

**Adsorption geometry determination of single molecules by atomic
force microscopy.**

SUPPLEMENTAL MATERIAL (SM)

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TIP PREPARATION

After cutting the PtIr tip *ex situ* by focused ion beam, it is *in situ* repeatedly indented into the Cu. We selected tips that had a frequency shift smaller than 2Hz at a tunnel set point of $I = 2\text{ pA}$ at 0.2V. The Cu tips were then terminated with a single CO or Xe by vertical manipulating CO or Xe on NaCl(2ML)/Cu(111). Unlike CO, Xe does predominately adsorb on steps to NaCl(3ML)/Cu(111) or next to molecules adsorbed prior to admitting Xe on the surface. Like CO it can be picked-up by approaching it at reduced voltage. The successful termination with CO or Xe can be checked by the tip specific STM contrast of adsorbates on the surface.

ADSORPTION HEIGHTS

Reasons for using z^ as a measure of adsorption height.* As a measure for the adsorption height we took the height z^* where the frequency shift Δf is minimal. In the following the rationale behind using z^* as a measure for distances is explained. The force on an inert tip being close to molecule on a surface is primarily composed out of an attractive component from the surface and the molecule and a repulsive component from the latter. After subtracting the surface contribution, we remain with polynomial decaying vdW and electro-static attraction and exponentially decaying Pauli repulsion [1, 2]. Accordingly, the maximal total vertical force gradient (minimum in the frequency shift), is very narrow and hence z^* well-defined. If we assume that the force on the tip from the induced electronic changes in the molecule and the surface upon adsorption can be neglected, a shift in the adsorption height will shift likewise both, the attractive and repulsive force, relative to the surface and hence z^* . By choosing chemically equivalent tip-molecule systems a change in adsorption height is directly reflected in z^* . Here we compare systems that qualify for these restrictions, namely pentacene with DIP, two polyaromatic hydrocarbons, and the olympicene family: olympicene, radical, and ketone, which differ in their chemical structure only by one atom. We used one CO (Xe) tip for the measurement on pentacene and DIP and another CO (Xe) tip for the measurement on the olympicenes.

There are other criteria that would also be suited for adsorption height determination and that should yield similar results. For example also $\arg \min_z \{F(z)\}$ corresponding to the

node of $\Delta f(z)$ or $\arg \min_z \{E(z)\}$ corresponding to the node of $F(z)$, or the node on $E(z)$ should lead to similar results. This is because usually we observe a very similar slope of the graphs of $E(z)$, $F(z)$, and $\Delta f(z)$ but being shifted in z by $\approx 0.45 \text{ \AA}$ with respect to each other [1]. Since z^* refer to the difference between the Δf minimum on the molecule and the substrate we expect that by choosing the minimum of $F(z)$ or $E(z)$ instead would lead to the same value. Therefore we expect similar results using these other criteria. Exceptions from this simple relationship are expected (i) in the case of height dependent tip relaxations, e.g., for a CO tip at small ($\lesssim 3.5 \text{ \AA}$) tip heights [3] or (ii) above the molecule border where $\Delta f(z)$ takes a different form and two local minima are observed [4]. However, the minimum of the force or energy are more challenging to reach without changing the tip or the molecule due to the smaller tip heights compared to the minimum in Δf . The change of the tip, i.e. dropping the atom/molecule functionalizing the tip is especially a problem when trying to reach $\arg \min_z \{F(z)\}$ (and even more $\arg \min_z \{E(z)\}$) above the bare substrate, which is needed for the z_{off}^* determination.

In principle, one would also expect differences in z^* due to variations in the charge density for example between the center and the border of the molecule [3]. In comparison with the calculated adsorption heights, however, we observe that this effect plays only a minor role.

Details of data acquisition. Next, a detailed description of the data acquisition and analysis is given. First we selected tips that showed a relatively small frequency shift of $\Delta f \lesssim 2 \text{ Hz}$ at a tunnel set point of 10 pS on NaCl(2ML)/Cu(111). Then we functionalized the tip with a single CO molecule or Xe atom by picking up CO or Xe on NaCl(2ML)/Cu(111). Thereafter we recorded a full 3D frequency shift map (usually 4500 to 5000 points in $\sim 16 \text{ h}$) by using variable tip approach on each molecule to be studied (for details see [4]). The molecules that are compared have been recorded with the identical tip. To limit the risk of moving or unintentional pick-up of the molecule, the maximal tip approach during the frequency shift map is set to a height where the turn around point in the force-distance spectrum was reached everywhere above the molecule but usually not above the substrate. Therefore, after recording the frequency shift map a reference spectrum above the substrate was taken and its z^* value determined. The zero point of the z^* is then set to this value. To extract z^* , the minimum of the $\Delta f(z)$ curve is approximated by a 4th order polynomial.

For a qualitative description of the adsorption height difference also the Δf contrast at constant height can be chosen. That is, molecules being more repulsive compared to another

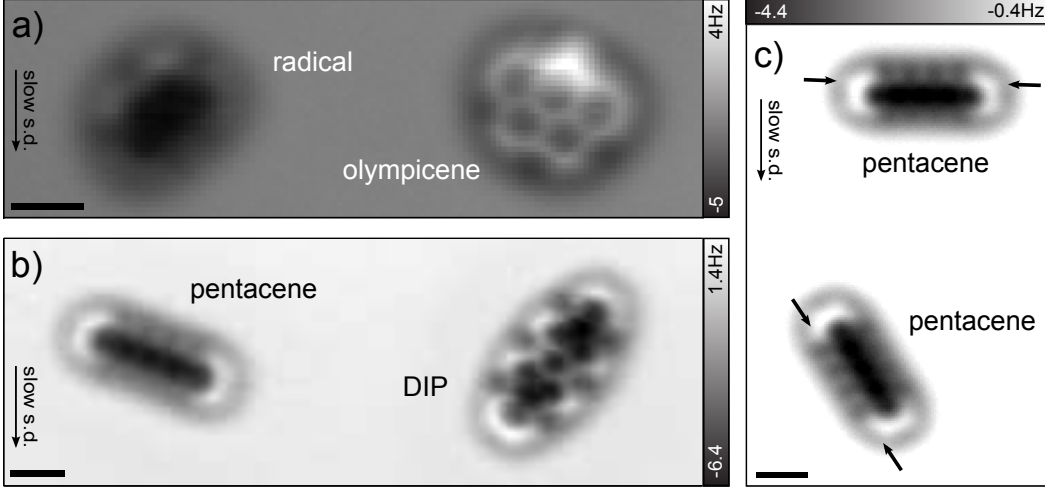


FIG. 1. Constant height AFM images with CO functionalized tips on radical and olympicene (a), on pentacene and DIP (b) and on two pentacenes (c). Height offsets (STM conductance set points in brackets) : -1.2 \AA ($G = 57 \text{ pS}$) in (a), -1.2 \AA ($G = 10 \text{ pS}$) in (b) and -2.2 \AA ($G = 10 \text{ pS}$) in (c). The arrows in (c) mark the pentacene site that is slightly up tilted. Scale bars: 5 \AA .

one at the same scan height are farther adsorbed. This simplified picture is of course only valid, if the molecules being probed are chemically equivalent for the tip. In the case of olympicene and radical (Fig. 1 (a)) it can be readily concluded from the constant height image that radical is closer adsorbed. The effective height difference, however, is difficult to quantify from the bare Δf information at constant height. In Fig. 1 (b) pentacene and DIP are mapped in constant height mode. Here we see that DIP seems to be slightly farther adsorbed. The strong dependence of the Δf contrast on the molecule tip separation, even render possible to detect the slight tilting of the pentacene along its short axis, see Fig. 1 (c). Note that the greater Δf value was always observed on the same molecule site with respect to the substrate (total 16 different pentacene molecules where measured), irrespective of the tip. That is, the two-fold symmetry along the molecules long axis is broken upon adsorption.

In Tab. I the adsorption heights from z^* , DFT+vdW^{surf} and XSW [5, 6] (if available) for pentacene, DIP, olympicene, ketone and radical are compared. Please note that z^* is translated into the absolute adsorption height by adding a tip and bias dependent offset z_{off}^* . For CO tips ($V = 0 \text{ V}$) we found that $z_{\text{off}}^* \sim 0.8 \text{ \AA}$ and for Xe tips ($V = 0 \text{ V}$) $z_{\text{off}}^* \sim 0.4 \text{ \AA}$. All the adsorption heights (besides the XSW values) are given for the molecule centers and extracted from a least mean square fit of a plane model for DIP, olympicene, ketone and

TABLE I. Comparison of adsorption heights from z^* , DFT+vdW^{surf} and XSW.

	AFM				DFT		XSW
	CO tip		Xe tip		z	θ	z
	z_c^*	θ	z_c^*	θ			
pentacene	1.51 Å	-	1.97 Å	-	2.32 Å	-	2.34 Å
DIP	1.76 Å	0.2°	2.14 Å	0.2°	2.61 Å	0.3°	2.51 Å
olympicene	2.38 Å	-2.6°	2.58 ± 0.03 Å	-1.1 ± 0.2°	2.85 Å	-0.4°	-
ketone	2.08 Å	5.4°	2.21 ± 0.01 Å	4.9 ± 0.1°	2.66 Å	5.9°	-
radical	2.06 Å	2.5°	2.08 ± 0.03 Å	3.3 ± 0.1°	2.62 Å	3.4°	-

radical and parabolic trough model for pentacene. For fitting the geometry models to z^* , those spectra were selected that were lying within the circumference of a molecular structure model. The model was placed manually regarding a constant height slab of the frequency shift map at a tip height where the structure was atomically resolved. The least mean squares error method is applied for parameter optimization since we assume the errors of z^* to be normally distributed and statistically independent and the standard deviation of z^* to be the same for all spectra. The adsorption height order from the DFT calculations is reproduced by the AFM measurements (for those molecules that were measured with the same tip, i.e., pentacene/DIP and olympicene/ketone/radical). Noteworthy, the calculated and experimental tilt angles are in excellent agreement. Please note that the error estimation procedure as described in the manuscript was only done for the Xe tip. The respective errors of θ and z_c^* for the CO tip are about 5 times greater because of the atomic corrugation in z^* , which is not considered in the simple plane model. Consequently, the residuals of z^* with respect to this plane are not normally distributed.

ADSORPTION SITES

To facilitate adsorption site discrimination of the molecules we scanned the molecule and the surface in constant height mode, but changed the height offset during the scan such that we scan at a smaller height z_s above the substrate and at a larger height z_m close to the molecule. This is done by either changing the height offset twice in the slow scan direction

in the sequence z_s , z_m , z_s or on every scan line in the vicinity of the molecule in the same sequence. The resolved surface grid around the molecule is then interpolated to the central part where the molecule is resolved. The substrate grid was adapted to each image. The deviation from an equilateral triangle is always $< 2^\circ$ and $< 0.05 \text{ \AA}$ from the inter-atomic Cu distance of 2.55 \AA on Cu(111).

The effect of the adsorption site on z^* was only small for our studied molecules. In contrast, by choosing adsorption sites for the calculations not observed experimentally, the adsorption geometry was in some cases significantly influenced. Despite complete relaxation of the structure, the potential energy surface was such that the molecules did not always relax to their ground state, depending on the initially chosen adsorption site. Hence, a fast measurement of adsorption sites as described here, allowing the determination of several molecules within feasible time (approx. 1 h per individual molecule), is desirable for supporting calculations.

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