Supporting information for

The electric field of CO tips and its relevance for atomic force microscopy

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Table of Contents

1 Model
1.1 Description of the tip-sample interaction potential
1.2 Fitting of the short range interactions
1.3 Cl vacancy on a NaCl/Cu(100) Surface
1.4 CO tilting: DFT versus model calculations
1.5 DFT calculation details
2. Interaction decomposed images
3. CO-Cu tips
3.1 Charge density of CO functionalized Cu tips in DFT
3.2 Electrostatics of CO functionalized Cu tips in DFT
3.3 Choice of dipole size
3.4 Effect of the extension of the electric fields created by the CO and Cu metal tip on the AFM images 12
4. Additional series of experimental measurements: tip sharpness

1 Model

1.1 Description of the tip-sample interaction potential

AFM images of a Cl vacancy on a NaCl(100) bilayer supported on Cu(100) (see section 1.3 for details) probed with a Cu metal cluster decorated by a CO molecule are simulated by minimizing the potential:

$$V = V_{tilt} + V_{vdW} + V_{SR} + V_{ES}$$
(S1)

for the probe relaxation.

The CO tilting is defined through:

$$V_{tilt} = \frac{1}{2} \kappa \delta^2 \theta^2 \tag{S2}$$

where δ = 302 pm is the lever arm (distance from the outmost Cu atom of the tip to the O of the CO probe), and κ = 0.24 N/m [1] is the spring constant (see section 1.4 for a discussion of this approximation).

As in the DFT calculations used to obtain the parametrization of the model, the vdW contribution is approximated using the DFT-D3 method [2]. All the atoms from the sample (Na, Cl, and Cu), the CO probe, and the metal tip, modeled by a 20 atom Cu cluster, are included in the calculation. Although absolute vdW forces depend on the size of the tip, the overall force contrast is well converged for this cluster size.

The short range (SR) contribution is approximated using a sum of pair-wise interactions between the CO probe and the Na(Cl) sample atoms. We have found that the best description of each of these interactions is obtained with a Morse potential:

$$V(r) = D_e \left(\left(1 - e^{-a(r-r_e)} \right)^2 - 1 \right),$$
(S3)

where D_e , a, r_e are the well depth, width of the potential, and equilibrium bond distances. The fitting procedure of these species-dependent parameters is described in the next subsection.

The electrostatic interaction (ES) is calculated from:

$$V_{ES} = \int \left(\rho_{CO}^0 + \rho_{metal}^0\right) \Phi_{sample}^0 d\mathbf{r}^3,\tag{S4}$$

where ρ_{CO}^0 and ρ_{metal}^0 are the charge density of the CO probe and the Cu metal tip, and Φ_{sample}^0 the electrostatic potential of the isolated surface. The charge distribution and the electrostatic potential are calculated using VASP [3] on a 3D uniform mesh with ≈ 0.075 Å grid spacing. The dipole correction is applied to all the calculations. A uniform 1D filter in the z direction is applied to the volumetric data to eliminate high frequency noise (λ =2 grid points). The charge distribution of the Cu tip is simulated by two opposite localized charged Gaussian distributions (width at half-maximum of 10 pm) separated by 106 pm, that provide a net 1.5 D dipole centered 53 pm from the last Cu atom (see section 3 for a discussion of this dipolar approximation for the Cu tip).

1.2 Fitting of the short range interactions

In order to parametrize the Morse potentials of the SR interaction, we perform static DFT force calculations (see section 1.5 for details on the DFT calculations details) on a clean NaCl bilayer on a 4-layer Cu(100) slab probed by a CO molecule on a 2v2 x 2v2 unit cell with a large vacuum (total cell size 15.9 Å x15.9 Å x 42 Å) (Fig. S1a-b). Force curves were calculated with a 25 pm interval on 3 different sites: Cl, Na, and bridge (defined as the midpoint between a Na and Cl site). Figs. S1c and S1d show the total and vdW forces obtained for those three sites (red, blue, and yellow markers correspond to the Cl, Na, and bridge sites in Fig. S1c-d). The electrostatic interaction is calculated, as in the model, from:

$$V_{ES} = \int \rho_{CO}^0 \, \Phi_{sample}^0 d\mathbf{r}^3 \tag{S5}$$

(Fig. S1e). Finally, the short range (SR) contribution (Fig. S1f) is obtained from:

$$V_{SR}^{DFT} = V_{total}^{DFT} - V_{vdW}^{DFT} - V_{ES},$$
(S6)

and fitted, through a least-squares method, to a sum of Morse potentials:

$$V_{SR} = \sum_{i=Na,Cl\ ions} D_e^i \left(\left(1 - exp[-a^i(|\mathbf{x} - \mathbf{x}^i| - r_e^i)] \right)^2 - 1 \right), \tag{S7}$$

where $|\mathbf{x} - \mathbf{x}^i|$ is the distance between the O atom in the CO probe and the corresponding ion, D_e^i (well depth), a^i (that controls the inverse of the width of the potential), and r_e^i (equilibrium bond distance) are the species dependent parameters determined by the fitting, and the sum extends to all the Na(Cl) atoms of the ionic surface.



Results for the total, vdW, electrostatic, and short range forces on the 3 sites are plotted in Fig. S1c-f.

Figure S1: a) Front view of the relaxed clean NaCl/Cu(100) surface used in the DFT spectroscopy calculations. b) Lateral view of the surface along with the CO probe. c) Total, d) vdW, e) electrostatics (ES), and f) short range (SR) forces for Cl (blue), Na (red), bridge (yellow) and hollow (gray) sites. Markers correspond to DFT data while the lines to calculations with the model. The Cl, Na, and bridge sites were used in the parametrization of the SR interaction, while the hollow site is calculated to show the ability of the model to reproduce the DFT results on any point of the surface.

Bullets correspond to the values obtained from DFT calculations while lines represent the results from the model. Note that the DFT-D3 theory is used to estimate the vdW interaction both in the DFT calculations and in the model; hence, markers and lines of Fig. S1d are identical. For the three sites, forces calculated with DFT and the model are in excellent agreement. Table S1 shows the fitted parameters.

	D _e (Hartree)	a (Bohr ⁻¹)	r _e (Bohr)
Na-CO	8.15E-15	1.62	12.82
CI-CO	7.65E-05	0.80	8.61

Table S1: Morse potential parameters fitted from DFT calculations. These parameters provide an excellent fit to the DFT force curves.

In order to assess the transferability of our model to sites different from the ones included in the SR fitting, we have tested the predictions of the model for a new site: a hollow position (defined as the midpoint between two Cl atoms). Fig. S1 shows the excellent agreement between the DFT calculations (grey markers) and the model (grey lines) on this site.

1.3 Cl vacancy on a NaCl/Cu(100) Surface

In the model, we simulate the surface imaged in the experiments with a single Cl vacancy on a NaCl bilayer supported on a 2-layer Cu(100) slab. We use a 6x6 surface unit cell and a large vacuum (33.7 Å x 33.7 Å x 48 Å)

(see Fig. S2). The main structural difference with respect to the clean NaCl bilayer is that Na ions adjacent to the vacancy shift away from the vacancy approximately 30 pm; while the Cl ions shift towards the vacancy by 15 pm (Fig. S2b). In addition, the Cl ions adjacent to the vacancy also shift away from the substrate approximately 30 pm (Fig. S2c). Section 1.5 presents details of the DFT ionic relaxations carried out on this surface.



Figure S2: a) Cell used for the simulation of AFM images. The cell size is $(33.7 \times 33.7 \times 48)$ Å³. It includes a NaCl bilayer with a Cl vacancy (143 Cl atoms and 144 Na atoms), on 2 layers of Cu(100) (324 atoms). b) Top and c) lateral view of the atoms near the vacancy (area marked by dashed lines in the left panel). Na atoms adjacent to the vacancy relax away from the vacancy, while Cl atoms relax towards the vacancy. In addition, the Cl atoms shift away from the substrate.

1.4 CO tilting: DFT versus model calculations

In order to corroborate that the spring model with δ = 302 pm and κ = 0.24 N/m treats the CO tilting correctly, we have carried out DFT force calculations (see section 1.5 for details on the DFT calculations details) of a clean NaCl bilayer on a 4-layer Cu(100) slab probed by a Cu₂CO tip in a small (7.95 Å x 7.95 Å) unit cell (Fig. S3a). Fig. S3b shows DFT force curves with (dash) and without (solid) relaxation of the CO probe. Fig. S3c shows force curves calculated with the model on the sites mentioned above. The quantitative and qualitative behavior of the CO bending is well described by the model.

The arm length, δ = 302 pm, used to describe the tilt of the CO molecule on the Cu tip is obtained from DFT calculations of a CO molecule adsorbed on a 4 layer (111)-oriented Cu tip (Cu20 tip). It is the length from the O atom to the outmost Cu atom. This arm length is well converged for this tip size. It is worth noting that the CO bond length calculated from DFT is 115 pm, thus the C-Cu adsorption length is 187 pm.



Figure S3: a) Lateral view of DFT cell and Cu2CO probe used in calculation. b) Force curves with (dashed) and without (solid lines) CO tilting. The tip was moved in 25 pm intervals. c) Forces computed with the model (only the CO probe was used as a tip).

1.5 DFT calculation details

All density functional theory (DFT) calculations were carried out using project augmented wave functions (PAW) as implemented in VASP [3]. We have used the PBE exchange-correlation functional supplemented by semiempirical DFT-D3 van der Waals (vdW) interaction [2], a plane wave cuttoff of 400 eV, and fine electronic convergence ($E_{SCF} = 10^{-4}$ eV) on all calculations. Furthermore

- Section 1.2 calculations used a 3x3x1 grid for the sampling the Brillouin zone.
- Section 1.3 calculations used a 7x7x1 grid for the sampling of the Brillouin zone and ionic relaxations were considered converged when forces were less than 10⁻² eV/Å.
- Section 1.4 calculations used the Γ point for the sampling of the Brillouin zone and ionic relaxations were considered converged when forces were less than 1x10⁻² eV/Å.

2. Interaction decomposed images

In the main text, we discuss the FM-AFM image contrast of a Cl vacancy on a NaCl bilayer supported on a Cu substrate in terms of the short-range, electrostatics, and van der Waals contributions to the total probe-sample force (Fig. 3 of the main text). Fig. S4 illustrates the decomposition of the frequency shift (Δ f) in terms of each of these interaction components.



Figure S4: a) Total frequency shift with (solid) and without (dashed lines) relaxation of the CO probe for the vacancy (green), Cl (blue), and Na (red) sites. b) Frequency shift decomposed spectroscopy for the above sites in terms of short range (solid), electrostatics (dashed), and van der Waals (dotted lines) interaction. Frequency shift decomposed images in terms of the above mentioned interactions for c) $z_T = 375$ pm and d) $z_T = 650$ pm. In order to highlight the influence of each contribution on the total frequency shift, the frequency shift limits are scaled to keep the frequency shift range in all contributions equal to the total frequency shift range.

Fig. S5 shows 4 sets of force decomposed images as well as tip relaxation for probe-sample distances z_{τ} = 1000 pm, 650 pm, 400 pm, 375 pm, and 300 pm. Forces are again decomposed in terms of short-range, electrostatics, and van der Waals contributions. Images in the bottom row illustrate the tilting of the CO probe. The lines show trajectories of the O atom when the tip is scanned along a rectangular grid. Between 1100 pm and 650 pm no tilting occurs. At 400 pm already significant tilting of the CO tip occurs and the O avoids the Cl sites. At 300 pm the oxygen atom almost exclusively moves above the Na sites.



Figure S5: Total force and force decomposed images in terms of short-range (SR), electrostatic (ES), and vdW interactions contributions for $z_T = 1000 \text{ pm}$, 650 pm, 400 pm, 375 pm, and 300 pm. In order to highlight the influence of each contribution on the total force, the gray scale in all of the images corresponds to the variation range of the total force. The bottom row represents CO tilt. The lines show trajectories of the O atom when the tip is scanned along a rectangular grid (only half of the grid points used to construct the images are shown). Notice that the probe relaxes toward the Na site (low electronic density) and is more pronounced as the tip height distance decreases.

3. CO-Cu tips

3.1 Charge density of CO functionalized Cu tips in DFT

Fig. S6 shows the electronic charge density from which the electrostatic potentials of the tips (Fig. 4 in the main text) were obtained. Figs. S6a-b show the charge density along the xz-plane of the CO molecule and a 4 layer (111)oriented Cu tip (Cu20 tip) functionalized with a CO molecule. The charge density around the oxygen of the CO molecule is only slightly altered by the coupling to the Cu tip. This is confirmed by Figs. S6c-d that show the xyplane averaged electronic charge density of both the CO molecule and CuCO tip in the full range of the charge density and centered around the CO molecule. This result suggests that the electrostatic behavior of the compound Cu-CO tip is additive.

The charge densities were calculated in VASP using project augmented wave functions (PAW) [3]. We have used the PBE exchange-correlation functional, a plane wave cuttoff of 400 eV, fine electronic convergence ($E_{SCF} = 10^{-4}$ eV), the Γ point for the sampling of the Brillouin zone, and a fine 3D uniform mesh with ≈ 0.075 Å grid spacing for the charge distribution.



Figure S6: Electronic charge density of a) CO molecule and b) CuCO tip. c) Full range and d) zoom of the xy-plane averaged charge density of both the CO molecule and CuCO tip.

3.2 Electrostatics of CO functionalized Cu tips in DFT

Fig. S7a shows the z-component of the electric field (E_z) of a 4 layer (111)-oriented Cu tip (Cu20 tip) functionalized with a CO molecule. As mentioned in the main text, the electric field of the CO-Cu tip retains the shape of the CO's electric field (Fig. 4a in the main text) close to the apex. The electron cloud of the oxygen's lone pair creates a

dome-shape electric field near the apex. The Cu tip reduces the strength and extent of the negative dome by surrounding it with a positive electric field.

The charge distribution that produces this field can be approximated by replacing the Cu tip by a dipole of 0.7 D centered 53 pm away from the outmost Cu atom. The size and origin position of the dipole are obtained by a least-squares fitting of the E_z of a Cu20 tip along the axis of symmetry (shown as blue line/markers on Fig. S7c). This dipolar approximation reproduces very well the E_z for larger tip clusters, but fails for tips with less than 4 metal layers. Fig. S7c shows how the E_z of the compound CO-Cu tip (green markers) along the symmetry axis can indeed be described quantitatively as the sum of the contributions from the CO molecule and the +0.7 D dipole representing the tip (green line). Fig. S7b, further confirms this additivity showing that, now in all three dimensions, the Cu-CO tip's E_z calculated with DFT shares the same quantitative and qualitative behavior as the CO-0.7 D dipole's field.



Figure S7: z-component of the electric field (E_z) of a) a CO-Cu tip and b) a 0.7 D dipole and a CO. c) E_z along the symmetry axis of the tip for the CO tip (red marker), Cu tip (blue marker), 0.7 D dipole (blue line), CO-Cu tip (green marker), and 0.7 D dipole plus a CO (green line). The Cu tip's E_z is approximated well by a 0.7 D dipole placed 53 pm from the apex atom (away from the tip). The E_z of the CO-Cu tip is approximated well by the separate fields of the CO probe and the Cu tip.

3.3 Choice of dipole size

In the previous section, we showed that replacing the Cu metal tip by a 0.7 D dipole is a good approximation for the E_z of CO-Cu tips calculated with DFT. However, for the Cl vacancy on the NaCl bilayer, such a small dipole underestimates the electrostatic tip-sample interaction and does not reproduce the experimental contrast of the vacancy at large probe-sample distances, where it appears brighter than the surrounding Cl sites (see Figs. 1a-e in the main text). This is true both for calculations performed with our model as well as for DFT force calculations of this surfaced probed by CO-Cu tips.

The choice of dipole size necessary to reproduce the experimental contrast is difficult. We have chosen it as the smallest dipole needed to reproduce the contrast inversion near the vacancy around $z_T = 500$ pm illustrated in Figs. 1e-g of the main text: While the vacancy is brighter than the adjacent Cl sites in Fig. 1e, they are imaged with similar frequency shift in Fig. 1f, and, finally, Cl ions become brighter in Fig. 1g. Fig. S8 shows that the model reproduces this behavior with a dipole of roughly 1.5 D, approximately twice the value calculated from DFT.

Admittedly, larger dipoles seem to reproduce better the experimental contrast for large probe-sample distances ($z_T > 700 \text{ pm}$). This is illustrated in Fig. S9 where AFM images for the far distance regime are simulated using different dipoles. It is not clear if this discrepancy between the calculated and the effective dipole necessary to

reproduce the experiments reflects the limitations of a pure, perfectly ordered Cu tip to represent the real metal tip structure, an incorrect description of the charge density around the vacancy by the PBE exchange-correlation functional or it arises from a failure in the description of other interactions, like vdW, which are relevant in this distance regime.



Figure S8: Constant-height profiles across the vacancy site using the CO probe and 0 D, 0.7 D, 1.1 D, 1.5 D, 2.5 D, and 5 D dipoles as a Cu tip. Profiles were calculated along the diagonal (following X shape feature) at $z_T = 500$ pm. b) Difference in frequency shift between the vacancy site and Cl ions adjacent to vacancy. A 1.5 D dipole is roughly the minimum dipole size needed to image these two sites with equal frequency shift.



Figure S9: Theoretical AFM images of a Cl vacancy in bilayer NaCl on Cu(100) using a CO probe and dipoles of 0, 0.7, 1.5, and 5 D acting as a Cu tip. The probe-sample distance, z_T , decreases from 1100 to 500 pm. The frequency shift limits corresponding to black (more negative) and white are indicated in the bottom right of each panel. Scale bars correspond to 1 nm.

3.4 Effect of the extension of the electric fields created by the CO and Cu metal tip on the AFM images

Fig. S10a shows the contribution to the electrostatic interaction of the Cu metal (1.5 D dipole), CO probe, and the compound CO-1.5D tip on the vacancy (green), Cl (blue), and Na (red) sites. The main difference between the electrostatic interactions of the CO probe and the compound CO-1.5D tip is obtained on the vacancy site (solid vs. dashed lines). At far distances, the 1.5 D dipole, being 250 pm behind the CO probe (behind the O atom), only probes electrostatically extended sites such as the vacancy. Furthermore, as discussed in the main text, at close probe-sample distances, the short range interaction is the dominant contribution on the contrast formation. Thus, the dipole only contributes to the contrast of the vacancy site with respect to the Cl/Na sites. On the contrary, the very localized electric field of the CO probe is the one responsible for the atomic resolution of the NaCl lattice. These conclusions are clearly illustrated in Figs. S10b-d that show images of the electrostatic interaction at $z_T = 650$ pm using the CO probe, a 1.5 D dipole, and the composite CO-1.5 D probe.



Figure S10: a) Electrostatic interaction of the isolated CO probe (dashed), a 1.5 D dipole simulating the metallic tip (dotted), and the CO-1.5 D probe (solid lines) for the vacancy (green), Cl (blue), and Na (red lines) sites. Electrostatic interaction image using b) isolated CO probe, c) a 1.5 D dipole acting as a Cu tip, and d) the composite CO+1.5 D probe at z_T = 650 pm.

Fig. S11 provides an explanation for this behavior in terms of the lateral extension, 650 pm away from the probe, of the E_z of a) the CO probe and b) the Cu apex (1.5 D dipole) apex. The electric field of the metal apex extends over several lattice positions while the CO's is localized to a single atomic position. Effectively, the metal apex averages the periodic Cl⁻/Na⁺ charges. However, near the vacancy, the metal apex is able to probe the extended vacancy's net positive charge.



Figure S11: Lateral distribution of the E_z of a) the CO probe and b) the 1.5 D dipole (that replaces the Cu tip charge distribution) in the NaCl top surface plane. The composite CO+1.5 D probe is at z_T = 650 pm (as in Fig. S10). The atomic positions of the Cl vacancy on NaCl surface are superimposed. The electric field of the metal tip extends over several lattice sites and effectively averages out the opposite contributions of Na⁺ and Cl⁻ ions to the electrostatic interactions. The field of the CO molecule, confined to a single atomic position, is responsible for the atomic-scale lattice resolution.

4. Additional series of experimental measurements: tip sharpness

Fig. S12 shows an additional series of experimental AFM raw data of a Cl vacancy acquired with a different CO tip. In this case, the total change in tip height *z* between panels (a) and (h) was 1680 pm. For the largest tip heights, the vacancy cannot be resolved anymore. The overall smaller absolute values in frequency shift are a fingerprint of the metal tip behind the CO molecule being sharper than the one used for the experiments in Fig. 1. Even so, the relative contrast between the different sites (Na, Cl, and vacancy) and the tip-sample distances associated contrast changes very much resemble those in Fig. 1. These results show that the macroscopic tip shape/size does not play a decisive role on the local electric field that is relevant for imaging and further corroborates the generality of our findings.



Figure S12: Experimental constant-height AFM measurements for a Cl vacancy with a CO tip different from the one used in the experiments shown in Fig. 1 of the main text. Scale bars correspond to 1 nm.

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