

Quantitative Atomic Force Microscopy with Carbon Monoxide Terminated Tips

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Noncontact atomic force microscopy (AFM) has recently progressed tremendously in achieving atomic resolution imaging through the use of small oscillation amplitudes and well-defined modification of the tip apex. In particular, it has been shown that picking up simple inorganic molecules (such as CO) by the AFM tip leads to a well-defined tip apex and to enhanced image resolution. Here, we use the same approach to study the three-dimensional intermolecular interaction potential between two molecules and focus on the implications of using molecule-modified AFM tips for microscopy and force spectroscopy experiments. The flexibility of the CO at the tip apex complicates the measurement of the intermolecular interaction energy between two CO molecules. Our work establishes the physical limits of measuring intermolecular interactions with scanning probes.

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Scanning probe methods have been the workhorse of nanotechnology in obtaining atomic-scale structural and electronic information. While earlier experiments relied mostly on scanning tunneling microscopy (STM) [1–4], noncontact atomic force microscopy (AFM) has recently revolutionized the field of atomic-scale imaging by the impressive demonstrations of atomic resolution on bulk and ultrathin insulators and atomic identification and manipulation at room-temperature on semiconductor surfaces [5–10]. Improvements in AFM instrumentation have further extended these possibilities as demonstrated by the structural characterization of single crystal surfaces and isolated organic molecules with unprecedented spatial resolution [11–15]. These advances are based on the use of a quartz tuning fork force sensor operating with very small tip oscillation amplitudes, down to a fraction of an Ångström [16,17]. As a consequence, the measured frequency shift Δf (proportional to the force gradient) is dominated by the short range (chemical) forces allowing the interaction energies to be measured down to the atomic scale [10,14,16–19].

Previous experiments have shown that using a carbon monoxide terminated tip (formed by controlled vertical manipulation of CO from the sample surface onto the tip) yields a well-defined tip apex and enhanced image resolution [12,20]. Here, we use the same approach and present precise measurement of intermolecular forces between two CO molecules: one adsorbed on the Cu(111) single crystal substrate and the other on the AFM tip as schematically illustrated in Fig. 1. The frequency shift, Δf , is measured as a function of tip-sample distance (z direction) and lateral distance between tip and the adsorbed CO molecule. By performing this experiment with a metal-terminated and a CO-terminated tip, a three-dimensional map of the intermolecular interaction potential with

subatomic resolution is obtained. At sufficiently large intermolecular separations this approach yields the “true” intermolecular interaction, i.e., a combination of chemical repulsion (due to the Pauli exclusion principle) and van der Waals (vdW) attraction, as a function of the distance and angle between the two aligned CO molecules. Comparison of the experimental results with detailed

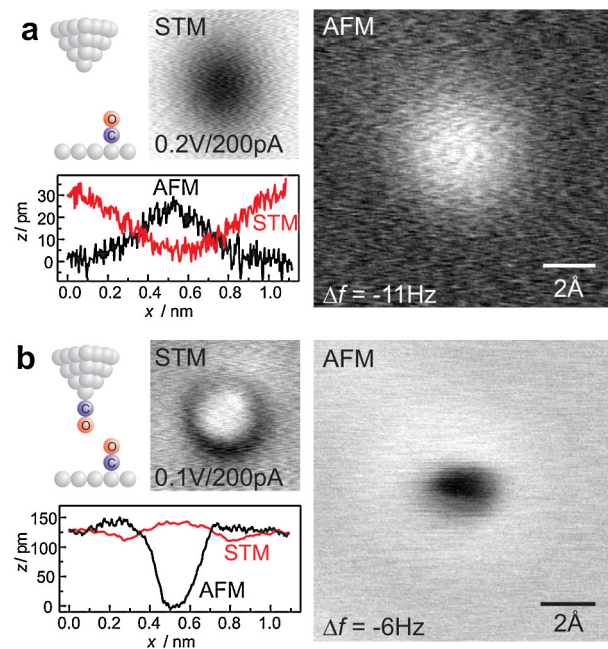


FIG. 1 (color online). STM and AFM images of a CO molecule adsorbed on Cu(111) surface acquired with (a) a clean metal tip and (b) a tip that is terminated by a CO molecule. The line profiles are taken from the images across the middle of the CO molecule. All images are $11 \times 11 \text{ \AA}^2$. Images were recorded under constant current (STM) or frequency shift (AFM) with setpoints indicated in the figure.

density-functional theory (DFT) calculations also shows the limits of atomically resolved force spectroscopy as the adsorbed CO molecules reorient when the Pauli repulsion becomes too strong at short tip-sample distances.

We carried out the experiments on the (111)-terminated copper single crystal, which was cleaned by several sputtering-annealing cycles. The AFM and STM experiments (LT-STM equipped with the QPlus force sensor, Omicron Nanotechnology GmbH) were carried out in ultra-high vacuum (base pressure $<10^{-10}$ mbar) at $T = 4.7$ K. The QPlus sensor (resonance frequency 21 575 Hz and quality factor of 21 600) was used in the frequency modulation mode with a tip oscillation amplitude of $A = 67$ pm. All the AFM experiments were carried out at zero bias voltage. The tip was cleaned by controlled contact with the copper surface, resulting in a copper-coated tip. A CO molecule was vertically manipulated onto the tip as described previously and it adsorbs with the carbon atom toward the metal tip [12,21]. The presence and orientation of the CO molecule on the tip was verified by the shape and the characteristic change in the STM contrast of imaging another CO molecule from a depression (metal tip) to a protrusion (CO terminated tip) as illustrated in the insets of Figs. 1(a) and 1(b) [12,21]. AFM images acquired under constant frequency shift conditions are shown in Figs. 1(a) and 1(b) with a clean metal tip and a CO terminated tip, respectively. CO imaged with a metal tip appears as a protrusion (height ca. 25 pm as can be seen in the cross-sectional profile shown in Fig. 1(a) indicating that there are attractive interactions between the tip and the CO molecule on the surface. Decreasing the Δf setpoint further results in lateral manipulation of the CO molecule. In contrast, CO appears as a depression—provided that the Δf setpoint is sufficiently negative—when imaged with a CO-terminated tip. This indicates that we are able to approach the CO sufficiently close such that repulsive short range chemical interactions contribute significantly to the total force gradient. This reduces the total attractive (Δf is still negative) interaction and the tip has to approach the surface to maintain constant Δf . Again, decreasing the Δf setpoint further resulted in lateral manipulation of the CO along the surface. In either case, there is no evidence of the threefold symmetry of the underlying Cu(111) surface [12,15,17,22].

To get a more quantitative handle on the interaction of the tip (either metallic or functionalized with a CO molecule) with the CO on the surface, we acquired constant height line scans at different tip-sample distances over the CO molecule. The results obtained with a CO terminated tip are shown in Fig. 2(a). Before further analysis of the frequency shift directly above a CO molecule, the measured background signal (independent of the lateral position) due to the vdW interaction between the tip and the Cu substrate was subtracted from the line scans [see Fig. 2(b)]. It can be seen that the background-corrected signal is

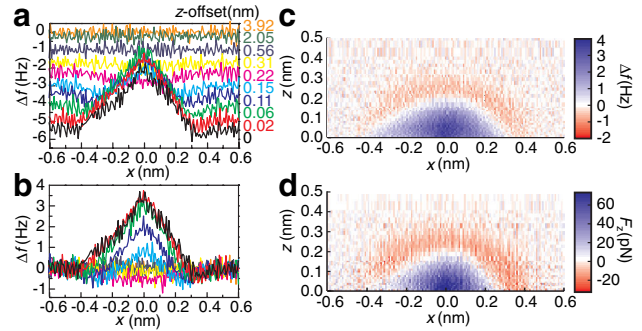


FIG. 2 (color online). Mapping the force landscape over a CO molecule. (a) Frequency shift measured by constant height line scans over a CO molecule with a CO molecule adsorbed at the tip apex. Numbers indicate the z height of the line scans with respect to the closest achievable tip-sample separation; i.e., $z < 0$ results in lateral manipulation of the CO. (b) Same data after removing the constant background due to the Cu(111) substrate. (c) The background-corrected Δf and (d) the corresponding vertical force F_z landscape presented in a color scale plot for the CO terminated tip as a function of the horizontal position and tip-sample distance.

attractive at large tip-sample distances ($z > 0.2$ nm). As we reduce the tip-sample separation, we find an increasing repulsive interaction that starts to saturate at the closest achievable distances ($z < 50$ pm). The data are represented in a color scale plot in Fig. 2(c), where x is the lateral position ($x = 0$ indicates the position directly above the CO molecule) and z the tip-sample distance. The height $z = 0$ is taken as the closest achievable tip-sample separation; approaching the tip more closely resulted in lateral manipulation of the adsorbed CO molecule. We used the Sader-Jarvis method to convert the measured Δf to the vertical force F_z [23]. The calculated vertical force map obtained with a CO terminated tip over an adsorbed CO molecule is shown in Fig. 2(d). It indicates the presence of both attractive (red) and repulsive (blue) regions depending on the lateral and vertical position of the tip. We have carried out the same experiment using a clean metallic tip and consistent with the AFM imaging, we only detect attractive force between the metallic tip and adsorbed CO molecule.

The interaction potential between the tip and the substrate can be obtained by integrating the vertical force. The results for the background-corrected potential values are shown in Figs. 3(a) and 3(b) for the CO-terminated and clean metal tips, respectively. As already suggested by the force maps, the interaction between the CO-terminated tip and the adsorbed CO molecule have both repulsive and attractive contributions, whereas only attractive contributions are present with a clean metal tip. To obtain further insight into the measured interaction energy maps, we have carried out a DFT (ADF 2009.01B program with the dispersion corrected Perdew-Burke-Ernzerhof functional and triple-zeta plus double polarization basis

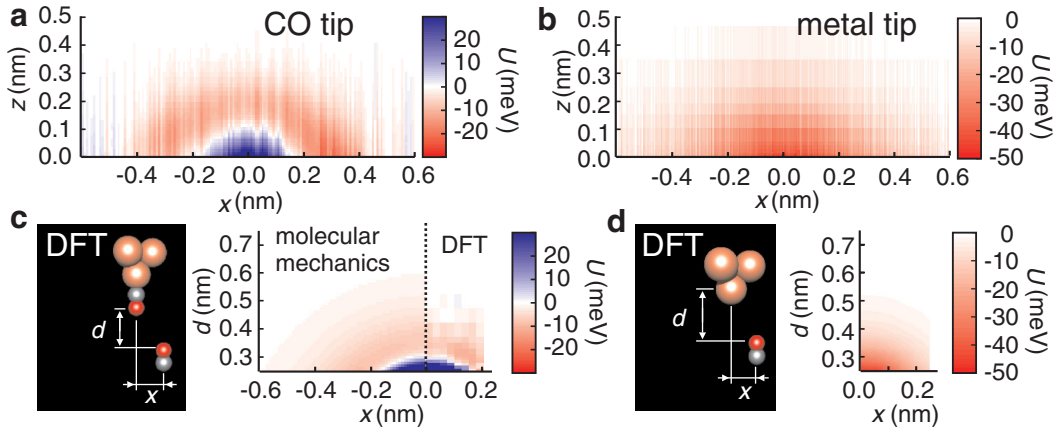


FIG. 3 (color online). Experimental interaction energy obtained by integration of vertical force data with (a) a CO terminated and (b) a clean metal tip. (c) Calculated interaction energy between two CO molecules based on molecular mechanics between two isolated CO molecules and DFT calculations between a CO molecule and a CO adsorbed on a Cu_4 cluster. (d) The corresponding DFT calculation for the interaction energy between a Cu_4 cluster and an isolated CO molecule.

set [24–26]) and molecular mechanics (COMPASS force field [27]) calculations. The molecular mechanics calculations were included to validate the use of the semiempirical vdW correction in the DFT calculations. The results for two isolated CO molecules (based on molecular mechanics) are shown in the left half of Fig. 3(c). The other half of the panel shows the interaction energy calculated by DFT between an isolated CO molecule and a CO molecule adsorbed on a Cu_4 cluster, which serves as a simple model of the AFM tip. The DFT results agree well with the force field-based calculation. As can be seen, these model calculations without geometry relaxation agree with the experiment in a semiquantitative fashion. They correctly reproduce the magnitude and extent of the attractive part of the interaction potential, which is mostly due to attractive vdW interaction between the two CO molecules. However, both DFT and molecular mechanics overestimate the repulsive potential at short distances, which we will show to result from the elasticity of the adsorbed CO molecules (vide infra).

The purely attractive interaction in the case of a clean metal tip can also be reproduced by the DFT calculations, where we use a Cu_4 cluster as a very simple model of the AFM tip and calculate its interaction with an isolated CO molecule [Fig. 3(d)]. The negative U is due to the attractive vdW interaction and, at shorter distances, chemical bonding between the last tip atom and the oxygen atom in CO.

We have carried out more detailed DFT calculations including Cu_4 and Cu_{10} clusters as simple models of the tip and the substrate, respectively, in order to understand why the measured repulsive interaction between two CO molecules is much weaker than that calculated between two aligned CO molecules [Fig. 4(a)]. The geometries of the Cu clusters were fixed, and the CO molecules were allowed to relax (with no symmetry restrictions) to minimize the total energy of the system. As can be seen in the calculated geometries at different distances, both CO

molecules undergo relaxation as the tip-substrate distance is decreased. This reduces the repulsive interaction and brings the calculated interaction energy [(blue circles] significantly closer to the experimental results [(red squares)] [Fig. 4(b)]. Hence, chemical repulsion between the CO molecules is relaxed at the expense of weaker bonding of the CO molecules to the Cu atoms of the tip and substrate, respectively.

What is actually measured in our experiment? This is generally problematic in AFM, where it has been realized that the tip structure and relaxation usually has to be considered in understanding the force response [28–30]. The background correction procedure implies that we are measuring the energy difference (ΔU) between a CO molecule adsorbed on the tip on top of a clean Cu(111) surface (U) and on top of a CO molecule adsorbed on the substrate (U') (at a given tip-sample separation) [see Fig. 4(b)]:

$$\begin{aligned} \Delta U = & U'_{t-\text{CO}(s)} + [U'_{s-\text{CO}(s)} - U_{s-\text{CO}(s)}] \\ & + [U'_{s-\text{CO}(t)} - U_{s-\text{CO}(t)}] + [U'_{t-\text{CO}(t)} - U_{t-\text{CO}(t)}] \\ & + U'_{\text{CO}(s)-\text{CO}(t)} \end{aligned} \quad (1)$$

where $\text{CO}(t)$ and $\text{CO}(s)$ refer to the CO molecule adsorbed on the tip and substrate. In the absence of relaxation, all the terms in the parentheses are zero. Based on the data shown in Fig. 3, we can estimate that the $|U'_{t-\text{CO}(s)}| < 10$ meV even for the shortest distances shown in Fig. 4. In this case, it is possible to extract the interaction energy between the two CO molecules [$U'_{\text{CO}(s)-\text{CO}(t)}$] directly from the experiment as it forms the major contribution to the measured interaction energy. However, if the CO molecules structurally relax, the terms in the parentheses are nonzero. While $|U'_{s-\text{CO}(t)} - U_{s-\text{CO}(t)}|$ is small as vdW forces between the substrate and CO adsorbed on the tip are not very sensitive to the small changes in the orientation and

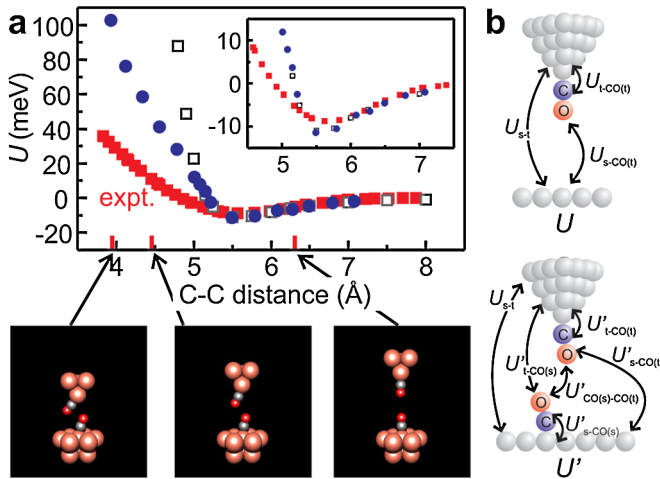


FIG. 4 (color online). Effect of relaxation on the force distance curves. (a) The experimental background-corrected interaction energy directly above a CO molecule [filled (red) squares, data taken from Fig. 3(a)] compared with DFT calculation of two isolated CO molecules without geometry relaxation (open gray squares) and the full model that includes Cu_4 and Cu_{10} clusters as tip and substrate models, respectively, and where the CO molecules are allowed to relax [filled (blue) circles]. Inset is a zoom-in into the attractive regime. The DFT energies correspond to the experimental situation, that is, the energy difference between a CO-modified tip approaching a bare metal substrate or an adsorbed CO molecule. The tip-sample distance in the experimental data has been shifted to overlay the vdW part of the interaction potential with the theoretical predictions. The lower images show the relaxed geometry at tip-substrate distances indicated by the arrows. (b) Schematics of the different interaction energy terms for the case of an CO-terminated tip on top of a clean metal substrate [top, term $U_{s-\text{CO}(s)}$ not indicated] and on top of an adsorbed CO molecule (bottom).

rotation of the CO, this is not necessarily the case for $|U'_{s-\text{CO}(s)} - U_{s-\text{CO}(s)}|$ and $|U'_{t-\text{CO}(t)} - U_{t-\text{CO}(t)}|$. The decreased repulsion between the CO molecules due to the geometric relaxation occurs at the expense of these adsorption energy terms. Finally, the problem with the $U'_{t-\text{CO}(s)}$ term is that it cannot be directly measured experimentally as it is the interaction between the tip and the relaxed CO geometry.

It is striking that the interaction potential between two adsorbed CO molecules measured with an AFM resembles so accurately the potential between two isolated CO molecules. This implies that the electron distribution in either CO molecule is not substantially perturbed by bonding to the tip and copper substrate (in agreement with earlier findings [31]), and that the CO molecules do not change their absorption geometry as a function of the tip-sample distance. However, at close tip-sample distances, chemical repulsion between the CO on the tip, and the molecule under investigation can cause atomic reconfiguration, which limits the achievable resolution both in imaging and force spectroscopy. These effects are expected to be

general and occur in all noncontact AFM experiments employing molecule-terminated tips.

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