

Electrospray deposition of fullerenes in ultra-high vacuum: *in situ* scanning tunneling microscopy and photoemission spectroscopy

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Abstract

Electrospray deposition of fullerenes on gold has been successfully observed by *in situ* room temperature scanning tunneling microscopy and photoemission spectroscopy. Step-edge decoration and hexagonal close-packed islands with a periodicity of 1 nm are observed at low and multilayer coverages respectively, in agreement with thermal evaporation studies. Photoemission spectroscopy shows that fullerenes are being deposited in high purity and are coupling to the gold surface as for thermal evaporation. These results open a new route for the deposition of thermally labile molecules under ultra-high vacuum conditions for a range of high resolution surface science techniques.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electrospray ionization provides a highly promising route for the deposition of non-volatile molecules onto surfaces in ultra-high vacuum (UHV). The technique, widely used in mass spectroscopy to introduce large and fragile biomolecules into the gas phase [1], has been successfully applied to the ambient deposition of materials with a wide range of uses, from batteries to biotechnological thin films [2]. The technique has also been applied in vacuum for the deposition of polymers and biomolecules [3, 4]. More recently, we demonstrated that the electrospray event could be performed in a high vacuum environment [5] for the deposition of carbon nanotubes from a liquid suspension, with investigation by *ex situ* atomic force microscopy [6].

Deposition of carbon structures such as nanotubes and fullerenes by electrospray presents a promising pathway

to the *in vacuo* deposition of interesting thermally labile molecules. Preparation of arrays of such molecules in UHV opens up the possibility of using a large range of techniques for the characterization of these systems such as high resolution photoemission spectroscopy (PES) and scanning tunneling microscopy (STM). Moreover, the potential for surface contamination during preparation is greatly reduced in comparison to ambient deposition methods.

The formation of molecular ions by electrospray involves drawing a solution through a highly charged narrow capillary. The resulting electric field is sufficient to overcome the surface tension of the liquid and create a Taylor cone shape at the tip of the capillary [7], whereupon a cone-jet of highly charged liquid particles is formed [8]. These particles then undergo a cascade of Coulomb fission [9] and desolvation events, producing progressively smaller droplets and, in some cases, individual ions. The ions or nanoscale droplets can then be transported through a differentially pumped vacuum system to impinge on a surface held in UHV.

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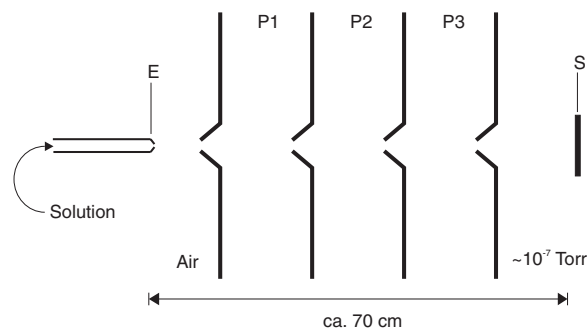


Figure 1. Schematic illustration of the electro spray system. The emitter tip (E) is at ambient pressure. The spray passes through a three-stage differentially pumped system (P1 and P2 are pumped by scroll pumps, P3 is pumped by a turbomolecular pump) and into a vacuum chamber to impinge on the sample surface (S) in the low 10^{-7} Torr range during operation. See text for more information.

Here we present a room temperature UHV STM and PES study of fullerenes deposited onto an Au(111) surface using *in situ* electro spray deposition. We confirm by STM that C_{60} may be deposited onto the surface and resolved with molecular resolution, decorating the step edges at low coverages. Upon deposition of multilayers, hexagonal close-packed islands of C_{60} are observed with a periodicity of 1 nm. These results are consistent with previous work where deposition was carried out by thermal evaporation [10]. C 1s PES shows no evidence of co-adsorption of solvent molecules and that the peak line-shape changes are consistent with deposition of layers of C_{60} on the surface [11]. Autoionization measurements and observation of C 1s shake-up features show that the deposited C_{60} is coupled to the surface in the monolayer as for thermally deposited films.

2. Experimental details

The design of the electro spray apparatus is shown schematically in figure 1. In these experiments dilute solutions (typically $<1 \text{ mg ml}^{-1}$) of C_{60} (99.5% purity) in a matrix of toluene:acetonitrile (4:1 by volume) were prepared by ultrasonication. The solution was passed to a stainless steel emitter (E, $100 \mu\text{m}$ tip internal diameter, New Objective) held at a voltage of between 1.5 and 2.0 kV, where the electro spray is created at ambient pressure. The spray enters the system through a skimmer cone and passes through a further three differentially pumped skimmers (0.5 mm diameter) before entering the UHV preparation chamber (base pressure 5×10^{-11} Torr both in Nottingham and at the SRS). With the gate valve open to the electro spray system in the absence of spray, the pressure in the preparation chamber is in the mid 10^{-9} Torr range, which gives a direct indication of the level of contamination due to air entering the first aperture. During electro spray operation the pressure rises to the low 10^{-7} Torr range, the additional pressure being due solely to the solvent molecules of toluene and acetonitrile (this was confirmed by quadrupole residual gas analysis in Nottingham). The total distance from the tip to the sample (E–S) is approximately 70 cm. The sample was aligned by shining a laboratory light source through the final two apertures of the electro spray system.

An $8 \text{ mm} \times 4 \text{ mm}$ gold on mica sample (1500 \AA thickness, Agilent) was used as a substrate for the STM studies. Prior

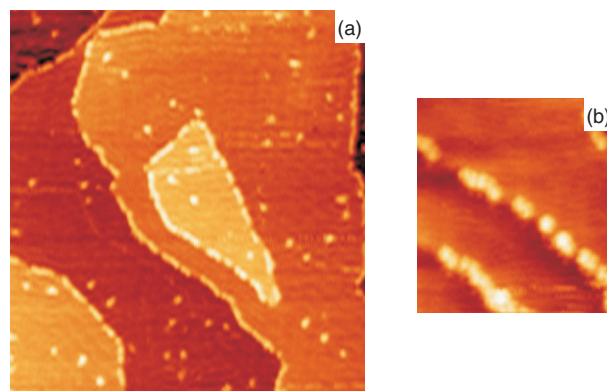


Figure 2. (a) STM image ($107.8 \text{ nm} \times 117.6 \text{ nm}$, -0.70 V , 0.03 nA) of C_{60} decorating step edges of a Au(111) surface following electro spray deposition; (b) high resolution image ($22 \text{ nm} \times 24 \text{ nm}$, -0.70 V , 0.03 nA) showing step-edge decorative features.

to deposition, the sample was prepared by repeated cycles of sputtering (Ar^+) and annealing ($\sim 600^\circ\text{C}$) until a clear herringbone reconstruction pattern could be observed on the Au(111) surface by STM [12]. STM measurements were conducted in an adjoining chamber with a base pressure of 5×10^{-11} Torr. The STM was operated in constant current mode at room temperature using a chemically etched tungsten (W) tip that was cleaned in UHV by electron bombardment prior to use. The WSxM package was used to process the STM images [13].

PES studies were carried out at the UK Synchrotron Radiation Source (SRS), Daresbury, on beamline 5U.1 using a concentric hemisphere electron energy analyzer (VG-CLAM). A $10 \text{ mm} \times 10 \text{ mm}$ gold single crystal was used as the substrate for these measurements. The sample surface was cleaned by Ar^+ sputter and anneal cycles, as in the STM experiments. Cleanliness was verified by observing no detectable C 1s signal ($h\nu = 390 \text{ eV}$) and only gold features in the survey spectra. Total yield near edge x-ray adsorption fine structure (NEXAFS) was taken by use of the sample drain current.

3. Results

3.1. Scanning tunneling microscopy

Initially the sample was aligned several millimeters below the direct line of sight of the electro spray. The sample was then exposed to 1 h of electro spray deposition of C_{60} solution. The resulting STM images (figure 2) show decoration of the step edges, indicative of a low coverage of C_{60} at the surface [10], suggesting that the C_{60} molecules are mobile on the surface after spraying. A blank solution (containing no C_{60}) was sprayed for the same duration with the sample in the same position. The resulting images showed no step-edge features (figure 3), confirming that the features in figure 2 are due to adsorbed C_{60} molecules and not to a residual solvent effect. However, in the cases of both the C_{60} and blank solutions some disruption in the herringbone reconstruction is observed in the images. It is speculated that this disruption is caused by the transfer of energy to the surface by the impinging molecules.

A realignment of the sample caused significant changes in the total coverage of C_{60} . The clean sample was adjusted to be

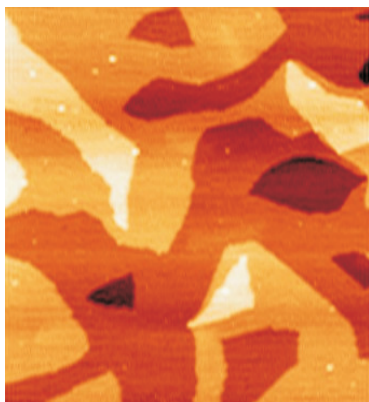


Figure 3. STM image (220 nm \times 240 nm, -1.80 V, 0.03 nA) of a Au(111) surface after 1 h electro spray of toluene/acetonitrile mixture.

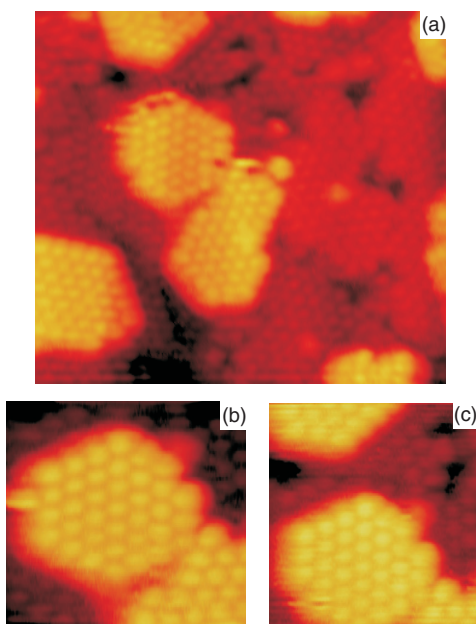


Figure 4. (a) STM image (26.4 nm \times 24 nm, +2.00 V, 0.03 nA) of C_{60} multilayers deposited by electro spray; (b) high resolution image of central region of (a) (9.7 nm \times 9.2 nm, +2.00 V, 0.03 nA) showing hexagonal close-packed islands of C_{60} ; (c) image (9.7 nm \times 10.6 nm, +2.00 V, 0.03 nA) as (b).

directly in line of sight with the electro spray and was exposed to 30 min spray of the same C_{60} solution. The resulting STM images (figure 4) clearly show at least two layers of hexagonal close-packed structures with an average periodicity of 1 nm. The periodicity of 1 nm (an average of the periodicity of rows of features from figures 4(b) and (c)) agrees with previous studies of close-packed islands of C_{60} [10]. The creation of ordered islands on the surface also indicates that the molecules have a similar mobility upon electro spray deposition as after thermal sublimation.

3.2. Photoemission spectroscopy

Figure 5 shows the C 1s core level spectra for monolayer (ML) and multilayer (~ 3.5 ML) coverages taken at $h\nu = 390$ eV to

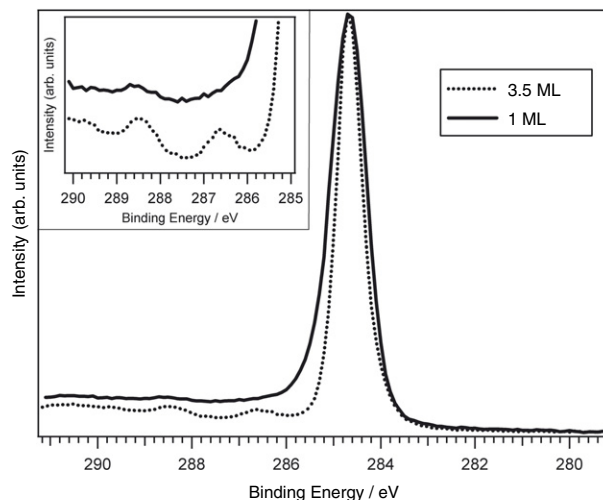


Figure 5. C 1s core level spectra for an electro sprayed monolayer and multilayer (3.5 ML) films ($h\nu = 390$ eV). Spectra have been normalized to the top of the peak and shifted on the binding energy scale for ease of comparison. The inset shows the shake-up features on the high binding energy side of the C 1s peak.

avoid a large gold Auger feature and to place the C 1s peak on a small background. Surface coverages were estimated by using the ratio of the C 1s to Au $4f_{7/2}$ peaks and referencing them to a monolayer prepared by annealing a multilayer deposition at ~ 670 K until the ratio of peaks remained constant and the C 1s line-shape remained the same. A single peak is observed in figure 5 for the monolayer, attributed to C_{60} . No evidence for co-deposition of solvent is observed in the C 1s region, where a higher binding energy feature would be expected for the $-CN$ group of acetonitrile. This was also supported by the lack of features in the N 1s region of the spectrum (not shown), which rules out acetonitrile (CH_3CN) adsorption. The line-shape and shake-up features of the C 1s peak also closely matched core-level spectra from thermally deposited C_{60} [11], suggesting that any co-deposition of toluene was below detectable limits. The C 1s line-shape changes from an asymmetric shape in the monolayer to a more Gaussian-like profile for multilayers. The shake-up features on the higher binding energy side of the C 1s peak are very weak in the monolayer spectrum, but become more pronounced in the multilayer spectrum.

Resonant photoemission spectra (RPES) was also performed to monitor the highest occupied molecular orbital (HOMO) participator in the prepared surfaces. RPES (also commonly known as autoionization) provides information about the decay of core-excited states (the final state in NEX-AFS) [14]. The participator pathway is detailed in figure 6, where a core-hole excited state decays by the initially excited electron (specifically from the lowest unoccupied molecular orbital (LUMO) in these experiments) fills the core-hole which excites an electron from the HOMO to the vacuum level. If the adsorbate is electronically coupled to the substrate then charge transfer can occur from unoccupied molecular levels lying above conduction band edge [15–17]. This charge transfer depopulates the unoccupied adsorbate levels, reducing the participator intensity compared to a decoupled system [18].

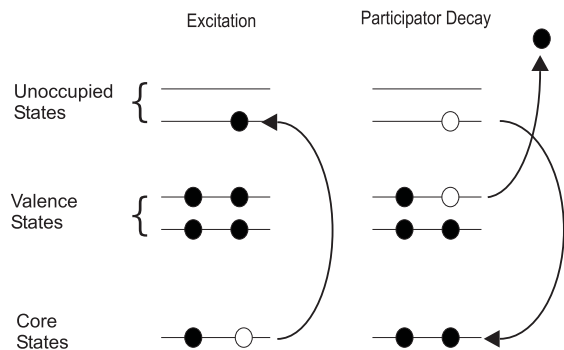


Figure 6. Schematic of the participator decay process.

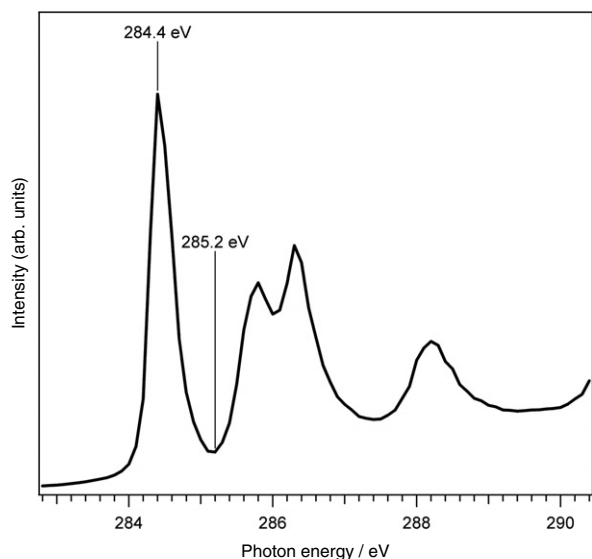


Figure 7. C 1s edge NEXAFS spectrum of multilayers (3.5 ML) of C_{60} electro spray deposited on Au(111). The photon energies of on-resonance (284.4 eV) and off-resonance (285.2 eV) photoemission spectra are indicated around the LUMO.

Figure 7 shows a NEXAFS spectrum, showing the π^* region, taken from the multilayer preparation, which shows π^* features matching those previously reported for thick films of C_{60} on gold [11]. Two valence band spectra were taken at $h\nu = 284.4$ eV (on LUMO resonance) and at $h\nu = 285.2$ eV (off resonance) for all preparations. These spectra were then normalized to the C 1s second-order photoemission peak (to ensure that photoemission intensity was normalized, not shown). The off-resonance ($h\nu = 285.2$ eV) spectrum for each preparation was subtracted from the on-resonance ($h\nu = 285.2$ eV) spectrum from the same preparation to yield the RPES spectra in figure 8. Whilst this method does not provide an absolute measure of the participator intensity (as a small amount of participator intensity is present in the off-resonance spectrum) it provides a consistent and expedient estimate, as no fitting of the C 1s second-order feature is required. This estimate is adequate for the purpose of these experiments. The RPES spectra show a decrease in participator intensity for both the electro sprayed and annealed monolayers compared to the multilayer preparation, with the latter having a greater reduction in intensity.

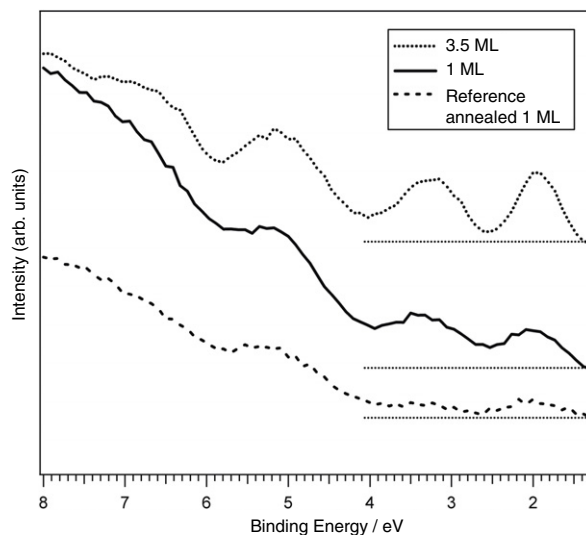


Figure 8. RPES spectra for electro spray deposited films of C_{60} on Au(111) and a reference annealed monolayer taken at an excitation energy of 284.4 eV. The spectra are shifted on the binding energy scale so that the HOMO participator lies at 2.0 eV for ease of comparison. See text for more information.

4. Discussion

The STM images clearly show the appearance of features that can be attributed to individual C_{60} molecules on the surface of the gold substrate. There is some disruption of the Au(111) herringbone reconstruction visible at low coverages. It is speculated that this disruption could arise from energetic collisions of charged C_{60} and solvent molecules; however, this disruption appears not to result in the embedding of adsorbates or the creation of pits in the surface. At high coverages, the formation of hexagonal islands of C_{60} indicates that the molecules have a similar mobility, after electro spray deposition, as thermally deposited C_{60} .

Turning to the PES, there is a clear line-shape change between in the monolayer and multilayer coverages, in good agreement with the previously reported change from a Doniac–Sunjic shape in a monolayer to a more Gaussian shape in a thick film of C_{60} thermally evaporated onto a Au(110) surface [11]. This result, along with the fact that no other observed features in the C 1s or N 1s core level spectra can be attributed to the co-deposition of solvent molecules, indicates that C_{60} is being deposited intact and with an undetectable level of solvent contamination. The C 1s shake-up features (figure 5, inset) are only weakly observed in the monolayer as compared to the multilayer preparation. This broadening of the shake-up features can be understood as the hybridization of occupied and unoccupied molecular states and the substrate conduction band [19], providing strong evidence for the chemisorption of the electro sprayed monolayer.

The RPES spectra also support the conclusion that the monolayer is chemisorbed to the surface in a similar way to films prepared by thermal evaporation, by showing a reduction in HOMO participator intensity over the LUMO resonance attributed to charge-transfer to the electronically coupled substrate. The slight increase in participator intensity

compared to the reference annealed monolayer can be attributed to the fact that the latter has been subjected to a prolonged period of heating, resulting in a more ordered monolayer, whereas the electro sprayed monolayer is likely to have more disorder resulting in the presence of a small amount of uncoupled C₆₀ trapped above the layer in direct contact with the surface.

The above results demonstrate the great potential for the use of electro spray deposition in the growth of thin films of carbon nanostructures on surfaces under UHV conditions and, moreover, as a general technique for depositing non-volatile molecules in vacuum. The microscopic and spectroscopic measurements are in strong agreement with previous studies and suggest that deposition by electro spray forms very similar thin films as other UHV deposition methods.

It is also interesting to note that since the additional pressure above the steady-state leakage pressure of $\sim 5 \times 10^{-9}$ Torr is due to the spray itself, the deposition pressure can be reduced by decreasing the flow into the system. This results in a corresponding reduction in the flux of molecules and is therefore more suited for the studies of individual molecules and sub-monolayer coverages.

5. Conclusion

In situ deposition of fullerenes by electro spray has been successfully performed at pressures in the low 10^{-7} Torr range and provides a route to the controlled deposition of endohedral fullerenes and similar thermally labile nanostructures. STM and PES of our C₆₀/Au(111) surfaces show similar features to those observed after thermal evaporation and formation of ordered islands, and this suggests that the molecules are similarly mobile following electro spray deposition and chemisorbed to the surface in a similar fashion. These initial investigations show that electro spray deposition is a valid alternative to thermal evaporation to achieve a range of coverages of fullerene molecules in vacuum, from sub-monolayer to multilayer films.

Acknowledgments

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References

- [1] Fenn J B, Mann M, Meng C K, Wong S F and Whitehouse C M 1989 Electro spray ionization for mass-spectrometry of large biomolecules *Science* **246** 64–71
- [2] Jaworek A 2007 Electro spray droplet sources for thin film deposition *J. Mater. Sci.* **42** 266–97
- [3] Rauschenbach S, Stadler F L, Lunedei E, Malinowski N, Koltsov S, Costantini G and Kern K 2006 Electro spray ion beam deposition of clusters and biomolecules *Small* **2** 540–7
- [4] Lyon J E, Cascio A J, Beerbom M M, Schlaf R, Zhu Y and Jenekhe S A 2006 Photoemission study of the poly(3-hexylthiophene)/Au interface *Appl. Phys. Lett.* **88** (22)
- [5] Swarbrick J C, Taylor J B and O'Shea J N 2006 Electro spray deposition in vacuum *Appl. Surf. Sci.* **252** 5622–6
- [6] O'Shea J N, Taylor J B, Swarbrick J, Magnano G, Mayor L C and Schulte K 2007 Electro spray deposition of carbon nanotubes in vacuum *Nanotechnology* **18** 035707–10
- [7] Ganan-Calvo A M 1997 Cone-jet analytical extension of Taylor's electrostatic solution and the asymptotic universal scaling laws in electro spraying *Phys. Rev. Lett.* **79** 217–20
- [8] Tuft D, Achtzehn T, Muller R, Huber B A and Leisner T 2003 Coulomb fission: Rayleigh jets from levitated microdroplets *Nature* **421** 128
- [9] Uematsu I, Matsumoto H, Morota K, Minagawa M, Tanioka A, Yamagata Y and Inoue K 2004 Surface morphology and biological activity of protein thin films produced by electro spray deposition *J. Colloid Interface Sci.* **269** 336–40
- [10] Altman E I and Colton R J 1992 Nucleation, growth and structure of fullerene films on Au(111) *Surf. Sci.* **279** 49–67
- [11] Maxwell A J, Bruhwiler P A, Nilsson A, Martensson N and Rudolf P 1994 Photoemission, autoionization, and x-ray-absorption spectroscopy of ultrathin-film C₆₀ on Au(110) *Phys. Rev. B* **49** 10717–25
- [12] Barth J V, Brune H, Ertl G and Behm R J 1990 Scanning tunneling microscopy observations on the reconstructed Au(111) surface—atomic-structure, long-range superstructure, rotational domains, and surface-defects *Phys. Rev. B* **42** 9307–18
- [13] Horcas I, Fernandez R, Gomez-Rodriguez J M, Colchero J, Gomez-Herrero J and Barro A M 2007 WSxM: a software for scanning probe microscopy and a tool for nanotechnology *Rev. Sci. Instrum.* **78** 013705
- [14] Nilsson A 2002 Applications of core level spectroscopy to adsorbates *J. Electron Spectrosc. Relat. Phenom.* **126** 3–42
- [15] Schnadt J et al 2003 Excited-state charge transfer dynamics in systems of aromatic adsorbates on TiO₂ studied with resonant core techniques *J. Chem. Phys.* **119** 12462–72
- [16] Schnadt J et al 2002 Experimental evidence for the sub-3 fs charge transfer from an aromatic adsorbate to a semiconductor *Nature* **418** 620–3
- [17] Schnadt J, O'Shea J N, Patthey L, Krempasky J, Martensson N and Bruhwiler P A 2003 Alignment of valence photoemission, x-ray adsorption, and substrate density of states for an adsorbate on a semiconductor surface *Phys. Rev. B* **67** 235420
- [18] Bruhwiler P A, Karis O and Martensson N 2002 Charge-transfer dynamics studied using resonant core spectroscopies *Rev. Mod. Phys.* **74** 703–40
- [19] Enkvist C, Lunell S, Sjogren B, Svensson S, Bruhwiler P A, Nilsson A, Maxwell A J and Martensson N 1993 C(1s) shakeup spectrum of C-60—global charge-transfer satellites and their relation to the x-ray threshold singularities in macroscopic systems *Phys. Rev. B* **48** 14629–37