Probing Superexchange Interaction in Molecular Magnets by Spin-Flip Spectroscopy and Microscopy

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

[1] Department of Physics, Tsinghua University, Beijing 100084, China
[2] Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China
* Corresponding author. E-mail: qkxue@mail.tsinghua.edu.cn

Abstract. **We report on a direct study of the superexchange mechanism in cobalt phthalocyanine (CoPc) single crystalline thin films by using a low temperature scanning tunneling microscope (STM). High resolution STM images were used to determine the stacking geometry of the molecules, which were found to form one-dimensional antiferromagnetic chains in the films. Collective spin excitations in individual molecular chains were measured with spin-flip associated inelastic electron tunneling spectroscopy. The spin-flip spectra give both the spin configuration of the chains and the superexchange coupling strength between molecules. By spatially mapping the spin-flipping channels with sub-molecular precision, we are able to explicitly identify the specific molecular orbitals that mediate the superexchange interaction between the CoPc molecules.**

I.   INTRODUCTION

Orbital overlapping, a fundamental process in chemical bonding, magnetism and so on, usually results in short-ranged interaction between atoms due to the localization of atomic wave functions. Interaction over a larger distance cannot be simply achieved by this process, and the superexchange mechanism (1, 2), where a bridging molecule or ion mediates higher-order virtual hopping processes, has to be invoked. The superexchange interaction is responsible for the magnetism in a wide range of materials including transition metal oxides (3) and strongly correlated electronic systems (4). It also exists in the ultracold atoms in optical lattices (5), as well as in the charge and energy transfer of molecular systems (6). As a typical superexchange pathway in molecular magnetism (7-9), the non-magnetic ligands mediate the magnetic coupling between well-separated transition metal ions. Owing to the lack of real-space imaging techniques with high spin sensitivity, the superexchange pathway was usually identified by model calculation. For the purpose of rational design and nano-scale engineering of molecular magnetic structures, it would be highly desirable to develop a technique by which the spin coupling information can be readily obtained with simultaneous ultrahigh spatial resolution.

Recently, inelastic electron tunneling spectroscopy (IETS) of individual molecules was achieved with a scanning tunneling microscope (STM). The molecular vibration (*10, 11*) and the light emission from single molecules (*12*) were excited by the highly localized tunneling electrons from an STM tip. The latest success of STM-IETS was the measurement of spin excitation, where the tunneling electrons transfer energy to the spin degree of freedom of individual Mn atoms or atomic chains via the spin-flip process (*13-15*). The spin-flip IETS provides direct information of spin distribution and coupling, and therefore opens new avenues to study magnetism at the nanometer scale. In this work, we studied the mechanism of superexchange interaction by the spin-flip IETS and microscopy with an STM operated at 400 mK and a magnetic field of 11 Te (*16-18*).

II.   RESULTS AND DISCUSSION

Ordered cobalt phthalocyanine (CoPc) crystalline thin films were found to be quantum antiferromagnets by probing their collective spin excitation spectra. The Co^{2+} ion in a CoPc molecule is coordinated to four pyrrole N atoms (Fig. 1A) and has a spin of $S = 1/2$. Based on the stacking geometry of the CoPc molecules determined by atomically resolved STM images (Fig. 1B-D), we conclude that the antiferromagnetic coupling is due to the superexchange interaction between the Co^{2+} ions through the well-developed π system of the phthalocyanine rings.

Fig. 1. CoPc multilayers on Pb. (**A**) Molecular structure of CoPc. (**B**) STM image (*V* = 0.9 V, *I* = 0.03 nA) of the self-assembled multilayers of CoPc molecules on Pb (111) film with a thickness of 26ML. (**C**) High resolution STM image showing the relative stacking of the 2nd and 3rd CoPc layers. The white and black dots indicate the centers of the molecules on the 2nd and 3rd layers, respectively. The lateral displacement between these two layers is clearly revealed. (**D**) Stacking geometry of CoPc molecules. The molecular layers are spaced ~3.5 Å apart. The inserts show the orientation and displacement between molecules in adjacent layers.

The *dI/dV* spectra at the center (Co^{2+} ion) of CoPc molecules from the third to the fifth monolayers are shown in Fig. 2A, where inelastic tunneling features (indicated by arrows in Fig. 2A) that are typical of spin-1/2 antiferromagnetic chains are clearly noted.

The spin excitation is described by the Heisenberg Hamiltonian

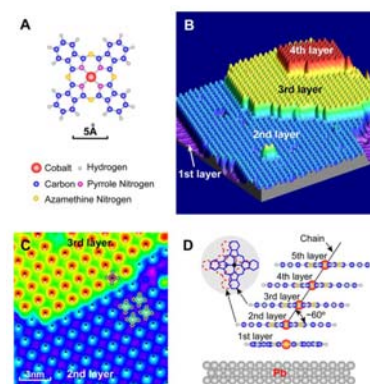$$H = J \sum_{i=1}^{N-1} \mathbf{S}_i \cdot \mathbf{S}_{i+1}$$

where $\mathbf{S}_i$ is the spin operator for the *i*th site, *J* is the exchange parameter and *N* is the number of molecules in the chain. A positive *J* value corresponds to an antiferromagnetic coupling. Figure 2B shows the excitation spectra calculated by diagonalizing Eq. 1 with $S = 1/2$ and $J \sim +18$ meV. The observed inelastic tunneling threshold energies (Fig. 2A) agree well with the calculation.

To unequivocally attribute the observed IETS to spin-flip, we measured the splitting of the singlet ($S_c = 0$) to triplet ($S_c = 1$) transition on a molecule in the third layer under magnetic field. The single step in Fig. 2A splits to three distinct steps in Fig. 2C, corresponding to the three magnetic quantum numbers 0 and ±1 of the excited state whose three-fold degeneracy is lifted by the magnetic field as schematically shown in Fig. 2D. The unequal spacing of the splitting in Fig. 2C reflects the effect of magnetocrystalline anisotropy.

The observed antiferromagnetic ordering of the molecular chain is a result of the superexchange interaction between the nearest-neighboring Co^{2+} ions via a pyrrole N atom in the phthalocyanine ring, as indicated by the dotted lines

Fig. 2. Spin-flip spectra of individual CoPc chains. (**A**) Spectra acquired with the STM tip positioned on different thickness of the molecular layers. The tunneling gap was set at $V = 50$ mV, $I = 0.2$ nA. The bias modulation was 1 mV (rms) at 1991 Hz. The arrows indicate the inelastic tunneling threshold voltages. The curves are offset vertically for clarity. (**B**) Eigenstates of the Heisenberg Hamiltonian with S = 1/2. The energy levels are labeled by the total spin of the chain S_c. The exchange parameter *J* is obtained by comparing the threshold voltages in (**A**) with the excitation energies of the Heisenberg chain. (**C**) Spectra taken on the third layer at different magnetic fields. The STS were acquired at a set point of $V = 10$ mV and $I = 0.15$ nA at $T = 0.4$ K. The arrows indicate the three steps induced by 11 T magnetic field. The lock-in modulation was 0.05 mV at 1991 Hz. (**D**) Schematic of the spin singlet to triplet transition. The triplet states are labeled by the magnetic quantum number S_z.

in Fig. 3A. Generally, the superexchange interaction depends on the symmetry of the molecular orbitals, the orthogonality relationship between the relevant molecular orbitals and the stacking mode. It arises when the magnetic orbital α is nonorthogonal to an orbital X of the common ligand between α and β (Fig. 3B). An electron on X can transfer to α and the remaining unpaired electron on X enters into a direct exchange with another magnetic orbital β. As a result, α and β are magnetically linked by the bridging orbital X.

We can resolve the specific molecular orbitals that involve in the superexchange interaction using the spin-flip imaging together with the first-principles simulation. The bridging orbital was visualized by the image constructed from the *dI/dV* signal when the dc bias voltage was fixed at the conductance
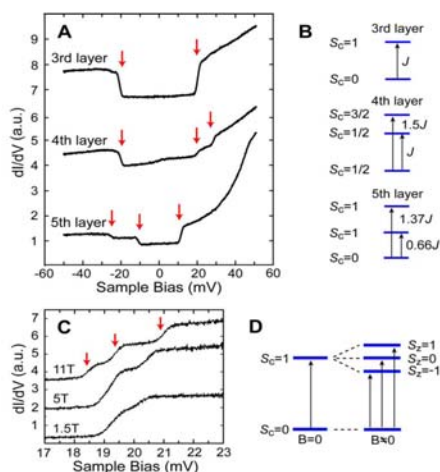
step (–17.2 mV). The obtained spatial mapping of the inelastic tunneling channels (Fig. 3C) is considerably distorted from the D_{4h} symmetry of the CoPc molecule: the charge density is reduced at the benzene ring adjacent to the intervening N atom (indicated by a dashed circle in Fig. 3C). The superexchange pathway involves an E_g orbital (X in Fig. 3B) of the well-developed π system of the phthalocyanine ring, the $3d_z^2$ (β in Fig. 3B) of the same molecule, and the $3d_z^2$ (α in Fig. 3B) of the neighboring molecule.

Fig. 3. Superexchange mechanism. (**A**) Illustration of the superexchange interaction in a molecular chain. The pyrrole N atoms mediate the magnetic coupling between Co^{2+} ions. (**B**) Spin configuration in superexchange. The bridging N atom is marked by a red dot. The nodal plane (dashed line) of the E_g orbital passes through two pyrrole N atoms and the central Co^{2+} ion. (**C**) Spin-flip image of a CoPc molecule on the third layer at $T = 0.4$ K. The bias voltage was fixed at -17.2 mV during mapping. The modulation was 2mV at 799 Hz. The molecular structure is superimposed on the image. The dashed circle indicates the bridging N atom. (**D**) Charge density of E_g orbital yielded by the first-principles calculation. The yellow and blue regions represent the different phases (+ or −) of the wave-function.

Molecular magnetic materials show great potential in spin-based electronics and quantum information technology as a result of the rich structure of organic chemistry (*19*). The spin-flip spectroscopy and microscopy reported here provide direct information of spin distribution and coupling, and enable our study and understanding of molecular magnetism down to the single molecular level.
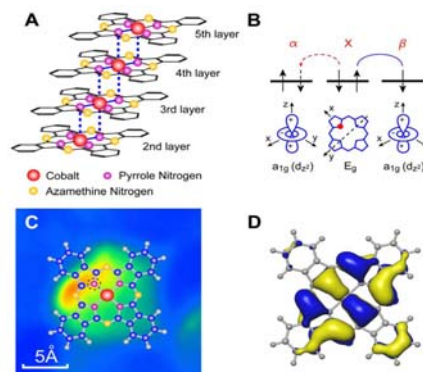
REFERENCES

[1] H. A. Kramers, *Physica* **1**, 182 (1934).
[2] P. Anderson, *Phys. Rev.* **79**, 350 (1950).
[3] R. M. White, *Quantum Theory of Magnetism* (Springer-Verlag, Berlin, 2007).
[4] P. A. Lee, N. Nagaosa, X. G. Wen, *Rev. Mod. Phys.* **78**, 17 (2006).
[5] S. Trotzky, *et al.*, *Science* **319**, 295 (2008).
[6] V. May, O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH, Berlin, 2001).
[7] O. Kahn, *Molecular Magnetism* (Wiley-VCH, New York, 1993).
[8] J. S. Miller, A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **33**, 385 (1994).
[9] J. S. Miller, *Inorg. Chem.* **39**, 4392 (2000).
[10] R. C. Jaklevic, J. Lambe, *Phys. Rev. Lett.* **17**, 1139 (1966).
[11] B. C. Stipe, M. A. Rezaei, W. Ho, *Science* **280**, 1732 (1998).
[12] X. H. Qiu, G. V. Nazin, W. Ho, *Science* **299**, 542 (2003).
[13] A. J. Heinrich, J. A. Gupta, C. P. Lutz, D. M. Eigler, *Science* **306**, 466 (2004).
[14] C. F. Hirjibehedin, C. P. Lutz, A. J. Heinrich, *Science* **312**, 1021 (2006).
[15] C. F. Hirjibehedin *et al.*, *Science* **317**, 1199 (2007).
[16] X.-C. Ma *et al.*, *Proc. Natl. Acad. Sci.* **104**, 9204 (2007).
[17] Y. S. Fu *et al.*, *Phys. Rev. Lett.* **99**, 256601 (2007).
[18] S. H. Ji *et al.*, *Phys. Rev. Lett.* **100**, 226801 (2008).
[19] N. Tsukahara *et al.*, *Phys. Rev. Lett.* **102,** 167203 (2009).