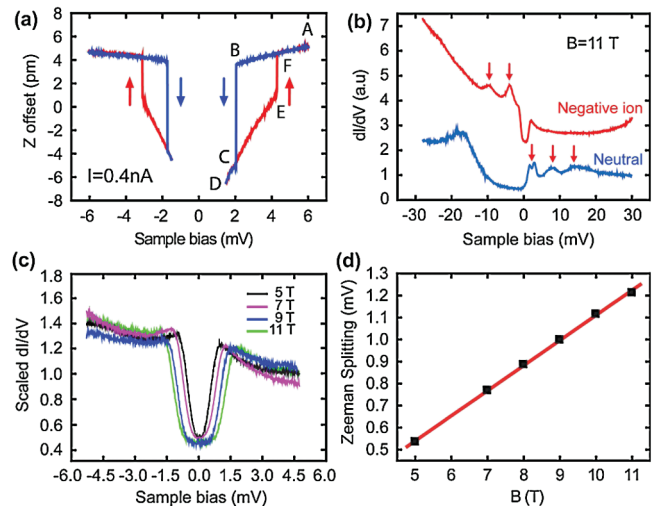

FIG. 2 (color). Charge states of an $N = 2$ spin chain. (a) $Z - V$ curves performed on a CoPc molecule in the third layer at a constant current of 0.4 nA. The forward ($A \rightarrow B \rightarrow C \rightarrow D$) and backward ($D \rightarrow C \rightarrow E \rightarrow F$) scans are indicated by arrows. (b) Differential conductance spectra of the spin chain before and after charging. With 11 T magnetic field, the Zeeman splittings for negative ion and neutral molecule are 1.23 meV and 1.32 meV, respectively. The dI/dV signal was measured with a modulation of 0.2 mV (rms) at a tunneling gap of $V = 8$ mV and $I = 0.1$ nA. The vibronic peaks are indicated by red arrows. (c) Spin-flip IETS of the negatively charged state at different magnetic field. The data were recorded with a modulation of 0.05 mV on bias. (d) Magnetic field dependence of the Zeeman energy in (c). The line intercepts the y-axis at -0.03 ± 0.02 meV.

quence of bias voltage ramping. Subsequently, the charge states are determined by their characteristic features in STS, respectively.

After the LUMO is moved below the Fermi level by tuning the z offset, the vibronic states are visible at the negative bias [upper curve in Fig. 2(b)] and the pair of molecules becomes singly charged. In magnetic field, the conductance over the charged molecules is reduced near zero bias [see also Fig. 2(c)] due to spin-flip inelastic tunneling through Zeeman splitting [Fig. 3(a)]. The IETS steps shift consecutively to higher energy with magnetic field [Fig. 2(c)]. A linear fitting of the threshold energy for inelastic process as a function of the magnetic field yields a g-factor of 1.97 [Fig. 2(d)]. In contrast, the dI/dV spectrum [lower curve in Fig. 2(b)] for neutral molecules does not show similar features near zero bias. Therefore, one can use spin-flip IETS, which is sensitive to the charge states, to conveniently distinguish between charged and neutral spin chains by their different response to external magnetic field.

As a matter of fact, the dI/dV spectrum of neutral molecules can still exhibit the Zeeman effect, but in a different way, i.e., through the elastic tunneling channels [Fig. 3(b)]. As shown in the lower curve in Fig. 2(b), the first vibronic peak of the LUMO splits under strong magnetic field. Usually, it is difficult to see the Zeeman splitting of a molecular orbital in STS because the width of peak corresponding to the resonant tunneling to an orbital is often much broader than the Zeeman energy. But in our case, the LUMO state is well isolated from the metallic substrate by the first CoPc layer, which greatly reduces the width of resonance. In strong magnetic field, the Zeeman

splitting becomes comparable to the peak width and can be resolved in STS.

In an inelastic tunneling process, the coupling between tunneling electrons and local spins is nonresonant and the process can be viewed as an impact scattering [23]. More specifically to the charged state, the tunneling electrons interact with the three electrons on a pair of coupled molecules through the exchange interaction, leading to local spin excitation. On the other hand, the elastic tunneling into the LUMO state of neutral molecules is a resonant process. The dI/dV spectrum of this process depends on the tunneling matrix element between the initial state, where the adsorbate stays neutral, and the final state, where a temporary negative ion is formed. In both of the nonresonant inelastic [Fig. 3(a)] and resonant elastic [Fig. 3(b)] tunneling processes, a charged state with three electrons on two d_{z^2} orbitals is involved.

To understand the observed STS in more detail, we model the spin chain by one-dimensional Hubbard Hamiltonian,

$$H = \epsilon \sum_{i=1}^{N} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{i\sigma} + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow} + t \sum_{i=1}^{N} \sum_{\delta} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{i+\delta\sigma},$$
(1)

where the operator $c_{i\sigma}^{\dagger}$ creates an electron with spin σ at the d_{z^2} orbital of ion i with energy ϵ and Coulomb repulsion U. t is the tight-binding hopping term. The summation over δ is limited to the nearest neighbors of i. Usually, $U \sim 1$ eV, $t \sim 0.1$ eV and $t \ll U$. The two-site Hubbard Hamiltonian describes the spin chain with $N = 2$. If only two electrons occupy the pair of ions, Eq. (1) reduces to the Heisenberg Hamiltonian $H = JS_1S_2$, where $J = 4t^2/U$ [24]. The ground state is antiferromagnetic [Figs. 1(d) and 1(e)] since J is positive.

The charged state is described by the two-site Hubbard Hamiltonian with three electrons. Exact diagonalization of the Hamiltonian shows that both the ground and the excited states of a singly charged chain of two spins are doublets with $2t$ as the excitation energy [Fig. 3(c)] [25]. In magnetic field, the eigenstates split into two levels. The splitting is given by the Zeeman energy $\Delta = g\mu_B B$. Both elastic and inelastic tunnelings require the participation of the ground state of Eq. (1), and therefore show the signature of Zeeman splitting in their dI/dV spectra [Fig. 2(b)] [26], however, in different ways.

The charging of a spin chain is also observed on some molecules on the fourth layer, where three spins are antiferromagnetically coupled. As shown in Fig. 4(a), the two steps at ± 19 mV [16] indicate the spin-flip process for a neutral spin chain with $N = 3$. The spin-flip excitation is well described by the Heisenberg model, which gives an excitation energy of J [see the insert of Fig. 4(a)]. The peak right above the Fermi level is the LUMO of the molecules. The vibronic structure is not clearly resolved possibly because of the superimposing of other electronic structures, such as the Kondo resonance. The ground state of
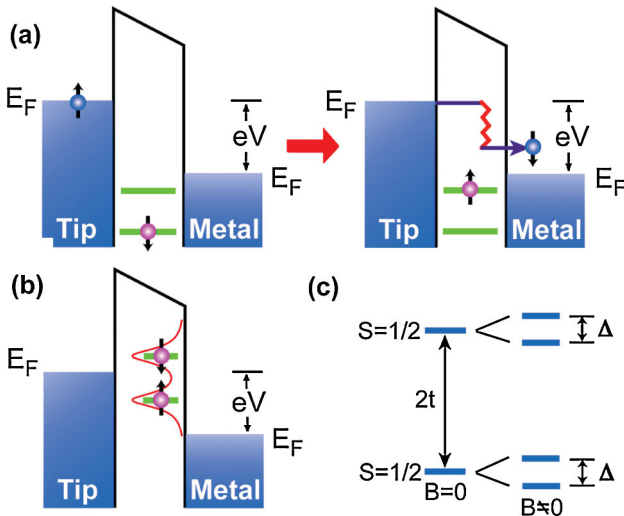

FIG. 3 (color). Zeeman effect in the resonant and nonresonant tunnelings. (a) Nonresonant inelastic tunneling through Zeeman splitting. (b) Resonant elastic tunneling through Zeeman splitting. (c) Eigenstates of the two-site Hubbard Hamiltonian with three electrons. The levels are split under magnetic field. Δ is the Zeeman energy.
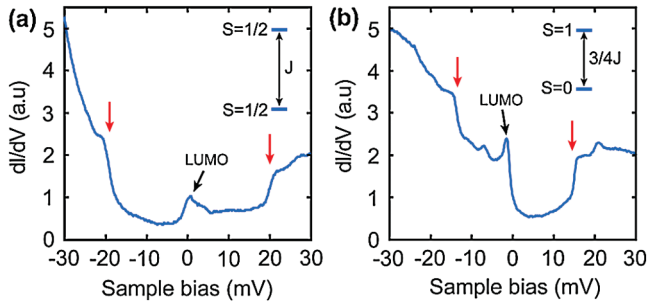
FIG. 4 (color).   Charge states of an $N = 3$ spin chain. (a) STS of the neutral state. The tunneling gap is set by $V = 50$ mV and $I = 0.08$ nA. The insert shows the first two energy levels of a neutral chain with $N = 3$. The threshold voltages for inelastic tunneling are indicated by red arrows. (b) STS of the charged state. The tunneling gap is set by $V = 25$ mV and $I = 0.3$ nA. The insert shows the first two energy levels calculated by the three-site Hubbard model with four electrons.

three coupled molecules carries spin-1/2, which may induce a weak Kondo peak at Fermi level. Similar to the situation in the third layer, the $N = 3$ spin chains can be charged by moving the LUMO below Fermi level with the help of electrostatic effect. Figure 4(b) shows the STS of a charged chain of three molecules. The threshold voltages (indicated by arrows) for spin-flip tunneling shift from ± 19 mV for neutral state to ± 14 mV for charged state. The Hubbard model [Eq. (1)] has to be employed again to calculate the spin-flip spectra of a charged spin chain with $N = 3$. The exact diagonalization yields the first excitation energy of $3/4J$ [insert of Fig. 4(b)], which is in close agreement with the observed STS.

In summary, we have demonstrated the capability of STM to manipulate and probe the charge states of single spin chains. Spin-flip IETS not only characterizes single spins but also emerges as a technique to detect single-electron charging in the nanometer scale. In this approach, the identification of charge states no longer relies on the indirect information induced by additional charges residing on adsorbates. To observe the spin-flip IETS, an insulating buffer is needed to increase the lifetime of spin excitations [13–16]. This requirement is usually satisfied in those experiments of charging single atoms or molecules [8–12], where a polar insulating film stabilizes the negatively charged state of adsorbates by its large ionic polarizability. Thus, we expect that the spin-flip IETS is generally applicable for directly detecting the charge states of single atoms in the experiments.

Furthermore, we have shown that magnetic structure could be manipulated at the atomic level by altering the charge states of molecules. This may lead to molecular spintronics devices with fully electrical control [27]. Applications, such as spin shift register [28] and channels for quantum communications [29], are envisioned.

*xc@mail.tsinghua.edu.cn
†qkxue@mail.tsinghua.edu.cn

[1] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, and P. L. McEuen, Nature (London) **407**, 57 (2000).
[2] J. Park *et al.*, Nature (London) **417**, 722 (2002).
[3] W. Liang, M. P. Shores, M. Bockrath, J. R. Long, and H. Park, Nature (London) **417**, 725 (2002).
[4] S. Kubatkin *et al.*, Nature (London) **425**, 698 (2003).
[5] A. Nitzan and M. A. Ratner, Science **300**, 1384 (2003).
[6] N. A. Pradhan, N. Liu, C. Silien, and W. Ho, Phys. Rev. Lett. **94**, 076801 (2005).
[7] Y. Gohda and S. T. Pantelides, Nano Lett. **5**, 1217 (2005).
[8] J. Repp, G. Meyer, F. E. Olsson, and M. Persson, Science **305**, 493 (2004).
[9] S. W. Wu, N. Ogawa, and W. Ho, Science **312**, 1362 (2006).
[10] F. E. Olsson, S. Paavilainen, M. Persson, J. Repp, and G. Meyer, Phys. Rev. Lett. **98**, 176803 (2007).
[11] M. Sterrer *et al.*, Phys. Rev. Lett. **98**, 096107 (2007).
[12] L. Giordano *et al.*, Phys. Rev. Lett. **101**, 026102 (2008).
[13] A. J. Heinrich, J. A. Gupta, C. P. Lutz, and D. M. Eigler, Science **306**, 466 (2004).
[14] C. F. Hirjibehedin, C. P. Lutz, and A. J. Heinrich, Science **312**, 1021 (2006).
[15] C. F. Hirjibehedin *et al.*, Science **317**, 1199 (2007).
[16] X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).
[17] N. Tsukahara *et al.*, Phys. Rev. Lett. **102**, 167203 (2009).
[18] Y. S. Fu *et al.*, Phys. Rev. Lett. **99**, 256601 (2007).
[19] S. H. Ji *et al.*, Phys. Rev. Lett. **100**, 226801 (2008).
[20] X. H. Qiu, G. V. Nazin, and W. Ho, Phys. Rev. Lett. **92**, 206102 (2004).
[21] Z. Q. Liu, X. X. Zhang, Y. X. Zhang, and J. Z. Jiang, Spectrochim. Acta, Part A **67**, 1232 (2007).
[22] S. W. Wu, G. V. Nazin, X. Chen, X. H. Qiu, and W. Ho, Phys. Rev. Lett. **93**, 236802 (2004).
[23] N. Lorente and M. Persson, Phys. Rev. Lett. **85**, 2997 (2000).
[24] J. Callaway, *Quantum Theory of the Solid State* (Academic Press, San Diego, 1991).
[25] In principle, it is possible to observe the excitation energy $2t \sim 0.2$ eV in IETS. However, the spectrum in this range is dominated by the elastic tunneling into the electronic states of sample, which overshadows the IETS signal.
[26] The vibronic peaks of the charged state at the negative bias do not exhibit Zeeman splitting because the molecules are mainly at the ground state at ultralow temperature. At the negative bias, a majority of the tunneling electrons are only from the split level with lower energy under magnetic field.
[27] R. Hanson and D. Awschalom, Nature (London) **453**, 1043 (2008).
[28] G. D. Mahan, Phys. Rev. Lett. **102**, 016801 (2009).
[29] A. Bayat, D. Burgarth, S. Mancini, and S. Bose, Phys. Rev. A **77**, 050306(R) (2008).