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Hybridization-induced oscillatory magnetic polarization of C₆₀ orbitals at the C₆₀/Fe(001) interface

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We have studied the electronic and magnetic properties of the interface between C₆₀ molecules and a Fe(001) surface. X-ray absorption spectroscopy and x-ray magnetic circular dichroism studies of C₆₀ monolayers on Fe(001) surfaces show that hybridization between the frontier orbitals of C₆₀ and continuum states of Fe leads to a significant magnetic polarization of C₆₀ π*-derived orbitals. The magnitude and also the sign of this polarization were found to depend markedly on the excitation energy. These observations underline the importance of tailoring the interfacial spin polarization at the Fermi level of ferromagnet/organic semiconductor interfaces for applications in organic spintronics. © 2011 American Institute of Physics. [doi:10.1063/1.3595269]

Organic spintronics, which combines the strong potential of both spintronics and organic and/or molecular electronics for the development of next-generation nanoelectronics, is a promising research field that has received a strongly increasing amount of attention during the last decade.¹ Due to the weak spin-orbit coupling and hyperfine interaction in organic semiconductors (OSCs), the spin polarization of carriers can potentially be maintained for long times,² providing good prospects for robust spin manipulation and readout.

So far, the most promising results involving spin-dependent electronic transport in devices comprising organic, carbon-based materials have been obtained for vertical, current-perpendicular-to-plane geometries (notable exceptions being graphene³ and carbon nanotubes⁴) for which clear spin-valve signals have been observed in lateral devices. In such vertical devices, OSCs are used either as a tunnel barrier^{5,6} or charge/spin transport spacer^{6–8} placed between two ferromagnetic electrodes. Although spin-valve behavior has been consistently observed in devices encompassing several different OSCs, e.g., tris(8-hydroxyquinolino)aluminum,^{6,7} pentacene,⁹ and rubrene,¹⁰ the microscopic mechanisms governing the magnetotransport behavior remain poorly understood, in part due to the often ill-defined hybrid interfaces in the devices. This understanding may be improved upon exploiting the electronic structure and magnetic properties of *well-defined* interfaces between ferromagnetic electrodes and OSCs.^{6,11}

In this study, we focus on C₆₀ molecules, which are especially interesting for organic spintronics because of the absence of hydrogen nuclei and the associated spin-dephasing mechanism by hyperfine coupling¹² (the 99% predominant ¹²C isotopes have zero nuclear spin).

Thin films of C₆₀ molecules on Fe(001) were prepared *in situ* at beam line D1011 of the MAX-Laboratory in Lund, Sweden (base pressure 10⁻¹⁰ mbar). MgO(001) substrates were annealed (450 °C, 1 h) to obtain clean and restructured surfaces,¹³ on top of which a Fe film of several nanometer thick was grown at 150 °C, using a mini e-beam evaporator.

Epitaxial growth of Fe(001) was verified with low energy electron diffraction (LEED), as shown in Fig. 1(a). C₆₀ was deposited onto Fe(001) by thermal evaporation from a simple custom-built Knudsen-cell, monolayers (MLs) were obtained by annealing at 280 °C for one minute to desorb weakly bound overlayers. The x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) spectra were measured at room temperature in the total electron yield (TEY) mode. The angle of incidence of the photon beam was set to 70° relative to the sample normal. XMCD

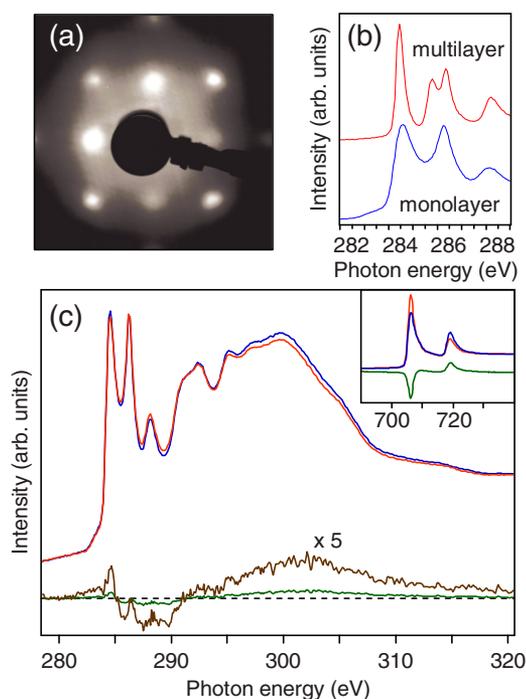


FIG. 1. (Color online) (a) LEED pattern of an epitaxial bcc-Fe (001) film on MgO(001); (b) XAS spectra of a multilayer and monolayer of C₆₀ on Fe(001); (c) C K-edge and Fe L-edge (inset) XAS and XMCD spectra of a ML C₆₀/Fe(001) sample. The XMCD spectra were obtained by taking the difference between the XAS data recorded with parallel and antiparallel alignment of the magnetization and photon helicity.

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spectra were recorded by reversing the helicity of the circularly polarized photons with respect to the (in plane) magnetization (in remanence, after applying a magnetic field pulse of 250 Oe) of the Fe layers. All the XAS and XMCD measurements were normalized to the incident photon flux using the TEY of a gold grid, onto which a fresh layer of gold was deposited prior to the measurements.

The LEED pattern in Fig. 1(a) of Fe(001) on MgO(001) reveals a well-ordered (1×1) spot pattern, without any additional distinct features of, e.g., a granular structure, indicating a high degree of structural order in the Fe film due to a good lattice match of MgO ($a=4.213 \text{ \AA}$) and Fe ($a=2.866 \text{ \AA}$) upon a 45° in-plane rotation of the Fe layer.¹⁴ Figure 1(b) shows the C *K*-edge XAS spectra of a multilayer and ML of C₆₀ on Fe(001), recorded with a photon line width of about 100 meV. The multilayer spectrum, which is identical to previously published spectra of solid C₆₀ (see, e.g., Ref. 15), was recorded on a C₆₀ film with a thickness between 2 and 5 nm, as estimated from the attenuation of the Fe *L*-edge XAS intensity. The peaks in the XAS spectra represent various core-excited states derived from virtual molecular orbitals. The first peak at 284.45 eV excitation energy is related to the lowest unoccupied molecular orbital (LUMO). In the core-excited state, the threefold degeneracy of the LUMO is lifted by the presence of the core-hole, such that the $5t_{1u}$ level (in icosahedral, I_h , symmetry) splits into three levels with slightly different energy eigenvalues. However, as has been shown by theoretical modeling,¹⁶ only one of these states contributes significantly to the C *K*-edge spectrum due to the large difference in oscillator strengths. Essentially the same holds for the LUMO+1 and LUMO+2 orbitals, which give rise to peaks at 285.80 eV and 286.35 eV photon energy, respectively.

The ML C₆₀ spectrum is dominated by two considerably broadened peaks compared to those in the multilayer spectrum, indicating orbital hybridization at the interface. Similar hybridization-induced spectral changes, including the merging of the LUMO+1 and LUMO+2 resonances into a single peak and a shift to higher energy of the LUMO peak, have been observed for C₆₀ adsorbed on, e.g., Al and Au.¹⁵ The peak broadening and LUMO-shift, from 284.45 eV (multilayer) to 284.55 eV (ML), which have previously been found to scale with the bond strength,¹⁵ indicate strong interfacial bonding between C₆₀ and Fe. We also note a small but clearly visible shoulder in the ML C₆₀ XAS spectra at about 283.5 eV, which we attribute to (partial) occupation of the LUMO due to electron transfer from Fe to C₆₀, in analogy with previous reports for C₆₀ on Cu(111).¹⁷

Recently published theoretical and experimental results^{18,19} show that the hybridization between the orbitals of organic molecules (or graphene²⁰) and ferromagnetic metal (*3d*) valence band states can lead to sizeable interfacial magnetic moments and spin polarization of π -conjugated states in carbon-based systems. For graphene on Ni(111),²⁰ a particularly strong C *K*-edge XMCD signal of about 5% of the XAS intensity has been observed, reflecting the significant degree of mixing between C p_z and Ni *3d* derived states at the interface.^{21,22} To investigate the magnetic properties of the interface between the ML C₆₀ and Fe, which is also characterized by strong hybridization effects as discussed above, we analyze the XMCD spectra of both the Fe *L*_{2,3}-edge and C *K*-edge. From Fig. 1(c), we can observe a significant di-

chromic signal (of about 3% of the XAS intensity) at the C *K*-edge of the ML C₆₀/Fe(001) system. This strong XMCD signal indicates a sizeable magnetic moment on the C₆₀-Fe hybridized orbitals. *K*-edge dichroism, involving *s* to *p* dipole transitions, is usually attributed to the orbital moment in the final state (see Ref. 23 and references therein), which in turn depends on spin-orbit coupling. Therefore, even though the C *K*-edge XMCD probes orbital polarization, it is intimately connected to the spin polarization of the hybrid states. Depending on the excitation energy, an inversion of the polarization of the C₆₀ derived π^* states with respect to that of the Fe layer is evident from the change in sign of the XMCD signal across the C(*1s*) $\rightarrow \pi^*$ resonance. In particular, the LUMO-related transition has an XMCD signal that is opposite to that of the Fe *L*₃-edge [inset in Fig. 1(c)], corresponding to a magnetic polarization of the LUMO-derived orbital that is also opposite to that of the Fe surface. Our results might be interpreted in terms of an oscillatory interfacial spin polarization, induced by the hybridization between carbon p_z orbitals and Fe *3d* majority and minority bands. Such a scenario is similar to the recently published theoretical and experimental (spin-polarized scanning tunneling microscopy) results on the complex, energy-dependent spin polarization of aromatic molecules on Fe/W(110).¹⁹ For these systems, viz., benzene, cyclopentadienyl radicals, and cyclooctatetraene on 2 ML Fe/W(110) substrates, first-principles density functional theory calculations show that the hybridization of out-of-plane π and π^* orbitals with metal *d*-states leads to an oscillatory behavior of the spin polarization versus binding energy of electronic states on the molecules with respect to that of the metal substrate bands. Our experimental observations tentatively support a similar picture for C₆₀ on Fe(001), and underline the crucial role played by the hybridization effects between different molecular π^* (and π) orbitals and metal *3d* surface bands in determining the magnetic properties of the interfaces. These effects may be exploited to tune the interfacial spin polarization, and thereby influence spin-polarized charge carrier injection, at properly engineered, structurally and electronically well-defined organic/ferromagnetic metal interfaces.

It is an interesting question whether the hybridization of C₆₀ orbitals with Fe *3d* states significantly affects the spin-dependent electronic structure of the Fe surface atoms. If so, one would expect to observe a change in the orbital and/or spin moments in the Fe *L*-edge XMCD spectra upon adsorption of C₆₀ onto Fe. However, such effects are difficult to observe in samples comprising several nanometer thick Fe films, due to the significant contribution of bulk Fe atoms to the XAS yield (even for partial electron yield measurements the probing depth is several nanometer), obscuring effects due to bonding between C₆₀ and the Fe surface. Accordingly, additional samples incorporating a low coverage of Fe (significantly less than 1 ML) on Co(several nanometer)/MgO(001) were prepared, such that the majority of Fe atoms (if not all) will reside at the surface. Since the magnetic moments of the Fe atoms are aligned with the magnetization of the Co layers, such samples can be easily magnetized in-plane and characterized in remanence. Figure 2 shows the corresponding Fe *L*-edge XMCD spectra, of the same sample before and after the deposition of a C₆₀ overlayer. The spectra are normalized to the *L*₃-peak height of the XAS sum spectra for parallel and antiparallel alignment between the

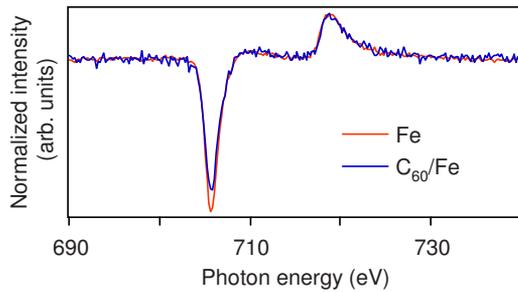


FIG. 2. (Color online) Fe L -edge XMCD spectra of sub-ML Fe on Co/MgO(001) before and after adsorbing C_{60} .

magnetization and photon helicity. After adsorbing C_{60} , the Fe L_3 -edge XMCD signal is somewhat suppressed while the L_2 edge remains unaffected (within the experimental error), indicating a reduction in, in particular, the orbital magnetic moments on the Fe atoms due to hybridization between Fe and C_{60} electronic states. Applying the XMCD sum rules²⁴ to the integrated XMCD spectra shows a slight reduction in the spin magnetic moment (of about 1%–2%), consistent with partial electron transfer to the C_{60} molecule. The orbital moment, which is especially sensitive to hybridization effects, is reduced by roughly a factor of 3. It should be pointed out, however, that this experiment does not provide direct quantitative information on the effects of C_{60} adsorption on the spin and orbital magnetic moments of an actual Fe(001) surface. However, it serves to illustrate the qualitative effects of chemical bonding between C_{60} and Fe on the Fe magnetic moments, and is in agreement with our observations of a strong, hybridization-induced XMCD effect at the C K -edge of ML $C_{60}/Fe(001)$ samples. The results are also in qualitative agreement with the bonding-induced modification of the spin polarized Fe $3d$ -derived interfacial electronic structure of aromatic molecules on Fe/W(110) reported in Ref. 19, and the calculated reduced magnetic moments of surface Ni atoms at graphene/Ni(111) interfaces.²¹

In conclusion, the C K -edge XAS spectra show evidence of significant hybridization between C_{60} orbitals and Fe continuum states, and mixing between C_{60} $\pi(\pi^*)$ orbitals and Fe $3d$ wave functions leads to a distinct, oscillatory magnetic moment of C_{60} -derived interfacial electronic states due to spin-orbit coupling in the hybridized final state, as is evident from C K -edge XMCD spectra. The oscillatory nature of the polarization of these states close to E_F is important in the light of spin-polarized charge injection across the interface. Gaining control of the interfacial spin polarization at well-defined hybrid interfaces is an essential ingredient for systematically engineering the performance of future organic and molecular spintronic devices.

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