Supplementary Information

Estimation of CO Contamination

As noted in the main text, background adsorption of residual CO from the vacuum chamber gives rise to a peak in our RAIR spectra in the vicinity of 2100 cm^{-1}. Since substantial co-adsorption with CO may alter our interpretation of the data concerning nitrogen-containing species, we aim here to provide an estimation of the maximum coverage of the contaminating adsorbate. In so doing, we note that the sample was cleaned before each individual experimental run. This involved sputtering, followed by cooling of the sample and its mount to around 100 K, and finally a flash anneal of the sample to 900 K. After this last step, the sample was rapidly cooled, and monitoring RAIR spectra during this process allows us to conclude that CO adsorption only occurred below about 213 K (Supplementary Figure 1a). By the time the sample reached 100 K, the peak corresponding to CO would have a height (i.e. ΔR/R) of around 0.2-0.3%. This height would then increase gradually, reaching around 0.5% after about an hour of further exposure to the chamber's residual atmosphere (Supplementary Figure 1b). For reference, the experiments reported in the main text (Figures 2, 8 and 9) were completed within about half of this time, with CO peak heights substantially below 0.5%.

Although not directly comparable, due to different experimental geometries and the use of different single-crystal surface facets, it may be worth noting straight away that previous RAIRS experiments show much greater peak heights under deliberate CO exposure of various copper surfaces. For instance, Raval et al. [1] report ΔR/R values of a little over 1% for their nominally clean Cu{111} surface (i.e. before deliberate exposure to CO) rising to over 7% at 0.45 L exposure, before dropping back to around 6% at 0.75 L. The peak in ΔR/R was reckoned to coincide with formation of a (√3x√3)R30^0 LEED pattern, at an inferred coverage of 0.33 ML, and the reduction of peak height at higher coverages is a consequence either of electronic effects or tilting induced by the proximity of neighbouring molecules. From this, we learn (a) that our much smaller ΔR/R values probably indicate a much smaller CO coverage, and (b) that estimation of low coverages by comparison of ΔR/R against values obtained at high coverage is complicated by reduction of the effective CO dipole in densely packed conditions.

We turn, therefore, to consideration of temperature-programmed desorption (TPD) data, where the area under desorption peaks should provide a reliably quantitative measure of surface coverage. We have performed a series of control experiments, in which we first prepared a nominally clean sample (as described above) and then deliberately dosed CO at 100 K to a chosen exposure prior to conducting a TPD run (Supplementary Figure 1c). From these, we see that the coverage of CO increases linearly with exposure only up to 0.5 L, after which the uptake reduces, leading eventually to effective saturation of the surface after about 5 L exposure. The temperature corresponding to the peak maximum is roughly constant, at around 205 K, during the linear regime, but reduces sharply to around 170 K as we approach saturation, indicating an overlayer phase transition driven by the increase in coverage.

Against these findings, we may compare the results of background exposure to residual CO at a temperature of 100 K. TPD traces obtained after 24 or 36 minutes, corresponding to nominal exposures of 0.67, and 1.00 L, respectively, yield peaks with maxima at 203 K (consistent with the low-coverage surface phase) and areas rising from roughly 15% to around 16% of that corresponding to CO saturation (Supplementary Figure 1c). It is noteworthy that these areas are much lower than might have been expected based on similar exposures from our control experiments, but this may readily be explained as an artefact of the way pressures are measured in the UHV chamber. During background dosing, the partial pressure of CO may reasonably be assumed to be fairly uniform throughout the chamber, so the reading of the pressure gauge should give an accurate assessment of the partial pressure that pertains at the sample itself. During deliberate dosing, however, gas is continually entering the chamber through a leak valve, whilst being continually removed by pumping, giving rise to a non-trivial pressure gradient. In our experimental geometry, we expect the partial pressure reading from the gauge during dosing to be an overestimate of that which pertains at the sample itself, although we emphasise that the two values should be linearly related. We cannot, therefore, directly compare exposures between deliberate dosing and background regimes. We certainly can, however, draw meaningful

comparisons between TPD peak areas obtained during background exposure and those obtained at saturation during deliberate dosing. The question that remains, then, is what coverage constitutes saturation for CO on Cu{311}?

To answer this crucial question, we first note that Papp and Pritchard [2] studied this system and reported a series of LEED patterns consistent with coverages increasing continuously from 0.67 ML to 0.83 ML whilst the exposure increased from about 0.7 L to around 1.2 L. That is to say, the apparent coverage increased by no more than around 0.03 ML for each additional 0.1 L exposure over this range. Saturation was finally achieved at 1.3 L exposure, suggesting that the corresponding coverage probably does not much exceed 0.86 ML (or 0.132 mol.cm^{-2}, given a primitive surface unit cell area of 10.84 Å^2).

As a further check on this logic, we may also turn to other reported experiments for similar systems. For example, saturation coverage on the Cu{110} surface (certainly the most structurally similar to our own Cu{311} surface) has previously been estimated as 0.77 ML [3]. Expressed as an areal density, this corresponds to 0.138 mol.cm^{-2} (given a primitive surface unit cell area of 9.24 Å^2) which is just 5% higher than the estimate we derive from Papp and Pritchard [2]. Converting back to the Cu{311} system, this would correspond to a coverage of 0.90 ML. Estimates from the Cu{111} and Cu{100} surfaces, where saturation coverages of 0.52 ML [1] and 0.70 ML [4] have been reported, yield areal densities of 0.152 mol.cm^{-2} and 0.178 mol.cm^{-2} (given respective cell areas of 5.66 Å^2 and 6.53 Å^2) but both are much less similar to the Cu{311} surface than is the Cu{110} surface. We therefore estimate the saturation coverage for CO on Cu{311} to be 0.88 ML (midway between the result derived from experiments conducted on the surface itself and on its most similar analogue).

On this basis, the peak areas obtained after background exposure, which it will be recalled are only about 15-16% as large as those obtained at saturation, would correspond to CO coverages in the range 0.13-0.14 ML (using the 0.88 ML estimate for saturation coverage) over the period from 24-36 minutes from commencement of the experiment. The interesting portions of the experiments reported in the main paper generally occurred within the first 12 minutes, however, and we therefore estimate that the CO coverage will rarely, if ever, have exceeded about 0.12 ML whilst acquiring the data discussed.
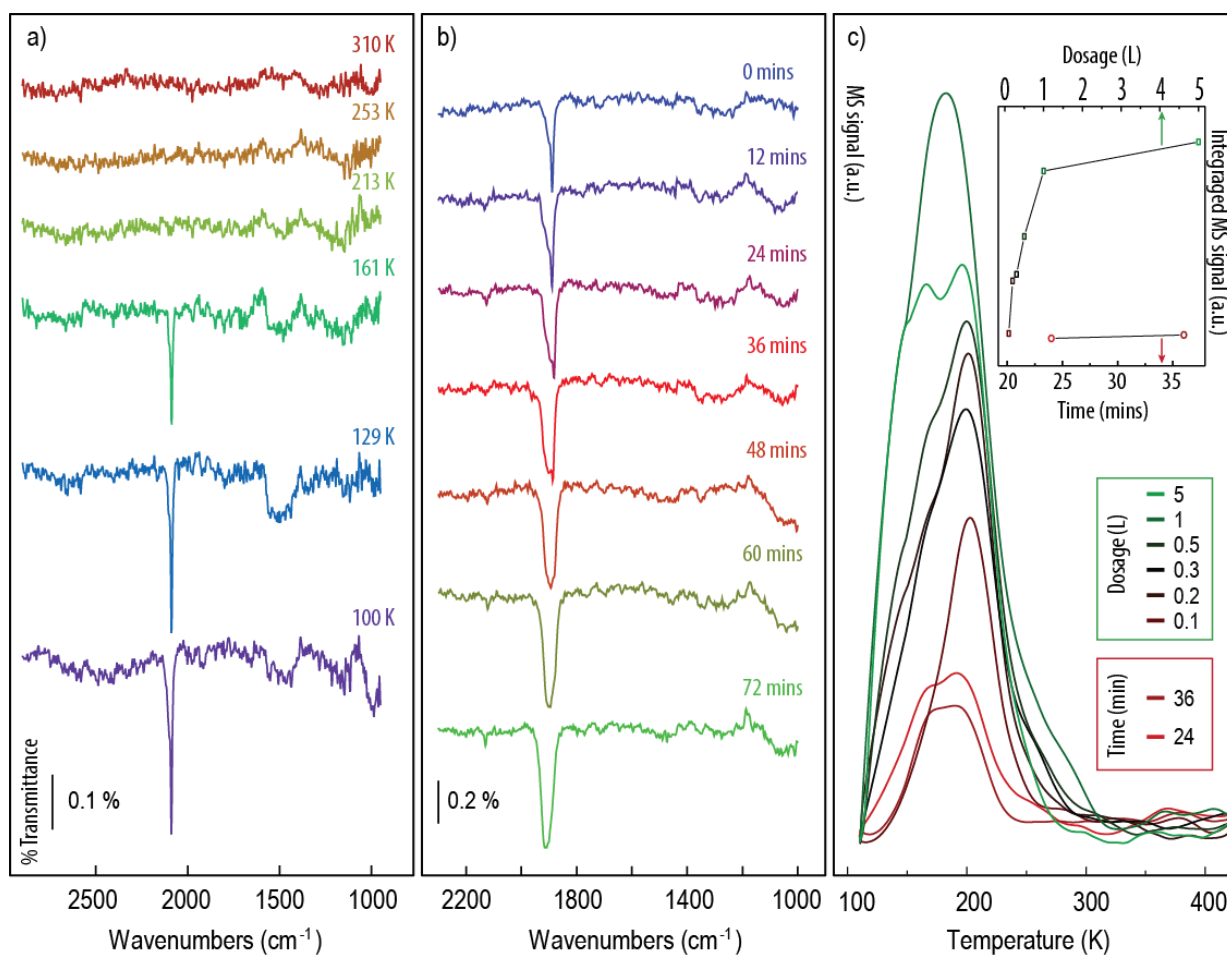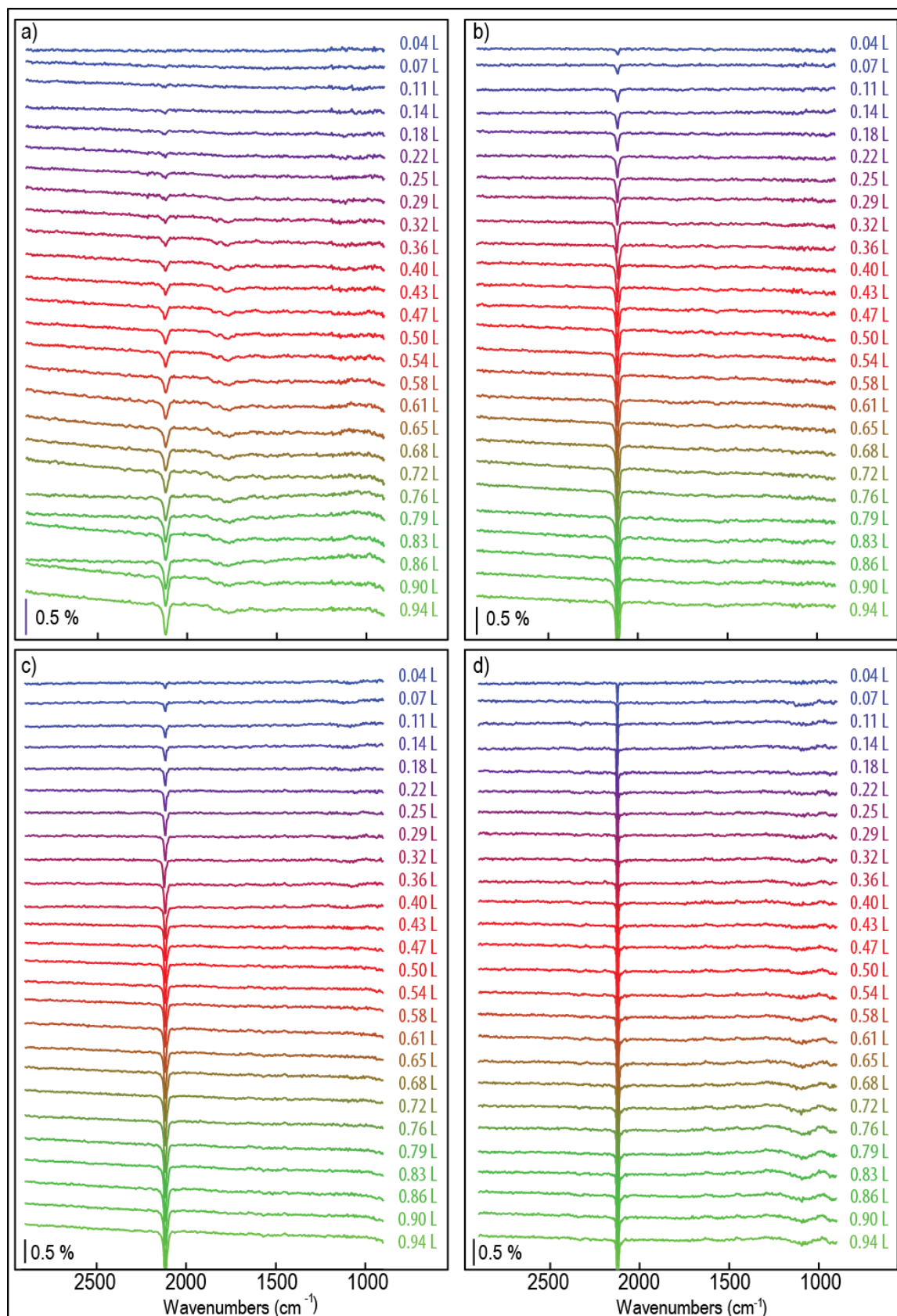
Supplementary Figure 1. a) RAIR spectra of a recently cleaned Cu{311} single crystal as it cools down from flash anneal; and b) as a function of time at 100 K; c) Temperature programmed desorption data (m/z = 28) of a Cu{311} surface rested at 100 K for 24, and 36 minutes (comparable timeframes to RAIRS experiments), as well as CO exposure at various dosages; Insert graph shows the area under the TPD curves.
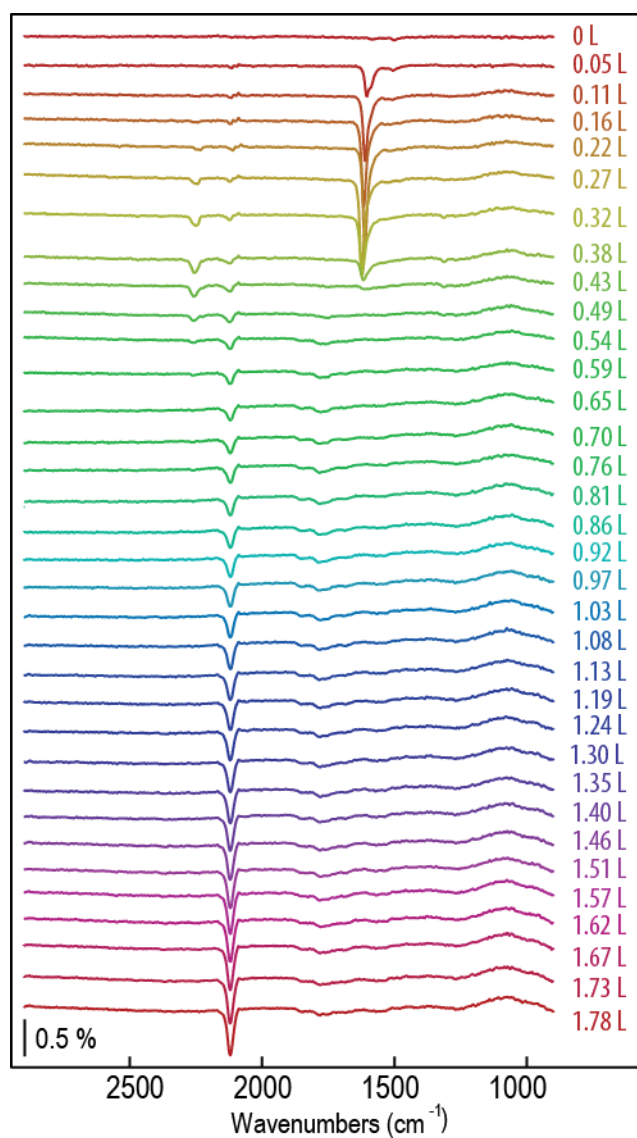
Supplementary Figure 2. RAIR spectra following the adsorption of NO onto a Cu{311} single crystal. The single crystal was held at 100 K, dosing pressure of 6 x 10^{-10} mbar, 400 scans/spectra with a resolution of 4 cm^{-1}.
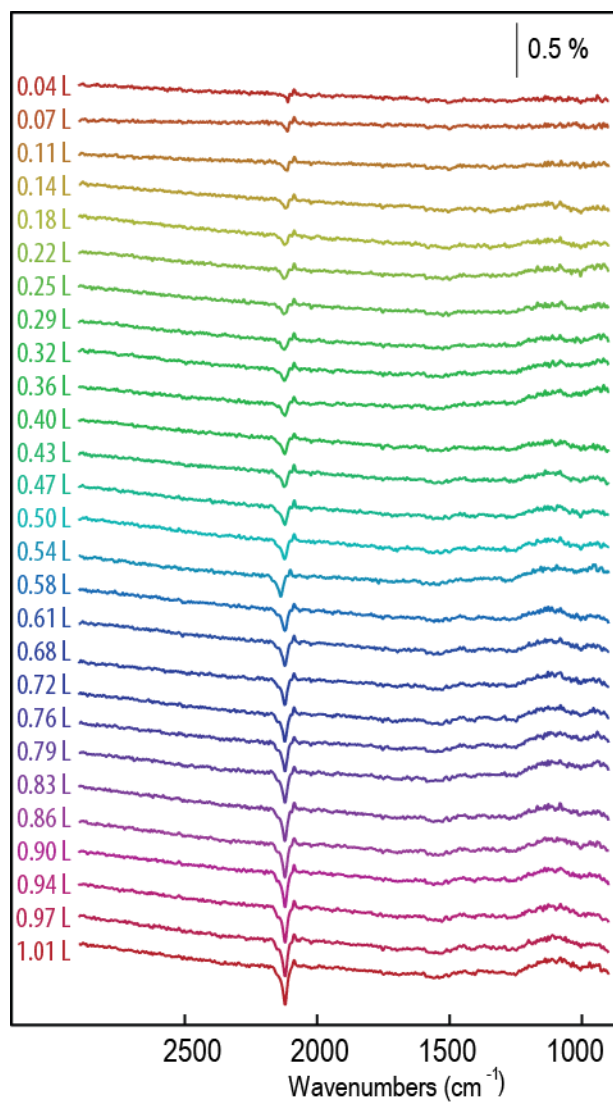
Supplementary Figure 3. Coverage-dependent RAIR spectra following the adsorption of NO on Cu{311} at temperatures of a) 150 K; b) 200 K;

Supplementary Figure 4. RAIR spectra following the adsorption of NO onto a O-Cu{311} single crystal at various oxygen coverages. Labels a) - d) correlate to pre-dosed oxygen with the LEED patterns shown in Supplementary Figure 5.
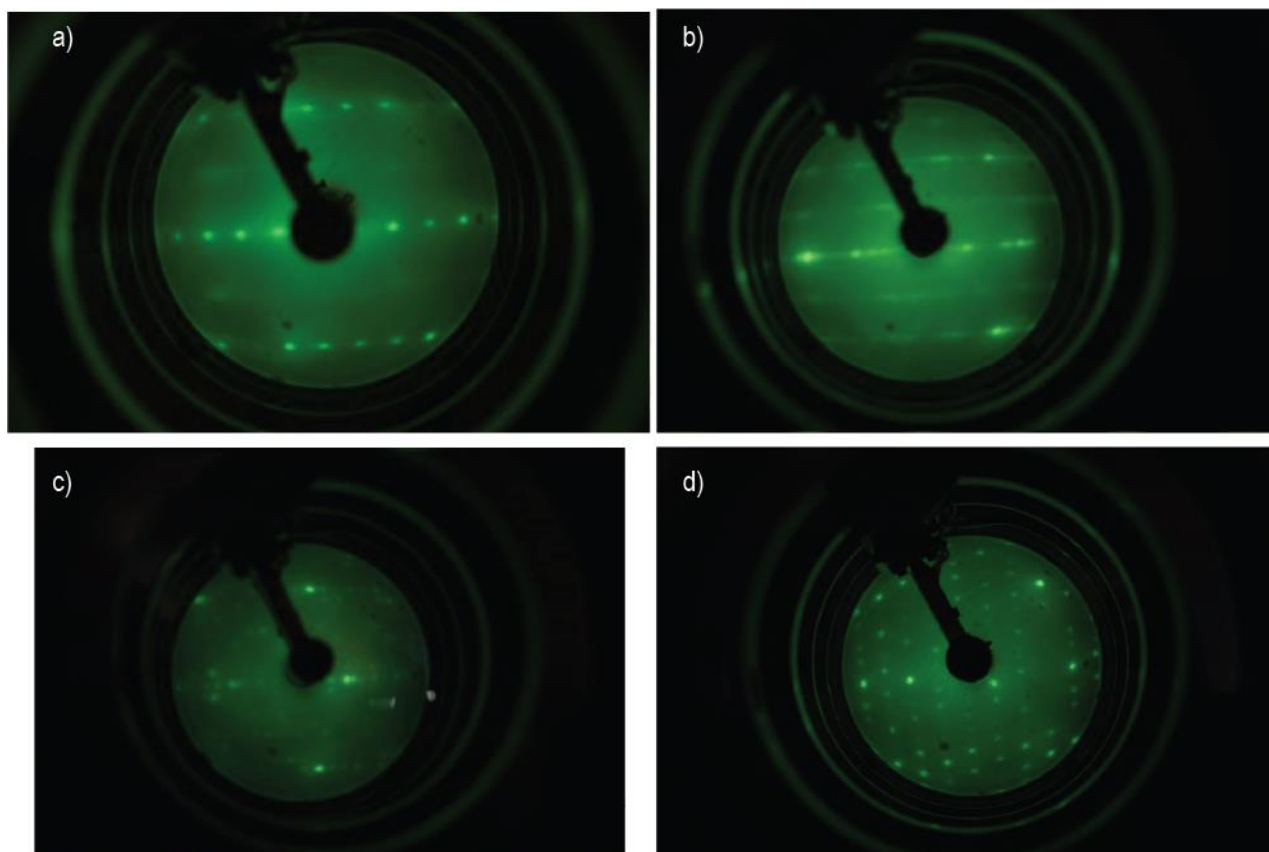
Supplementary Figure 5. LEED patterns obtained at increasing oxygen coverage on Cu{311}, showing a) a (1x2) pattern at relatively low coverage; b) a streaked pattern at higher coverage; c) and d) complex patterns at yet higher coverage.

Calculated Geometries

Calculated geometries corresponding to Figs. 3-6 of the paper are provided in the archive file named geomfiles.tar, each being in CASTEP's seed.geom file format. These may most easily be opened by the free software Jmol, or some similar application. These files typically contain several intermediate structures from the geometry optimisation procedure, with the final frame containing the local minimum obtained by that process. File naming should be self-explanatory in relation to figure numbering, and we include five further files (corresponding to adatom adsorption and tilted molecular desorption) that are mentioned in the text but not included in any of the figures.

Unscaled Vibrational Frequencies

Her we tabulate the unscaled frequencies that arise directly from our CASTEP calculations, alongside the scaling factors used to convert to the values quoted in the paper. All of the frequencies given for NO and N_2O_2 correspond to N-O stretch modes, while all of those given for N_2O are for the highest-frequency mode (N-O and N-N stretches in antiphase).

Description	Scaling Factor	Unscaled Frequency	Scaled Frequency
NO(g)	0.933	2007 cm^{-1}	1872 cm^{-1}
NO(a) bridge	0.933	1658 cm^{-1}	1547 cm^{-1}
2NO(a) bridge (close)	0.933	1731 cm^{-1}	1615 cm^{-1}
N_2O_2(a) bound thru N	0.933	1535 cm^{-1}	1432 cm^{-1}
N_2O_2(a) bound thru O	0.933	882 cm^{-1}	823 cm^{-1}
N_2O(g)	0.912	2438 cm^{-1}	2224 cm^{-1}
N_2O(a) bound thru N	0.912	2422 cm^{-1}	2209 cm^{-1}
N_2O(a) bound thru O	0.912	2423 cm^{-1}	2210 cm^{-1}
O/ N_2O(a) bound thru N	0.912	2431 cm^{-1}	2217 cm^{-1}
O/ N_2O(a) bound thru O	0.912	2432 cm^{-1}	2218 cm^{-1}

References

1. Raval, R., et al., *FT-RAIRS, EELS and LEED studies of the adsorption of carbon monoxide on Cu(111)*. Surface Science, 1988. **203**(3): p. 353-377.
2. Papp, H. and J. Pritchard, *The adsorption of Xe and CO on a Cu(311) single crystal surface.* Surface Science, 1975. **53**(1): p. 371-382.
3. Hollins, P., K.J. Davies, and J. Pritchard, *Infrared spectra of CO chemisorbed on a surface vicinal to Cu(110): The influence of defect sites.* Surface Science, 1984. **138**(1): p. 75-83.
4. Hirschmugl, C.J., et al., *Adsorbate-substrate resonant interactions observed for CO on Cu(100) in the far infrared.* Physical Review Letters, 1990. **65**(4): p. 480-483.