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Meeting-report

Atomic Force Microscopy Imaging of Individual CO Molecules Adsorbed on a Cu(111) Surface

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CO-functionalized atomic force microscopy (AFM) refers to attaching a single CO molecule onto a metallic Cu tip (C bonded with Cu). This CO molecule serves as a molecular probe, enabling the direct probing of atomic/subatomic features of the specimen in real space. As of now, CO tip AFM has achieved numerous accomplishments, such as imaging complex molecular [1] and surface structures [2], distinguishing bond orders [3], and identifying different functional groups [4] or atomic species [5]. Our recent work has also achieved the controlled manipulation of a single chemical bond [6] and the direct observation of electron orbital signatures [7]. Despite the significant achievements of CO tip AFM, a fundamental question remains unresolved – determining the absolute height between the CO tip and the sample during imaging.

We can only measure the relative tip height concerning a setpoint in the experiment. This accounts for why negative heights are often reported on experimental images. In theory, researchers have obtained data from different models ranging from less than 3 Å to over 15 Å. The uncertainty in tip height prevents us from precisely discerning how the tip interacts with the sample and identifying the exact nature of what we had probed. We employed a combined experimental and theoretical approach to address this puzzle. Our experiments were conducted using a combined STM/AFM system (CreaTec) under ultrahigh vacuum conditions and at a temperature of 4.8 K. The qPlus sensor had a resonance frequency of 33 KHz with a spring constant k = 1,800 N/m, which dropped to 31 KHz after gluing on a Pt/Ir tip. The quality factor in our measurement was about 20,000. For the theoretical aspect, we utilized real-space pseudopotential calculations [8] based on density functional theory (DFT) to simulate AFM images [9-10] at different tip heights and compute the force spectra.

In our experiment, we constructed the system using a CO-functionalized AFM tip mounted on a qPlus sensor to perform AFM imaging of CO molecules adsorbed on a Cu(111) surface at different tip heights. Our experimental AFM images (Figs. 1 (A-C)) and AFM images simulated by DFT (Figs. 1(D-F)) showed good agreement. Although we could not determine the absolute tip height experimentally, through simulation, we could infer that the bond-like feature between COs occurs at around 2.9 Å, implying that Fig. 1(B) was taken at a tip height of ~ 2.9 Å.

Furthermore, to obtain more accurate imaging heights for each image, we conducted vertical force measurements directly above a surface CO (Fig. 2A). By comparing the experimentally measured force curve (Fig. 2B) with the force curves (Fig. 2C) calculated using DFT, we found that the use of local density approximation (LDA - CA) [11] overestimates the force equilibrium tip height, while the generalized gradient approximations (GGA - PBE) [12] underestimate the tip height. As a result, we mixed our calculation results by a certain proportion so that the shape of the calculated force curve could better match the experimentally measured curve (Fig. 2D). By doing this, we found that the force equilibrium height is 3.2 Å, and the bond-like feature between COs starts to appear at 2.9 Å, which is in the repulsive regime.

Our work demonstrates that AFM imaging can be conducted in the attractive regime and under the dominance of Pauli repulsion, accurately pinpointing the imaging height. We also elucidate why AFM images are often height-dependent and distorted at small tip heights. When imaging in the repulsive regime, we can observe additional fine structures of the specimen. Our findings can play a crucial role in advancing the capabilities of AFM in characterizing complex molecular systems [13].

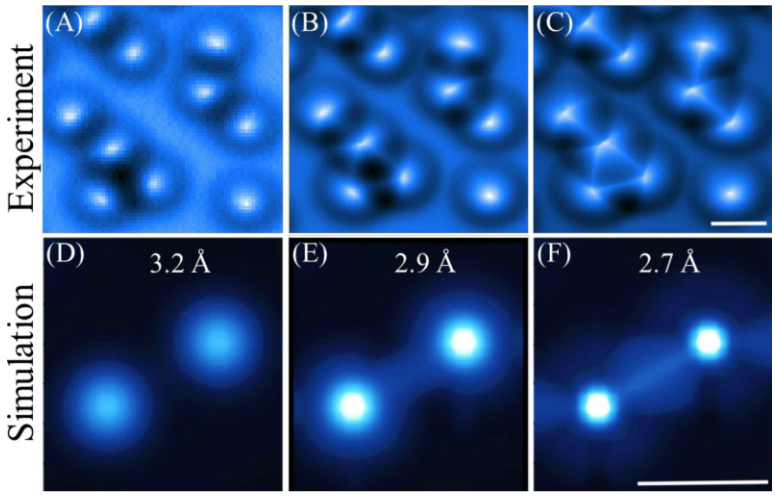

Fig. 1. (**A-C**) Experimental and (**D-F**) simulated AFM images of CO clusters on a Cu(111) surface (CO tip). The tip heights in our simulated images are 3.2, 2.9, and 2.7 Å, as labeled in the figure. Scale bars in (**C**) and (**F**) = 4.4 Å, the CO-CO separation distance.

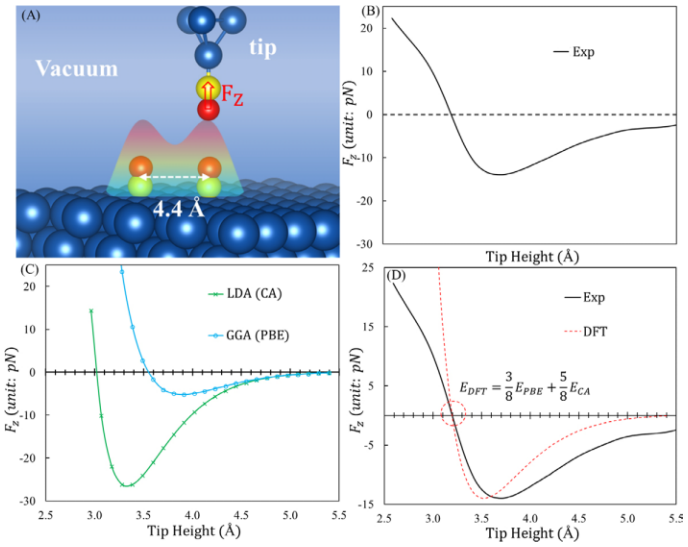

Fig. 2. (**A**) A schematic figure of the tip-sample system. (**B**) Experimentally measured and (**C-D**) theoretically calculated vertical force Fz (pN) acting on the CO tip when it is placed on the top of a surface CO. (**C**) shows the results calculated by solely using LDA (CA) and GGA (PBE). (**D**) shows the results calculated by combining PBE and CA. The red dashed circle shows the force equilibrium tip height is 3.2 Å.

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