Electronic Supplementary Material for Chemical Communications
Measuring Si-C_{60} chemical forces via single molecule spectroscopy

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I. EXPERIMENTAL DETAILS

A. Sample preparation

Our experiments were carried out in a commercially-supplied (Omicron Nanotechnology GmbH) low temperature scanning tunnelling microscope (STM)-FM-AFM atomic force microscope (AFM) instrument (using qPlus sensors) with a typical base pressure in the STM chamber (with the cryostat filled) of better than 1 x 10^{-11} mbar. Si(111) samples (boron doped, 10 - 20 mΩ cm) were first degassed at 600°C for a period of six to eight hours before flash-annealing to approximately 1200°C. During the flash anneal cycles we ensured that the chamber pressure did not exceed 5 x 10^{-10} mbar. After holding the sample at 1200°C for a period of order 20 seconds, the temperature was rapidly decreased to $\sim$ 800°C and then the current through the sample was slowly reduced to zero over the course of approximately 5 minutes. Direct current heating was used throughout the degassing and flash anneal process. C_{60} was deposited from a simple source comprising a Ta envelope with a small ($\sim$ 1 mm diameter) hole on one side which was heated by direct current. The chamber pressure during C_{60} deposition was below 3 $\times 10^{-9}$ mbar.

B. qPlus AFM set-up and tip preparation

The qPlus FM-AFM measurements were carried out at 77 K. Commercial tuning fork sensors (Omicron GmbH) were used throughout. At the time of our experiments, these sensors did not have a separate connection to the tip in order to measure the tunnel current signal. Moreover, in Omicron systems the bias voltage is usually applied at the input to the tunnel current pre-amp, rather than at the sample (which is at ground potential). Both of these aspects of the instrument design can lead to significant issues with crosstalk between the tunnel current, frequency shift, and damping channels unless this effect is recognised and compensated/removed. Given the importance of acquiring “clean” frequency shift data (i.e. free of the influence of the tunnel current channel) for our measurements we describe in the following section the strategy we have adopted to ensure that the df spectra we acquire are not compromised by cross-talk. (Further detail on our experimental set-up and the uncertainties associated with qPlus FM-AFM measurements can be found in the Supplementary Information file for Sweetman *et al.*[1]. On the latter point it is perhaps worth noting that a calibration (GA Shaw, NIST, US) of the tuning fork spring constant for the Omicron sensors we use yields a value of 2.6 ± 0.4 kN - appreciably greater than the “expected” 1.8 kN/m value.). The z piezo displacement is calibrated via STM measurements of the bilayer step height on the Si(111) surface.

The resonant frequency of the tuning forks we use lies in the 20 kHz - 25 kHz range with Q values ranging between 1,000 and 10,000 (at 77 K). We determine the Q of the tuning fork via impulse excitation using the slip-stick motor. This produces a damped harmonic response which when transformed to Fourier space yields a Lorentzian function. We subsequently fit the Lorentzian curve to extract the free resonant frequency and the Q value. It is important to note that the measured Q value depends not only on the coupling of the tuning fork to the end of the piezo tube but on the position of the tube within the slip-stick motor.

As described elsewhere[1–3], we do not heat - or otherwise treat, e.g. sputter - the W tips used in our experiments to prepare them for measurements. Instead, we use standard STM methods - in either conventional STM mode or dynamic STM mode, where the tip is oscillated at its resonant frequency - such as voltage pulsing, crashing the tip into the sample surface, and high current/high bias imaging to coerce the tip into a state where it provides atomic resolution. (Due to the cross-talk issues noted above, it is worth noting that in many cases the tuning fork can “self-excite” during voltage pulsing or high bias imaging. This can on occasion lead to severe crashing of the tip). We are therefore confident that the original oxide-covered W tip is terminated by silicon before we start FM-AFM measurements on the surface. Scanning electron microscope imaging of some of our tips, coupled with energy dispersive X-ray analysis, has provided evidence to support this hypothesis. (We mention in passing that automated probe optimisation methods recently developed in our group[4] will play an increasingly important role in “tuning” the tip structure for our FM-AFM experiments in future.)

Either self-excitation, or “active” driving of the tuning fork with a sinusoidal waveform provided by the phase-locked loop (PLL) electronics, was used in our experiments. In both cases the amplitude of the tuning fork was held constant. A separate external lock-in was used to monitor the amplitude of the tuning fork oscillation throughout our experiments.

We use the Omicron “twin regulator” feature to transition during a scan from dynamic STM, where the feedback signal is the tunnel current channel, to NC-AFM where the feedback regulates the frequency shift at a setpoint value. After transitioning to FM-AFM (using a very low frequency setpoint) we reduce the bias voltage slowly ($\sim$ 20 mV/second) so as not to perturb the tuning fork oscillation. We then increase the frequency shift setpoint (df_{sp}) to the point where atomic or molecular resolution is achieved. In general, this procedure is sufficiently well-controlled so that we avoid inadvertent changes in the tip structure or modification of the sample surface during the transition. As can be seen from a comparison of Fig. 2(a) and 2(b), this procedure, if carried out using appropriate feedback parameters and scan speeds, also does not lead to inadvertent manipulation of adsorbed C_{60} molecules.

C. Eliminating cross-talk

Given the now well-recognised crosstalk problem with the first generation Omicron qPlus sensor design[1], it is important that we describe how we ensure that our df and damping measurements are free of the influence of the tunnel current channel. Before doing so, we highlight that even with a separate connection to the tip to measure the tunnel current (I_t) "independently" there can still be an influence of the I_t channel on the tuning fork sensor dynamics. For example, on a different commercial qPlus FM-AFM system (Createc) used in our labs, it is not unusual for a fork to "self-oscillate" at relatively modest setpoint tunnel currents ($\sim$ 1 nA) during conventional STM imaging. (Second generation Omicron sensors which have a separate wire for the tunnel current connection exhibit a similar effect). Moreover, as Weymouth *et al.*[5] have recently highlighted, there can be important *physical* effects underlying the coupling of the tunnel current and df channels on semiconductor surfaces even in the absence of any crosstalk due to instrumental artifacts.

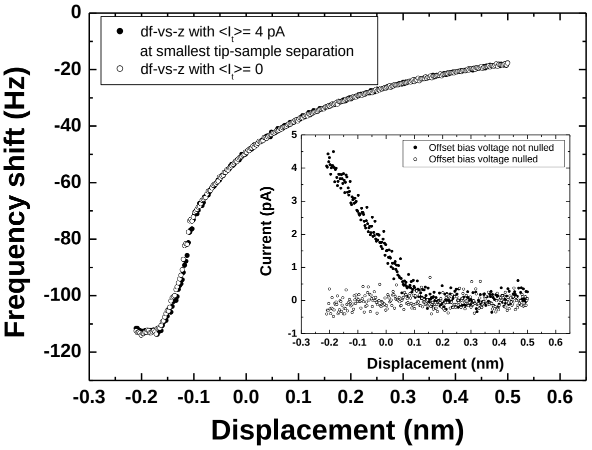

FIG. S1: Frequency shift vs tip displacement, d$f(z)$, spectra measured above an adatom of the Si(111)-(7x7) reconstruction using FM-AFM at 77 K with (open circles) and without (filled circles) the bias voltage set to 0 V. The inset shows the tunnel current variation in both cases. The df(z) spectra for both bias settings overlap. (Oscillation amplitude: 0.1 nm)

For these reasons we prefer to measure tip-sample interactions in the absence of a tunnel current. To do so we reduce the bias voltage to zero. This can of course result in an appreciable contact potential difference and, therefore, a long-range electrostatic force between tip and sample[2]. We therefore have to be particularly careful in removing the long range background from the df(z) spectra in order to extract the short-range force[6].

For small average tunnel currents, $< I_t >$, of order pA to tens of pA, the level of cross-talk is negligible. To demonstrate this we show in Fig. S1 raw d$f(z)$ spectra measured above an adatom of the Si(111)-(7x7) surface for a bias voltage of zero (which results in zero tunnel current - see inset) and a small bias voltage sufficient to produce an average tunnel current of 4 pA at the smallest tip-sample separation. The d$f(z)$ spectra overlap within experimental error. (The damping spectra (not shown) similarly agree within experimental error). Hence, small tunnel currents do not influence the frequency shift or damping channels. Nonetheless, in order to ensure that we entirely eliminate potential tunnel current-induced contributions to the frequency shift[5], we operate at zero bias. We have also attempted to measure the magnitude of the displacement current present in our experiments using a strategy similar to that adopted by Muller *et al.*[7] which involves measurement of the AC current which is 90° out of phase with the (modulated) tunnel current. We did not observe a displacement current contribution above the noise floor of the tunnel current preamplifier used in our measurements ($\sim$ 1 pA).

II. ISOLATING THE SHORT-RANGE FORCE

The extraction of short range force data from d$f(z)$ measurements is fraught with difficulty, particularly when the long range electrostatic potential due to the contact potential difference is not removed (as in our case). (However, even with data where the long range electrostatic force contribution has been small due to a fortuitous close match of the work functions of the tip and sample, we have still found that the short range force data are extremely sensitive to the background subtraction technique). We use long-range force distance curves, extending out well into the tip-sample separation range where the frequency shift variation is flat, to extract an accurate long-range background d$f(z)$ spectrum which we then subtract from the data

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[1] See http://qplus.forum-motion.net/ for discussion on this topic

[2] It is perhaps worth pointing out that this contact potential difference cannot drive a tunnel current. Without an external bias the Fermi levels in tip and sample are aligned and a net current cannot flow.

acquired over a shorter z range. In the case shown in Fig. 1 in the paper the power law fitted to the frequency shift data was of the form

$$df = \frac{A}{(z+B)^C} + D \quad (1)$$

Even relatively minor offsets in z (at the level of 10 pm) can significantly change the extracted short range df curve. We therefore examine carefully the residuals in the fitting of the long range background to determine as accurate a value of the short range df "cut-off" as possible. (We shall discuss the procedure we use in detail in a future paper[6]).

In order to isolate the short range force above C_{60} molecules we use a different procedure: first acquire a background spectrum above the clean silicon substrate; offset this spectrum to correct for the z position of the tip above the C_{60} molecule (the necessary offset can be taken directly from the topographic FM-AFM image); and then subtract the background spectrum from the d$f(z)$ curve measured above the C_{60} molecule.

As is noted in the main paper, the apparent height of the C_{60} molecules in our FM-AFM images is typically between 0.01 and 0.1 nm, much less than the van der Waals diameter of ∼ 1 nm. This "discrepancy" is not particularly surprising, however, as the apparent height of the molecule depends on the variation in the total tip-sample force above the molecule as compared to that above the Si(111)-(7x7) surface. In order to ensure that we do not displace the molecules during a scan we operate at a low frequency set-point such that we do not attain atomic resolution on the (7x7) reconstruction. This means that the tip is rather far from the sample surface during qlus imaging.

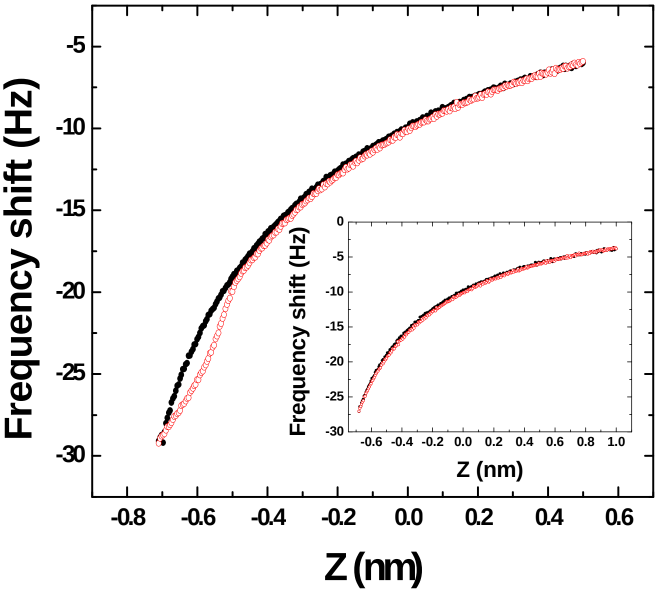

FIG. S2: Frequency shift (df)-vs-tip displacement (z) curves acquired above a molecule-free region of the Si(111)-(7x7) surface during the acquisition of a FM-AFM image of adsorbed C_{60} (similar to that shown in Fig. 2(b) of the paper). Clear hysteresis arising from the chemical interaction of the tip and sample is observed when the tip is moved closer to the surface by ∼ 7.1 Å from the imaging feedback position (i.e. the 0 position on the x-axis of the graph). Inset: A d$f(z)$ curve acquired before that shown in the figure. In this case the tip was not extended sufficiently far to interact with the surface and no hysteresis (or evidence of a change in curvature of the d$f(z)$ curve which would indicate a chemical interaction) is observed.

To gain an estimate of just how far the tip is above the underlying adatoms of the (7x7) reconstruction while scanning C_{60} (e.g. Figs. 3 and 4 in the main paper) in FM-AFM mode, we use d$f(z)$ spectra taken in the molecule-free regions of the surface (which, as described above, we routinely acquire in any case in order to determine the background contribution to the spectra taken above C_{60} molecules). To observe a strong interaction with the Si(111) adatoms in d$f(z)$ spectra typically required that the tip was moved closer to the sample by 6.6 (± 0.5) Å from the z position defined by the frequency setpoint used for imaging. We define "strong interaction" as the point at which the minimum of the d$f(z)$ function has been reached and the slope of the curve has changed sign or, as shown in Fig. S2 below, where we first observe hysteresis between the approach and retract d(f)-vs-z spectra.

Typical spectra are shown in Fig. S2. The inset shows the approach and retract curves when the tip is moved forward a maximum of 6.8Å from the constant frequency shift feedback position. No hysteresis is observed. When the tip is moved forward an additional 0.3 Å during the spectrum (as shown in the main figure in Fig. S2), however, strong hysteresis is observed. From this we ascertain that the tip is approximately 7Å above the Si(111)-(7x7) surface while scanning C_{60} in the "weak imaging" mode to which we refer in the paper. This is somewhat smaller than the 10 Å van der Waals diameter of C60 but, interestingly, very close to the hard sphere diameter of 7.1Å.

III. SUB-MOLECULAR RESOLUTION

Although we have observed submolecular structure which agrees very well with data in the literature[8, 9] (Fig. S3(a) - (d)), in many cases (e.g. Fig. S3(e)) we find that the contrast variations for our C_{60} images do not correlate well with the results of other experiments and DFT simulations[8–11]. This lack of agreement between many of the (dynamic-)STM images we have acquired and those previously published in the literature is, however, not particularly surprising. While there has been a considerable amount of effort expended in elucidating the origin of submolecular contrast in STM images of C_{60} molecules adsorbed on the Si(111)-(7x7) surface, it is only very recently that a key contribution to the image formation process, namely the tip state, has been considered in any detail[10].

The form of submolecular resolution observed in an STM, dynamic-STM, or NC-AFM image will depend strongly on the geometric and electronic structure of the tip. In two important combined experiment-theory studies over a decade ago, both Hou *et al.*[8] and Pascual *et al.*[9] elucidated the origins of sub-molecular contrast in high resolution STM images of C_{60} on Si(111)-(7x7), although there had been a number of previous studies which had also observed intramolecular features and attributed them to tunnelling into/out of specific molecular orbitals. The question of submolecular resolution has also been revisited more recently using both Hückel molecular orbital theory[11] and local density approximation (LDA) density functional theory[10]. In each case the authors highlight that the tip can play a substantial role in the image formation mechanism. The importance of the coupling of the molecular charge density variations to the tip state has been recognised by Hands *et al.*[11] - the tip-sample interaction necessarily weights the molecular orbital images to those contributions which have strong charge density in the tip direction. Rurali *et al.* used different tip types in their DFT simulations and conclude that the intramolecular contrast seen in STM images of C_{60} adsorbed on the Si(111)-(7x7) surface depends critically on the electronic structure of the probe.

As described above (and in the main paper in relation to Fig. 1), our tips are generally Si-terminated. Moreover, a silicon-terminated tip can form a variety of different structures at its apex[2] and each one of these can, in principle, give rise to a different set of submolecular contrast images. That the submolecular features seen in Fig. S3(e) arise from a tip which does not have the "ideal" structure comprising a single dangling bond aligned parallel with the surface normal is clear from the images of the (7x7) reconstruction acquired from the regions between the C_{60} molecules (inset to Fig. 3(e)). As first shown by Giessibl *et al.*[12], the relatively narrow spatial extent and large separation of the adatom dangling bond orbitals at the Si(111)-(7x7) surface enable an "inverse imaging" process to take place where the surface orbitals image the tip structure (and not vice versa as is usually the case). The distorted shape of the (7x7) adatoms seen in the contrast-enhanced dynamic-STM image shown in the inset to Fig. S3(e) is clear evidence that the tip apex is significantly more complicated than the idealized single protruding dangling bond structure.

Another highly plausible possibility, of course, is that the tip has picked up a C_{60} molecule and that it is the convolution of the orbitals of the "on-tip" C_{60} with those of the surface-bound molecule which produces the "anomalous" intramolecular contrast seen in Fig. 3(e). To check this hypothesis we have carried out a series of experiments involving the deliberate adsorption of a C_{60} molecule on the tip[13]. The interaction forces we measure for this type of "functionalized" probe are significantly smaller than those determined for the tip used to generate the images and data shown in Figs. 1 - 4 in the paper. In order to pin down the origin of the submolecular contrast variations observed in our images, we are currently collaborating with Dunn and co-workers[11] who are attempting to simulate the submolecular features observed in our images using the Hückel molecular orbital approach described in ref.[11].

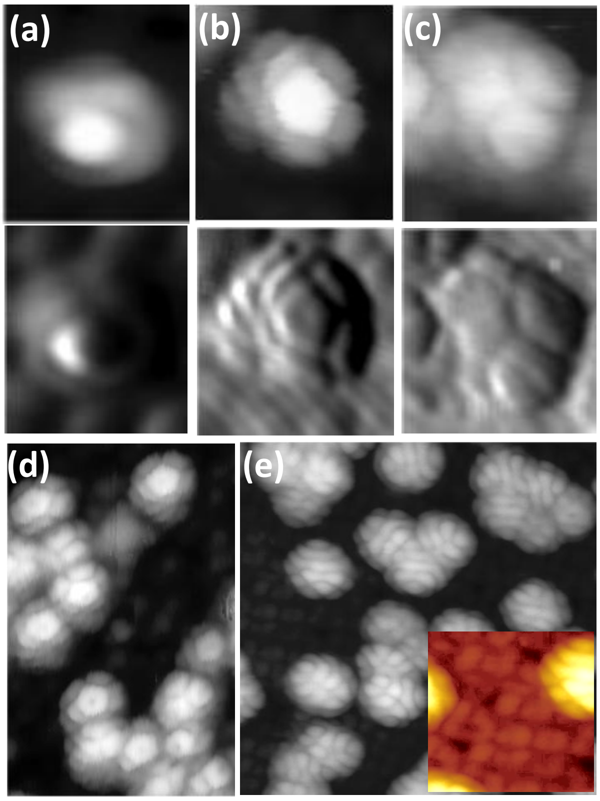

FIG. S3: Submolecular resolution dynamic STM images of C_{60} adsorbed on the Si(111)-(7x7) surface. (a)-(c) show constant average tunnel current topographs (top row) for different molecular orientations. Underneath each image is a low pass filtered (9 point average) tunnel current image acquired in parallel with the topograph. These three empty state images (V_b=+2.3 V) are in good agreement with previous experimental and theoretical data published by, for example, Pascual *et al.*[9], Hou *et al.*[8], Rurali *et al.*[10], and Hands *et al.*[11]; (d) A dSTM empty state image (V_b =+ 2.3 V) showing C_{60} molecules in a number of different bonding orientations; (e) Submolecular contrast arising from a different tip state than that used to acquire (a) - (d). The inset shows that the tip gives rise to "anomalous" imaging of the adatoms of the (7x7) surface[12].

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