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Molecular induced skyhook effect for magnetic interlayer softening

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Our first-principles study demonstrates for the first time that by increasing the molecule-surface binding strength, the interlayer magnetic coupling of a ferromagnetic metal can be drastically reduced with respect to that of a clean substrate. Importantly, for a weakly chemisorbed molecule the rehybridization of metal atomic d states within the molecule-induced surface geometry (geometrical effect) plays a crucial role in obtaining interlayer magnetic softening. On the contrary, for a strongly chemisorbed molecule the interlayer magnetic coupling is further reduced due to an interplay between the geometrical effect and the hybridization of atomic d states with molecular ones.

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The first experimental demonstration of room-temperature spin injection into bulk organic semiconductors [1] and the subsequent experimental measurement of the magnetoresistance effect in an organic spin valve device [2] opened the way to organic spintronics [3], where bulk organic spacers are used to manipulate the electron spin in solid-state devices [4]. On this basis, the next step was to employ the different physical and chemical properties of several single organic molecules to design devices with potential technological applications leading to the exciting field of molecular spintronics [5–7].

A mainstream research direction in molecular spintronics is to gain a fundamental understanding of how the interaction between a magnetic molecule with a magnetic substrate changes the properties of the molecular system. In this respect, many experimental investigations have explored the prospect of using single molecule magnets as basic functional units in molecular spintronic devices [8–13]. In parallel, several other studies have revealed the crucial role played by the creation of new interface hybrid organic-metal electronic states in molecular adsorption [14–16]. For instance, scanning tunneling microscopy experiments and density functional theory calculations proved that the chemisorption of nonmagnetic molecules onto a magnetic substrate leads to an inversion of the spin polarization at the molecular sites with respect to that of the substrate [14,15].

So far, less attention has been paid to the question how the molecule-surface interaction changes the properties of the underlying magnetic substrate. Recent theoretical simulations demonstrated that the chemisorption of a paracyclophane molecule onto a 1 monolayer (ML) Fe/W(110) magnetic substrate enhances the magnetic exchange interaction between surface atoms directly under paracyclophane (in-plane magnetic hardening effect) and leads to the formation of local molecule-surface magnetic units [17] embedded within the magnetic surface. The generality of these concepts has been revealed for other π-conjugated organic materials chemisorbed on magnetic surfaces; e.g., it was theoretically proposed and experimentally measured that the adsorption of π-conjugated systems such as coronene molecules and graphene nanoflakes onto a complex noncollinear magnetic surface like 1 ML Fe/Ir(111) leads to the creation of local organic-ferromagnetic units that can be switched with respect to the surrounding magnetic atoms [18]. Recently, we have also shown that the in-plane magnetic hardening effect can be selectively tuned via a molecular chemical functionalization process and even an in-plane magnetic softening of the surface exchange interaction is possible [19].

In this study we explore how nonmagnetic molecules can be employed to tune not only the strength of the in-plane but especially that of the interlayer magnetic exchange interactions of a magnetic substrate. More specifically, we have chosen two molecules that, although they have similar chemical compositions, are representative examples of two substantially different classes of molecule-surface systems: (i) weakly (σ-bonded molecule) and (ii) strongly (π-bonded molecule) interacting molecule-surface systems. In this way we demonstrate that the weak and strong chemisorption of organic molecules to prototypical magnetic surfaces lead (i) to a local hardening and/or softening of in-plane (intralayer) magnetic exchange interactions and (ii) to a local decrease in the interlayer magnetic coupling (magnetic interlayer softening effect) of surface atoms underneath the molecules regardless of the molecule-surface binding strength. Importantly, our first-principles simulations also reveal that the softening of the interlayer magnetic exchange coupling constants is mainly driven by a structural change of the surface (geometrical effect).

More precisely, in this *ab initio* study we have investigated the dioxan ($C_4O_2H_8$) and dioxin ($C_4O_2H_4$) molecules chemisorbed on 1 ML and 2 ML Fe/W(110), which are well-established substrates for molecular spintronic investigations [14,15,17]. It is important to note that in the dioxan molecule all C and O atoms have an sp^3-like hybridization, forming only σ bonds (i.e., dioxan is a σ system), whereas in the dioxin molecule the C atoms are sp^2 hybridized, forming π bonds (i.e., dioxin also contains a π system). As a consequence, we can expect a different strength of the corresponding molecule-surface interaction, which in turn can lead to qualitatively different changes in the intra- and interlayer magnetic exchange interactions.

To explore this scenario, we performed spin-polarized electronic structure calculations within the density functional

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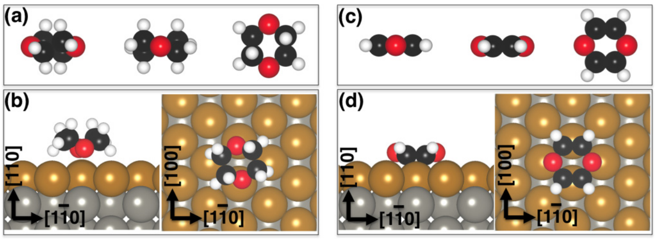

FIG. 1. (Color online) Side and top views of the (a) dioxan ($C_4O_2H_8$) and (c) dioxin ($C_4O_2H_4$) molecules and the ground-state geometries for (b) dioxan and (d) dioxin adsorbed on the magnetic substrate. Color code: light gray, hydrogen; black, carbon; red, oxygen; gold, iron; gray, tungsten.

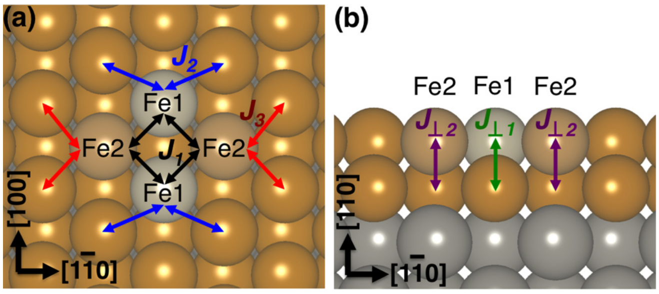

FIG. 2. (Color online) Labeling of the (a) in-plane and (b) inter-plane exchange coupling constants for 2 mL Fe/W(110).

theory framework [20,21] using the VASP program [22,23]. Data sets of the projector augmented-wave method [24] were employed in the flavor of the exchange correlation functional of Perdew, Burke, and Ernzerhof [25]. For relaxations the dispersion correction D3 of Grimme and coworkers was used [26] (for further details see the Supplemental Material [27]).

The ground-state geometries of both molecules are displayed in Fig. 1 for the case of 1 ML Fe/W(110). Note that on 2 ML Fe/W(110) the adsorption geometries are practically identical. As reported in Table I, the calculated adsorption energies indicate that the π-system dioxin interacts significantly more stronly with both surfaces compared to the σ-system dioxan.

This different binding energy strength is directly reflected in the molecule-surface geometries as depicted in Fig. 1, where the π-system dioxin ($C_4O_2H_4$) [see Fig. 1(d)] is overall closer to the surface than the σ-system dioxan ($C_4O_2H_8$) [see Fig. 1(b)] (see also the molecule-substrate distances reported in Supplementary Table I [27]). Therefore, the σ-system dioxan ($C_4O_2H_8$) is weakly chemisorbed and interacts with the magnetic substrate atoms only through the oxygen atoms, while the π-system dioxin ($C_4O_2H_4$) is strongly chemisorbed and interacts with its whole molecular plane formed by C and O with the surface Fe atoms. As a consequence, the molecule-surface hybridization is much stronger for the π-system dioxin compared to the σ-system dioxan (see also the discussion of the spin-polarized density of states SP-PDOS in the Supplemental Material [27]), which generally implies a molecule-specific change in the magnetic moments of the surface Fe atoms.

In particular, the adsorption of the σ-system dioxan ($C_4O_2H_8$) and the π-system dioxin ($C_4O_2H_4$) molecules onto the magnetic substrates modifies the magnetic moments of the four Fe atoms underneath, labeled Fe1 and Fe2 in Fig. 2. As reported in Table I, the magnetic moments of Fe atoms close to oxygen atoms are only slightly changed compared to those of the clean surface. However, in the case of the π-system dioxin, due to the strong hybridization, the magnetic moments of Fe1 atoms under the C-C bond are strongly reduced.

As discussed in Refs. [17–19], a change in the magnetic moments of the surface atoms as well as their interatomic distances upon molecular adsorption can also modify the strength of the magnetic exchange interactions between these surface atoms. Therefore we investigated the impact of σ-system dioxan and π-system dioxin adsorption on the magnetic exchange coupling constants between surface Fe atoms. Using an effective Heisenberg Hamiltonian as outlined previously [17,19], the calculated exchange couplings J's between Fe magnetic moments are listed in Table I and shown in Figs. 3 and 4, respectively.

As a common feature, the in-plane (intralayer) magnetic exchange coupling constant J_1 evaluated for the σ-system dioxan [see Fig. 3(a)] and the π-system dioxin [see Fig. 3(b)] on 1 ML Fe/W(110) is smaller than the clean surface value of 35.3 meV and indicates a softening of the magnetic interactions between the four Fe1 and Fe2 atoms. On the other hand, the exchange couplings J_2 and J_3 describing the magnetic interaction of the Fe1 and Fe2 with their nearest neighbors (clean surface Fe atoms) reveal the presence of a magnetic hardening for the σ-system dioxan, while this effect coexists with a softening one in the case of the π-system dioxin.

TABLE I. Adsorption energy E_{ads} [28] for each molecule (in eV), magnetic moments of Fe atoms underneath the molecules (in μ_B), and evaluated exchange coupling constants J's between surface Fe atoms for molecules on the surface and Fe/W(110) surface geometries induced by molecules (in meV).

		Magnetic moments		Molecule/surface					Molecular induced surface geometry				
Molecule/surface	E_{ads}	Fe1	Fe2	J_1	J_2	J_3	$J_{\perp 1}$	$J_{\perp 2}$	J_1	J_2	J_3	$J_{\perp 1}$	$J_{\perp 2}$
1 ML Fe/W(110)	–	2.5	2.5	35.3	35.3	35.3	–	–	35.3	35.3	35.3	–	–
Dioxan/1 ML Fe	1.10	2.5	2.3	24.8	41.2	41.4	–	–	22.4	34.8	38.5	–	–
Dioxin/1 ML Fe	3.20	1.2	2.5	28.8	32.0	48.2	–	–	26.5	33.6	34.6	–	–
2 ML Fe/W(110)	–	2.8	2.8	21.3	21.3	21.3	126.1	126.1	21.3	21.3	21.3	126.1	126.1
Dioxan/2 ML Fe	1.12	2.9	2.8	23.2	45.8	70.2	112.4	83.7	12.1	44.3	63.1	111.4	92.2
Dioxin/2 ML Fe	2.29	1.9	2.9	23.6	10.9	70.0	63.1	78.6	26.2	33.0	42.4	104.4	100.7

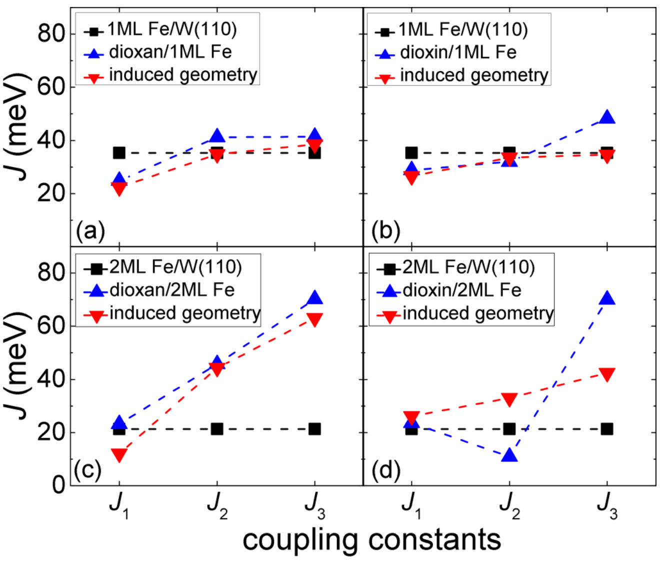

FIG. 3. (Color online) Visualization of the calculated in-plane exchange coupling constants for dioxan and dioxin on (a, b) 1 ML Fe/W(110) and on (c, d) 2 ML Fe/W(110), respectively.

In particular, this result correlates with the observation that for the π-system dioxin, Fe1 atoms below the C-C bonds [see Figs. 1(b) and 2(a)] have a strongly reduced magnetic moment. Note that a similar trend is observed for dioxin on 2 ML Fe/W(110). Nevertheless, for both molecules on this substrate the calculated exchange coupling J_1 reveals a magnetic hardening effect at variance with the corresponding outcome for 1 ML Fe/W(110).

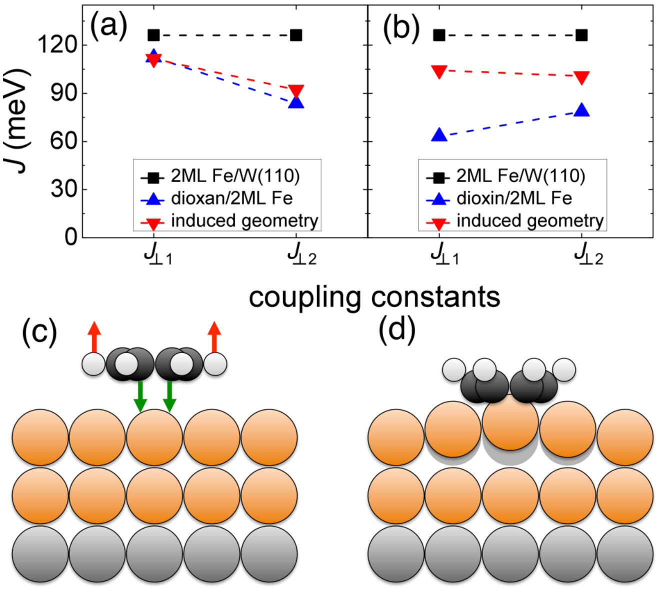

FIG. 4. (Color online) Visualization of the calculated interlayer exchange coupling constants for (a) the σ-system dioxan and (b) the π-system dioxin on 2 ML Fe/W(110). (c) Schematic of the different interactions between the molecular parts and the substrate. Hydrogen atoms are repelled from the surface, whereas the central part of the molecule (oxygen and/or carbon atoms) chemically interacts with the surface. (d) This induces a geometrical change, e.g., a lifting of the Fe atoms below the molecule, that leads to a decrease in interlayer magnetic exchange interactions.

Importantly, the magnetic hardening/softening effect in a hybrid molecule-surface system is related to an interplay between (i) an adsorbate-substrate hybridization effect and (ii) a geometrical effect describing the rehybridization process of the surface atom d states due to the surface structural changes upon molecular adsorption [17,19].

To clarify the role of the geometrical effect on the calculated magnetic exchange coupling constants $J_{1,2,3}$, the in-plane (intralayer) J's have been recalculated for relaxed molecule-surface structures but with the molecules removed (i.e., for the molecule-induced surface geometry). The values obtained are listed in Table I and visualized in Fig. 3. For the surface geometry induced by the σ-system dioxan on 1 ML Fe/W(110) the computed magnetic exchange coupling constants [see Fig. 3(a)] differ by a few milli–electron volts with respect to those evaluated for the hybrid molecule-surface system. This observation clearly demonstrates that for the σ-system dioxan on 1 ML Fe/W(110) the calculated exchange coupling J's are mainly due to a geometrical effect. On the other hand, for the π-system dioxin on the same substrate the magnetic exchange coupling constant J_3 [see Fig. 3(b)] evaluated for the molecule-induced surface geometry is significantly smaller than that of the hybrid system. This result implies that for dioxin molecule-surface hybridization is a key factor to explain the increase in magnetic exchange couplings. Note that a similar picture is obtained for the dioxan and dioxin molecules on 2 ML Fe/W(110).

At this point it is important to note that the adsorption of the σ-system dioxan and π-system dioxin on 2ML Fe/W(110) modifies the interlayer magnetic exchange coupling constants $J_{\perp 1,2}$ [see Fig. 2(b)] describing the magnetic interaction between the two Fe layers. As listed in Table I and shown in Figs. 4(a) and 4(b), in the case of both molecules the interlayer magnetic exchange couplings $J_{\perp 1,2}$ are reduced with respect to the corresponding clean surface values, indicating an interlayer magnetic softening effect. More specifically, the clean surface interlayer coupling constants of $J_{\perp 1} = J_{\perp 2} = 126.1$ meV are reduced to 112.4 and 83.7 meV for the σ-system dioxan and even more considerably decreased, to 63.1 and 78.6 meV, for the π-system dioxin, respectively.

An important question to be answered is the origin of this interlayer magnetic softening, i.e., whether it is a molecule-substrate hybridization effect or a geometrical one. In the case of the σ-system dioxan, the interlayer $J_{\perp 1,2}$ values evaluated for the molecule-induced surface geometry are very similar to those obtained for the molecule-surface system. In consequence, we conclude that this interlayer magnetic softening present in a weakly chemisorbed molecule-surface system (σ-system dioxan) is mainly a geometrical effect. It is also noteworthy that this result of our first-principles study is *qualitatively different* from that obtained in [17] and [19], where a magnetic hardening effect was attributed to a strong molecular-substrate hybridization. Nevertheless, for the strongly chemisorbed π-system dioxin one can note the rather large difference between the interlayer $J_{\perp 1,2}$ values calculated for the hybrid system and those obtained for the molecule-induced surface geometry. This observation clearly emphasizes the importance of molecule-substrate hybridization effects (i.e., interface hybrid states) for such a strongly chemisorbed system to weaken the magnetic exchange coupling of the Fe layers. In this regard, we also note here that previous theoretical calculations identified the decrease in the interlayer magnetic exchange coupling between the Co surface atoms with respect to their clean surface values due to the adsorption of a zinc methyl phenalenyl dimer onto the Co(111) surface as a key ingredient to explain the interface magnetoresistance effect measured in an organic zinc methyl phenalenyl–based spin valve device [29].

Furthermore, our simulations clearly indicate that the decrease in the interlayer magnetic exchange coupling is strongly related to an increase in the distance between the first-layer Fe atoms just below the oxygen atoms and the second-layer Fe atoms. More specifically, in the case of the σ-system dioxan (π-system dioxin) the interlayer distance between Fe1 (Fe2) and the second layer, 2.40 (2.42) Å, is slightly larger than the clean surface value of 2.35 Å. The mechanism responsible for the Fe1 and Fe2 atoms lifting is schematically depicted in Figs. 4(c) and 4(d). For the π-system dioxin, the hydrogen atoms are repelled from the ferromagnetic surface [30] with a H-Fe distance of 2.43 Å, while the π molecular plane strongly interacts with the Fe surface atoms, for which the shortest C-Fe (O-Fe) bond is 2.04 (2.15) Å. Overall this leads to a lifting of the Fe atoms and therefore a slight increase in the interlayer distance locally below the molecule. Additionally, the weak interaction of the σ-system dioxan with the substrate is mainly governed by the dative-like bonds between the oxygen sp^3 orbitals and the underlying Fe atoms, which also determine a lifting of these surface atoms.

To summarize, in our *ab initio* study we have investigated how weakly and strongly chemisorbed organic molecules adsorbed on 1 ML and 2 ML Fe/W(110) locally modify the strength of the intra- and interlayer magnetic exchange interaction between the Fe atoms. Upon molecular adsorption, on both substrates the intralayer magnetic exchange coupling constants evaluated in a Heisenberg model can be drastically modified (i.e., increased or decreased) compared to those on a clean magnetic surface. Interestingly, on 2 ML Fe on W(110), weak (σ-system) or strong (π-system) chemisorption of the organic molecule onto the magnetic substrate can locally lead to a decrease in the interlayer magnetic exchange interactions. Furthermore, for a weakly chemisorbed σ-system dioxan the decrease in the interlayer magnetic exchange coupling is due to a geometrical effect. In other words, the rehybridization of the iron d states in the molecule-induced surface geometry is the driving mechanism leading to hybrid molecule-surface magnetic units weakly magnetically coupled to the underlying magnetic substrate. For a strongly chemisorbed π-system dioxin, in addition to the geometrical effect, the molecule-substrate hybridization also plays a very important role in further locally decreasing the interlayer magnetic exchange interactions, which suggests an enhancement of the interlayer magnetic softening.

It is important to note that this effect is very important in spintronic devices, where different magnetic layers must be switched independently with respect to each other. For example, this general mechanism is responsible for the molecular induced interface magnetoresistance effect measured for other π-bonded systems on a different magnetic substrate, such as phenalenyl derivatives adsorbed on Co(111) [29].

As an outlook, the results reported in this work represent a necessary step to understanding how a weakly or strongly chemisorbed molecular system can be employed to induce a hardening and/or softening of the exchange interactions and rationally design nanopatterned magnetic surfaces with locally targeted magnetic properties on a molecular scale.

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[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.92.195407 for computational details, structural data, and SPPDOS on the metal side and molecular side.

[28] Note that the adsorption energy is defined as $E_{\text{ads}} = -(E_{\text{sys}} - (E_{\text{surf}} + E_{\text{molec}}))$, where E_{sys} is the total energy of the molecule-surface hybrid system, E_{surf} stands for the total energy of the specific Fe/W(110) surface, and E_{molec} represents the total energy of the molecules in the gas phase.

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