

## Adsorption energy of iron-phthalocyanine on crystal surfaces

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**Summary.** — The adsorption energy of iron-phthalocyanine (FePc) deposited on different crystal surfaces is studied by thermal desorption spectroscopy. A thin film of molecules has been absorbed on highly oriented pyrolytic graphite (HOPG), on graphene epitaxially grown on Ir(111), and on Au(110). Activation energies for the desorption of a molecular thin film and for the FePc single layer are determined at the three surfaces. The desorption temperature measured for the thin films is only slightly dependent on the substrate, since it is mostly dominated by molecule-molecule interactions. A definitely different desorption temperature is found at the single-layer coverage: we find an increasing desorption temperature going from HOPG, to graphene/Ir, to the Au(110) surface. The different adsorption energies of the first FePc layer in contact with the substrate surface are discussed taking into account the interaction and the growth morphology.

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### 1. – Introduction

In the framework of the development of advanced organic electronic devices, the molecule-substrate interaction is a fundamental parameter that influences the electron transport [1]. Metal-phthalocyanines (MPc,  $M-C_{32}N_8H_{18}$ ) are planar metal-organic molecules with conjugated orbitals [2], building block of potential new devices at the nano-scale. MPcs can self-assemble on templating surfaces able to drive well-ordered low-dimensional architectures [3-6], like other  $\pi$ -conjugated oligomers [7,8]. Their charge transport and delocalization are mainly due to the  $\pi$ -conjugation, whereas the central metal atom can be exploited to control their optical and magnetic properties [2].

Adsorption of metal-phthalocyanines on crystalline substrates may lead to a planar configuration, thanks to the interaction with the templating surface, and the subsequent layers may continue to build up a layered planar thin film. In particular, FePc can be

adsorbed in a planar configuration on weakly interacting surfaces like HOPG [9] as well as on stronger interacting metal surfaces, like Au(110) [5,6]. The anchoring of the molecules onto the substrate surface occurs *via* the organic macrocycles, while the central metal atom plays a role in determining the electronic [4] and magnetic properties of the system. An open question concerns the adsorption temperature in the different coverage phases, from the single-layer (SL) stage to the building-up of a molecular thin film (TF).

An effective method to determine the adsorption energies at these thin interface systems is the use of thermal desorption spectroscopy (TDS). With TDS, the deposited molecular layers are heated with a linear temperature ramp, while the masses of the desorption products are measured *via* a mass spectrometer. The adsorbed molecules desorb when the thermal energy exceeds the activation energy associated with the bond between the molecules for the thin film, or the bond between the first adsorbed layer and the substrate surface for the SL. The measured desorption temperatures can be related to the activation energies, giving information on the interaction strength between molecules in the TF, and between the molecule and the substrate surface, in the case of a single layer [10,11].

In this paper, we use different substrates, namely HOPG, graphene epitaxially grown on Ir(111), and Au(110), over which a FePc TF with nominal thickness of 20 nm has been grown. We chose these substrates since HOPG is a flat polycrystalline weakly interacting surface, graphene presents a natural corrugation linked to the moiré pattern originating from the slight lattice mismatch between carbon and Ir [12], and Au(110) is a metal with a natural  $(1 \times 2)$ -surface reconstruction. Through TDS we determine the FePc desorption temperature on the different surfaces, highlighting its dependence on the molecule-molecule and molecule-surface interaction. The major differences found at the SL coverage are discussed as depending on the specific electronic interaction with the substrate states.

## 2. – Experimental

Experiments have been carried out at the surface physics laboratory LOTUS in Rome in an ultra-high-vacuum (UHV) chamber equipped with all the facilities for sample preparation. HOPG sample has been cleaved prior to be placed inside the UHV chamber and cleaned by a sputtering-annealing treatment ( $\text{Ar}^+$  ions at 1 keV,  $T = 700^\circ\text{C}$ ). The Ir(111) clean substrate was prepared by  $\text{Ar}^+$  ion sputtering-annealing cycles (2.5 keV and  $1000^\circ\text{C}$ ), and subsequent annealing/oxygen-exposures cycles. The graphene single sheet was prepared by repeated cycles of  $\text{C}_2\text{H}_4$  dosing during annealing up to  $1200^\circ\text{C}$ , ensuring a well long-range-ordered layer. The graphene/Ir(111) sample was prepared in a different UHV chamber [13] and then air-transferred to the TDS UHV chamber. After transfer into UHV, cleaning was obtained by several subsequent annealing cycles at increasing temperatures up to about  $700^\circ\text{C}$ , revealing an excellent clean graphene recovering, as testified by the good low-energy diffraction (LEED) pattern [13]. The Au(110) clean surface has been obtained by means of a sputtering-annealing treatment with  $\text{Ar}^+$  ions at 1 keV,  $T = 500^\circ\text{C}$ .

FePc was evaporated in UHV from resistively heated quartz crucibles, the nominal thickness of the deposited layers was measured *via* an oscillating quartz microbalance. We prepared TFs with a thickness of about 20 nm, while a single-layer corresponds to  $\approx 3.5 \text{ \AA}$  nominal coverage. The overall pressure during deposition was in the low  $10^{-9}$  mbar range.

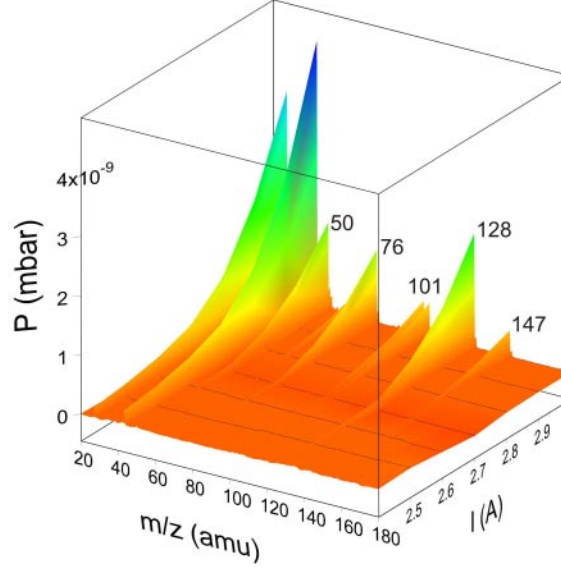


Fig. 1. – Identification of the FePc-derived masses followed in this experiment. Mass spectrum (pressure *vs.* mass,  $m/Z$ ) of FePc as a function of the FePc evaporator heating current.

The temperature was measured using a K-type (chromel-alumel) thermocouple mounted to the side of the sample, with an error of  $\pm 15^\circ\text{C}$ . Samples have been mounted on the head of a manipulator resistively heated through a W filament, capable to reach temperatures up to approximately  $700^\circ\text{C}$ . For the thermal desorption experiments, the sample temperature was ramped with a constant rate  $\beta = dT/dt = 0.3\text{ K/s}$ . The use of a quadrupole mass spectrometer allows the determination of partial gas pressures, where the flux intensity of the desorbing molecules is proportional to the ion current recorded by the mass spectrometer (given the high pumping speed in UHV). The recorded ion-current is directly proportional to the partial pressure of the corresponding desorbing component.

FePc has an atomic mass unit (amu) of 568, too large to be detected by our mass spectrometer which can scan masses up to 300 amu. The cracking pattern of the molecules is then helpful for choosing the masses to follow during the TDS experiment: in fig. 1, we report the mass spectrum (pressure *versus*  $m/Z$ , amu), recorded by the mass spectrometer as a function of the FePc evaporator current, where we can identify some of the cracking fingerprints of the FePc molecule, *i.e.* masses 50, 76, 101, 128, 147, originating from benzene and pyrrole components of the FePc molecules ( $\text{C}_4\text{H}_2$ ,  $\text{C}_6\text{H}_4$ ,  $\text{N}_2\text{C}_8\text{H}_4$ , etc.).

### 3. – Results and discussion

In fig. 2, we show the TD spectra of a FePc thin film adsorbed on three different substrates, namely HOPG, graphene/Ir(111), and Au(110). The desorption relative to a fragment of the benzene component ( $\text{C}_4\text{H}_2$ , 50 amu) is shown, however several mass

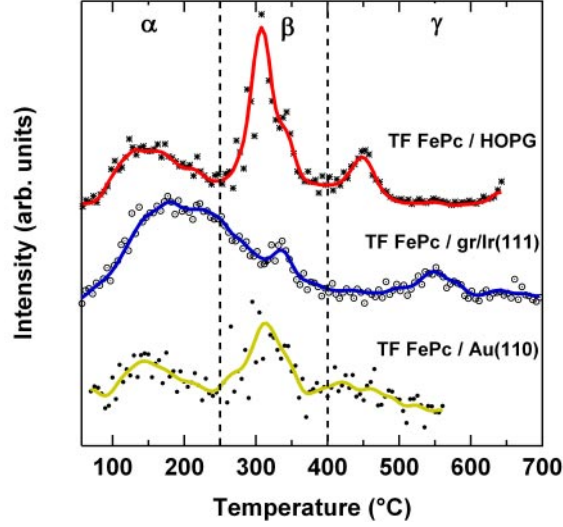


Fig. 2. – Thermal desorption spectra ( $m/z = 50$  amu vs. T) of a FePc TF adsorbed on three different surfaces: (from top to bottom) HOPG, graphene/Ir(111) and Au(110). Data are vertically stacked for clarity. Experimental data are reported as black symbols, continuous curves are obtained after a smoothing treatment of the data. Three temperature regions are observed, and indicated with  $\alpha$ ,  $\beta$  and  $\gamma$  (see text).

signals deriving from FePc were followed, all giving the same TDS behaviour, a sign that the molecule desorbs as a whole and there is not any fragmentation on the surface. Three temperature regions can be identified in the TD spectra of fig. 2: a low-temperature region up to about 250 °C (indicated with  $\alpha$ ), a middle-temperature region from 250 °C to 400 °C ( $\beta$ ), and a high-temperature region above 400 °C ( $\gamma$ ). The broad peak observed in the  $\alpha$  region is actually due to the desorption of disordered molecular layers from the sample manipulator and from the environment, it is thus a spurious signal also identified in a check experiment performed without crystal surfaces (not shown here). The rather narrow and distinct peak appearing in the  $\beta$  region just above 300 °C is common to all three systems (310 °C, 330 °C and 305 °C for FePc TF on HOPG, graphene/Ir and Au, respectively).

By looking at the third temperature region ( $\gamma$ ) in fig. 2, we can clearly identify a narrow peak at  $(450 \pm 15)$  °C for FePc on HOPG, a broader peak at  $(550 \pm 15)$  °C for FePc on graphene/Ir, while not any further structure is detectable for FePc on Au(110). In this latter case, we could heat the sample only up to 550 °C in order to avoid surface melting.

These desorption temperatures can be associated to corresponding activation energies. We first consider that the present interface systems are characterized by a first-order process, where the FePc molecules desorb leaving the surface without subsequent re-adsorption (see below). In these conditions, for analysing the TD spectra we can use the Redhead equation, correlating the activation energy  $E_A$  to the desorption temperature [14]

$$E_A = K_B T_{\max} \left[ \ln \frac{\nu T_{\max}}{\beta} - \ln \frac{E_A}{K_B T_{\max}} \right],$$

TABLE I. – *Activation energies (and corresponding desorption temperatures,  $\pm 15^\circ\text{C}$ ) of FePc TF and SL adsorbed on HOPG, graphene/Ir(111) and Au(110), as calculated with the Redhead equation (1).*

	HOPG	graphene/Ir(111)	Au(110)
FePc TF	$2.3 \pm 0.1 \text{ eV}$ ( $310^\circ\text{C}$ )	$2.4 \pm 0.1 \text{ eV}$ ( $330^\circ\text{C}$ )	$2.3 \pm 0.1 \text{ eV}$ ( $305^\circ\text{C}$ )
FePc SL	$2.8 \pm 0.1 \text{ eV}$ ( $450^\circ\text{C}$ )	$3.2 \pm 0.1 \text{ eV}$ ( $550^\circ\text{C}$ )	$> 3.2 \pm 0.1 \text{ eV}$ ( $> 550^\circ\text{C}$ )

where  $K_B$  is the Boltzmann constant,  $T_{\text{max}}$  is the desorption temperature,  $\nu$  is a frequency factor, and  $\beta$  is the heating rate. The term  $\ln(E_A/K_B T_{\text{max}})$  is small compared with the first term in brackets and can be approximated by a value of 3.64, and  $E_A$  vs.  $T_{\text{max}}$  is a linear relation. This approximation is valid assuming  $\nu = 10^{18} \text{ s}^{-1}$ , a reasonable value for adsorbed molecules. This is valid for first-order kinetic processes that are non-dissociative desorptions, without multiple process of readsorption, where the temperature peak does not change with coverage, as in the case under examination.

The desorption temperatures and the activation energy values calculated by means of the Redhead equation (1), are reported in table I.

We attribute the first desorption peak (around  $310\text{--}330^\circ\text{C}$ ) to the desorption of the flat molecular thin film adsorbed onto the sample surfaces, since it appears at comparable and low temperatures for all three substrates. It is thus compatible with physisorbed TFs dominated by molecule-molecule interactions, with an adsorption energy ( $2.3\text{--}2.4 \text{ eV}$ ) rather independent from the substrate. The desorption of the multi-layer leaves a single layer on each surface. In order to understand the role of the substrate in the interaction process with FePc, we should focus on the behaviour of this first molecular layer in direct contact with each surface. If the molecule-surface interaction is higher than the intermolecular forces, a desorption peak in a higher temperature range is expected. Focusing on the first two systems (FePc single-layer on HOPG and on graphene/Ir), we found a higher desorption temperature on graphene/Ir than on HOPG ( $550^\circ\text{C}$  and  $450^\circ\text{C}$ , respectively) even if they would be expected to be very similar, since graphene is essentially a single sheet of graphite and in principle we would not expect a different adsorption energy. This evidence indicates a different activation energy at the FePc single-layer coverage stage on the two surfaces,  $3.2 \text{ eV}$  and  $2.8 \text{ eV}$  for the SL FePc on graphene/Ir and on HOPG, respectively, which may be due to a different interaction strength. A different behaviour in the FePc adsorption on these two carbon systems has been found concerning the growth morphology of the molecular layers: a Volmer-Weber mode (island growth) is observed for FePc uptake on HOPG [15], while a Stranski-Krastanov growth (first single layer followed by islands) has been determined on graphene/Ir [13], while maintaining a planar orientation of the first and subsequent molecular layers [9, 13]. This different behaviour confirms the role played by the graphene substrate in the interaction with FePc molecules, although there is not any definite sign of electronic state interaction or mixing between FePc and graphene and/or Ir [16]. We can therefore identify as responsible of the higher interaction in these  $sp^2$ -C-based layers the regularly modulated moiré pattern generated by the growth of graphene on Ir(111), with the consequent chemical and geometrical corrugation of the graphene sheet. It exhibits very different local electronic structures influencing the self-assembling behaviour of the adsorbed molecules. At contrast with graphene/Ir, the HOPG surface is flat, and the adsorbed molecules are dominated by intermolecular interactions, while the substrate-molecule interactions are mainly responsible for the preferential orientation of the respective adlayer networks.

Finally, the FePc molecules well ordered at the SL stage on the Au(110) surface [5] present an enhanced molecule-substrate interaction, with respect to the C-based surfaces. In this case, FePc molecules have been shown to present a high electronic interaction characterized by a Au-*d* to molecular  $\pi$ -orbital mixing [5, 17], favoured by the presence of unfilled out-of-plane *d*-like states in the FePc molecules [5]. Thus, we expect an activation energy higher than that found on graphene and HOPG, and this is confirmed by the lack of a desorption peak relative to the single-layer up to 550 °C. As a consequence of the FePc-Au orbital mixing, the molecules stick to the gold surface with an activation energy higher than 3.2 eV, beyond the limits of gold surface melting. This energy is much higher than the 1.9 eV activation energy found for the complete desorption of a single layer of pentacene (a purely  $\pi$ -bonded system) from Au(110) [18], confirming the role of the central Fe metal in establishing the FePc interaction with Au.

#### 4. – Conclusions

The activation energy for FePc molecules adsorbed on three different crystal surfaces has been determined by thermal desorption spectroscopy. FePc flat multi-layers desorb at comparable temperatures on HOPG, graphene/Ir(111) and Au(110), corresponding to 2.3–2.4 eV activation energy, compatible with a weak molecule-molecule interaction. The FePc first layer interacts with Au(110) presenting an activation energy higher than 3.2 eV due to an actual orbital mixing between gold and the molecule. The FePc first layer presents a higher activation energy on graphene/Ir (3.2 eV) than on HOPG (2.8 eV), despite the analogous composition of the carbon sheet, because of the corrugated nature of the graphene sheet prepared on Ir. The exploitation of graphene/Ir as a template for molecular adsorption opens a new scenario for designing novel molecular architectures with new functionalities.

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