Supplementary Materials for

Bond-Order Discrimination by Atomic Force Microscopy

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Materials and Methods

Sample preparation

The Cu(111) single crystal was cleaned by several sputtering and annealing cycles, and about 10% of a monolayer (ML) coverage of NaCl was evaporated at 270 K. At this temperature, mainly bilayer islands of NaCl, i.e., NaCl(2ML)/Cu(111), are formed, with typical lateral dimensions of about 1000 Å. After the sample has been transferred to the microscope, CO was admitted to the chamber at a partial pressure of $2 \times 10^{-8}$ mbar and the shutter to the microscope was opened for a few seconds, resulting in a CO coverage on the order of $10^4 \mu m^{-2}$. Finally, the molecules to be investigated were evaporated thermally onto the sample, usually resulting in molecular coverages between $10^3 \mu m^{-2}$ and $10^4 \mu m^{-2}$. During CO adsorption and adsorption of the investigated molecules, the sample temperature was about 10 K. During all measurements the sample temperature was 5 K.

Tip preparation

As the tip, we used 25-μm-thick PtIr wire that was cut using a focused ion beam before being transferred into the LT-STM/AFM system. In the LT-STM/AFM the tip was further shaped by controlled indentations into the Cu substrate yielding a copper coated tip.

To modify a tip with a CO molecule, we followed the routine described by Bartels et al. (36) to pick up the CO from Cu(111). Alternatively, CO was picked up from bilayer NaCl on Cu(111) by approaching the tip at a sample bias of $V = 0.1$ V by 3.5 Å, starting from a tunneling set point of $I = 0.2$ A at $V = 0.2$ V above CO on NaCl(2ML)/Cu(111). A jump in the tunneling current indicated the successful transfer of the CO from NaCl towards the tip.

AFM operation

We used NC-AFM in the dynamic mode (37) and a force sensor in the qPlus geometry (23). The used sensor had a resonance frequency $f_0 = 28$ kHz, spring constant $k_0 \approx 1.8 \times 10^3$ N/m, and a quality factor of $Q \approx 50,000$ at 5 K. We used oscillation amplitudes $A$ between 0.3 Å and 0.5 Å. All AFM images were obtained in constant-height mode, i.e., the tip was scanned parallel to the surface with fixed tip height $z$. In the experiment, the tip height was set with respect to a reference height given by the STM set point above the uncovered substrate in the vicinity of the molecule. The offset for the tip height $z$ was calibrated by determining the tip height that yielded the minimum $\Delta f(x,y,z)$ above the investigated molecule and by setting this height to $z = 3.9$ Å. All other tip heights were then corrected by the same offset. The lateral position $(x,y)$ of the minimum $\Delta f(x,y,z)$ was found above the center of a $C_6$ ring for all three investigated molecules.
Supplementary Text

1. Data analysis

1.1. Measurement of frequency shift $\Delta f$ above bonds

To measure the frequency shift $\Delta f$ above individual bonds, we used constant-height AFM measurements typically at a tip height of $z = 3.7$ Å, i.e., a tip height 0.2 Å smaller than the tip height that yielded the minimum $\Delta f$ above the molecule. Such images were low-pass filtered and the maximum $\Delta f$ for a line profile perpendicular to the bond (see Fig. S1) was assigned as the $\Delta f$ value corresponding to the individual bond. Figure S1 shows the same data as in Fig. 3B, but low-pass filtered, with decreased contrast scale, and with the position of the line profiles indicated that were used to measure the $\Delta f$ values. For example, for the six $i$ bonds and the six $j$ bonds in Fig. S1 we obtained $\Delta f_i = [-5.36$ Hz; $-5.32$ Hz; $-5.31$ Hz; $-5.38$ Hz; $-5.38$ Hz] and $\Delta f_j = [-5.50$ Hz; $-5.55$ Hz; $-5.45$ Hz; $-5.45$ Hz; $-5.38$ Hz; $-5.41$ Hz], where the measurements correspond to the bonds counted clockwise, starting from the top in Fig. S1.

Usually we observed the highest $\Delta f$ contrast corresponding to bond order differences for $z = (3.7 \pm 0.1)$ Å. For tip heights larger than $z \approx 3.7$ Å, the contrast decreased with increasing $z$ because the electron density and therefore the measurement signal decreased when the tip is retracted. For smaller tip heights, relaxations of the CO have to be taken into account and, furthermore, tip asymmetries influence the measurements in a pronounced way. The latter is problematic for the $\Delta f$ contrast. Bright features inside the $C_6$ rings appeared for the smallest accessible tip heights as can be observed in Fig. 1D, Fig. 1E, and Fig. S2. We observed that the bright features usually are not centered within the $C_6$ rings and we assigned this to tip asymmetries. Depending on the exact tip structure, the stiffness of the CO could be different for different tilting directions, or the CO could be adsorbed at the tip under an angle with respect to the surface normal.

The bright features are most clearly visible at the smallest accessible tip heights ($z \approx 3.2$ Å). However, they start to contribute already for tip heights a few tenths of Å further away. This adds another component to the $\Delta f$ contrast that is not related to the bond order, but rather to the asymmetry of the tip used. For tip heights larger than 3.5 Å we observed no influence of these asymmetric features, and we therefore used tip heights of $z = (3.7 \pm 0.1)$ Å for bond order discrimination by $\Delta f$ contrast.

1.2. Measurement of apparent bond length $L'$

To measure the apparent bond length $L'$ from constant-height AFM images, we first applied Laplace filtering and then low-pass filtering to the images, as shown in Fig. 1F for $C_{60}$ and in Fig. S3 for HBC (same data as shown in Fig. 3C). After the filtering, the intermolecular bonds are observed as bright features, and by eye we fitted lines to the maxima corresponding to the bonds. The apparent bond length $L'$ was measured as the distance between the respective crossings of the lines. For the six $i$ bonds and the six $j$ bonds with the fitted lines indicated in Fig. S3, we obtained $L'_i = [1.44$ Å; $1.45$ Å; $1.50$ Å; $1.53$ Å; $1.45$ Å; $1.50$ Å] and $L'_j = [1.56$ Å; $1.67$ Å; $1.72$ Å; $1.65$ Å; $1.78$ Å; $1.67$ Å].
where the measurements correspond to the bonds counted clockwise, starting from the top, respectively.

Compared to the frequency shift, the apparent bond length seems to depend to a lesser extent on the tip height. In particular, the asymmetric bright features arising inside the C₆ rings for small tip separations seem to have no measurable influence on the apparent bond length. Therefore, we can measure the bond order related $L'$ at smaller $z$ than $\Delta f$. Measuring $L'$ at small tip separations has the advantage that bonds are imaged with increased resolution. We used tip heights $z$ from 3.6 Å down to 3.3 Å to measure apparent bond lengths.

2. DFT calculations

We calculated the tip/sample system with density functional theory (DFT) and applied a code with numerical atomic orbitals as basis functions (38), employing the Perdew-Burke-Ernzerhof exchange-correlation functional (PBE) (39) and a C₆ coefficient based van-der-Waals scheme (40). Note that the calculations only take into account the sample molecule and the Cu₂CO tip, i.e., no macroscopic vdW contribution that could arise due to the macroscopic tip or the substrate were added to the calculations. For this reason, attractive forces could be underrepresented in the calculations, giving a possible explanation for the larger $\Delta f$ values in theory (Fig. 2D) compared to the experiment (Fig. 1G).

The geometries of the sample molecules were determined by relaxing the atomic positions until the forces were smaller than $10^{-3}$ eV/Å. By comparison of the calculated bond lengths for PAHs with available X-ray diffraction data, e.g. for HBC (34), we estimated an error of about 0.01 Å for the calculated bond length of DBNP (in Fig. 4F).

For the calculation of the frequency shift, we used a CO molecule on a Cu dimer as a model for the CO-terminated tip, which has the advantage that it is rotationally symmetric and therefore does not induce any lateral directional preference of the CO tilting. The atoms of the sample molecule and the Cu dimer were kept fixed. The atoms of the CO molecule were relaxed until the forces were smaller than $10^{-3}$ eV/Å. The interaction energies of the tip and the sample molecule (without substrate) were calculated for various lateral positions with a lateral spacing of 0.1 Å and for tip heights ranging from $d = 3.95$ Å to $d = 3.35$ Å with a vertical spacing of 0.025 Å. To obtain the frequency shifts, the interaction energies were numerically differentiated twice with respect to $d$.

Calculation of the resulting forces upon lateral displacement of the O atom at the Cu₂CO tip yielded a calculated lateral spring constant of $k_{Cu2} = 0.5$ N/m. We also explored tips with CO attached to a Cu₃, a Cu₅, and a Cu₁₄ cluster, which resulted in lateral spring constants of $k_{Cu3} = 1.0$ N/m, $k_{Cu5} = 1.3$ N/m, and $k_{Cu14} = 0.3$ N/m, respectively. For an Au₅ cluster we obtained $k_{Au5} = 1.6$ N/m. Note that for all these tips, in contrast to the Cu₂ tip, the lateral spring constants also depend on the azimuthal direction due the broken cylindrical symmetry. The results compare reasonably well with the
estimated lateral spring constant of CO/Cu(111) of 2.1 N/m (31). However, our experimental data obtained on C₆₀ show a larger distortion compared to the calculations. Note that the maxima Δf(x) in the experiment (Fig. 1G) are found at larger absolute values of x compared to calculated line profiles (Fig. 2D). This indicates that the effective lateral spring constant in the experiment is smaller than the calculated \( k_{Cu2} = 0.5 \text{ N/m} \). Also the smaller calculated lateral spring constant of the COCu₁₄ tip with respect to the COCu₂ tip indicates that the lateral spring constant of \( k_{Cu2} = 0.5 \text{ N/m} \) overestimates the stiffness with respect to a macroscopic tip. However, calculations with clusters as large as 14 Cu atoms were too expensive to be carried out. On the other hand, the Cu₂ cluster seems better suited to model the tip than the Cu₃ and Cu₅ clusters, which show even larger lateral spring constants. In summary, we used the Cu₂ cluster as the metallic part of the tip in our calculations, because (i) its spring constant seems to be similar to that of a large Cu cluster (Cu₁₄), (ii) it shows spherical symmetry, and (iii) the small number of only 2 Cu atoms reduces the computational costs.

For a comparison of calculated images of the interaction energy with Δf images, it is important to note that interaction energy (E), vertical force (F), and frequency shift (Δf) are related to each other by differentiation along d and their images show similar features. If we compare the distance dependence of these quantities, we observe that their maxima are usually separated by 0.45 Å in d. That is, when the minimum interaction energy \( E(d)_{\text{min}} \) is found at \( d_0 \), then \( F(d)_{\text{min}} \) is usually found at \( d_0 + 0.45 \text{ Å} \) and \( Δf(d)_{\text{min}} \) is found at \( d_0 + 0.9 \text{ Å} \). Furthermore, the image of the interaction energy at d is qualitatively similar to the force image at \( d + 0.45 \text{ Å} \) and to the Δf image at \( d + 0.9 \text{ Å} \) (28). Therefore, the interaction energy calculated at \( d = 2.9 \text{ Å} \) (Fig. 2A) can be qualitatively compared to the Δf image calculated at \( d = 3.8 \text{ Å} \) and the experimental Δf map at \( z = 3.8 \text{ Å} \) (Fig. 1B). However, this simple comparison is not valid when relaxations of the tip geometry, which are distance-dependent, play an important role. Therefore, the comparison of the calculated energy at \( d_0 \) with the frequency shift at \( d_0 + 0.9 \text{ Å} \) cannot be used for small tip separations. In this case, the interaction energy E has to be calculated for several tip heights to extrapolate E(d) and Δf(d) has to be calculated as the second derivative of the interaction energy E with respect to d (as done in Fig. 2D). This and the relaxation of the whole tip-sample system make the calculations of entire Δf images including the relaxations too complex to be carried out within feasible time. The calculation of the Δf(x) line profiles (Fig. 2D) took about a week computation time on a large computer facility.

3. Statistical analysis of bond distances in C₆₀ in published X-ray structures

The analyses were carried out from the Cambridge Structural Database (CSD 2012, update 5.33) of the Cambridge Crystallographic Data Centre (CCDC). We only selected the structures without disorder, without crystallographic errors, without ions, obtained by single-crystal diffraction, and with a quality factor \( R_f < 0.075 \) and excluding organometallic complexes. Using these limitations, 62 X-ray structures of unsubstituted C₆₀ were selected. For each structure, the analysis was done on 60 \( p \) bonds (fusing a pentagon and a hexagon) and 30 \( h \) bonds (fusing 2 hexagons). The \( p \) bonds distances ranged from 1.41 Å to 1.575 Å with a mean value of 1.454 Å (median: 1.452 Å) and with
a statistical estimated standard deviation (esd) of 0.012 Å. The $h$ bonds distances ranged from 1.039 Å to 1.633 Å. The analysis was limited to error-free measurements in the range 1.30 Å to 1.55 Å and led to a mean value of 1.38 Å (median: 1.38 Å) with a statistical esd of 0.02 Å.
Fig. S1.
Constant-height AFM measurement of HBC on Cu(111) using a CO tip (low-pass filtered). Tip height $z = 3.7$ Å, amplitude $A = 0.3$ Å, sample bias voltage $V = 0.0$ V. The line profiles used for $\Delta f$ determination are indicated.
Fig. S2
Constant-height AFM measurements at minimal tip heights. (A) HBC on Cu(111) using a CO tip, tip height $z = 3.2$ Å, amplitude $A = 0.35$ Å, sample bias voltage $V = 0.0$ V. (B) DBNP on NaCl(2ML)/Cu(111) using a CO tip, $z = 3.2$ Å, $A = 0.48$ Å, $V = 0.0$ V. Note the asymmetric bright features inside the aromatic rings arising for such small tip heights. In the case of (A), the bright features appear with a relatively large lateral shift towards the top left of each ring. In the case of (B), the features appear with a lateral shift towards the left of each ring.
Fig. S3
Constant-height AFM measurement of HBC on Cu(111) using a CO tip (Laplace- and low-pass filtered). Tip height $z = 3.5$ Å, amplitude $A = 0.35$ Å, sample bias voltage $V = 0.0$ V. The lines used for the determination of the apparent bond lengths are indicated.
References and Notes


22. Supplementary materials are available on Science Online.


27. In the calculations, \( d \) denotes the distance between the O atom of the unrelaxed tip (i.e., for \( \Delta x = 0 \)) and the plane of the imaged atoms. In the experiment, the tip height was measured with respect to the STM set point; therefore, there is an offset with respect to \( d \). Comparison with theory (10, 28) shows that the minimum of \( \Delta f(d) \) above a carbon ring is usually found at \( d = 3.9 \) Å. By measuring the tip height that yielded the minimum of \( \Delta f(z) \) in the experiment and by setting this height to \( z = 3.9 \) Å, we determined the offset and adjusted all other tip heights of a measurement series by applying the same offset. Therefore, the experimental \( z \) values correspond to the theoretical \( d \) values and approximately reflect the atomic tip-sample separation.


33. C$_{60}$ and HBC could not be stably imaged by AFM on NaCl films with atomic resolution because they were laterally manipulated when using small tip heights. In contrast, DBNP could be imaged on bilayer NaCl on Cu(111) and was investigated on this surface to demonstrate that bond-order discrimination is possible on different substrates.


35. As vdW background forces also induce substantial tilting of the CO tip, the apparent bond length can only be compared if the vdW background is constant, which is given in the central part of planar molecules. The bond length measured for C$_{60}$ cannot be compared with the bond length measured for planar molecules, because the vdW background is not constant in the region around the $p$ and $h$ bonds due to the spherical shape of C$_{60}$, resulting in additional lateral distortions. However, the $p$ and $h$ bonds can be compared with each other because of their similar vdW background.


