

Supporting information for:
Structural Evolution of a Cyclooctatetraene
Adlayer on Cu(111) During Isothermal
Desorption

JA Lau,^{†,¶} I Calvo-Almazán,^{†,§} PSM Townsend,[†] DJ Ward,[†] AP Jardine,[†] W
Allison,[†] J Ellis,[†] BJ Hinch,[‡] and N Avidor^{*,†}

[†]*Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3
0HE, United Kingdom*

[‡]*Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New
Jersey 08854, USA*

[¶]*Present address: University of Goettingen, Institute of Physical Chemistry, Tammannstr.
6, 37077 Goettingen, Germany*

[§]*Present address: Material Science Division, Argonne National Laboratory, Argonne,
60439, Illinois, United States*

E-mail: na364@cam.ac.uk

Additional information on the diffraction pattern at 205K

For the impression of the reader, we provide figure S1, which shows the equivalent of a full 2D diffraction pattern. The actual measured diffraction pattern is the (smaller) section marked by the two dashed black lines, which represent the high symmetry directions of the Cu(111)

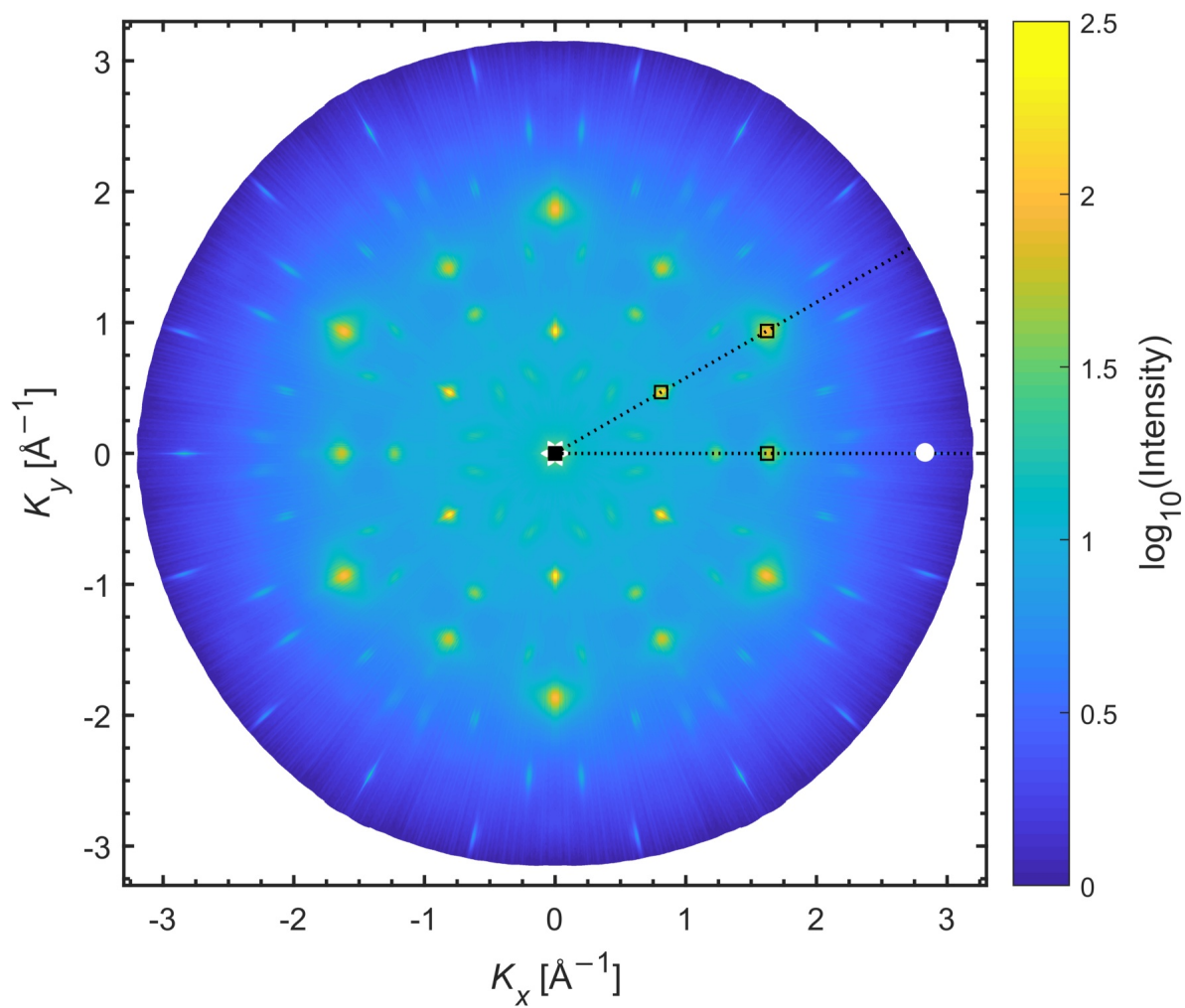


Figure S1: Replication of the measured diffraction pattern (marked in dashed black lines), to represent the equivalent of the complete diffraction pattern. The white circle marks the 1st order copper peak, and the three black squares mark peaks 4,8,11 as labeled in the main text.

surface. The pattern is then reflected across the high symmetry directions and replicated to create the full 2D pattern.

For completeness we provide a table (S1) of intensities of the diffraction peaks maximum, after subtracting the background using a second order fitted polynomial function.

Table S1: Peak intensities (I) after background subtraction, for peaks 1-14 as labeled in Fig. 1 of the main text. The diffraction positions are shown as well in parallel momentum transfer coordinates.

Peak	$K_x[\text{\AA}^{-1}]$	$K_y[\text{\AA}^{-1}]$	I [$10^{-12}A$]
1	0.60	0.13	8
2	0.96	0.00	1
3	1.22	0.02	31
4	1.63	0.01	58
5	1.91	0.00	2
6	2.24	0.15	2
7	2.84	0.00	25
8	0.80	0.47	228
9	1.44	0.59	11
10	2.06	0.49	6
11	1.61	0.94	92
12	2.24	1.06	7
13	2.84	0.92	5
14	2.41	0.47	0.3

Convolution of Two Diffraction Patterns

The eikonal formula represents the simplest method for calculation of diffraction intensities within the hard wall approximation to the helium-surface interaction potential, and relies on the hard wall corrugation function $\xi(\mathbf{R})$ where \mathbf{R} is a 2-D position vector.^{S1} It can be shown that a convolution of diffraction patterns is to be expected, respectively with substrate and adsorbate periodicities, if the adsorbate overlayer exhibits a corrugation that is modulated by the substrate of a differing lateral periodicity. Such a modulation could be caused by

small displacements of adsorbate species with respect to the long-range averaged positions, or by local changes in the electronic density of the adsorbate molecules due to spatially dependent binding configurations, or strengths with the substrate.

The eikonal formula for the structure factor $F(\Delta\mathbf{K})$ is given by

$$F(\Delta\mathbf{K}) = \frac{1}{S} \int e^{i\Delta\mathbf{K}\cdot\mathbf{R}} \cdot e^{i\Delta k_z \xi(\mathbf{R})} d\mathbf{R}, \quad (1)$$

where $\Delta\mathbf{K}$ and Δk_z are the surface parallel and perpendicular components of the scattering vector \mathbf{k} , respectively. S is the super-lattice unit cell area, \mathbf{R} is a position vector and $\xi(\mathbf{R})$ a corrugation function of the hard-wall potential energy surface. The eikonal formula for the diffraction pattern is simply a Fourier transform of the spatially varying phase factor $e^{i\Delta k_z \xi(\mathbf{R})}$, and can be evaluated at reciprocal lattice vectors, \mathbf{G} , associated with the super-lattice unit cell.

Assuming the total corrugation can be expressed as a sum of two contributions, $\xi(\mathbf{R}) = \xi_a(\mathbf{R}) + \xi_s(\mathbf{R})$, where ξ_a and ξ_s are the corrugation functions of the adsorbate and substrate-induced modulation, then $F(\Delta\mathbf{K})$ can be written as a Fourier transform of a product of two phase factor functions,

$$F(\Delta\mathbf{K}) = \frac{1}{S} \int e^{i\Delta\mathbf{K}\cdot\mathbf{R}} \cdot e^{i\Delta k_z \xi_a(\mathbf{R})} \cdot e^{i\Delta k_z \xi_s(\mathbf{R})} d\mathbf{R}. \quad (2)$$

Using the convolution theorem, and assuming the perpendicular momentum transfer Δk_z is a weak function of $\Delta\mathbf{K}$, $F(\Delta\mathbf{K})$ can be written as a convolution of the structure factors from both contributions,

$$F(\Delta\mathbf{K}) = \frac{S_a S_s}{S} (F_a * F_s)(\Delta\mathbf{K}). \quad (3)$$

From the Bragg condition for diffraction, the corrugation of the unmodulated adsorbate will result in a diffraction pattern with finite intensities at $F_a(\Delta\mathbf{K} = \mathbf{G}_a)$. Similarly, $F_s(\Delta\mathbf{K})$ will have finite values at $\Delta\mathbf{K} = \mathbf{G}_s$. \mathbf{G}_a and \mathbf{G}_s denote reciprocal lattice vectors of the adsorbate and substrate lattice, respectively.

The convolution of F_a and F_s will therefore have non-zero intensity at $\mathbf{G} = \mathbf{G}_a \pm \mathbf{G}_s$, as found in the case of the COT overlayer on Cu(111). We conclude that the adsorbate overlayer is indeed modulated with the periodicity of the substrate.

Analysis of Isothermal Desorption Data

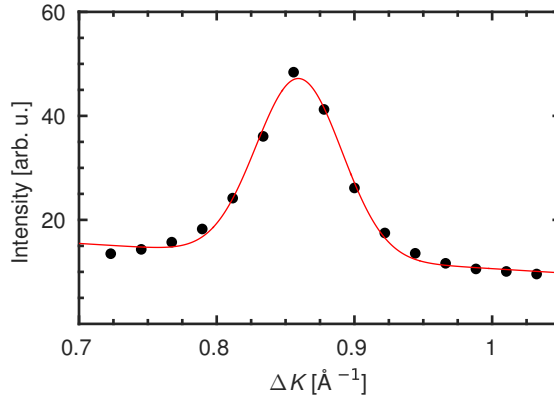


Figure S2: Example of fitting the one-dimensional diffraction scans (black circles) with a Gaussian function including a linear background (red line). The black circles represent the same data as the third curve in Fig. 3a of the paper showing the center of the diffraction peak ($\alpha = 30.0^\circ$).

As shown in Fig. 4c of the main text, the positions of the maxima in the consecutive 1D diffraction scans in ΔK (e.g. Fig 4a) were extracted as a function of time. Each 1D scan $I(\Delta K)$ was fitted with a Gaussian peak, $G(\Delta K)$, and a linear background signal (see Fig S2) of the form,

$$I(\Delta K) = G(\Delta K) + b \cdot \Delta K + c = \frac{A}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2} \left(\frac{\Delta K - \Delta K(t_i)}{\sigma}\right)^2\right) + b \cdot \Delta K + c. \quad (4)$$

The parameter $\Delta K(t_i)$ describes the center of the Gaussian function at time t_i at which the intensity was measured. The corresponding lattice constant $a(t_i) = 2\pi/|\Delta K(t_i)|$ is used to estimate the coverage, $\theta(t)$, relative to the 205 K monolayer coverage with $\Delta K = \Delta K_{205}$ using

$$\theta(t) = \left(\frac{a_{205}}{a(t)} \right)^2 = \left(\frac{\Delta K(t)}{\Delta K_{205}} \right)^2, \quad (5)$$

and assuming that the surface is uniformly covered by COT molecules.

As explained in the paper, the time-dependent decrease in coverage is attributed to desorption, which can be described using the Polanyi-Wigner equation for first-order desorption,^{S2}

$$-\frac{d\theta}{dt} = \nu(\theta) \cdot \theta \cdot \exp\left(\frac{-E_{\text{des}}(\theta)}{k_{\text{B}}T}\right). \quad (6)$$

Since the desorption experiment is carried out at constant temperature, the pre-exponential factor $\nu(\theta)$ and the desorption energy $E_{\text{des}}(\theta)$ only depend on the coverage. Because the change in coverage is relatively small (between 0.8 and 0.9), we assume that $\nu(\theta)$ is independent of coverage. Similarly, for the desorption energy a linear dependence on coverage is assumed,

$$E_{\text{des}}(\theta) = E_{\text{des}}^0 + a(\theta_0 - \theta). \quad (7)$$

E_{des}^0 and θ_0 are fit parameters and represent the desorption energy and coverage (expressed as number density with respect to the substrate surface atoms) at $t = 0$, respectively. a is a fit parameter representing the slope. Starting at θ_0 and $t = 0$, the temporal evolution of

the coverage $\theta(t)$ can be calculated by numerical integration. For that, $d\theta/dt$ in Eq. 6 is approximated by $\Delta\theta/\Delta t$ to evaluate $\theta(t + \Delta t) = \theta(t) + \Delta\theta(t)$ at each time step. The function $\theta(t)$ with parameters E_{des}^0 , θ_0 and a is then fitted to the experimental coverage decay shown in Fig. 4c.

The coverage regime, in which the experiment was done, is narrow. To avoid excess in fit-parameters, we assume a pre-exponential factor of $\nu = 1 \times 10^{13}$ Hz. Under that assumption, we find that $\theta_0 = 0.88 \pm 0.01$ ML (density of 0.096 with respect to the number of Cu(111) surface atoms), $a = 6.0 \pm 0.7$ eV and $E_0 = 1.045 \pm 0.003$ eV. Extrapolation to near saturation coverage (density of 0.11) and to zero coverage, yields desorption energies of 0.96 ± 0.01 and 1.62 ± 0.07 eV, respectively. More extensive measurements (for example, monitoring the desorption for longer time and at different temperatures) would allow ν to fitted as a function of the coverage.

References

- (S1) Ellis, J.; Rohlfing, D.; Hinch, B.; Allison, W.; Willis, R. A new method for the calculation of helium diffraction intensities from complex surfaces. *Vacuum* **1988**, *38*, 347–351.
- (S2) King, D. A. Thermal desorption from metal surfaces: A review. *Surf. Sci.* **1975**, *47*, 384–402.