Orthogonal Interactions of CO Molecules on a One-Dimensional Substrate

Min Feng,[†] Pepa Cabrera-Sanfelix,[‡] Chungwei Lin,[†,⊥] Andres Arnau,[‡] Daniel Sánchez-Portal,[‡] Jin Zhao,[§] Pedro M. Echenique,[‡] and Hrvoje Petek[†,*]

[†]Department of Physics and Astronomy and Petersen Institute for NanoScience and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States, [‡]Donostia International Physics Center (DIPC), San Sebastián, Donostia, Spain, Centro de Física de Materiales (CFM-MPC), CSIC-UPV/EHU, San Sebastián 20018, Spain, and Departamento de Física de Materiales, UPV/EHU, Facultad de Quimica, San Sebastián, Spain, and [§]Physics Department, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui, China. [⊥]Present address: Department of Physics, University of Texas at Austin, Austin, Texas 78712-0264.

ABSTRACT We investigate the chemisorption structure of CO molecules on the quasi-one-dimensional Cu(110)-(2 × 1)-O surface by low-temperature scanning tunneling microscopy and density functional theory. Contrary to flat metal surfaces, where CO molecules adsorb in an upright geometry and interact through repulsive intermolecular interactions, we find the most stable adsorption structure of single CO molecules to be at Cu atoms of substrate Cu—O— chains with the Cu—CO unit bent by ∼±45° in two equivalent structures at low coverages. At higher coverages, CO molecules combine in the same structure into highly ordered single-molecule-wide rows perpendicular to the substrate chains in an approximately 8 × 1 full monolayer structure. First-principles calculations attribute the unprecedented chemisorption behavior of CO molecules to lifting of the host Cu atoms by 1 Å from the surface Cu—O— chains, in order to optimize the bonding and reduce the repulsive interactions with the substrate. This structural distortion enables short-range intermolecular dipole—dipole attraction and creates orthogonal long-range surface-mediated repulsion leading to unusual self-assembly of CO molecules into coherent nanometer scale molecular grating structures.

KEYWORDS: carbon oxide · self-assembly · Cu(110)-(2 × 1)-O surface · dipole—dipole attraction · surface-mediated repulsion · nanograting

The chemical bonding of CO on metals has featured prominently in developing theories of chemisorption and heterogeneous catalysis at solid surfaces.[1−10] The Blyholder model describes the essence of CO—metal interaction in terms of charge donation from the occupied CO-5σ orbital to the metal and back-donation from the metal d-bands to the unoccupied CO-$2\pi^*$ orbitals.[1] This basic picture is confirmed by theoretical calculations employing constrained space orbital variation (CSOV) of the adsorbate and substrate, which identify the flow of charge in response to covalent and electrostatic interactions, as well as atom-selective X-ray spectroscopy.[11,12] The orbital hybridization involving the σ and π^* interactions favors CO molecule chemisorption in vertical geometry, with the C atom binding typically to an atop substrate metal atom.[13] The upright geometry imposes short-range repulsive intermolecular dipole—dipole interactions, which suppress molecular aggregation at low coverages, and forces neighboring molecules to tilt away from the preferred vertical configuration in opposing directions for neighboring molecules at high coverages, as a compromise with the chemical bonding to the substrate.[10,14,15] Consequently, the submonolayer chemisorbed CO molecular overlayer structures on metal surfaces are usually disperse.[14] By contrast, for metals with deeply bound or nonexistent d-bands, the π^* type interactions are not available and CO molecules physisorb in a reclined geometry.[13] Thus, CO molecule adsorption structure on metals is a compromise of several competing interactions, whose strength depends on the electronic structure of the metal substrate. The conventional picture of the CO chemisorption structure can therefore be upset for surfaces with uncommon electronic and chemical properties, where different components of the interaction can dominate over others.[16] This is particularly true when one tries to extrapolate from the behavior of CO molecules on flat metal surfaces, where substrate distortion is energetically costly, to real catalytic systems, where the substrate atom coordination is reduced and substrate distortion is an integral aspect of the catalytic activity.[10,17−19]

In this study, we present a low-temperature scanning tunneling microscopy (LT-STM) and first-principles theory study of CO molecules interacting with a low-dimensional surface, namely, Cu(110)-(2 × 1)-O (Cu(110)—O). We find that when CO molecules

* Address correspondence to petek@pitt.edu.

Received for review August 9, 2011 and accepted October 7, 2011.

10.1021/nn203041c

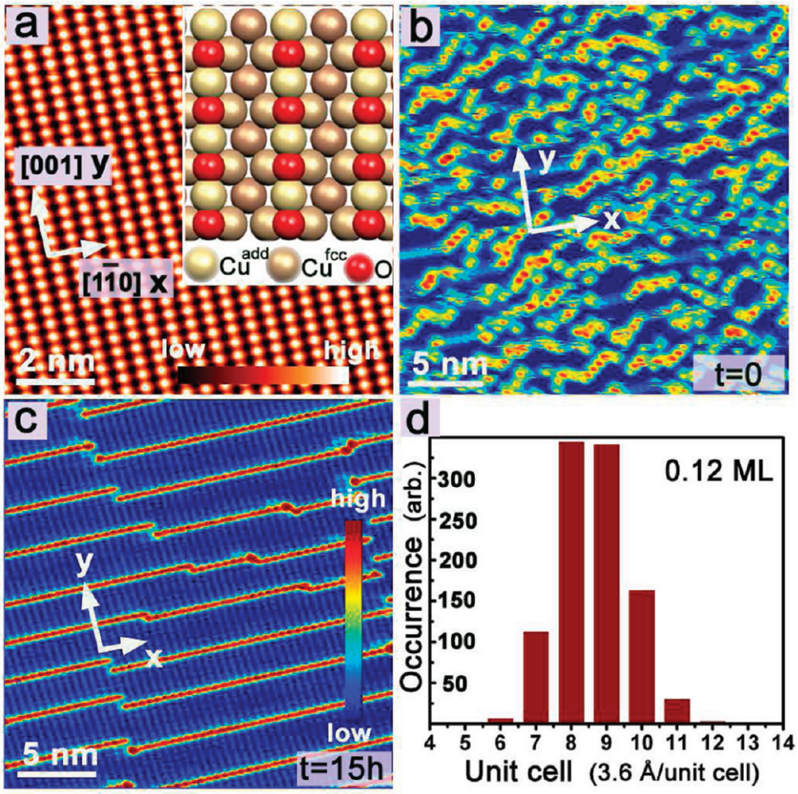

Figure 1. (a) STM image of the Cu(110)−O surface and its ball model (inset). Cu atoms confer bright contrast. (b) STM images acquired immediately and (c) 15 h after dosing CO on the Cu(110)−O surface at 77 K; the CO nanograting forms spontaneously. (d) Histogram of the nearest CO row separations in (c), for which the CO coverage is 0.12 ML.

chemisorb on quasi-one-dimensional Cu−O− chains of the substrate they induce large substrate distortions. Specifically, each CO molecule pulls its host Cu atom by an unprecedented 1 Å from the Cu−O− chain, and, as if were on a hinge, this distortion enables the Cu−CO unit to tilt in orthogonal direction to the chain by ∼±45° from the surface normal. The unique CO chemisorption structure enables attractive dipole−dipole interaction among tilted CO molecules orthogonal to Cu−O− chains, and simultaneously, the strain along the Cu−O− chains introduced locally by CO adsorption poisons adsorption of additional molecules for several unit cells along the same chain. Through these anisotropic attractive and repulsive interactions, CO molecules assemble into single-molecule-wide rows to form a coherent nanograting structure on the Cu(110)−O surface.

Because our theoretical modeling shows that the interplay between the unusual electronic structure of Cu−O− chains and Blyholder-type interactions with covalent bonding and electrostatic repulsive components leads to the structure distortion and unusual self-assembly, they could be expressed on other strongly interacting surfaces. The surface energy of flat metal surfaces, however, is usually too large for CO to induce comparable distortion. Rather, the large distortion should be more facile on low-dimensional surface features of particular catalytic activity.[20−24] Indeed, it has been shown that CO molecules gain chemisorption energy by interacting with low-dimensional features on metal surfaces, such as steps and kinks. Moreover, CO molecules are also able to lower the coordination number of substrate atoms and thereby generate low-dimensional features on 2D surfaces[25] and within catalytic zeolites.[17] Thus, studies of the chemisorption behavior of CO molecules on atomically defined low-dimensional features such as Cu−O− chains on the Cu(110)−O surface can reveal subtle aspects of Blyholder-type interactions that may play an important role in catalytic chemistry.

RESULTS AND DISCUSSION

Experiments were performed in an LT-STM instrument at both 4.5 and 77 K. The focus is the 77 K behavior because here the CO molecules have sufficient mobility to self-organize into thermodynamically stable structures.

Figure 1a shows an STM image and ball structure of the bare Cu(110)−O surface; the bright contrast corresponds to Cu atoms within Cu−O− chains.[26] The Cu(110)−O surface is anisotropic with Cu−O− chains running along the ⟨001⟩, or *y*-direction, forming a parallel array in the ⟨1$\bar{1}$0⟩, or *x*-direction. The electronic structure and chemical bonding of Cu−O− chains have been characterized by angle-resolved photoemission spectroscopy (ARUPS), scanning tunneling microscopy/spectroscopy, optical spectroscopy, and theory.[27−30] The surface electronic band dispersions

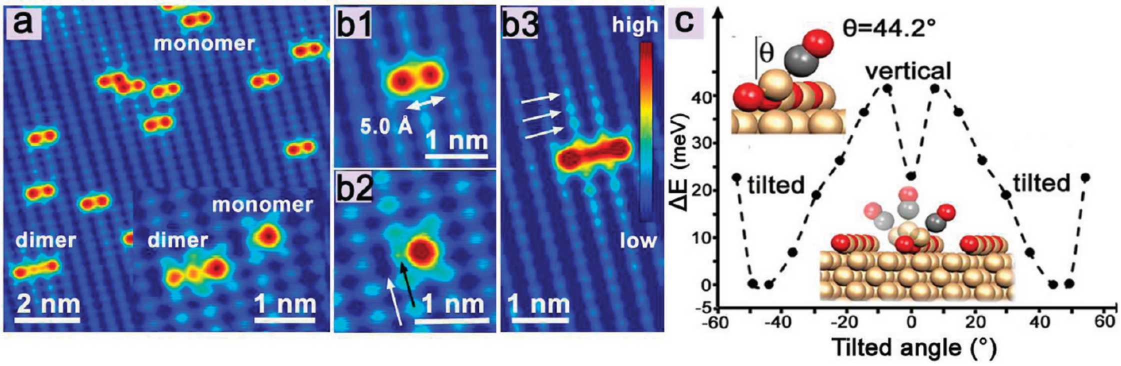

Figure 2. (a) STM images of CO monomers and dimers on the Cu(110)−O surface. The monomer and dimer appear to be two-spot and three-spot images, respectively, at 77 K. For a monomer, their symmetric and asymmetric appearances at 77 and 4.5 K (inset) indicate the tilted interconverting and tilted frozen structures, respectively, which are also reproduced in high-resolution images (b1,b2). (b3) STM image shows bright, bias-voltage independent topographic contrast attributed to distortion Cu−O− chains near adsorbed CO molecules. The white arrows indicate that the enhanced contrast decays within a distance of ~4 × 3.6 Å units. (c) Ball model structure of CO on the Cu−O− chain from DFT, and the total energy curve for the metronomic motion of the Cu−CO unit between the equivalent tilted forms.

measured by ARUPS and parametrized by a tight binding model portend 1D electronic character along Cu−O− chains in the *y*-direction, weak coupling both among Cu−O− chains in the *x*-direction, and to the bulk bands of the substrate.[13,30−33] Figure 1b shows the overlayer structure obtained immediately after dosing ~1.0 Langmuir of CO at 77 K onto the Cu(110)−O surface. Initially, CO molecules assume a dense disordered structure corresponding to ~0.5 ML coverage. After aging the sample for 15 h at 77 K, CO molecules collocate into rows in the *x*-direction, with nearly uniform row spacing in the *y*-direction of ~30 Å, thereby forming a highly ordered grating pattern at a reduced ~0.12 ML coverage (Figure 1c). Lower coverage surfaces start forming linear chain structures immediately after chemisorption, indicating that the evolution from the high-to-low coverage structures in Figure 1 is frustrated by the energetic cost of desorbing excess CO molecules from rapidly deposited, high-coverage overlayers. Although how the initially disordered structure evolves into the grating structure is an interesting topic,[25] our primary focus here is on the microscopic interactions responsible for the molecular self-assembly.

In order to characterize the coherence of the grating pattern, in Figure 1d, we plot a histogram of the inter-CO-row intervals. The distribution peaks at a spacing of 8−9 substrate lattice unit cells with a dimension of 3.6 Å. The histogram shows almost *no* separations below 7 lattice constants (~25 Å), signifying a steep onset of repulsion between CO molecules in the *y*-direction. After a grating structure is formed, additional CO molecules dosed onto the surface at 77 K do not stick; apparently formation of CO rows poisons the surface with respect to chemisorption of additional CO molecules.

The structure of CO chemisorption at low coverage reveals the anisotropic interactions that are responsible for the self-assembly at ~0.12 ML coverage. Immediately after dosing 0.02 ML of CO, in Figure 2a, we observe mostly CO monomers and a few dimers. A striking feature is that at 77 K the majority of CO monomers appears as a pair of identical high contrast spots straddling the host Cu atoms and separated by 5 Å in the *x*-direction, that is, much further than the 1.2 Å bond length of a CO molecule. Such binary images of single CO molecules on solid surfaces are unprecedented. Our DFT calculations, however, provide an intriguing explanation. Unlike 2D substrates,[33] CO molecule chemisorbing on the Cu(110)−O surface lifts its host Cu atom by 1.0 Å from the 1D Cu−O− chain (Figure 2c). Moreover, the entire Cu−CO unit tilts in *x*-direction by ±44.2° from the surface normal into one of two equivalent energy minima. Another metastable minimum is predicted in the vertical CO configuration with 22 meV higher energy and a barrier to tilting of 20 meV (see Figure 2b). The tilted is favored over the vertical structure by the dipole−image dipole interaction.

The general shape of the potential energy curve in Figure 2c is confirmed by cooling the sample to 4.5 K. Quenching the thermal motion freezes CO molecules mainly into one of the two tilted minima (Figure 2a, inset) and occasionally into vertical configuration above the host Cu atom. At 4.5 K, the vertical molecules eventually convert irreversibly to the titled geometry, confirming their metastable nature. Thus, we attribute the binary image of CO molecules at 77 K to the flipping of the Cu−CO unit between the two tilted minima during the STM measurement.[34]

STM imaging cannot easily quantify the height of CO molecules above the surface plane. We point out, however, that there are several indirect clues of the lifting of host Cu atom. The first, as indicated in Figure 2b1, is the separation between two high contrast spots of ~5 Å at 77 K. Simply tilting a CO molecule ±44.2° without pulling the host Cu atom will produce a separation smaller than the observed value. The second is the

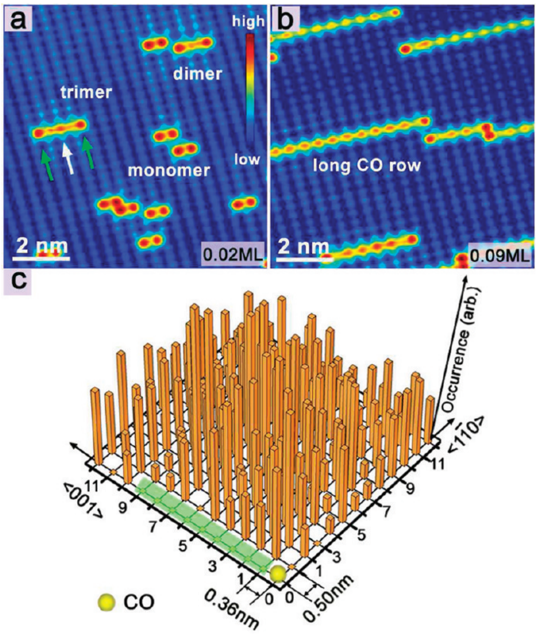

Figure 3. (a) STM images of CO adsorption on the Cu(110)$-$O surface with the coverage of 0.02 ML at 77 K. (b) STM image after dosing more CO onto (a) showing the propensity for CO molecules to assemble into rows at 0.09 ML. (c) Distribution of CO molecules around sampling monomers in (a) along the *x*- and *y*-directions at 0.02 ML. Note that *no* CO molecules adsorb within nine unit cells on the same Cu$-$O$-$ row (green highlight).

high-resolution STM image of isolated titled frozen CO monomer at 4.5 K (Figure 2b2), for which the observed bright substrate lattice contrast (marked by the black arrow) suggests that the host Cu atom is displaced from the Cu$-$O$-$ chain toward the CO molecule and the region between the host Cu and the opposite Cu$-$O$-$ chain has a darker contrast (marked with the white arrow) compared with the regions without CO adsorption. The observed contrast is consistent with the Cu atom being pulled from the chain and the whole Cu$-$CO unit being tilted. Finally, we observe a bias-independent Cu atom contrast rising from within 4 unit cells in the *y*-direction on each side of CO adsorption site (Figure 2b3), suggesting that the Cu atoms close to the CO molecule on the same Cu$-$O$-$ chain are also lifted above the bare surface plane.

We now show that the exceptional chemisorption structure of CO molecules in Figure 2c is the crux of their anisotropic self-assembly on the Cu(110)$-$O surface. At low CO coverage (~0.02 ML; Figure 3a), CO molecules mostly exist as monomers and dimers. Occasionally, some trimers and even longer aggregates can be found. In consecutive STM images, we observed that CO monomers gradually combine to form dimers or trimers. After dosing more CO molecules onto the substrate, longer linear structures aligned exclusively in the *x*-direction form immediately (Figure 3b).

In Figure 3a,b, we describe two features of the longer rows. First, within CO dimers, trimers, and long rows, STM contrast of the outwardly tilted terminal CO molecules is of higher contrast (green arrows), like for the monomer, but the internal contrast is considerably of lower contrast (white arrow). Second, the internal high contrast appears above the Cu$-$O$-$ chain (white arrow in Figure 3a) and not between Cu$-$O$-$ chains as expected for tilted molecules. We attribute the different contrast for terminal and interior molecules to their different environments: a tilted terminal molecule interacts with the Cu$-$O$-$ chain, like the monomer, whereas a tilted interior molecule interacts with the neighboring tilted Cu$-$CO unit. Concerning the location of the interior high contrast, this feature is STM bias-dependent. For most images, we employ a bias voltage of 0.6 V because it makes concurrently resolving the Cu atoms within the Cu$-$O$-$ chain and imaging CO molecules feasible. At this bias, an unoccupied surface state derived from the Shockley surface state of the bare Cu(110) surface contributes to the imaging, causing the high contrast to appear above Cu$-$O$-$ chains (see Supporting Information). For bias voltages below the surface state, the high contrast is between Cu$-$O$-$ chains, as expected for the tilted structures. A more complete discussion is given in the Supporting Information. We emphasize that the high contrast of the monomer and of terminal groups is independent of the bias or the tip condition.

These observations indicate a CO$-$CO attraction along *x*-direction. Figure 3c shows a histogram of the nearest-neighbor distances from sampling CO monomers within 12 lattice sites along both the *x*- and *y*-directions. This analysis shows that, remarkably, on the same Cu$-$O$-$ chain *no* other CO molecule adsorbs within 9 lattice sites, whereas on different chains, they seemingly distribute randomly. These two features confirm that pairs of CO molecules experience short-range attraction on adjacent Cu$-$O$-$ chains and long-range repulsion on the same chain.

The observed features of CO chemisorption on the Cu(110)$-$O surface are explained by DFT calculations. We will elaborate the pronounced chemisorption-induced structural distortion. To describe the CO bonding to Cu(110)$-$O, we calculate the interaction of a single CO molecule at various heights over a Cu atom of the Cu$-$O$-$ chain for a (4×4) supercell of the (2×1) surface unit cell. Figure 4 compares the projected density of states (PDOS) onto the host Cu atom 3d orbitals and adsorbate C and O atom 2p orbitals, which combine into lowest unoccupied molecular orbital (LUMO) of $2\pi^*$ symmetry for Cu$-$C distances of 1.81 and 4 Å. The distances correspond to, respectively, the chemisorbed CO interacting with the distorted Cu$-$O$-$ chain and free CO interacting with the undistorted chain. Figure 4 shows that, in agreement with the Blyholder model,[1] CO bonding to the Cu(110)$-$O surface involves hybridization of the $2\pi^*$ LUMO and host Cu atom 3d orbitals.

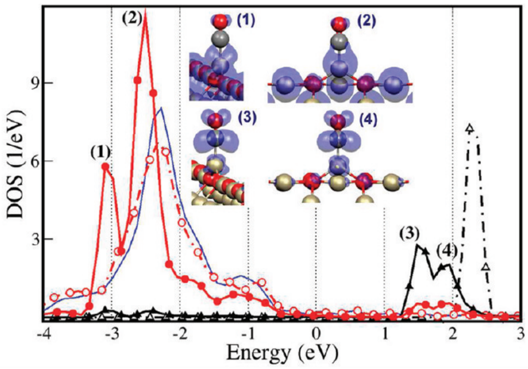

Figure 4. PDOS onto Cu 3d (circles) and CO 2p (triangles) orbitals relative to the Fermi level. The dashed lines are for CO at 4 Å above the undistorted (*i.e.*, no hybridization) host Cu atom. The full thick lines are for chemisorbed CO above a displaced Cu at the optimized bond length of 1.81 Å. The thin blue line (without ligands) shows the PDOS of the nearest-neighbor Cu atom. The charge density isocontours show the occupied Cu $3d_{xz}$ (1), $3d_{yz}$ (2), and the unoccupied CO $2\pi^*$ orbitals (3,4) that are primarily responsible for the chemical bond. The charge density plot (3) shows the hybridization channel between C $2p_x$ and Cu $3d_{xz}$, whereas (4) is between C $2p_y$ and Cu $3d_{yz}$.

To see why CO chemisorption causes the substrate distortion, we first consider the chemical bonding of the unperturbed Cu$-$O$-$ chains based on the previous experimental and theoretical studies and our DFT calculations.[30,31] Of the six bands formed by the interaction of Cu 3d and 4s orbitals with the O 2p orbitals, the lowest five bands are readily observed and assigned in ARUPS spectra.[13,30,31] The most stable 1D bonding band of a Cu$-$O$-$ chain forms through the hybridization of Cu $3d_{3y^2-r^2}$ and O $2p_y$ orbitals.[35] Its antibonding counterpart is the least stable band, which has not been observed in ARUPS, and its assignment remains controversial.[13,30,31] According to our DFT calculation, this band is of $3d_{3y^2-r^2}$ and O $2p_y$ origin, but it also contains some Cu 4s character. This 4s component couples strongly with the Shockley surface state of the clean Cu(110) at $\bar{Y}$ point (unpublished data). This coupling results in two new branches of bands, which simultaneously have components from Cu $3d_{3y^2-r^2}$, Cu 4s, O $2p_y$ of the Cu$-$O$-$ chain, and from clean Cu(110) Shockley surface states. The upper branch of these two interacting bands is readily observed in scanning tunneling spectroscopy measurements at 0.56 eV above the Fermi level, E_F.[26,30] The lower branch is pushed below E_F, hybridizing with the bulk Cu states, which makes it difficult to observe.

Now we analyze the CO adsorption energy gain based on the Blyholder model. The interaction consists of bonding back-donation interactions, where the Cu 3d orbitals transfer some charge to the unoccupied Cu $2\pi^*$ orbitals, and repulsive donation interaction, where according to CSOV analysis[11] the lone pair 5σ orbital causes the polarization of primarily Cu 4s charge toward the substrate. On the ground of symmetry, the bonding interaction cannot involve the highest (partially) occupied states from the Cu$-$O$-$ chain because the Cu $3d_{3y^2-r^2}$, Cu 4s orbitals, do not hybridize with CO $2\pi^*$. The symmetry-allowed interaction with $3d_{xz}$ and $3d_{yz}$ orbitals is weak because they are engaged in deep (-2 eV below the Fermi level, E_F) fully occupied 2π symmetry bands. Therefore, without distortion of the chain, the hybridization of the Cu 3d and CO $2\pi^*$ orbitals is small.[5] Lifting of the host Cu atom by 1 Å, however, induces a local rehybridization and simultaneously raises the energy of Cu $3d_{yz}$ orbitals so that they become partially unoccupied. This allows Cu atoms both to maintain the conjugation of the distorted Cu$-$O$-$ chain and to accommodate bonding between Cu $3d_{xz}$ and $3d_{yz}$ and CO $2\pi^*$ orbitals, as shown in Figure 4. Such rehybridization is more favorable for a 1D substrate, rather than a 2D substrate, because the relatively low energy cost of chain distortion can be met by more favorable interaction between the Cu atom and CO molecule. The local character of the induced electronic perturbation of the distorted chain is evident in Figure 4 from the similarity between the PDOS of the host Cu atom 3d orbitals when the CO molecule is at 4 Å and that of the nearest-neighbor Cu atoms on the Cu$-$O$-$ chain when CO is chemisorbed.

In addition to the π back-donation bonding interaction, the Cu$-$O$-$ chain distortion is also favored by ionic interactions. A Bader analysis of the clean surface assigns charges of $+0.6e$ and $-1.0e$ to the Cu and O atoms, respectively, implying a net transfer of $-0.4e$ from the substrate. The upward shift of the host Cu atom also reduces further its polarizible 4s electron density by a Smolukowski smoothing effect and allows the CO molecule to avoid the negatively charged O atoms. Both factors reduce the Coulomb as well as the Pauli repulsion associated with the CO 5σ orbital donation.[6,36,37] Such polarization of charge away from the host Cu atom has been identified in CSOV analysis as an important factor in stabilizing a CO$-$metal bond.[11] Therefore, we conclude that both maximizing the bonding back-donation and reducing the repulsive donation components of the CO surface interaction favor the strong, local distortion of the Cu$-$O$-$ chain.

We now explain the attractive interaction responsible for the formation of CO rows. Being perpendicular to Cu$-$O$-$ chains, along which the surface electrons propagate, the attraction is unlikely to be substrate-mediated. More pertinent is chemisorption-induced charge redistribution and the correspondingly induced dipole. The large displacement of Cu atom enhances the dipole of the Cu$-$CO complex (*via* back-donation), giving the calculated value of $-0.123e$ Å. The consequent dipole$-$dipole interaction is repulsive for vertical[14,15] but can become attractive for tilted CO molecules. The tilting, which is already present in CO monomers, occurs predominantly in the same direction within a CO molecule row consistent with the dipole–dipole attraction. We confirmed this interpretation by comparing the calculated chemisorption energy for a tilted monomer, a pair of CO molecules tilted in the *x*-direction on adjacent Cu–O– chains, and an infinite CO row. Consistent with the dipolar mechanism, we found the dimer to be stabilized by ~10 meV per molecule, increasing to ~20 meV per molecule for the infinite row. The additive character of the attraction and the order-of-magnitude of the energy gain calculated with a simple point dipole model are also consistent with the dipolar origin (unpublished data). We therefore conclude that the direct dipole–dipole attraction drives the formation of uniformly tilted rows of nearest-neighbor CO molecules.

Finally, we discuss the CO–CO repulsion along the same Cu–O– chain. In calculations for configurations containing 1, 2, and 4 CO rows per supercell composed of 1 × 8 surface unit cells (*i.e.*, corresponding to periods of 8, 4, and 2 Cu–O units), the adsorption energy per CO molecule decreases from 603 to 573 and 509 meV as the coverage increases. In principle, one could expect repulsion between dipoles of Cu–CO complexes along the chain, but the energy difference of nearly 100 meV, the length scale of interaction, and sensitivity to alternating the tilt direction are inconsistent with this mechanism.

The distortion of the Cu–O– chain upon CO adsorption provides a useful clue for a different mechanism. The STM images show evidence for lifting of Cu atoms near the pulled host Cu atom, which decays within a distance of ~4 × 3.6 Å units (Figure 2b3). The fact that the grating period is twice the topographic distortion length suggests an intimate connection between them. Given the 1D character of Cu–O– chains, the lifted Cu atoms act as strong scattering centers for the electrons in the antibonding Cu 3d$_{3y^2-r^2}$–O 2p$_y$ band. For a single CO molecule, this scattering and its effect on the total energy are reduced by the rehybridization at the adsorption site. The proximity of two CO adsorbates, however, imposes additional constraints that render rehybridization less effective and, therefore, translate into an effective intermolecular repulsion. A quantitative model for such intrachain repulsion will be presented elsewhere (unpublished data).

CONCLUSIONS

We have observed the self-assembly of CO molecules into a nanoscale grating pattern on the 1D highly anisotropic Cu(110)–O surface and explained it in terms of orthogonal short-range dipole–dipole attraction and long-range surface-mediated repulsion. Our work illustrates how formation of a chemical bond through specific electron donating and withdrawing between an adsorbate and 1D dispersive states of the substrate can impact the surface geometrical and electronic structures. The interactions we observe are favored by the substrate distortion by making available the Cu 3d$_{xz}$ and 3d$_{yz}$ orbitals for the bonding interaction and polarizing Cu 4s electron density away from the adsorption site. The same interactions favor chemisorption-induced surface restructuring at step and kink defects on 2D surfaces and other reduced coordination sites that may confer enhanced reactivity. We point out that in Cu-substituted zeolites CO molecules are postulated to bind to Cu atoms with similar bidentate bonding to the neighboring O molecules.[17,18] The fact that such structures form through breaking of other Cu–substrate bonds suggests that this is a particularly favorable bonding motif between CO and Cu, which is unavailable for 2D Cu surfaces. The ability of CO molecules to induce pronounced surface distortion represents a exemplary behavior that may be especially significant in the context of reactivity of low-dimensional active sites on catalytic surfaces.

METHODS

The fully saturated Cu(110)–O reconstructed surface was prepared as described in ref 38. The substrate is nearly atomically perfect over micrometer-wide terraces. CO molecules were dosed onto a Cu(110)–O substrate *in situ* at 77 K. Constant current topographic STM images were acquired using a bias voltage of 0.6 V (positive bias means that electrons tunnel from the occupied tip state to the unoccupied substrate state) and a typical current of 0.1 nA.

DFT calculations were performed using the VASP code[39] with a well converged 400.0 eV plane-wave cutoff, the Perdew–Wang 1991 functional,[40] and the projector augmented wave method. The Cu substrate was represented by a slab of 5–15 layers. For all of the lateral supercells considered, the number of k-points was consistent with a 6 × 10 × 1 k-sampling of the (2 × 1) substrate unit cell.

Acknowledgment. We thank G. Benedek for discussions. The research in Pittsburgh was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-FG02-09ER16056, and the W.M. Keck foundation. Some of the calculations were performed in the Environmental Molecular Sciences Laboratory at the PNNL, a user facility sponsored by the DOE Office of Biological and Environmental Research. The research in San Sebastian was supported by the Ministerio de Cienciae Innovación (FIS2010-19609-C02-00) and G.V.-UPV/EHU (IT-366-07).

Supporting Information Available: Additional experimental data on clarifying STM images of CO rows and the geometry of CO within CO rows. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Blyhoder, H. Molecular Orbital View of Chemisorbed Carbon Monoxide. *J. Phys. Chem.* **1964**, *68*, 2772–2777.
2. Eastman, D. E.; Cashion, J. K. Photoemission Energy-Level Measurements of Chemisorbed CO and O on Ni. *Phys. Rev. Lett.* **1971**, *27*, 1520–1523.

3. Greuter, F.; Heskett, D.; Plummer, E. W.; Freund, H. J. Chemisorption of CO on Co(0001): Structure and Electronic Properties. *Phys. Rev. B* **1983**, *27*, 7117–7135.
4. Hoffmann, R. A Chemical and Theoretical Way To Look at Bonding on Surfaces. *Rev. Mod. Phys.* **1988**, *60*, 601–628.
5. Hammer, B.; Morikawa, Y.; Nørskov, J. K. CO Chemisorption at Metal Surfaces and Overlayers. *Phys. Rev. Lett.* **1996**, *76*, 2141–2144.
6. Föhlish, A.; Nebergy, M.; Bennich, P.; Triguero, L.; Hasselström, J.; Karis, O.; Pettersson, L. G. M.; Nilsson, A. The Bonding of CO to Metal Surfaces. *J. Chem. Phys.* **2000**, *112*, 1946–1958.
7. Wimmer, E.; Fu, C. L.; Freeman, A. J. Catalytic Promotion and Poisoning: All-Electron Local-Density-Functional Theory of CO on Ni(001) Surfaces Coadsorbed with K or S. *Phys. Rev. Lett.* **1985**, *55*, 2618–2621.
8. Over, H.; Kim, Y. D.; Seitsonen, A. P.; Wendt, S.; Lundgren, E.; Schimid, M.; Varga, P.; Morgante, A.; Ertl, G. Atomic-Scale Structure and Catalytic Reactivity of the RuO$_2$(110). *Surf. Sci.* **2000**, *287*, 1474–1476.
9. Kelkkanen, A. K.; Lundqvist, B. I.; Nørskov, J. K. van der Waals Effect in Weak Adsorption Affecting Trends in Adsorption, Reactivity, and the View of Substrate Nobility. *Phys. Rev. B* **2011**, *83*, 113401–113404.
10. Freund, H.-J. Model Studies in Heterogeneous Catalysis. *Chem.—Eur. J.* **2010**, *16*, 9384–9397.
11. Bagus, P. S.; Hermann, K.; Bauschlicher, C. W., Jr. On the Nature of the Bonding of Lone Pair Ligands to a Transition Metal. *J. Chem. Phys.* **1984**, *81*, 1966–1974.
12. Nilsson, A.; Pettersson, L. G. Chemical Bonding on Metal Surface. In *Model Systems in Catalysis: Single Crystals to Supported Enzyme Mimics*; Rioux, R. M., Ed.; Springer Verlag: New York, 2010; pp 253−274 .
13. Kuhlenbeck, H.; Freund, H.-J. Adsorption on Metals. In *Handbook of Surface Science*; Horn, K., Scheffler, M., Eds.; Elsevier: Amsterdam, 2000; Vol. 2, pp 670−747 .
14. Ahner, J.; Mocuta, D.; Ramsier, R. D.; Yates, J. T., Jr. Adsorbate−Adsorbate Repulsions: The Coverage Dependence of the Adsorption Structure of CO on Cu(110) as Studied by Electron-Stimulated Desorption Ion Angular Distribution. *J. Chem. Phys.* **1996**, *105*, 6553–6558.
15. Kato, H.; Okuyama, H.; Ichihara, S.; Maki, K.; Yoshinobu, J. Lateral Interactions of CO in the (2 × 1)p2mg Structure on Pd(110): Force Constants between Tilted CO Molecules. *J. Chem. Phys.* **2000**, *112*, 1925–1936.
16. Schimka, L.; Harl, J.; Stroppa, A.; Grüneis, A.; Marsman, M.; Mittendorfer, F.; Kresse, G. Accurate Surface and Adsorption Energies from Many-Body Perturbation Theory. *Nat. Mater.* **2010**, *9*, 741–744.
17. Rejmak, P.; Sierka, M.; Saucer, J. Theoretical Studies of the Cu(I) Sites in Faujasite and Their Interaction with Carbon Monoxide. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5446–5456.
18. Davidová, D.; Nachtigallová, D.; Bulánek, R.; Nachtigáll, P. Characterization of the Cu$^+$ Sites in High-Silica Zeolites Interacting with the CO Molecule: Combined Computational and Experimental Study. *J. Phys. Chem. B* **2003**, *107*, 2327–2332.
19. Van Hove, M. A.; Somorjai, G. A. Adsorption and Adsorbate-Induced Restructuring: A LEED Perspective. *Surf. Sci.* **1994**, *299/300*, 487–501.
20. Zambelli, T.; Wintterlin, J.; Trost, J.; Ertl, G. Identification of the "Active Sites" of a Surface-Catalyzed Reaction. *Science* **1996**, *273*, 1688–1690.
21. Vang, R. T.; Honkala, K.; Dahl, S.; Vestergaard, E. K.; Schnadt, J.; Laegsgaard, E.; Clausen, B. S.; Norskov, J. K.; Besenbacher, F. Controlling the Catalytic Bond-Breaking Selectivity of Ni Surfaces by Step Blocking. *Nat. Mater.* **2005**, *4*, 160–162.
22. Yates, J. T., Jr. Surface Chemistry at Metallic Step Defect Sites. *J. Vac. Sci. Technol., A* **1995**, *13*, 1359–1367.
23. Vattuone, L.; Savioa, L.; Rocca, M. Bridging the Structure Gap: Chemistry of Nanostructured Surfaces at Well-Defined Defects. *Surf. Sci. Rep.* **2008**, *63*, 101–168.
24. Henderson, M. A.; Szabo, A.; Yates, J. T., Jr. Direct Observation of Adsorbate−Adsorbate Repulsions along a One-Dimensional Array: CO on the Steps of Pt(112). *Chem. Phys. Lett.* **1990**, *168*, 51–55.
25. Thostrup, P.; Vestergaard, E. K.; Lægsgaard, E.; Besenbacher, F. CO-Induced Restructuring of Pt(110)-(1 × 2): Bridging the Pressure Gap with High-Pressure Scanning Tunneling Microscopy. *J. Chem. Phys.* **2003**, *118*, 3724–3730.
26. Corriol, C.; Hager, J.; Matzdorf, R.; Arnau, A. Surface Electronic Structure of O(2 × 1)/Cu(110): Role of the Surface State at the Zone Boundary-Point in STS. *Surf. Sci.* **2001**, *600*, 4310–4314.
27. Cortona, P.; Sapet, C. LCAO Study of the Cu(110)(2 × 1)O Surface. *Surf. Sci.* **2005**, *585*, 155–162.
28. Hager, J.; Matzdorf, R. Surface State Lifetime in Quasi-One-Dimensional Oxygen Stripes on Cu(110). *Surf. Sci.* **2006**, *600*, 2581–2586.
29. Stahrenberg, K.; Herrmann, T.; Esser, N.; Richter, W. Surface Optical Properties of Clean Cu(110) and Cu(110)-(2 × 1)-O. *Phys. Rev. B* **2000**, *61*, 3043–3047.
30. Tjeng, L. H.; Meinders, M. B. J.; Sawatzky, G. A. Relationship between Atomic and Electronic Structure of Clean and Oxygen Covered Copper (110) Surface. *Surf. Sci.* **1990**, *233*, 163–183.
31. Courths, R.; Cord, B.; Wern, H.; Saalfeld, H.; Hüfner, S. Dispersion of the Oxygen-Induced Bands on Cu (110): An Angle-Resolved UPS Study of the System p(2 × 1)O/Cu(110). *Solid State Commun.* **1987**, *63*, 619–623.
32. Berge, K.; Goldmann, A. Electronic Interchain Interactions of the Cu(110) (2 × 1) O Surface: An Angle-Resolved Photoemission Study. *Surf. Sci.* **2003**, *540*, 97–106.
33. Lorente, N.; Ueba, H. CO Dynamics Induced by Tunneling Electrons: Differences on Cu(110) and Ag(110). *Eur. Phys. J. D* **2005**, *35*, 341–348.
34. According to the Arrhenius description, assuming the pre-exponential factor to be the vibrational frequency at the order of 10^{12} Hertz and using the calculated energy barrier, the interconverting rate between two CO tilted minimum is roughly 10$^{8-9}$ Hertz at 77 K and 10^{-32} at 4.5 K, consistent with the observed two-spot image at 77 K and one-spot image at 4.5 K.
35. Pforte, F.; Gerlach, A.; Goldmann, A.; Matzdorf, R.; Braun, J.; Postnikov, A. Wave-Vector-Dependent Symmetry Analysis of a Photoemission Matrix Element: The Quasi-One-Dimensional Model System Cu(110)(2 × 1)O. *Phys. Rev. B* **2001**, *63*, 165405.
36. Nilsson, A.; Pettersson, L. G. M. Chemical Bonding on Surfaces Probed by X-ray Emission Spectroscopy and Density Functional Theory. *Surf. Sci. Rep.* **2004**, *55*, 49–167.
37. Gajdos, M.; Eichler, A.; Hafner, J. CO Adsorption on Close-Packed Transition and Noble Metal Surfaces: Trends from *Ab Initio* Calculations. *J. Phys.: Condens. Matter* **2004**, *16*, 1141–1164.
38. Feng, M.; Lee, J.; Zhao, J.; Yates, J. T., Jr.; Petek, H. Nanoscale Templating of Close-Packed C$_{60}$ Nanowires. *J. Am. Chem. Soc.* **2007**, *129*, 12394–12395.
39. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169.
40. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1992**, *46*, 6671–6687.