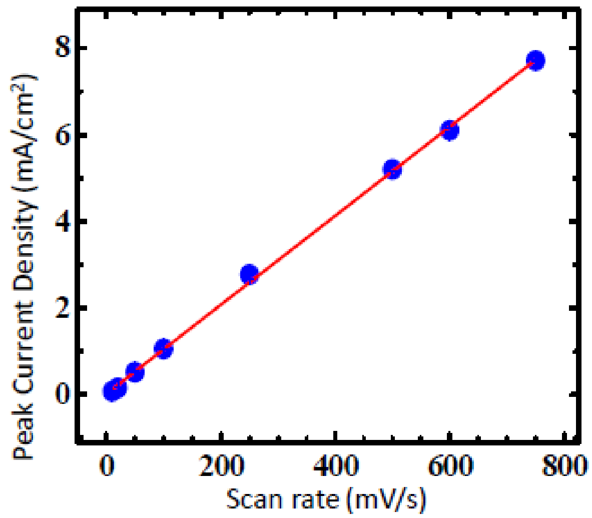
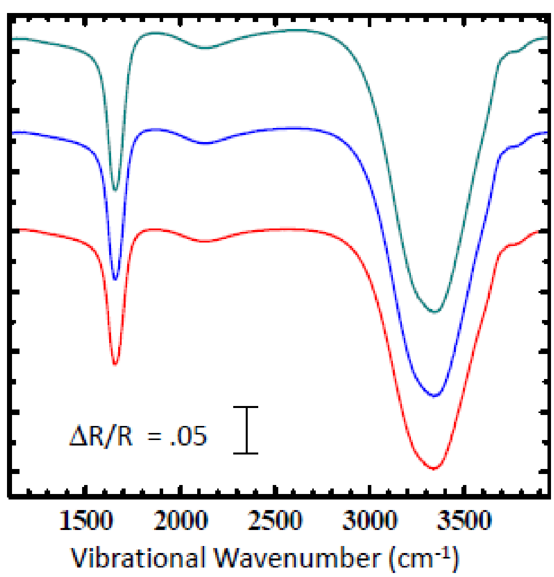
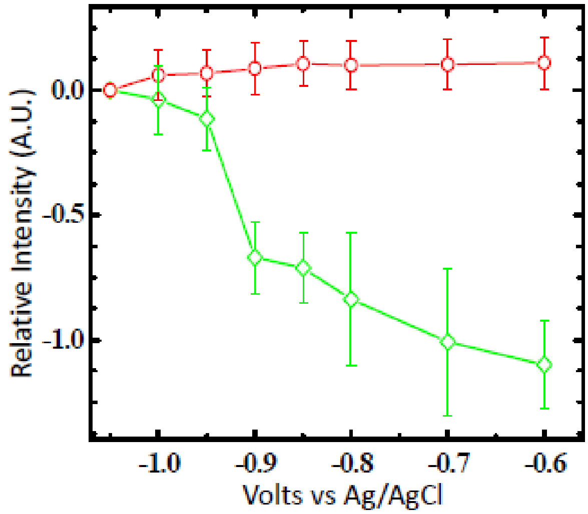
Supporting Information:



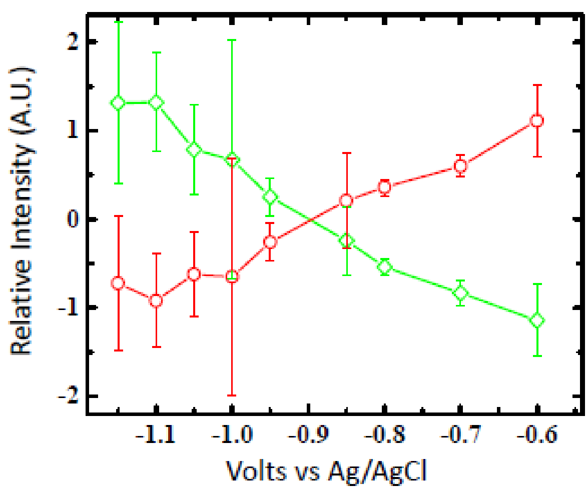
S. I. **Figure A.** Dependence of the peak current density of the anodic scan on sweep rate for Cu(110) in 0.1 M NaF saturated with CO. The error bars are indicated by the symbols' sizes.



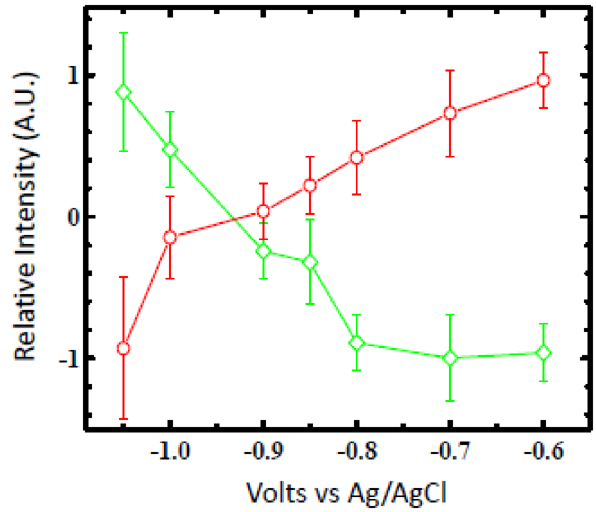
S. I. **Figure B**. SNIFTIRS spectra for Cu(110) in argon saturated 0.1 M NaF. Sample potentials (from top to bottom): -1.00, -0.80 and -0.60 V. The reference potential was -1.20 V. The spectra have been offset for clarity



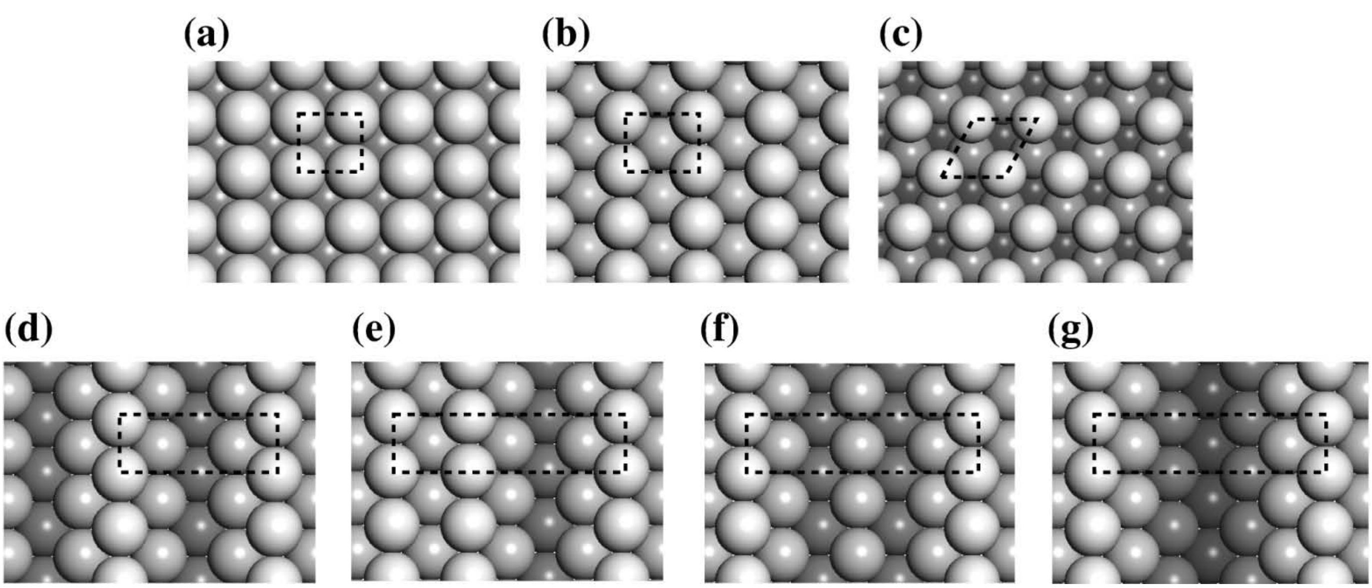
S.I. **Figure C1.** Relative intensities of the SNIFTIRS CO stretching bi--modal vibrational bands obtained from non-linear regression fits for Cu(111) in 0.1 M NaF. The circles and diamonds correspond to the high and low energy lobes, respectively.



S.I. **Figure C2.** Relative intensities of the SNIFTIRS CO stretching bi--modal vibrational bands obtained from non-linear regression fits for Cu(110) in 0.1 M NaF. The circles and diamonds correspond to the high and low energy lobes, respectively.

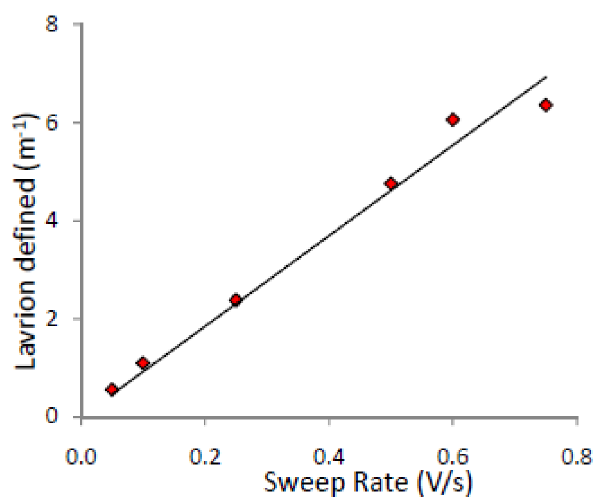


S.I. **Figure C3.** Relative intensities of the SNIFTIRS CO stretching bi--modal vibrational bands obtained from non-linear regression fits for Cu(100) in 0.1 M NaF. The circles and diamonds correspond to the high and low energy lobes, respectively.



S.I. Figure D: Hard-sphere models of the different Cu-surface onto which CO adsorption has been studied: (a) Cu(100), (b) Cu(110), (c) Cu(111), (d) Cu(110)-(2×1) single-MR, (e) Cu(110)-(3×1) single-MR, (e) Cu(110)-(3×1) double-MR, (f) Cu(110)-(3×1) triple-MR. In each figure the unit cell is indicated as dashed box.

Laviron 'Trumpet' Plot Analysis Method: The method for obtaining experimental rate constant values from electrochemical measurements has been described previously(see Laviron 1979, Journal of Electroanalytical Chemistry) and will be reviewed briefly here. For a quasi-reversible electron transfer reaction, the dependence of the cathodic and anodic peak potentials on the log of the sweep rate observed in Figure 4 resembles a classical trumpet plot. Laviron's calcuations for the dependence of m^{-1} ($m = (RT/F)*(k/n\nu)$) on peak potential separation, ΔEp, were fitted to a third order polynomial, which was then used to obtain the values m^{-1} at different sweep rates from the experimental ΔEp results (R, T, F, n, and ν have the usual meanings and k is the rate constant in s^{-1}). The rate constant k was obtained from $k = (F/RT)/S$, where S is the slope of the results shown in S.I. Figure E.



S.I. Figure E: Data for Laviron trumpet plot analysis. m^{-1} vs sweep rate (V/s)

The slope of the line is 9.2 ± 0.3