Supplementary Information

Strong substrate mediation of attractive lateral interactions of CO on Cu(110)

José A. Garrido Torres[‡], Kirsten L. Finley[‡], Herbert A. Früchtl, Paul B. Webb[*], Renald Schaub[*]

EaStCHEM and School of Chemistry, University of St Andrews, KY16 9ST, St Andrews, UK

Corresponding Authors: * RS: renald.schaub@st-andrews.ac.uk; PBW: pbw@st-andrews.ac.uk

Author Contributions: ‡ These authors contributed equally.

SI1. STM-induced lateral manipulation of CO molecules on the Cu(110) surface

The single-molecule manipulation experiments were performed in constant height mode. The tip was first moved to the desired starting position, and from there was moved along the desired line of manipulation to the final position and back again to the starting point whilst recording data in normal imaging mode (constant current). The feedback signal was then turned off and the tip moved again from the starting to the final position this time in constant height mode, with a bias voltage of 1 V and an additional tip-sample offset of 4.5 Å for increased tip-molecule interaction. Finally, the tip moved back to the starting position acquiring data in imaging mode. The tip was moved laterally in both the $[1\bar{1}0]$ and the [001] direction i.e. perpendicular and parallel to the alignment of the CO molecular chains respectively.

SI2. DFT calculations: Identification of the preferred adsorption sites for CO on Cu(110)

Four different input geometries were optimized to corroborate the preference for the “top” and “short-bridge sites”. The “top” and “short-bridge” geometries are calculated to be the two most stable configurations for CO adsorbed on Cu(110). As illustrated in **Figure S1**, when starting from the “top” and “long-bridge” configurations, the CO molecules relax to “top” sites. In a similar manner, when starting from “hollow” or “short-bridge” sites, the CO molecules migrate to “short-bridge” sites after optimization. Therefore, our discussions in the main paper are based of the analysis of these two structures only.

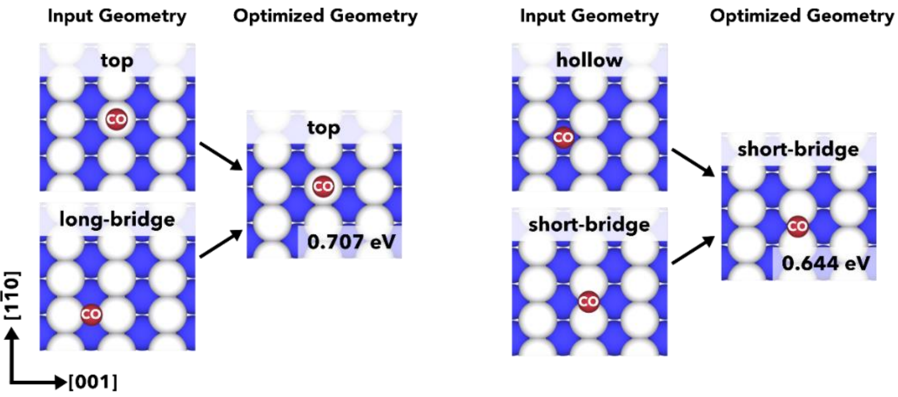

Figure S1. Top views of the input geometries probing the “top”, “long-bridge”, “short-bridge” and “hollow” adsorption sites for CO on Cu(110), and corresponding optimized geometries resulting from relaxation. White (blue) spheres represent the Cu atoms belonging to the first (second) layer of the surface. Red spheres represent the CO molecules. The corresponding calculated adsorption energies are indicated.

SI3. DFT calculations: Identification of the energy barriers for diffusion of CO on Cu(110)

The Nudged Elastic Band (NEB) calculations reported in **Figure S2** show the three different pathways that CO molecules could adopt to diffuse from one top to another adjacent top site. The most energetically favorable reaction path occurs through the $[1\bar{1}0]$ direction (in red). The energy barrier through the [001] direction is 400 meV higher than when following the $[1\bar{1}0]$ direction. The highest energy barrier is found for translation involving a combination of the [001] and $[1\bar{1}0]$ directions (in green) which is 510 meV higher than when diffusing through the most favourable translational coordinate.

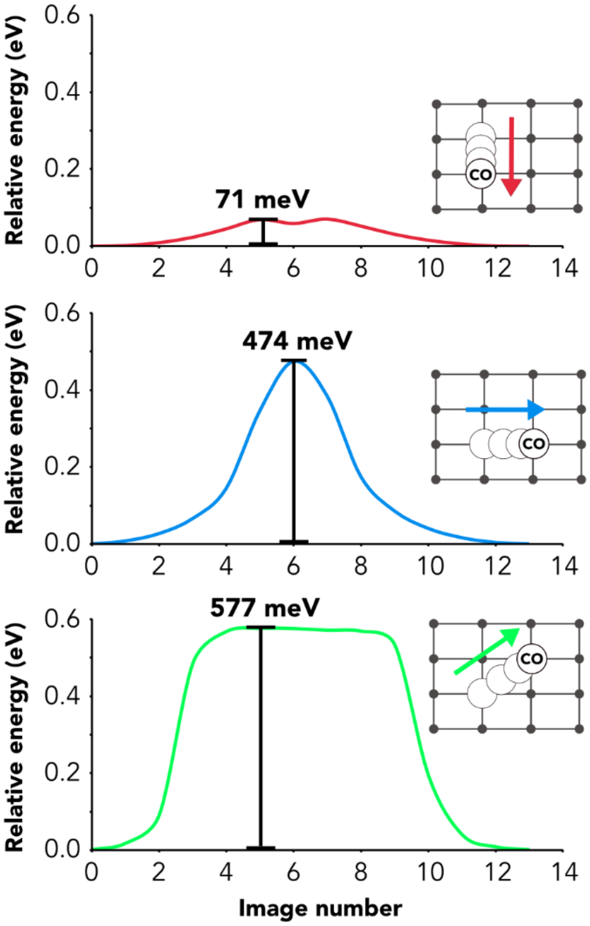

Figure S2. NEB calculations for the lateral displacement of a CO molecule from one top to the adjacent top site following the $[1\bar{1}0]$ (top), [001] (middle) and a combination of the two previous directions (bottom). The corresponding energy barriers are indicated for the three different diffusion paths.