Strain-induced tuning of the magnetocrystalline anisotropy of single molecules

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(Dated: December 24, 2014)

An important goal in device technology is the construction and addressability of nanomagnets, which are stable against small external fluctuations for sufficiently long timescales. This requires the knowledge on how to create large anisotropy barriers in atomic-scale structures on substrates. Recent works have shown that a careful choice of the surrounding, such as adsorption sites or an organic ligand lead to sizable magnetocrystalline anisotropy in atoms on surfaces. It can be traced back to the particular ligand field splitting and spin-orbit coupling in the partially filled energy levels. The ligand field splitting is accompanied by the annihilation of the orbital moment in all or at least two spatial directions due to mixing of states with opposite magnetic quantum number. Effective orbital moments emerge from the admixture of low-lying excited states and can be treated as second order perturbation. Spin-orbit coupling then gives rise to magnetocrystalline anisotropy.

Tunable control of the magnetocrystalline anisotropy is difficult to achieve, because it demands a handle to continuously shift the energy levels. So far this has only been achieved by pulling molecules in break junction configurations, which lack the precise control of the contact point of the force field.

One way to tune properties of nanoobjects on surfaces continuously with a high degree of control consists of bringing the tip of an STM close to or even into contact with the sample. This has been used to intentionally shift surface or molecular states in energy, change the Kondo screening, or the (anti-)ferromagnetic coupling strength.

Here, we develop a strategy to precisely tune the magnetocrystalline anisotropy in metal-organic complexes. We study and manipulate an iron porphyrin in two different oxidation and spin states adsorbed on Pb(111) by means of scanning tunneling microscopy and inelastic scanning tunneling spectroscopy (ISTS). We observe spin excitations in both molecules and utilize these to characterize changes in the magnetocrystalline anisotropy. To resolve changes in anisotropy, a very good energy resolution is required. Thus, we employ a superconducting tip and substrate to probe the magnetic excitations in the single molecules. We then use the force exerted by the tip of our microscope to affect the molecules with picometer precision and thus modify the ligand field and magnetocrystalline anisotropy.

Our experiments are carried out in a Specs JT-STM operating at a base temperature of 1.2 K. The Pb(111) surface was cleaned by repeated sputter/anneal cycles until a clean, superconducting surface was obtained. Pb is a type I superconductor with a critical temperature of 7.2 K. At 1.2 K its energy gap has a width of $2\Delta = 2.7$ meV. To increase the energy resolution beyond the Fermi-Dirac-limit of normal metal tips, we covered the bulk W-tip with superconducting Pb by controlled indentation into the clean surface, until the tip showed a bulk-like superconducting order parameter $\Delta$.

Spectra of the differential conductance ($dI/dV$) as a function of the sample bias were acquired using conventional lock-in technique at a frequency of 912 Hz with an ac bias modulation ($V_{\text{mod}}$). Iron-octaethylporphyrin-chloride (Fe-OEP-Cl, structure model as inset in Fig. 1h) was sublimated from a crucible at 490 K onto the clean Pb(111) surface held at 120 K. To enhance self-assembly into ordered domains, the sample was then annealed to 240 K for 180 s and transferred into the STM.

On the bare Pb(111) surface, the $dI/dV$ spectra of the superconductor -- superconductor tunneling junction is then characterized by a gap region around the Fermi level ($E_F$), enclosed by sharp resonances of quasi-particle excitations at $eV = \pm 2\Delta$ (Fig. 1b, upper plot). The doubling of the size of the superconducting gap is due to the convolution of the BCS-like (Bardeen–Cooper–Schrieffer) density of states (DoS) of tip and sample. The shoulder-like features at $\pm 6.7$ and $\pm 11.2$ meV are signatures of the strong electron-phonon coupling in Pb and correspond...
The porphyrin molecules self-assemble in ordered monolayer islands of quasi-hexagonal structure, with the ethyl-groups clearly visible in the STM images (see Fig. 1b). About two thirds of the molecules exhibit a bright protrusion in the center, which we identify as the Cl ligand upon adsorption (in the following referred to as Fe-OEP-Cl). The second type of molecules shows a bright excitation of Fe-OEP. The dI/dV spectra are acquired above clean Pb(111) (up), Fe-OEP-Cl (middle), and Fe-OEP (low), respectively \( (V_{\text{mod}} = 50\mu\text{V}_{\text{rms}}) \). (c) Scheme illustrating the opening of an inelastic tunneling channel at a threshold of \( \epsilon U = 2\Delta + \varepsilon \) in a superconductor – superconductor junction.

FIG. 1. Fe-OEP on Pb(111). (a) Topographic image of a molecular island on Pb(111) \( (V = 130 \text{ mV}, J = 60 \text{ pA}) \). Molecules with an axial Cl ligand appear with a protrusion in the center (Fe-OEP-Cl, left in the inset), molecules without Cl ligand exhibit a depression in the center (Fe-OEP, right). (b) ISTS on Fe-OEP-Cl and Fe-OEP. The dI/dV spectra are acquired above clean Pb(111) (up), Fe-OEP-Cl (middle), and Fe-OEP (low), respectively \( (V_{\text{mod}} = 50\mu\text{V}_{\text{rms}}) \). (c) Scheme illustrating the opening of an inelastic tunneling channel at a threshold of \( \epsilon U = 2\Delta + \varepsilon \) in a superconductor – superconductor junction.
and field splitting and yields a high-spin $S = 5/2$ ground state with singly occupied $d$-levels. The spin-pairing energy in this case is larger than the energy level difference. The magnetocrystalline anisotropy results from the admixture of electronically excited states of reduced total spin (e.g., $E_1$ and $E_2$ in Fig. 3). Furthermore, the lifting of the Fe center out of the pyrole plane leads to a relatively large Fe–surface distance, which makes the Fe$^{3+}$ insensitive to variations of the adsorption site.

In the case of Fe-OEP, the Fe$^{2+}$ lies in the square-planar ligand field of the porphyrin macrocycle. The in-plane position of the Fe$^{2+}$ yields shorter Fe–N distances and a larger ligand field splitting, in particular the energy of the $d_{xz}$ level is strongly increased compared to Fe-OEP-Cl. This results in the intermediate spin ($S = 1$) ground state $E_0$ as depicted in Fig. 3. Since the splitting between the $d_{x^2-y^2}$ and $d_{z^2}$ is small in Fe(II) porphyrins [29], there is a strong admixture of $E_1$ and $E_2$ to the ground state and hence a large magnetocrystalline anisotropy. The admixture of these lowest lying states yields contributions to the orbital moments $\Lambda_{xx}$ and $\Lambda_{yy}$ in $x$ and $y$ direction, respectively, but not to $\Lambda_{zz}$, the orbital moment in $z$ direction [31]. Therefore the resulting anisotropy is easy-plane, i.e., $D > 0$, as we can write $D = -\lambda^2/2(2\Lambda_{zz} - \Lambda_{xx} - \Lambda_{yy})$ [31], with $\lambda$ being the spin-orbit coupling constant. At the same time, the shorter Fe–surface distance compared to Fe-OEP-Cl results in a higher sensitivity to variations in the adsorption site. The atomic environment underneath the Fe$^{2+}$ ion mainly affects the $d_{zz}$ and $d_{xy}$ levels, because they extend towards the surface, resulting in slight variations of $\Lambda_{xx}$ and $\Lambda_{yy}$, and, therefore, $D$ and $E$ (note: $E = -\lambda^2/2(\Lambda_{xx} - \Lambda_{yy})$). The interaction with the surface also explains the reduction of the $D_{4h}$ symmetry evidenced by the non-zero $E$ parameter.

The above shown sensitivity of the zero field splitting to small variations in the environment provides access to a controlled tuning. With this intention, we approach the tip of the STM to the center of the molecules. The presence of the tip alters the ligand field, while we simultaneously record ISTS curves at varying tip–sample distances. Figure 4 presents $D$ as a function of tip displacement $\Delta z$ as extracted from spectra acquired above Fe-OEP-Cl. We observe an exponential increase in $D$ with decreasing tip–sample distance (negative $\Delta z$; cf. also Ref. [7]). In the case of Fe-OEP (see Fig. 4), first both excitation peaks shift to higher energies and reach a maximum at $\Delta z \approx -200$ pm. With a further decrease in distance, both peaks shift to energies lower than the initial ones until, at $-330$ pm, the junction becomes unstable. Figure 4 shows the extracted values of $D$ vs. $\Delta z$ [32]. From $\Delta z = 0$ to $-200$ pm the axial anisotropy $D$ slightly increases, before it rapidly decreases with further decreasing distance.

The opposed variations in the zero field splitting of the two species are understood considering the changes in geometry induced by the approaching tip. In the case of Fe-OEP-Cl, the tip potential acts (mainly) on the Cl ligand and attracts the Cl towards the tip. In turn, the Cl–Fe bond length increases and the Fe ion relaxes towards the molecular plane, decreasing the Fe–N bond length. The resulting changes of the ligand field splitting are sketched in Fig. 4b): the $d_{z^2}$ ($d_{x^2-y^2}$) orbital shifts down (up) in energy as the Fe–Cl (Fe–N) distance

FIG. 2. Inelastic excitations. (a) High-resolution ISTS spectrum of Fe-OEP-Cl (25 $\mu$V$_{rms}$). The two excitations of 1.4 and 2.8 meV identify the $S = 5/2$ state with a magnetocrystalline anisotropy parameter $D = 0.7$ meV [7]. (b) The zoom on the ISTS spectrum of Fe-OEP unveils two inelastic resonances of equal intensity at 12.6 and 14.0 meV (50 $\mu$V$_{rms}$). As guide for the eye, the spectrum of pristine Pb(111) is superimposed as dotted line. (c) Scheme of the zero field splitting in Fe-OEP and Fe-OEP-Cl. For Fe-OEP we detect, additionally to the main anisotropy axis, an in-plane distortion (rhombicity), which gives rise to the parameter $E$. (d) Distributions of $E$ and $D$ as measured for 71 different Fe-OEP molecules (measured at 4.5 K).

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FIG. 3. Sketch of the electronic ground ($E_0$), first ($E_1$), and second ($E_2$) excited state in the case of: (a) high-spin ($S = 5/2$) Fe$^{3+}$ in a square-pyramidal ligand field (as in Fe-OEP-Cl); (b) intermediate spin ($S = 1$) Fe$^{2+}$ in a square-planar ligand field [29] (as in Fe-OEP). Note that in (a) $E_1$ (degenerate) and $E_2$ are of reduced total spin compared to $E_0$, while in (b) the spin is conserved. Energies not to scale.
increases (decreases). These changes increase the overall ligand field splitting and decreases the total energy difference $E_2 - E_0$, which also includes the spin pairing energy. The reduced energy difference between ground and excited states increases their admixture according to perturbation theory. This yields larger orbital moments $\Lambda_{xx}$ and $\Lambda_{yy}$ and, therefore, increased magnetocrystalline anisotropy.

In the case of Fe-OEP, the tip exerts a force directly on the Fe$^{2+}$ ion. The potential drags the Fe$^{2+}$ out of the molecular plane, increasing the Fe–N bond length. While the $d_{x^2-y^2}$ decreases in energy, the $d_{xz}$ orbital shifts up due to the presence of the tip. The increased energy difference between $d_x$ and $d_{xz}$ increases also the energy difference $E_1 - E_0$, which decreases the admixture of the excited state and reduces the magnetocrystalline anisotropy. Furthermore, this scenario accounts for the slight increase in $D$ between $\Delta z = 0$ and $-200 \text{ pm}$. In the absence of the tip, the attractive surface potential mimics an axial ligand and drags the Fe ion slightly below the molecular plane. The potential of the approaching tip then counterbalances the surface potential. It pulls the Fe$^{2+}$ back into the molecular plane and increases the Fe–surface distance with the magnetocrystalline anisotropy being increased.

A large magnetic anisotropy in nanoscale structures is important to stabilize magnetic states[33]. In thin metallic films [34][35] and clusters [36], an external electric field can be applied to tune the magnetic anisotropy. For single atoms, so far only static control of the magnetocrystalline anisotropy has been achieved by a choice of the adsorption site on surfaces [1][3][37][39]. In the chemical approach organic ligands are used to determine the ligand field splitting and magnetocrystalline anisotropy[21]. Our approach provides the flexibility to continuously tune the magnetocrystalline anisotropy by modifying the geometry of the atomic-scale surrounding. Furthermore, it shows how the anisotropy may serve as a highly sensitive probe to identify variations in the atomic scale interactions, which are, e.g., induced by the presence of the tip.

This research has been supported by the DFG grant FR2726/4, ERC grant NanoSpin and the focus area "Nanoscale" of Freie Universität Berlin.

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