Hydrogen-Bonded Assembly of Methanol on Cu(111)

Timothy J. Lawton[1], *Javier Carrasco*[2], *Ashleigh E. Baber*[1], *Angelos Michaelides*[3] *and E. Charles H. Sykes*[1,*]

Department of Chemistry, Tufts University, 62 Talbot Avenue, Medford, MA 02155, Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, E-28049, Madrid, Spain, and Thomas Young Centre, London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, UK.

*charles.sykes@tufts.edu

Supplementary Information

At 30 K, even with the mild scanning conditions used, over time interactions between the STM tip and the MeOH molecules on Cu(111) lead to a disruption of the overlayer structure. This is demonstrated in Figure S1A. Prior to recording the image on Figure S1A, the area highlighted by the white box was scanned once: a full up and down sequence. Figure S1A is the subsequent image taken after zooming out from the original area. It is clear from the image that scanning over this area has perturbed the MeOH structures. Figure S1B shows how disordered the overlayer becomes after two more full up and down scans in the same area. To obtain the most unperturbed images possible, a certain area was only scanned up and down once and the least perturbative imaging

[1] Tufts University.
[2] Instituto de Catálisis y Petroleoquímica, CSIC.
[3] University College London.

conditions were used (very low tunneling current and bias <1 V) in order to minimize the molecule-tip interactions. Larger scale images also exhibited less tip induced disorder as the contact time per molecule was lower. Despite this experimental difficulty we can be confident that the ordered assemblies we report are equilibrium structures characteristic of the system itself and not caused by the influence of the STM tip as repeated imaging always resulted in disruption of the assemblies and a loss of order.

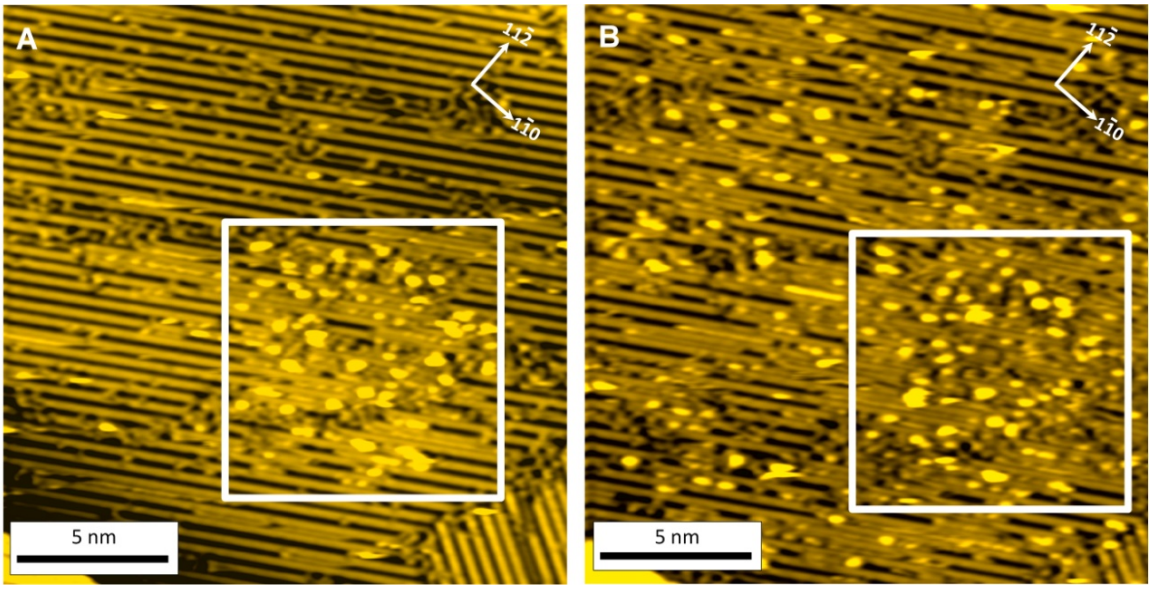

Figure S1: STM images taken at 28 K after a 140 K anneal reveal the difficulties in imaging the system for extended periods of time. A) The white box highlights a smaller area scanned immediately prior to image A being taken and indicates that over time the STM tip perturbs the surface structures. B) The same area taken two scans after A showing disruption of the MeOH chains in the whole image. Imaging conditions: A), B) -0.7 V, 2 pA

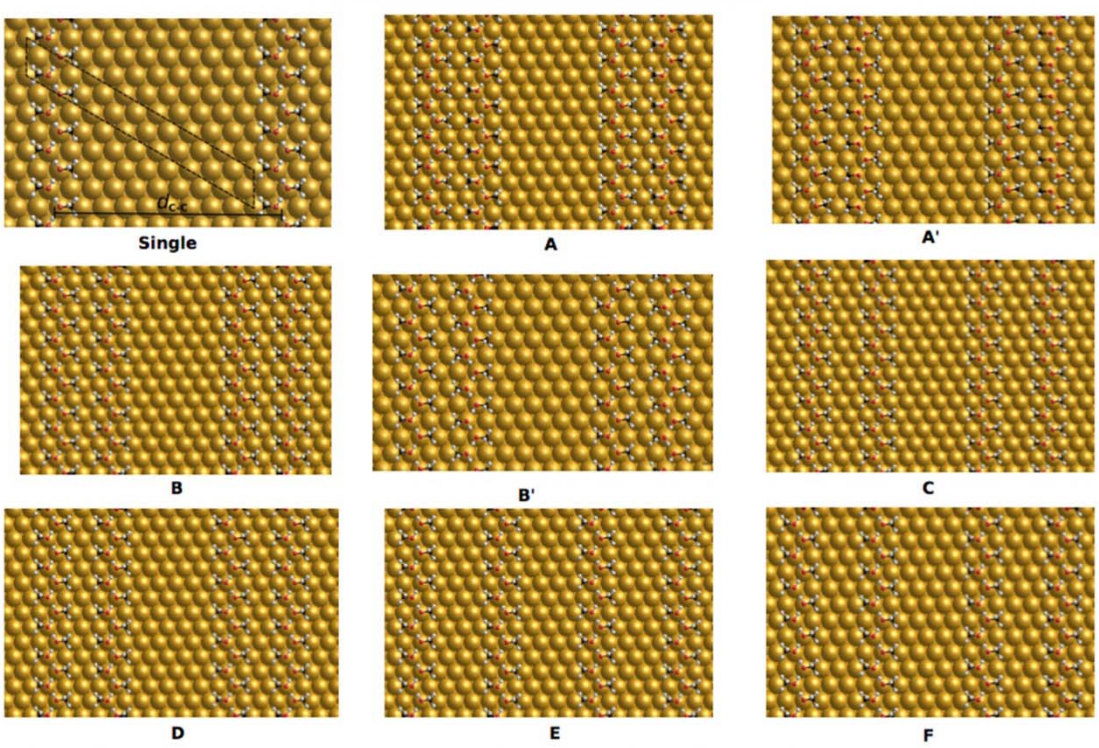

Figure S2: DFT calculated models for double chains of MeOH hexamers separated by different distances, with adjacent methyl groups aligned or staggered and with hydrogen bonding directions running parallel and anti-parallel. All models are based on a $7\sqrt{3}$ x $\sqrt{3}$ surface unit cell (shown in model A) with 1 x 7 x 1 k-points.

Table S1: Calculated distances and adsorption energies calculated for all the models above in Figure S2 and an isolated MeOH hexamer.

Chain-chain interactions

Model	Short $d_{C\text{-}C}$ (Å)	Long $d_{C\text{-}C}$ (Å)	E_{ads} (meV/MeOH) optB88-vdW
Single chain	27.12	27.12	699
A	-	-	(667)
A'	7.14	19.83	670
B	7.64	19.31	685
B'	7.66	19.29	685
C	10.24	16.70	683
D	9.03	17.92	682
E	12.79	14.16	685
F	11.59	15.36	685
Hexamer	-	-	688

From the table it is clear that isolated single chains are more stable than hexamers. In general chains with methyl groups facing each other are less stable than chains with the methyl groups in a zig-zag conformation. No effect due to the direction of the hydrogen-bonded network in adjacent MeOH chains was observed. Chains B and B' have parallel and antiparallel hydrogen-bonded networks respectively but the adsorption energies are equivalent.

Table S2: Calculated distances for two models of double chains from above. A' has methyl groups aligned and B has the methyl groups staggered.

Model	Short *d*c-c (Å)	Long *d*c-c (Å)	Eads (meV/MeOH) optB88-vdW
Single chain	27.12	27.12	699
A'	7.14	19.83	670
B	7.64	19.31	685
A'A'	7.15	8.27	662
BB	7.55	7.93	**688**
Hexamer	-	-	688

Focusing on two different models from Figure S1, A' and B. Model B is found to be more stable having methyl groups staggered. The double chains can pack as close as 6 copper atoms without an energy penalty being as stable as an isolated double chain (Model B). Model BB exhibits a Peierls like distortion with 2 different chain-chain spacings.

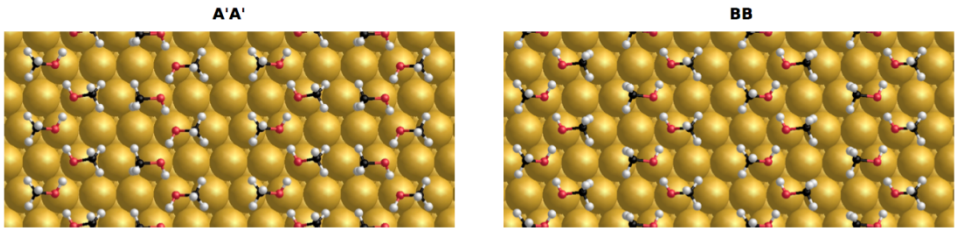

Figure S3: Two models of methanol double chains packed together revealing a Peierls like distortion.

According to previous TPD results, MeOH desorbs intact from Cu(111) by 165 K.[1] Figure S4 shows STM images of a Cu(111) surface before and after MeOH adsorption/desorption. Figure S4A is an STM image of a clean Cu(111) surface

exhibiting native impurities with a density of ~ 8 impurities per 38,900 Cu atoms. Figure S4B is the same size as Figure S4A for comparison after the MeOH layer has been desorbed at 165 K. In Figure S4B the impurity density is 27 per 38,900 Cu atoms, a negligible difference compared to clean Cu(111). This result demonstrates that MeOH adsorption on Cu(111) occurs without decomposition down to <0.1% ML.

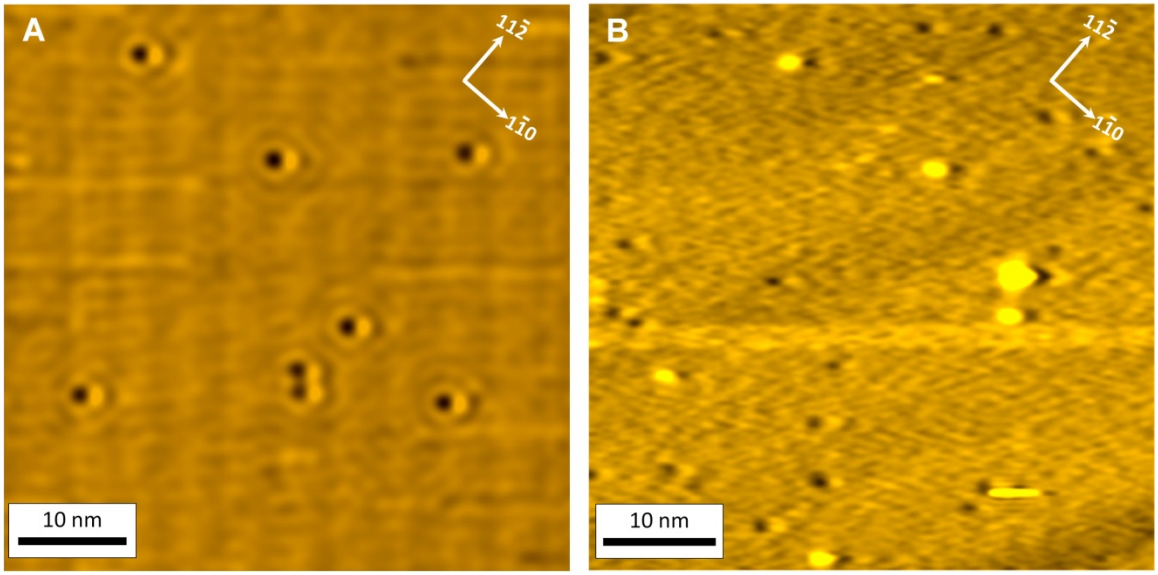

Figure S4: A) STM image of a bare Cu(111) terrace exhibiting native impurities that image as depressions. Impurity density is 0.02%. B) STM image of Cu(111) terrace taken after exposure to MeOH and a 165 K anneal. The terrace is mostly bare with some depressions that look similar to those on clean Cu(111). Impurity density is 0.07%. Imaging conditions: A) RT, -0.2 V, 200 pA B) 28 K, -0.8 V, 2 pA.

Reference:

1 S. M. Johnston, A. Mulligan, V. Dhanak and M. Kadodwala, *Surface Science*, 2003, **530**, 111-119.