



Experiment title: *Do Atoms Encapsulated in Fullerene Cages 'Feel' The Effects of Adsorption?: An XSW Investigation of Ce@C₈₂ on Si Surfaces*

Experiment number:

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Report is on following pages.

ABSTRACT

The key objective of our recent (July 15th – 22nd) experiment on ID32 was to determine whether an atom encaged in a fullerene molecule (in this case, Ce in Ce@C₈₂) modified its intramolecular position as a result of adsorption on a solid surface. Ce 3d photoemission and Ce MNN X-ray standing wave (XSW) spectra were acquired for bulk films and monolayers of Ce@C₈₂ on Ag(111), both at room temperature and at a temperature of 100 K. (At the latter temperature the intramolecular motion of the Ce atom is effectively quenched). Although data analysis is still ongoing, the measured Ce coherent fraction at room temperature and at 100 K is close to zero. Furthermore, the XSW profiles for a Ce@C₈₂ monolayer at room temperature and 100 K are almost identical, strongly suggesting that static disorder - rather than intramolecular motion or vibrational dynamics – gives rise to the very low coherence in the standing wave profiles.

EXPERIMENT

Ce@C₈₂ molecules were deposited using an evaporation source mounted on a liner transfer arm which could be isolated from the ID32 end station by means of a gate valve. We find - in common with other groups [1] – that the flux of endofullerene molecules from the deposition source is both rather low and critically dependent on the history of the source (the flux falls off dramatically as a function of deposition time). Hence, to ensure that a sufficiently high coverage of endofullerene material is initially deposited, the evaporation source is moved to within a centimetre of the sample surface and a multilayer (bulk-like) film deposited. This thick film is subsequently annealed at 300°C to produce a monolayer. Fig. 1 shows scanning tunnelling microscope (STM) images (acquired in Nottingham) of a very low coverage and (inset) ~ 0.5 ML of Ce@C₈₂ on the Ag:Si(111)-(√3 x √3)R30° surface [2].

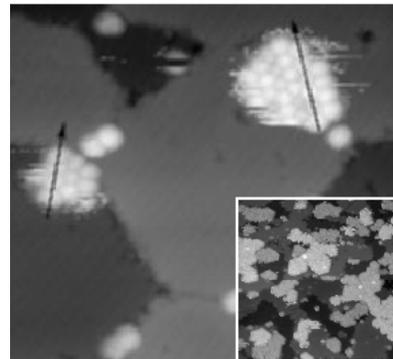


Fig. 1 STM images of Ce@C₈₂ on the Ag:Si(111)-(√3 x √3)R30° surface. Individual molecules within small ordered islands are clearly visible in the main image whereas the inset shows the morphology of a sample with a coverage of ~ 0.3 ML.[2]

Although our original proposal suggested that Si(111) would be used as a substrate, it proved to be far from straight-forward to provide the facility on ID32 to anneal to 1500 K (as required for Si(111) sample flashing) and ensure that a temperature of 100 K was achievable at the sample surface. While there are *ex situ* wet chemical methods that may be used to allow low temperature (~ 800 K) processing of Si samples, in our experience the quality (in terms of carbon contamination) of Si(111) surfaces prepared in this way is much poorer than those flashed at elevated temperatures. Hence, following discussion with the local contact, it was decided to use Ag(111) as a substrate, alleviating many experimental difficulties.

The Ag(111) crystal [3] was prepared via conventional sputter-anneal cycles. A sharp (1x1) pattern with low diffuse background was observed from the clean crystal, with no evidence of oxygen or carbon-related photoemission or Auger peaks observed in overview photoemission scans. Ce 3d photoemission and MNN Auger spectra were acquired in constant initial state and constant final state modes respectively using a hemispherical electron analyser (Physical Electronics) positioned at an angle of 45° to the incoming X-rays. The X-ray energy corresponding to back-reflection from the (111) lattice planes of the Ag(111) crystal is ~ 2633 eV (at room temperature).

RESULTS AND DISCUSSION

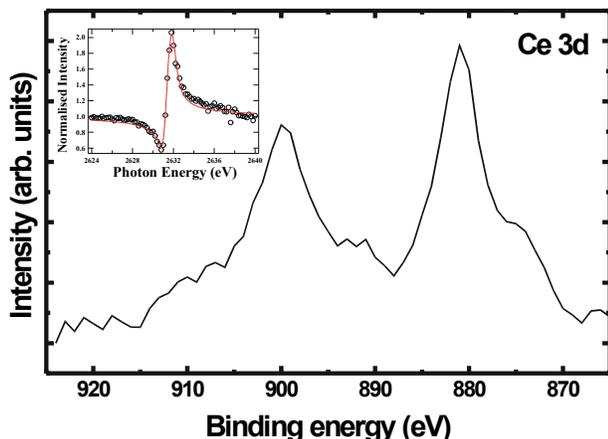


Fig. 2 Ce 3d photoemission spectrum ($h\nu = 2650$ eV) from a Ce@C₈₂ monolayer on Ag(111). The inset is the NIXSW Ag 3d profile from the clean Ag(111) sample.

Fig. 2 shows a Ce 3d photoemission spectrum measured from a Ce@C₈₂ monolayer on Ag(111). The inset is an Ag 3d NIXSW profile for the (111) reflection from the Ag(111) crystal. Note that it is clear that non-dipole effects contribute strongly to both our Ag- and Ce-related photoemission XSW spectra and we are currently carrying out a detailed analysis of these effects for the latter spectra (which is facilitated by the Ce MNN Auger NIXSW data we have acquired).

Ce 3d XSW profiles from bulk films and monolayers of Ce@C₈₂ measured at room temperature and at 100 K are associated with very low values of coherent fraction, F_C (indeed, F_C is effectively zero for all spectra) (see Fig. 3). Ce MNN XSW spectra (not shown) - although having a lower peak height due to the absence of the non-dipole effects that contribute to the photoemission-derived XSW profiles - also exhibit an incoherent lineshape. (Note that for a distribution of atoms associated with a coherent fraction of 0, the yield, Y_P , reduces to $1 + R$ (where R is the reflectivity of the Bragg peak) *in the dipole approximation*. Hence the XSW spectrum is simply a reflectivity curve offset by a value of 1 from the X-axis [4]).

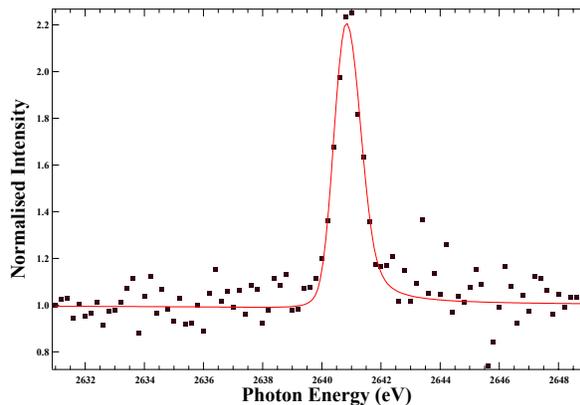


Fig. 3 Ce 3d XSW spectrum for a Ce@C₈₂ monolayer on Ag(111), measured at 100K. The coherent fraction is very close to zero.

The absence of any appreciable difference in the XSW profile for a Ce@C₈₂ monolayer measured at room temperature compared to that acquired at 100 K strongly suggests that static disorder in the atomic positions underlies the absence of coherence in the spectra. In addition, we did not observe the dramatic changes in XSW peak height for bulk and monolayer endofullerene films that have been very recently reported for La@C₈₂ on Cu(111) [5].

CONCLUSIONS

In conclusion, our XSW study of Ce@C₈₂ on Ag(111) clearly shows that adsorption does not strongly affect the distribution of atomic positions inside the endofullerene cage. We find no evidence for occupation of a specific intramolecular Ce bonding site resulting from the endofullerene-surface interaction. The absence of a strong cage-mediated Ce-surface interaction is perhaps not so surprising on the basis of our recent resonant photoemission (RESPES) and X-ray absorption spectra from covalently bound Ce@C₈₂ monolayers on Si(111) [6]. The RESPES and NEXAFS spectra for the Ce@C₈₂:Si(111) system clearly show that there are negligible changes in overall Ce valence induced via the strong covalent interaction (despite the clear hybridisation of fullerene cage orbitals and Ce electronic states visible in the RESPES spectra).

ACKNOWLEDGEMENTS

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REFERENCES

1. P. Rudolf; MRC Hunt, private communication
2. Li Wang, KHG Schulte, PH Beton, P. Moriarty, M. Kanai, and TJS Dennis, in preparation
3. We thank Dr. VR Dhanak of Daresbury Laboratory for lending us the Ag(111) single crystal.
4. See, for example, F. Schreiber et al., Surf. Sci. **486** L519 (2001) and references therein
5. C. Ton-That et al., Phys. Rev. B **68** 04524 (2003)
6. KHG Schulte, Li Wang, MA Phillips, P. Moriarty, M Kanai, TJS Dennis, S. Patel, and VR Dhanak, in preparation