Retraction for Chemical Communications:

Measuring Si-C60 chemical forces via single molecule spectroscopy

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We, the named authors, hereby wholly retract this *Chemical Communications* article, because on reanalysis of the original raw data we found errors had been introduced during the data processing that affect the conclusions of the paper. The amplitude calibration used was incorrect and this error led to an overestimation of the resultant forces. This means that the force measurements most likely arise from a C_{60} interaction and not a Si cluster - C_{60} interaction as originally claimed.

Signed: Cristina Chiutu, Andrew Stannard, Adam M. Sweetman and Philip Moriarty, University of Nottingham, Nottingham, 23 December 2013

Retraction endorsed by Robert D. Eagling, Editor, Chemical Communications

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COMMUNICATION

Measuring Si-C₆₀ chemical forces *via* single molecule spectroscopy†‡

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We measure the short-range chemical force between a silicon-terminated tip and individual adsorbed C_{60} molecules using frequency modulation atomic force microscopy. The interaction with an adsorbed fullerene is sufficiently strong to drive significant atomic rearrangement of tip structures.

The fullerene family of molecules continues to play a central role in a variety of scientific fields. As outlined in a recent review,¹ C₆₀ and its various functionalised and modified "siblings" not only have underpinned a variety of scanning-probe-based single molecule (and sub-molecular) imaging,^{2–4} spectroscopy,^{5,6} and manipulation^{7–9} experiments but they still attract considerable attention in relation to key topical areas in nanoscience.

A particularly intriguing emerging area of fullerene-related science relates to the development of hybrid carbon–silicon nanostructures. Mélinon *et al.*¹⁰ have highlighted the wealth of interesting fundamental and applied science which is accessible by controlling dimensionality and bonding interactions in carbon–silicon compounds and devices. A prototypical system of particular interest in this context, and which has been studied in some depth by Mélinon and co-workers,^{11–13} involves the exohedral bonding of Si atoms and clusters to the free C₆₀ cage. There has also been a substantial surface science effort focussed on a very similar problem: the nature of the interaction of C₆₀ with silicon surfaces.¹

Comprehensive theoretical studies have predicted a range of (meta)stable structures for a variety of Si_mC_{60} clusters.^{11,14} To date, however, an experimental determination of the short-range chemical force or interaction potential associated with Si–C₆₀ bonding has been lacking. Here we describe the use of frequency modulation atomic force microscopy (FM-AFM) to quantify the chemical force between a silicon-terminated tip and C₆₀ molecules adsorbed on Si(111)–(7 × 7).

Our experiments were carried out at 77 K in a commerciallysupplied (Omicron Nanotechnology GmbH) scanning tunneling microscope (STM)-frequency modulation (FM)-AFM instrument. A qPlus sensor¹⁵ was used for the FM-AFM measurements. We discuss important subtleties associated with our approach to qPlus

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imaging-including our measurement protocols, tip preparation procedures, and data analysis methods--in the ESI.†

In order to confirm the silicon termination of the tips used in our experiments[†], we ensure that the forces and energies extracted from df(z) spectra acquired on the clean Si(111)- (7×7) surface are comparable to those expected for silicon– silicon interactions on the basis of theoretical calculations¹⁶ and previous experimental work.^{17,18} To do this we measure df(z) curves above adatoms of the Si(111)–(7 × 7) surface. Fig. 1 shows the short-range force resulting from the transformation of the measured frequency shift data using the method of Sader and Jarvis.¹⁹⁺ We also include in the insets the frequency shift curve acquired above a corner-hole of the (7×7) reconstruction (so as to show the long-range behaviour of the df(z) spectrum) and a constant frequency shift FM-AFM image of the Si(111)– (7×7) surface. The maximum force attractive value in Fig. 1 (\sim 2 nN) and the overall form of the force curve agree well with previous work,¹⁶⁻¹⁸ providing strong evidence that the tips we use are indeed silicon-terminated.

Fig. 2(a) is a dynamic scanning tunnelling microscopy (dSTM) image of a submonolayer coverage of C_{60} on the Si(111)–(7 × 7) surface. Strong intramolecular contrast, which



Fig. 1 Force vs. displacement curve acquired above an adatom of the Si(111)– (7×7) surface with a silicon-terminated tip. Insets: long-range frequency shift (df) vs. z spectrum acquired over a corner-hole of the (7×7) reconstruction; constant frequency shift FM-AFM AFM image of Si(111)– (7×7) (acquired with a different sensor). Scan parameters: oscillation amplitude (A_0) = 0.5 nm (pk–pk = 1 nm); setpoint df = -21.6 Hz; $V_b = 0$ V. Scale bar: 1 nm.

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Fig. 2 (a) Dynamic STM image of a submonolayer coverage of C_{60} on the Si(111)–(7 × 7) surface. Strong intramolecular contrast is observed arising from the convolution of the tip electronic structure with the fullerene molecular orbitals.† (Scan parameters: A_0 : 1.5 nm; $V_{\rm b}$ = +2.3 V; $I_{\rm t}$ = 300 pA.) (b) FM-AFM image of the same molecules shown in (a). A_0 : 0.25 nm; $V_{\rm b}$ = 0 V; frequency shift (d*f*) setpoint = -11.0 Hz. Scale bars: 1 nm.

varies from molecule to molecule, is observed in the dSTM image. The contrast variations we observe are rather different to those reported in previous work^{2,5,20} but this is entirely to be expected given the key role that the tip state—and its associated coupling to the charge density variations in the fullerene molecule—plays in the image formation mechanism.^{20,21} †

The corresponding zero bias FM-AFM image for the adsorbed C_{60} molecules is shown in Fig. 2(b). We image with a frequency setpoint corresponding to the onset of molecular resolution. This precludes simultaneously attaining atomic resolution on the surrounding (7 × 7) surface but we find that at even moderately higher |df| values than that used for scanning (typically a few Hz larger), the C_{60} molecules are either displaced or picked up due to the interaction with the tip. (This effect can, however, be exploited to controllably manipulate individual molecules.)^{9,22} The apparent height of the C_{60} molecules in the qPlus AFM image is thus very much smaller than the diameter of the molecule and falls in the range 0.01 to 0.08 nm for the "weak imaging" parameters we use. The height of the tip above the surrounding Si(111)–(7 × 7) surface (*i.e.* in a molecule free region) is ~0.7 nm under these scan conditions.[†]

The force vs. displacement curves extracted from frequency shift spectra measured above a number of C₆₀ molecules (using an approach similar to that employed by Ternes et al.²³ for atomic adsorbates) are plotted in Fig. 3(a). The maximum force we measure for this particular tip is ~ 1 (±0.2) nN. This is somewhat lower than the values determined by Hobbs and Kantorovich²⁴ on the basis of their DFT calculations-they predicted a maximum force in the 1.5 to 2 nN range. Their calculations, however, were for a C_{60} molecule adsorbed on the Si(100) surface rather than the Si(111)– (7×7) reconstruction. Moreover, for the tip structure and experimental conditions used to acquire the data shown in Fig. 3, we did not observe a strong variation in the force curves from molecule to molecule nor, unlike the case for Hobbs and Kantorovich's simulated spectra, did we see strong differences in the force curves as a function of position on a given C_{60} molecule. Smaller oscillation amplitudes coupled with lower noise measurements (the phase-locked loop bandwidth was relatively high during the data acquisition for Fig. 3) will improve our ability to distinguish small force variations.

Both the attractive and repulsive regimes of the experimentally determined force curves in Fig. 3 have a slope which is shallower than that predicted by DFT.²⁴ The DFT calculations,



Fig. 3 (a) Short-range force curves extracted from df vs. z spectra for the molecules labelled as A–C in the FM-AFM image shown in the inset; (b) the corresponding interaction potentials. (The potential energy curves are particularly sensitive to the details of the background subtraction procedure for the df data†; the uncertainties for each curve are correspondingly high, ~30%.) Scale bar: 1 nm.

however, use an idealized single dangling bond tip which is unlikely to accurately represent the apex of the experimental tip. The influence of the tip structure is of course also reflected in the measured binding energies (Fig. 3(b)), which are significantly lower than those predicted by theory for the bonding of a silicon atom to a C_{60} molecule.^{11,12} Those theoretical studies, however, concern the interaction of a single free silicon atom with a C_{60} cage where the preferred bonding mechanism, as for fullerene adsorption on silicon surfaces, involves the breakage of a C=C double bond and the formation of two Si–C bonds. This type of reaction pathway will be severely constrained by the back-bonding of the outermost Si atom(s) at the tip apex.

A perhaps more appropriate system to consider in the context of our experiments is the Si_mC_{60} cluster family.^{13,14} Although the tip used to generate the spectra shown in Fig. 3 was extremely stable and produced highly reproducible force-distance curves, this is certainly not always the case. As Fig. 4 illustrates, the force curves we measure are *critically* dependent on the tip, i.e. a silicon cluster of unknown geometry. The four curves shown in Fig. 4(a) are raw df(z)spectra acquired above the same molecule (inset to Fig. 4(b)). The tip apex used to acquire the data of Fig. 4 is clearly much less structurally robust than that used for the measurement in Fig. 3 and substantial modifications occur during the acquisition of each spectrum (although molecular resolution is maintained throughout—see inset to Fig. 4(b)). The observation of strong hysteresis between the "forward" and "reverse" spectra is a clear signature of atomic level rearrangements driven by the formation of Si-C₆₀ chemical bonds. Fig. 4(b) shows that the maximum attractive force can vary wildly depending on the tip structure and the dynamics of Si-C₆₀ bonding-the largest negative forces in Fig. 4(b) are ~ 0.6 nN and > 2.5 nN.



Fig. 4 (a) A series of df(z) spectra measured above the C₆₀ molecule shown in the inset to (b). (Offset in df for clarity.) The tip approach and retract curves are distinguished by arrows. (b) The force curves, F_{iii} and F_{iv} , extracted from plots (iii) and (iv). Upper inset: 3D rendered (but unfiltered) dSTM image of the C₆₀ molecule. (Scale bar: 1 nm.) Lower inset: line profile overlaid over a constant frequency shift image of the molecule acquired in parallel with the spectroscopic curves. Molecular resolution was retained throughout. $A_0 = 0.5$ nm; $df_{sp} = -15.4$ Hz.

In conclusion we have measured the chemical force between silicon-terminated tips and adsorbed C_{60} molecules using FM-AFM. The measured force curves and maximum attractive force depend critically on the tip structure. There is considerable scope to extend these experiments to incorporate strategies to ascertain the bonding geometry of the outermost tip atoms^{25,26} and to improve the force sensitivity so as to measure the variation of the Si–C₆₀ chemical interaction with submolecular resolution.

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