

Does an Encapsulated Atom 'feel' the Effects of Adsorption?: X-ray Standing Wave Spectroscopy of Ce@C₈₂ on Ag(111)

Richard A. J. Woolley,^{*,†} Karina H. G. Schulte,[†] Li Wang,[†] Philip J. Moriarty,[†]
Bruce C. C. Cowie,[‡] Hisanori Shinohara,[§] Mito Kanai,^{||} and T. John S. Dennis^{||}

*School of Physics and Astronomy, The University of Nottingham,
Nottingham, England, NG7 2RD, ESRF, B.P. 220, F-38043 Grenoble Cedex, France,
Department of Chemistry, Nagoya University, Nagoya 4640-2804, Japan, and
Department of Chemistry, Queen Mary, University of London, England, E1 4NS*

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ABSTRACT

A comparison of normal incidence X-ray standing wave (NIXSW) spectra from bulk films and monolayers of Ce@C₈₂ on Ag(111) clearly shows that the Ce atom does not adopt a preferred intramolecular bonding site as a result of adsorption. NIXSW profiles measured at room temperature and 100 K are each associated with a coherent fraction of zero, indicating a high level of static (rather than vibrational) disorder in the intramolecular Ce positions.

Endohedral fullerenes, or *incar*-fullerenes,¹ where one or more atoms are encapsulated in a fullerene cage, represent an exotic and fascinating state of condensed matter.² The size of the fullerene cage and the nature of the atom (or atoms) contained within it both determine the molecule's physical properties. To some extent the band gap can be tuned and the electronic properties of the molecule tailored by careful selection of the encapsulated element. Fullerene adsorption on many metal surfaces results in ionic bond formation,³ suggesting that a monolayer film of endohedral fullerenes will have different properties than those of the bulk. Understanding surface–fullerene interactions and the degree of isolation the cage provides is of vital importance if the potential of endohedral fullerenes for use in molecular electronics and other exotic nanoscale devices, such as qubits,⁴ are to be realized. However, although a considerable number of groups have focused on the bulk properties^{2,5,6} of endohedral fullerenes, there has been relatively little work on the interaction of these molecules with solid surfaces. Of this surface-related work the vast majority has involved scanning tunneling microscopy (STM) measurements,⁷ and while STM is a powerful tool to determine molecular adsorption sites, it provides little information on bond character

or electronic structure. Furthermore, and of key importance for the study of endohedral fullerenes, STM yields very limited (if any) information on the atom within the cage.

To date there has been just one study, performed by Ton-That et al.,⁸ to locate the encapsulated atom within an *adsorbed* endohedral fullerene. This group observed differences in the intensity of the XSW profiles for multilayer and monolayer films which were interpreted as arising from increased order in the La positions. Furthermore, following cooling of the film (to quench vibrational dynamics), the encapsulated lanthanum was proposed to adopt a preferred intramolecular bonding site due to charge transfer between the molecule and the underlying Cu(111) surface. Here we discuss the effect on the intramolecular position when Ce@C₈₂, which is similar to La@C₈₂ in that both encapsulated atoms have a charge state close to +3,⁶ is adsorbed on Ag(111).

An effective structural probe for the endohedral fullerene family of molecules is X-ray standing wave (XSW) spectroscopy,⁹ or where the substrate has a large mosaicity such as a crystalline metal, normal incidence XSW (NIXSW).^{10,11} This technique is a particularly powerful probe of buried interfaces and has significant potential in the study of atomic positions *within* the fullerene cage. At the Bragg condition, for normal incidence the superposition of illuminating and backscattered X-rays produce a standing wave field which has a periodicity in intensity equal to that of the scattering

* Corresponding author. E-mail: richard.woolley@physics.org.

† University of Nottingham.

‡ European Synchrotron Radiation Facility (ESRF).

§ Nagoya University.

|| University of London.

planes. Varying the incident photon energy within the reflectivity range moves the standing wave nodal and antinodal planes with respect to the crystal lattice such that an atom “bathed” in the wave field will emit photoelectrons, Auger electrons, and/or X-ray photons with a predictable intensity,

$$Y_p = 1 + R + 2\sqrt{R}f_{co}\cos(\phi - 2\pi D)$$

where $R = |E_H/E_0|e^{i\phi}$ is the reflectivity and E_0 and E_H are the incident and Bragg reflected electric fields which produce the standing wave of phase ϕ . The terms which yield structural information are D , the coherent position (that is the distance of the absorber site as a fraction of lattice spacing from the diffracting planes), and f_{co} , the coherent fraction, i.e., the degree of order associated with site occupation. For a completely disordered system, such as a bulk incoherent film or a random arrangement of adsorbates, $f_{co} = 0$ and the resultant profile has the shape of a reflectivity curve where the value of D is meaningless.¹²

Fisher et al. have recently shown that considerable care must be taken in the interpretation of XSW data based on photoelectron yield measurements as nondipole effects can have considerable influence on the profile shape.¹³ An asymmetry parameter Q is introduced to account for the difference in photoemission intensity from incident and reflected X-rays:

$$Y_p = 1 + R(Q + 1)/(Q - 1) + 2\sqrt{R}[(Q + 1)/(Q - 1)]^{1/2}f_{co}\cos(\phi - 2\pi D)$$

A general formalism developed by Vartanyants and Zegenhagen¹⁴ includes multipole effects related to matrix elements that describe the scattering process, such as the photoionization energy, initial bound electron state, and the experimental geometry (however, currently only a description for the s state is available). Additionally, Lee et al.¹⁵ have shown that interference terms from the more rigorous treatment in Ref. 14 have little effect on the structural parameters D and f_{co} . Here we will treat the data in terms of Q and accept the systematic errors presented by the higher order interference, as they are expected to be negligible.

The spectroscopy experiments were performed at beamline ID32 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using a standard ultrahigh vacuum (UHV) surface science chamber. The substrate, a single crystal of Ag(111), was cleaned in UHV using standard argon ion sputter and annealing cycles. A sharp low energy electron diffraction (LEED) (1×1) pattern with low diffuse background was observed from the clean crystal, accompanied by no evidence of contamination in overview X-ray photoelectron spectroscopy (XPS) scans. Ce@C₈₂ molecules (the production of which is discussed elsewhere¹⁶) in a solution of CS₂ were transferred to a tantalum crucible, which was then thoroughly degassed at 100 °C under UHV for 24 h. Due to the very low deposition rate of endohedral fullerene molecules, the Knudsen cell containing them was held 1 cm

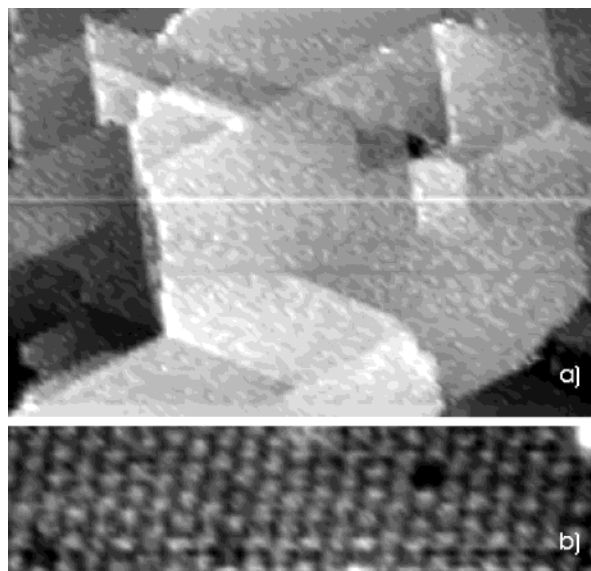


Figure 1. STM images of the bulklike Ce@C₈₂ film. The surface has a large-island morphology (a), consisting of close packed molecules (b). Image areas are 147 × 100 nm² and 21 × 5.5 nm², respectively.

away from the crystal surface using a custom built evaporator, until, after 30 min at an operating temperature of 580 °C, a multilayer (bulklike) film was grown. Gradually annealing this bulk film, while monitoring the ratio of substrate to Ce photoemission peaks, revealed that the multilayer desorbed at 300 °C, in accordance with previous experience of Ce@C₈₂ multilayer desorption on Ag:Si(111)–($\sqrt{3} \times \sqrt{3}$)R30°. Throughout the annealing process the Ce 3d to C 1s photoelectron intensity ratios remained constant at 0.7±0.05 ($h\nu = 2610$ eV). Photoemission spectra were recorded using a hemispherical electron analyzer (Physical Electronics) positioned at 45° to the incoming X-rays. NIXSW profiles were measured by recording the change in peak area for photoemission and Auger spectra, acquired in constant initial state and constant final state mode, respectively, while stepping through photon energy. In all recorded XSW spectra the reflectivity curve of the sample was used as a measure of instrumental broadening and the position of the Bragg peak.

Separate STM experiments were performed in the home laboratory (Nottingham) using a custom UHV system operating at room temperature. Bulk films of Ce@C₈₂ were grown in a fashion similar to the sample used for photoemission (however, a Ag:Si(111)–($\sqrt{3} \times \sqrt{3}$)R30° sample was used as the substrate). Figure 1 clearly shows that the bulk film consists of well-ordered close packed islands of endohedrals, and a detailed analysis of the STM data is underway.¹⁸

Prior to measuring the Ce-derived XSW spectra, a C 1s photoemission XSW profile derived from the C₈₂ cage was acquired. The cage diameter (~ 11.3 Å) is ~ 5 times the lattice spacing of the Ag(111) planes (2.36 Å), which produces an incoherent C 1s XSW profile bearing a very close resemblance to the reflectivity curve line shape, Figure 2. From the geometry of the C atoms in the endohedral fullerene, this absence of coherence is not unexpected. The key issue

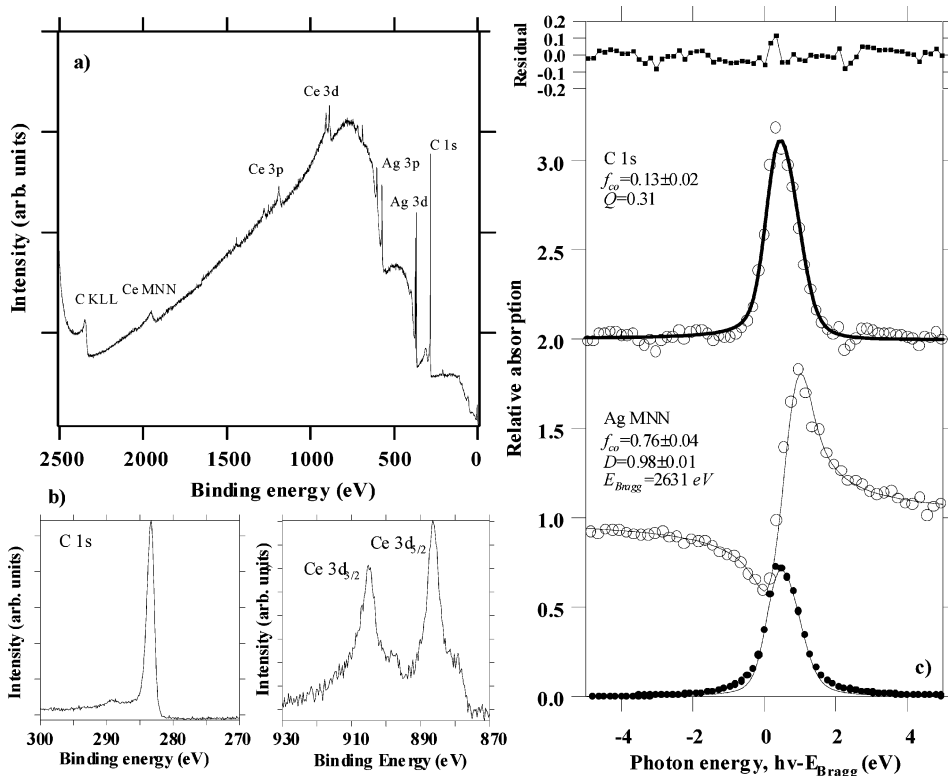


Figure 2. (a) Survey XPS spectrum from the bulklike Ce@C₈₂ film on Ag(111), (b) the C 1s and Ce 3d XPS spectra from a monolayer film used for NIXSW analysis. (c) NIXSW <111> profile from the Ag(111) substrate and corresponding reflectivity curve, which is similar in shape to the C 1s NIXSW <111> profile derived from the fullerene cage (displaced by 1 for clarity, its fitting residual is shown above).

motivating our XSW study of Ce@C₈₂ is, however, to ascertain whether adsorption on a metal substrate promoted an ordering of the *encapsulated* atom.

Ce 3d and MNN Auger XSW profiles for a bulk film and a monolayer (at 293 and at 100 K) are all very similar in shape (resembling a reflectivity curve) where the coherent fraction for each profile was effectively zero, Figure 3. The absence of any appreciable difference in the XSW profile for a Ce@C₈₂ monolayer measured at 293 K compared to that measured at 100 K suggests that static disorder associated with the distribution of the Ce intramolecular positions underlies the lack of any coherence in the XSW signal. In addition, there were no dramatic changes in peak height between bulk and monolayer films as reported very recently for La@C₈₂ on Cu(111),⁸ and interpreted in terms of an increase in coherent fraction. This may be due to differences in the monolayer preparation procedure; in our case the endohedral fullerenes were deposited onto a Ag(111) crystal held at room temperature and subsequently annealed, whereas in ref 8 the sample was held at 280 °C during the evaporation. Isomeric variations in the Ce@C₈₂ film may also be responsible. Shibata et al.¹⁹ have recently found that Ce@C₈₂ exists as a mixture of two isomers in a ratio of 4:1, and this mixture could possibly account for the absence of coherence if the cerium has a preferential bonding site that is dependent on the cage's symmetry.

In conclusion, our study of Ce@C₈₂ adsorbed on Ag(111) clearly shows that the presence of the surface does not strongly affect the distribution of intramolecular Ce bonding

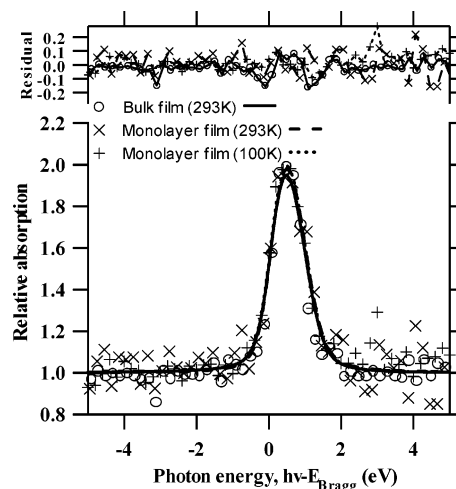


Figure 3. Ce 3d photoemission derived <111> NIXSW profiles from bulklike film and monolayer at 293 and 100 K. The corresponding coherent fractions for the monolayer are 0.04 ± 0.06 and 0.05 ± 0.06 , the associated error is twice the standard deviation from best fit to dynamical theory (lines). A $Q = 0.15$ was ascertained from the bulk profile assuming complete incoherence, $f_{co} = 0$.

positions. We find no evidence for occupation of a specific intramolecular Ce bonding site resulting from the endohedral fullerene–surface interaction. The absence of any increase in the coherent fraction on cooling to 100 K indicates that the disordering is not due to vibrational dynamics. This absence of a strong cage-mediated Ce-surface interaction is perhaps not so surprising on the basis of our recent

photoemission and X-ray absorption spectra from covalently bound Ce@C₈₂ monolayers on Si(111),¹⁷ which indicate that the Ce atom is remarkably well shielded from the outside chemical environment by the fullerene cage.

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