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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Imaging Long Range Charge Diffusion and interactions in metal/molecule hybrid structures**	**Experiment number**: HC-3469
Beamline:	**Date of experiment**: from: 13.09.2017 to: 17.09.2017	**Date of report**:
Shifts:	**Local contact(s)**: Chiara Cavallari	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Timothy Moorsom*, Bhoopesh Mishra*, Luke Higgins*, Oscar Cespedes.

REPORT

This experiment was intended to utilise the unique capabilities of the ID20 inelastic scattering beamline to observe the long range effects of a molecule-metal interface on molecular electronic structure. While previous synchrotron experiments in this system had revealed the formation of hybrid interface states at the boundary between molecular and metallic thin films, surface sensitive techniques were unable to explain the observed effects of thicker C_{60} films on the magnetic behaviour of metallic thin films, fig 1. Films were prepared with thicknesses from 0.002 μm to 1 μm. Samples were capped with aluminium to a thickness of 4.5 nm. Samples were characterised by VSM magnetometry in order to confirm the desired magnetic behaviour. [1]

Samples were loaded at grazing incidence with very small incident angles to maximise the length of the beam's path through the molecular layer. An initial measurement of a 1μm film revealed a K-edge with LUMO, LUMO+1, LUMO+2 and σ resonance visible. Compared to XAS data previously recorded in similar samples, the aromatic π resonances appear at higher energy.

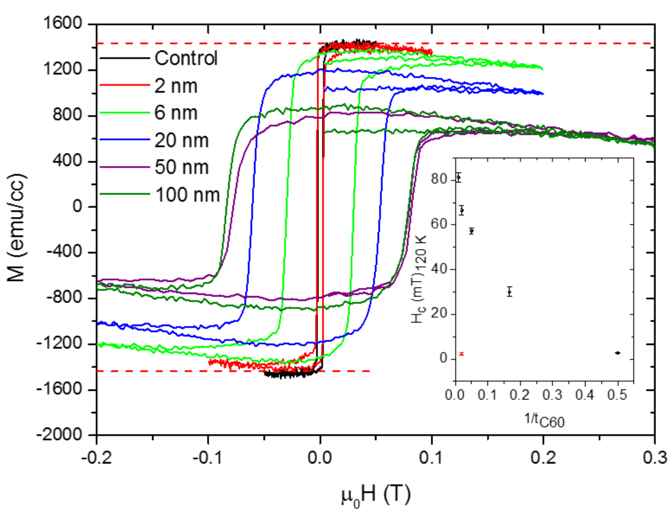

FIG. 1. Hysteresis loops in CoC_{60} bilayers obtained via VSM. The target was to observe films in the range of 200 - 20 nm, where the most significant changes in magnetic properties occur. The red dotted line marks the M_{sat} of the control sample in which a layer of alumina separates the C_{60} from the metal layer.

C_{60} thin films were probed at 6.5 keV. While 10 keV is typically used in this beamline, the lower energy was chosen to increase scattered intensity in a thin film. XRS spectra appear shifted in comparison to XAS spectra. This shift roughly corresponds to the on site Coulomb binding energy for a core-hole exciton in C_{60}. The spectra obtained are concurrent with previous XRS observations

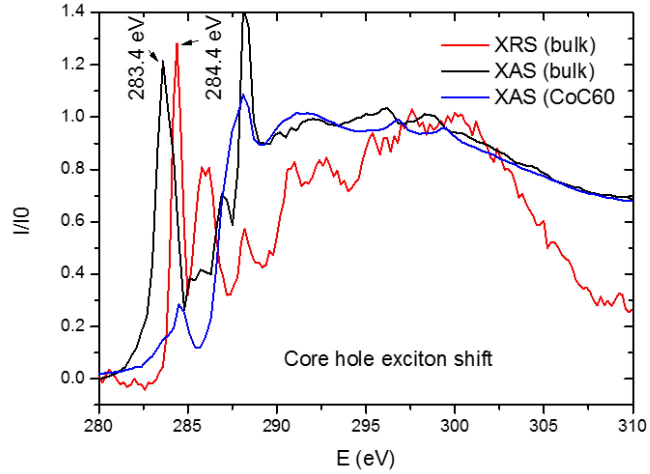

FIG. 2. Comparison of the K-edge in C_{60} films obtained via XAS and XRS. When a thin film of C_{60} is interfaced with a metal film, π resonances are supressed and a shoulder feature emerges close to the Fermi energy due to filling of hybrid interface states. This is the key feature which indicates coupling to the metal substrate.

of bulk C_{60} crystals with no indication of polymerisation or graphitic regions, fig 3. [4]

It was necessary to first deteremine the thinnest measureable sample. This was established as 50 nm, though the Lowest Unnocupied Molecular Orbital (LUMO) peaks were observable at 20 nm. However, 20 nm films were deemed to not provide a strong enough signal for small changes in the pre-edge structure to be visible.

Over time, the signal was seen to degrade and this was attributed to local heating of the substrate and subsequent evaporation of the moelcular layer. An attentuator was inserted to reduce the incident flux. The carbon K-edge was still clearly visible with attentuation of 70% while degredation was stabilised. Once the sample degredation was controlled, samples were measured with 1000,100,50 and 20 nm of C_{60} on cobalt thin films 5 nm thick 3. The expected hybridisation peak did not emerge in the thinnest observable sample. A 20 nm film was measured but it was not possible to obtain sufficient signal from this film within the allowable time frame. This indicates that in C_{60} films of at least 50 nm thickness, there is no shift in the energy of the LUMO due to the effect of the hybrid interface or formation of a mid-gap state. However, a relative suppression of the π orbital peaks was observed. This is commonly observed in thin films (1-3 ML) of C_{60} on metal substrates along with an increase in the FWHM of peaks close to the Fermi energy due to decay of excited states into the metal. [5] [6]

Samples which had been exposed to the beam at full intensity were analysed using Raman spectroscopy. This showed complete evaporation of the molecular layer directly under the beam. However, there was no evidence

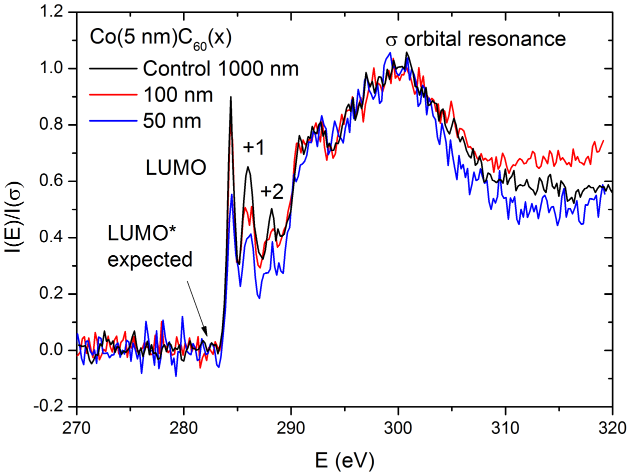

FIG. 3. K-edge spectra obtained for three of the measured samples. These show the spectra whcih emerge from a control sample comprising 1 μm of $C-60$ with no magnetic interface, a 100 nm layer of c_{60} on a cobalt thin film and a 50 nm thick layer on a cobalt thin film. In each case, the LUMO appears as a strong resonance followed by two higher order π orbitals. The broad feature above 290 eV is associated with σ bonds. The spectra are normalised to the σ peak as this should not change as part of π hybridisation with the substrate.

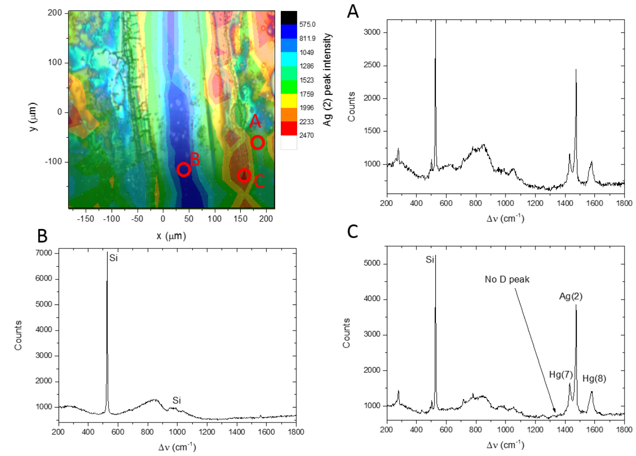

FIG. 4. Image of a region of the control film exposed to full beam intensity at 6.5 keV. The colour map shows the intensity of the Raman spectrum at 1420 cm^{-1} i.e the Ag(2) vibrational mode. At point B, Raman spectrum indicates total evporation. Point C scans a dark patch on the surface. This dark patch comprises C_{60} with no evidence of graphite. Point A is an unaffected region. None of the spectra showed evidence of graphitic remnants which would give the broad, characterisitc G and D peaks at 1300 and 1600 cm^{-1}.

on any part of the sample of C_{60} beign converted to graphite or amorphous carbon due to the lack of observable G and D peaks. This indicates that, while local heating of the substrate can evaporate molecular films, high energy x-rays do not cause breakdown of fullerene cages, fig 4.

OUTCOMES AND FUTURE WORK

This experiment established a new range of sensitivity for the ID20 instrument, demonstrating its efficacy in measuring carbon thin films down to 0.05 μm. Furthermore, the resilience of C_{60} to X-Rays at 6.5 keV has been demonstrated. However, this experiment was not able to establish the length scale over which a metallic interface has significant effects on the electronic sturcture of the C_{60} since the hybrid peak at 284 eV was not observed in any of the measured samplesl. This does establish an upper limit for these interactions, showing that the majority of molecules in a 50 nm thin film are non-interacting with the metal substrate.

Multilayer structures could be prepared which would also show hybrid interface effects. In sputtered films, this is undersireabel due to interdiffusion at the interface. However, there is the possibility of using a joint K-cell, e-beam evaporation chamber to deposit multilayer samples with lower interlayer variation. We plan to develop multilayer samples comprising 10s or even 100s of repeats such that the total thickness is many times greater than the bilayers used in this experiment. Since the data collected using ID20 has established the upper limit for detection of hybrid interface states, we expect multilayer films to show emerging hybrid states below 50nm in multlayer films.

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