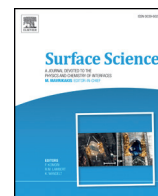




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Spins of adsorbed molecules investigated by the detection of Kondo resonance

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ABSTRACT

Surface magnetism has been one of the platforms to explore the magnetism in low dimensions. It is also a key component for the development of quantum information processes, which utilizes the spin degree of freedom. The Kondo resonance is a phenomenon that is caused by an interaction between an isolated spin and conduction electrons. First observed in the 1930s as an anomalous increase in the low-temperature resistance of metals embedded with magnetic atoms, the Kondo physics mainly studied the effects of bulk magnetic impurities in the resistivity. In the last 15 years it has undergone a revival by a scanning tunneling microscope (STM) which enables the measurement of the Kondo resonance at surfaces using an atomic scale point contact. The detection of the Kondo resonance can be a powerful tool to explore surface magnetism. In this article, I review recent studies of the surface spin of adsorbed molecules by the detection of the Kondo resonance. Researches on metal phthalocyanine (MPc) and porphyrin molecules will be examined. In addition, the Kondo resonance for double-decker lanthanoide Pc molecules will be discussed. Some of the double-decker Pc molecules show single-molecule magnet (SMM) behavior, which attracts attention as a material for electronic devices. For both classes, the ligand plays a crucial role in determining the parameters of the Kondo resonance, such as the Kondo temperature and the change of the shape from peak to Fano-dip. In addition, the spin in delocalized molecular orbital forms the Kondo resonance, which shows significant differences from the Kondo resonance formed by the metal spins. Since molecular orbital can be tuned in a flexible manner by the design of the molecule, the Kondo resonance formed by delocalized molecular orbital might expand the knowledge of this field.

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1. Introduction

Surface magnetism has a fundamental interest in which one can explore the influence of reduced dimensionality on magnetism [1–5]. It is also one of the key components for the development of quantum information devices, because the devices required for the quantum information processing, such as spintronics devices and quantum computing devices, much rely on the control of the surface magnetism [6].

Molecular spintronics is an emerging field of research that combines spintronics and molecular electronics [7]. Due to the weak spin–orbit coupling and hyperfine interactions, the spin coherence length in the organic material is longer than that in the inorganic materials for the electron transport [7], which makes the organic molecules suitable for spin transport material. Moreover, by combining with photochromism and electrochromism [8,9], the spin switching should be possible since

there is a strong correlation between the structure and electronic properties of molecules [10,11].

Much effort has been devoted to the development of spin detection techniques with an atomic scale resolution based on the scanning tunneling microscope (STM) and scanning tunneling spectroscopy (STS). These include spin polarized STM [12–15], inelastic tunneling spectroscopy (IETS) of spin flipping [16–18], and Larmor precession detection in the high frequency component of the tunneling current [19–22].

The observation of the Kondo resonance is another promising technique for examining spin at surfaces and interfaces. The Kondo effect is caused by the interactions between conduction electrons and localized spin [23]. The research of the Kondo resonance using STM has started for the observation of single magnetic atoms [24–29], which were followed by that for adsorbed molecules [30–53].

The Kondo resonance of a magnetic molecule is illustrated in Fig. 1(a), where a spin center of the molecule is placed in the gap between the STM tip and substrate. The electron in the singly occupied molecular orbital (SOMO) is specified by the energy ε , which is separated from the doubly-occupied state by the on-site Coulomb energy U . Through an interaction between the spin of the molecule

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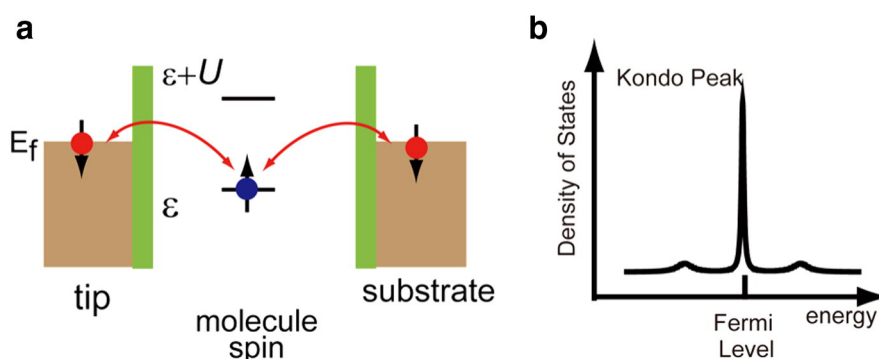


Fig. 1. (a) Schematic model of the Kondo resonance. ε and U represent the energy level of the singly occupied molecular orbital (SOMO) state and the Coulomb repulsion energy, respectively. (b) Schematic of a typical STS plot of the Kondo resonance.

and the conduction electrons, the Kondo resonance is formed. The Kondo resonance appears as a sharp feature of the density of states at the Fermi level in the STS spectra. In Fig. 1(b), it is illustrated as a sharp peak. The width of the peak is scaled with the Kondo temperature T_K that is one of the most important parameters in the Kondo physics [54]. Nagaoka et al. introduced a formula for the temperature dependence of the Kondo-peak width ($\Gamma(T)$):

$$\Gamma(T) = 2\sqrt{(\pi k_B T)^2 + 2(k_B T_K)^2} \quad (1)$$

where k_B is the Boltzmann constant and T_K is the Kondo temperature [55].

In addition, it is argued that T_K can be expressed by the following formula,

$$T_K \propto \exp(-\pi|\varepsilon|/m\Gamma_s) \quad (2)$$

where Γ_s is the peak width of the orbital responsible for the spin, and is originated from its hybridization with the surface, ε is the energy relative to E_F , and m is the degeneracy of the orbital [54,56]. Γ_s decreases with the increase of the distance between the spin and the substrate, which is due to the decrease of the hybridization between the orbitals containing the two.

In this article, recent studies of the Kondo resonance of adsorbed molecules are reviewed, focusing on phthalocyanine and porphyrin molecules. The manuscript consists of the following sections: 1. Introduction, 2. Experimental, 3. Kondo behavior of metal phthalocyanine, 4. Double Decker Pc and Kondo behavior, 5. Ligand effect for Kondo behavior, 6. Molecular ordering and Kondo resonance, and 7. Summary.

2. Experimental

STM has played important roles in the studies of molecules adsorbed on surfaces [57,58]. The use of cryogenic temperature improves the ability of STM for the molecular characterization from several view points. First, the motion of the molecules is frozen. Second, the energy resolution of the STS spectra can be improved because the tunneling electrons are in the thermal equilibrium with the sample temperature. The thermal broadening of the peak should be expressed with the following formula.

$$W = \sqrt{(5.4k_B T)^2 + W_1^2} \quad (3)$$

where k_B is the Boltzmann constant, T is the temperature, and W_1 is an intrinsic width of the peak [59]. The resolution linearly improves with the decrease of sample temperature. Most of the STM studies shown in this article employed the low temperature STM using liquid He.

3. Kondo behavior of metal phthalocyanine

The phthalocyanine (Pc) molecule, wherein four isoindoles are combined with nitrogen atoms, has been explored extensively, both from basic science and industry perspectives [60]. A Pc ligand is illustrated in Fig. 2(a), which tends to be a dianion. Pc ligand contains a metal atom at the center which can be of various kinds and this class of molecule is called as metal phthalocyanine (MPc). The metal atom becomes a dication to be the counter of the dianion Pc in a neutral molecule. A typical STM image of H_2Pc molecules adsorbed on Au(111) surface is shown in Fig. 2(b). Each molecule appears as a cross and its diagonal direction is aligned to one of the three close-packed directions of Au(111). The cross shape is commonly observed for various MPc molecules on Au(111) [61].

The Co-phthalocyanine (CoPc) molecule has a spin of $S = 1/2$ in vacuum [62] which is located in the d_z^2 orbital. Zhao et al. examined the Kondo state of CoPc adsorbed on Au(111). No Kondo feature is observed for the CoPc deposited on Au(111) surface. However, it appears with an abnormally high Kondo temperature, $T_K \sim 200$ K, when the chemical surrounding or environment is modified via selective dehydrogenation by applying electrical pulses. While four lobes are clearly resolved in the topographic image before dehydrogenation, they are merged into a circular cloud after the pulse application. The DFT calculation shows no magnetic moment for the Co ion in the undistorted CoPc, which is recovered after the dehydrogenation [63].

Nonmagnetic Co^{2+} for the non-distorted CoPc molecule adsorbed on Au(111) was confirmed by other experimental [64] and theoretical [65] studies. In those reports, the disappearance of the spin is explained by the filling of the d_z^2 state as a result of the charge-transfer from the substrate.

More recently, Stepanow et al. examined X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) for the same system [66]. They showed that $3d$ magnetic moment exists in the d_z^2 state for the multilayer film of CoPc, as expected from the behavior of an isolated CoPc molecule. However, the local magnetic moment of Co^{2+} is zero for the monolayer film of CoPc on Au(111) for both in-plane and out-of-plane directions. Although this is consistent with the results of DFT calculation [63], the underlying physics is more complex than a simple filling of the d_z^2 orbital by the charge transfer from the substrate. They incorporated the charge fluctuations in the initial and final states by assuming a Co d^7 configuration with an additional substrate electron that can hop to the Co ion. Consequently, it can create a d^8 configuration at a higher energy. The ground state wave function is a coherent superposition of the form $|d^7, 1\rangle$ and $|d^8, 0\rangle$, where the additional electron represents the state of the surface. The results show an agreement with both circularly and linearly polarized XAS.

It is interesting to notice that the singlet is formed for the $|d^7, 1\rangle$ configuration when it couples to the low-spin $|d^8, 0\rangle$ state. This is explained by a mixing of the two d_z^2 states, and the decrease of the

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