

# A spin polarized He metastable beam investigation of the adsorption of L-cysteine on magnetic surfaces

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## ABSTRACT

We report first results on the deposition of L-cysteine (Cys), a fundamental amino-acid, on a magnetic substrate. Molecules have been deposited under ultra-high vacuum conditions on Fe(100) films. Electronic and magnetic properties of adsorbed molecules have been investigated by spin polarized metastable deexcitation spectroscopy (SPMDS). The spectra show a growth dynamics apparently similar to the one already reported on coinage metal surfaces with the formation of a strongly-bound thiolate species (S–Fe bond) and weakly-bound second-layer molecules. SPMDS revealed the spin-polarized character of an Auger (Penning) deexcitation peak related to a Cys molecular orbital. Interestingly, these spin-polarization effects, ascribed to the interaction with the magnetized substrate, vanish before the first layer completion, suggesting a possible correlation with the SAM assembly properties.

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## 1. Introduction

The spectroscopy of electrons ejected following He<sup>+</sup> deexcitation at surfaces (MDS, MAES or MIES) is known for many years as a valuable tool for the investigation of the valence band of adsorbed layers [1–5]. In particular, the enhanced sensitivity to molecular adsorbates, through the Auger (Penning) deexcitation (AD) process, stimulated the application of MDS to self-assembled organic monolayers (SAMs) [6–10]. Recently, we have exploited MDS for the study of L-cysteine layers grown on noble metal surfaces [11,12]. Cysteine (Cys, HS–CH<sub>2</sub>–CH(NH<sub>2</sub>)–COOH) is a fundamental amino acid that forms strong chemical bonds with surfaces [13–18]. Interaction of Cys with metals, notably gold, finds applications in many fields such as electrode modification [19], proteins immobilisation [20], fabrication of selective channels for molecular separation [21], heterogeneous catalysis [22]. On a more fundamental ground, Cys has been exploited in studies on chiral recognition at surfaces [23] and about the assembly of complex molecular chiral nanostructures [24–27]. Studies on Cys SAMs mainly focused on gold and copper [28] substrates. Apparently, transition metals have been ignored. Here we report first results on L-cysteine SAMs deposited under ultra-high vacuum (UHV) conditions on a Fe substrate. This study is aimed to gather

information both on the Cys–Fe interaction and on the interplay between SAM morphology and surface magnetism. In this respect we also present spin-polarized MDS measurements. Spin-polarized He<sup>+</sup> beams were employed in pioneering experiments to probe spin correlation effects in charge-exchange processes [29] and are a well established tool to study the magnetic properties of adsorbates. Even though most SPMDS studies dealt with simplest adsorbates, notably atomic oxygen [30,31], more recently there have been interesting developments regarding organic molecules, such as pentacene [32] and benzene [33]. The interest for complex organic adsorbates is fostered by their relevance as materials for novel spintronic devices. In fact, the relatively weak spin-orbit and hyperfine interactions in these materials lead to spin relaxation times much longer than those observed in inorganic materials, thus making them ideally suited for applications requiring spin transport and manipulation [34,35]. For instance, organic materials may efficiently replace metallic spacers between ferromagnetic electrodes in spin valve devices. In this respect, the growth of ordered SAMs can be envisaged as a tool for obtaining molecular spacers with ultimate control over the spacer thickness and transport properties [36] while the knowledge of the electronic states and spin polarization of molecules adsorbed on ferromagnetic electrodes, particularly for the orbitals of the molecule pointing to the second electrode, can be exploited to select suitable molecules and optimize the device. SPMDS, with its exclusive sensitivity to the spin-polarized density of surface states spilling out into the vacuum, may give interesting contributions to this promising research field.

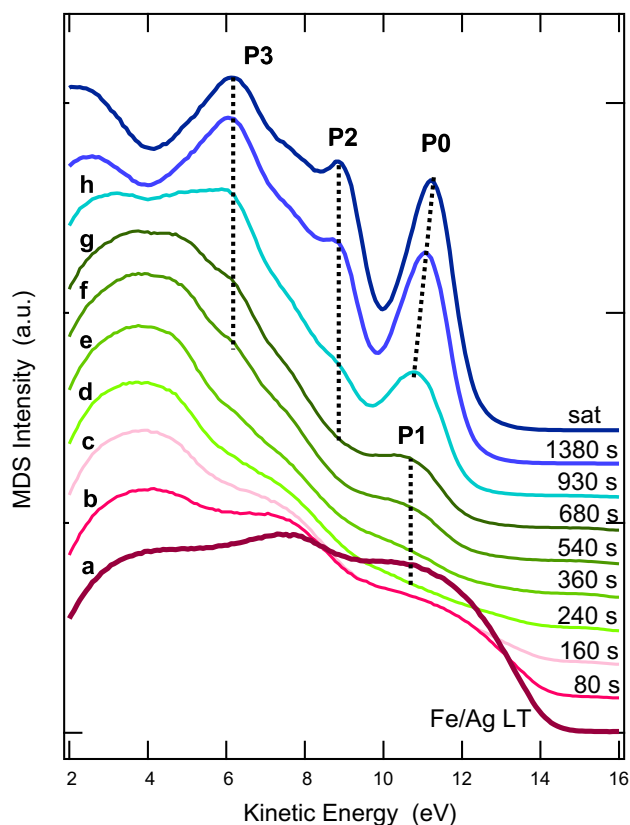
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## 2. Experimental

The experimental apparatus has been extensively described elsewhere [31,37]. Here we report the essentials. The  $\text{He}^+$  beam is produced in a nozzle-skimmer dc-discharge source. The intensity of the  $\text{He}^+(2^3S)$  fraction on the sample is of the order of  $10^{11}$  at/s with a spot diameter of 1 mm. The populations of  $\text{He}^+(2^1S)$  and UV photons are about 10% and 5% of  $\text{He}^+(2^3S)$ , respectively.  $\text{He}^+(2^3S)$  atoms are spin-polarized by optical pumping along a quantization axis defined by a weak magnetic field. The effective polarization of the  $\text{He}^+$  beam, including  $\text{He}^+(2^1S)$  atoms, is 84%. The kinetic energy distribution curves (EDCs) of the emitted electrons are measured by means of a spectrometer characterized by an acceptance angle of about 0.4 sr, and energy resolution adjustable in the 100–300 meV range.

The Ag(100) substrate has been prepared according to well-known procedures [37]. Fe films have been deposited at about 150 K, in order to minimize surface segregation of Ag [37]. Cleanliness of the Ag substrate and of Fe films prior to Cys deposition has been checked by MDS spectra. Iron films are highly reactive and efficiently capture background gas species which are revealed by MDS with high sensitivity. Cys deposition has been accomplished in UHV by means of a molecular beam [11]. L-Cysteine powders (purity 99%, Sigma) were used after re-crystallization in Milli-Q water. An operating temperature of about 100 °C was chosen to avoid Cys cracking. The pressure rise in the analysis chamber during deposition amounts to a few  $10^{-10}$  mbar. We have performed several Cys deposition experiments, with the substrate at 150 K or at room temperature (RT).



**Fig. 1.** MDS spectra measured during deposition of cysteine at 150 K. P1 is related to surface-bound molecules. P0 and P2 are related to orbitals localized on the SH group of weakly bound second-layer molecules [12]. More details in the text.

## 3. Results and discussion

Fig. 1 shows the typical evolution of EDCs observed during slow rate deposition of Cys on Fe at 150 K.

Curve a (thick reddish line) is the spectrum of the freshly deposited Fe films. It originates from the two-step Resonant Ionization + Auger Neutralization (RI + AN) de-excitation process typical of transition metals [2]. This spectrum has been quantitatively analysed in previous works, and can be approximated as the self-convolution of an effective surface density of states [37,31]: considering the spectrum from the highest to the lowest kinetic energy, the first slope, rising above 14 eV KE is related to AN electrons coming from the metal Fermi energy, while the second less intense bump is due to surface impurities (segregated Ag, O, OH, CO) [37]. The spectral evolution following Cys deposition is comparable to the one observed on other metal surfaces [Cu(100), Ag(100) and Au(110)], discussed in Ref. [11] and in more details in Ref. [12]. Initially, Cys adsorption induces a strong attenuation of the Fe-related features. Adsorbed molecules progressively “shields” the substrate from the incoming  $\text{He}^+$  and, increasing the exposure, two Penning features start to develop at about 10.6 (P1) eV KE and at 6.2 eV KE (P3). Going on with Cys exposure, the P3 feature evolves into a relatively intense peak with side shoulders. The position of the highest energy peak progressively shifts right. At saturation, the highest KE peak, P0, can be found at 11.3 eV KE while another narrow structure, P2, can be observed at 9 eV KE. The saturation spectrum is identical to those observed for all surfaces so far investigated, including oxidised surfaces [11,12]. Density Functional Theory (DFT) calculations of the electronic structure of the free neutral molecule [12], strongly suggest that P0, the Highest Occupied Molecular Orbital (HOMO), and P2, have to be assigned to the “unreacted” SH group of second-layer molecules, progressively masking the P1 feature. The orbitals corresponding to the P0–P2 pair are strongly affected by the Cys–metal reaction through the SH termination, and in fact those spectra characterized by the intense P1 peak (g–h) resemble those obtained at the monolayer stage on other metal substrates [12]. In the case of coinage metals [12], the most effective procedure to obtain a single layer consisted of a prolonged deposition at low temperature (or at RT), beyond saturation of the MDS spectrum, followed by a mild annealing or even prolonged exposure to the metastable helium beam which ensured detachment of weakly-bound second layer molecules. For the Fe/Ag films of this paper, such procedure led to a pattern (not shown) which was intermediate between curves g and h of Fig. 1. Thus according to the extensive discussion of Ref. [12], peak P1 is assigned to first-layer thiolate molecules. On the contrary, P3 is clearly related to a non-bonding orbital scarcely affected by the molecule–surface bond [12].

Regarding SPMDs, we have measured the so-called asymmetry [31,37], defined as

$$A^{\text{expt}}(E) = \frac{1}{P} \frac{I_{\downarrow}^{\text{expt}}(E) - I_{\uparrow}^{\text{expt}}(E)}{I_{\downarrow}^{\text{expt}}(E) + I_{\uparrow}^{\text{expt}}(E)} \quad (1)$$

where  $P$  is the polarization degree of metastable helium beam impinging on the surface and  $I_{\downarrow/\uparrow}^{\text{expt}}(E)$  are the experimental energy distributions of electrons ejected following the deexcitation of metastable atoms with polarization antiparallel ( $\downarrow$ ) or parallel ( $\uparrow$ ) to the surface magnetization vector.

Asymmetry curves corresponding to spectra of Fig. 1 are reported in Fig. 2. The asymmetry curve obtained on freshly deposited films (curve a) has been thoroughly discussed in previous works [37,31]: the positive feature at high KE related to Fe electronic states close to the Fermi energy, most probably  $d$  states protruding into the vacuum with a possible contribution from  $s$  states.

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