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## **Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study**

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## Chapter 4

# Spectroscopic Observation of a Hydrogenated CO Dimer Intermediate During CO Reduction on Cu(100) Electrodes

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*Carbon dioxide and carbon monoxide (CO) can be electrochemically reduced to useful products such as ethylene and ethanol on copper electrocatalysts. The process is yet to be optimized and the exact mechanism and the corresponding reaction intermediates are under debate or unknown. In particular, it has been hypothesized that the C-C bond formation proceeds via CO dimerization and further hydrogenation. Although computational support for this hypothesis exists, direct experimental evidence has been elusive. In this work, we detect a hydrogenated dimer intermediate (OCCOH) using Fourier transform infrared spectroscopy at low overpotentials in LiOH solutions. Density functional theory calculations support our assignment of the observed vibrational bands. The formation of this intermediate is structure sensitive, as it is observed only during CO reduction on Cu(100) and not on Cu(111), in agreement with previous experimental and computational observations.*

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## 4.1 Introduction

A considerable number of experimental observations as well as density functional theory (DFT) calculations have established that CO<sub>2</sub> and CO reduction on copper electrodes forms C<sub>1</sub> and C<sub>2</sub> products through different reaction pathways.<sup>47, 49-50, 52, 57</sup> The formation of C<sub>1</sub> and C<sub>2</sub> products has been shown to be highly sensitive to copper surface structure and electrolyte pH.<sup>51, 59, 61, 63-64, 91, 127</sup> Hori et al.<sup>61</sup> showed that the CO to CH<sub>4</sub> reduction follows a concerted proton-electron transfer mechanism, in stark contrast with C<sub>2</sub>H<sub>4</sub> production, the rate-limiting step of which is not sensitive to pH and only involves an electron transfer. As a result, on the pH corrected RHE reference scale, the formation of ethylene from CO depends on pH while that of CH<sub>4</sub> does not.<sup>61, 63</sup> Furthermore, Schouten et al. showed that C<sub>2</sub>H<sub>4</sub> formation takes place preferentially at Cu(100) electrodes without simultaneous CH<sub>4</sub> formation, which indicates that the reaction paths towards CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> must bifurcate in the early stages of CO reduction.<sup>61</sup> Specifically, a C<sub>2</sub> intermediate that requires only electron transfer to be formed, namely a negatively charged CO dimer, has been proposed as the first C-C coupled intermediate.<sup>49, 51, 53</sup> Various recent computational works have studied the structural sensitivity of this intermediate, and concluded that the formation of the dimer is indeed favored both thermodynamically and kinetically on Cu(100) sites compared to Cu(111).<sup>53-54, 58</sup>

However, there is still no direct experimental evidence that proves CO dimerization in aqueous solution during CO reduction on copper electrodes, and the existence of the dimer is mostly a logical deduction from experimental and computational results. In this chapter, we provide experimental evidence for the formation of a hydrogenated CO dimer (OCCOH) at low overpotentials during CO reduction on Cu(100) electrodes in LiOH solution, employing in situ Fourier transform infrared spectroscopy (FTIR), and support our interpretation by detailed DFT calculations.

## 4.2 Experimental

Prior to each electrochemical experiment, the glassware used was stored overnight in a solution of  $\text{KMnO}_4$  that was rinsed with a mixture of ultra clean water (Millipore MilliQ, resistivity  $> 18.2 \text{ M}\Omega$ ), 20 ml/l of hydrogen peroxide and 1 ml/l of concentrated sulfuric acid. The glassware was further cleaned by boiling 4 times in Millipore MilliQ water. A coiled platinum wire was used as counter electrode and a reversible hydrogen electrode (RHE) in the same electrolyte was used as reference electrode.

The copper electrodes used were 99.99% copper disks with a diameter of 6mm, purchased from Mateck and aligned to  $< 0.5^\circ$  accuracy. Prior to every experiment, the electrodes were electropolished and characterized as described elsewhere.<sup>91</sup>

The electrolytes were made from ultra-pure water (Millipore MilliQ, resistivity  $> 18.2 \text{ M}\Omega$ ) and high purity reagents (Sigma Aldrich TraceSelect). Before every experiment, Argon (Linde, 6.0) was bubbled through the electrolyte for 15 minutes in order to remove air from the solution, and during the experiments argon was kept flowing above the solution.

FTIR measurements were performed with a Bruker Vertex 80 V Infrared spectrophotometer.<sup>128</sup> The electrochemical cell was assembled on top of a  $60^\circ$   $\text{CaF}_2$  prism, and the electrode was situated against this prism to form a thin layer. The measurements were performed under external reflection. FTIR spectra were obtained from an average of 100 scans with a resolution of  $8 \text{ cm}^{-1}$  at the selected potentials. Every spectrum was obtained by applying single potential steps compared to the reference potential (+0.1 V). The spectra are shown as  $(R-R_0)/R_0$  where R is the reflectance at the sample potential and  $R_0$  is the reflectance at the reference potential. Thereby the ratio  $\Delta R/R_0$  gives positive bands for the formation of species at the sample potential, while negative bands correspond to the loss of species at the sample potential. P-polarized

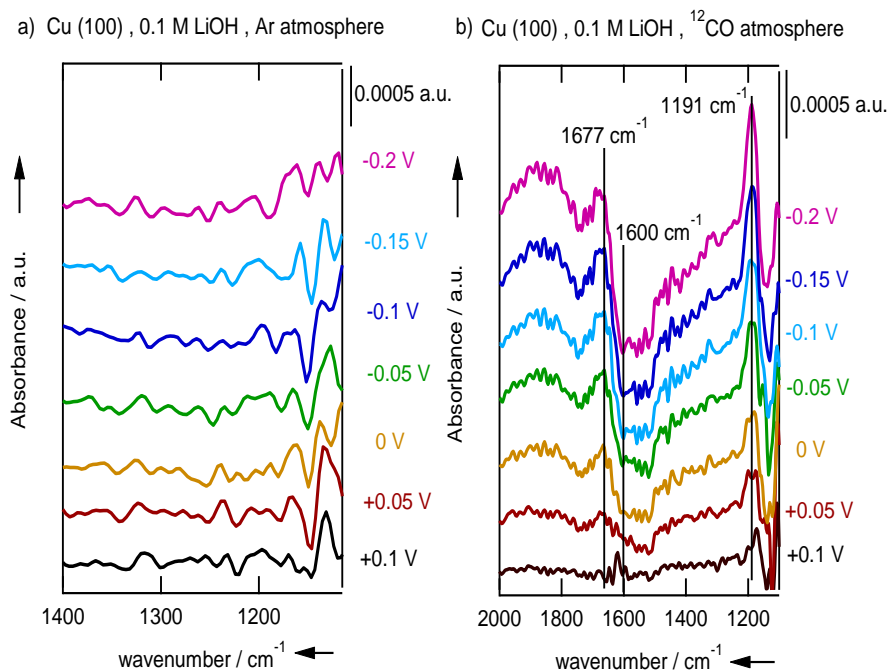
light was used to probe species both near the electrode surface and in solution.

The vibrational frequencies were calculated by means of DFT calculations using the VASP code<sup>112</sup> with the PBE exchange-correlation functional<sup>113</sup> and the projector augmented wave (PAW) method.<sup>114</sup> The Cu(100) surfaces were modelled with (3×2) 4-layer-thick slabs. The vertical separation between periodically repeated images was more than 16 Å and dipole corrections were applied. The structures were optimized allowing the adsorbates and the two topmost layers to relax in all directions, while fixing the 2 bottom layers at the optimized bulk positions. The relaxations were carried out with a plane-wave cut-off of 450 eV, using the conjugate-gradient scheme until the maximum force on any atom was below 0.05 eV Å<sup>-1</sup>. The Brillouin zones were sampled with 6×8×1 Monkhorst-Pack meshes.<sup>115</sup> The Fermi level of the surfaces was smeared using the Methfessel-Paxton method<sup>116</sup> with an  $k_B T = 0.2$  eV, and all energies were extrapolated to 0 K.

The vibrational frequency analysis was made using the harmonic oscillator approximation with two displacements in each direction plus the ground state.

### 4.3 Results and discussion

Figure 4.1 shows the potential-dependent absorbance spectra of Cu(100) in 0.1 M LiOH solutions in Argon atmosphere (Fig.4.1a, left panel) and in CO atmosphere (Fig.4.1b, right panel). The reference spectrum is taken at +0.1 V and additional spectra are provided for +0.05, 0.00, -0.05, -0.10, -0.15 and -0.2 V (all reported potentials are on the RHE scale). First of all, in Argon atmosphere the absorption spectra do not display any bands. After CO is bubbled through the solution, three bands appear at 1677, 1600 and 1191 cm<sup>-1</sup>. The band at 1600 cm<sup>-1</sup> corresponds to the O-H bending mode of H<sub>2</sub>O. This band causes fluctuations in the baseline of the spectra making it difficult to identify



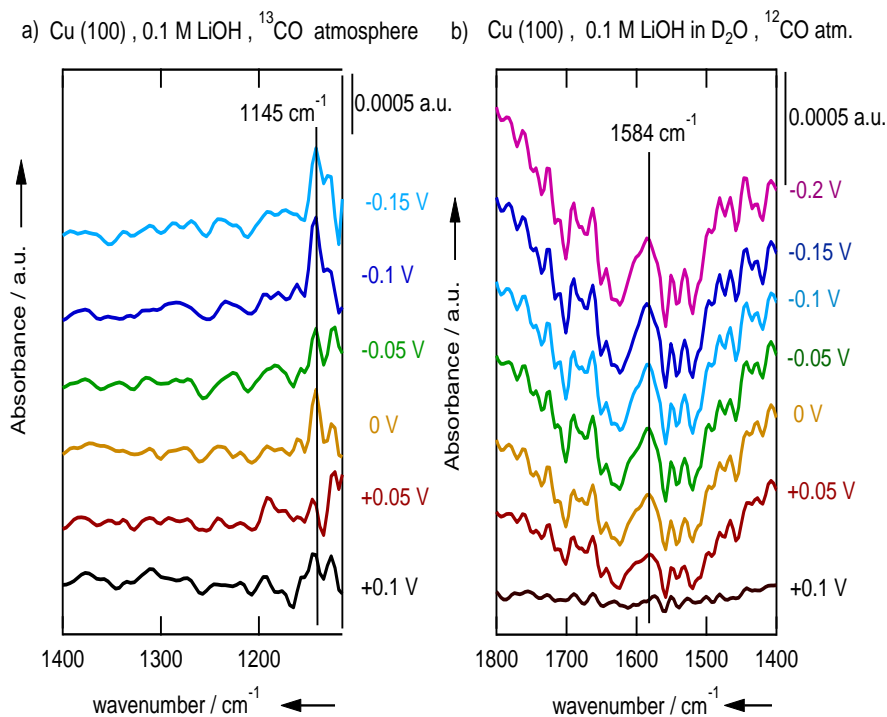
**Figure 4.1:** . Potential-dependent absorbance spectra for Cu(100) in the a) absence and b) presence of CO in a 0.1 M LiOH solution. Reference spectrum recorded at +0.1 V vs. RHE. Highlighted bands and their corresponding frequencies are indicated with a vertical line at 1191 cm<sup>-1</sup> for <sup>12</sup>C-OH stretching, 1145 cm<sup>-1</sup> for <sup>13</sup>C-OH stretching, 1677 cm<sup>-1</sup> for C=O stretching and 1600 cm<sup>-1</sup> for O-H

other bands in this wavenumber range. The band at 1677 cm<sup>-1</sup> corresponds to the C=O stretching<sup>129-131</sup> of CO adsorbed on hollow sites on Cu(100), in agreement with DFT calculations (see Figure 3 below). The intensity of the band for CO at multi bonded sites increases with more negative electrode potential. In alkaline media, the absolute potential (on the SHE scale) is more negative compared to acidic conditions and, consequently, the band for CO at multifold sites dominates the spectra.<sup>132-135</sup>

Simultaneously with the CO-related band, a band at 1191 cm<sup>-1</sup> associated with C-OH stretching<sup>136</sup> grows in the spectra.

Importantly, when CO reduction was performed under the exact same conditions on a Cu(111) electrode (see Appendix III, Figure AIII.1), the band at  $1191\text{ cm}^{-1}$  and the band corresponding to C=O stretching at  $1677\text{ cm}^{-1}$  were not observed. In order to ensure that the band at  $1191\text{ cm}^{-1}$  comes from a C-containing species, both the blank spectrum and a spectrum taken with isotopically labeled carbon  $^{13}\text{CO}$  were recorded. Figure 4.1a shows the absorbance spectra on Cu(100) without CO. The absence of the band at  $1191\text{ cm}^{-1}$  strongly suggests that the signal appearing in CO atmosphere comes from a C-containing species. Moreover, when the absorbance spectra were obtained in  $^{13}\text{CO}$  atmosphere (see Figure 4.2, left panel), the band shifts from  $1191\text{ cm}^{-1}$  to  $1145\text{ cm}^{-1}$ . The shift of approximately  $45\text{ cm}^{-1}$  matches the expected shift for the absorption spectra of  $^{13}\text{C}$  compared to  $^{12}\text{C}$ ,<sup>137</sup> confirming that the band at  $1191\text{ cm}^{-1}$  comes from a C-containing species.

As mentioned before, water exhibits a wide O-H bending band in the  $1650\text{-}1450\text{ cm}^{-1}$  range, which prevents the straightforward observation of vibrations from other species in this wavenumber range. For this reason, CO reduction on Cu(100) was performed in  $\text{D}_2\text{O}$ ; the corresponding spectra are shown in Figure 4.2b (right panel). In  $\text{D}_2\text{O}$  electrolyte, the range of  $1650\text{-}1450\text{ cm}^{-1}$  is free of water bands, allowing for the identification of additional bands. Unfortunately,  $\text{D}_2\text{O}$  has an O-D bending band at  $1209\text{ cm}^{-1}$  masking the C-OH stretching band. Interestingly, Figure 4.2b shows that in  $\text{D}_2\text{O}$  electrolyte at  $+0.05\text{ V}$  and more negative potentials a band appears around  $1584\text{ cm}^{-1}$ , which corresponds to a C=O stretch but is not adsorbed CO.



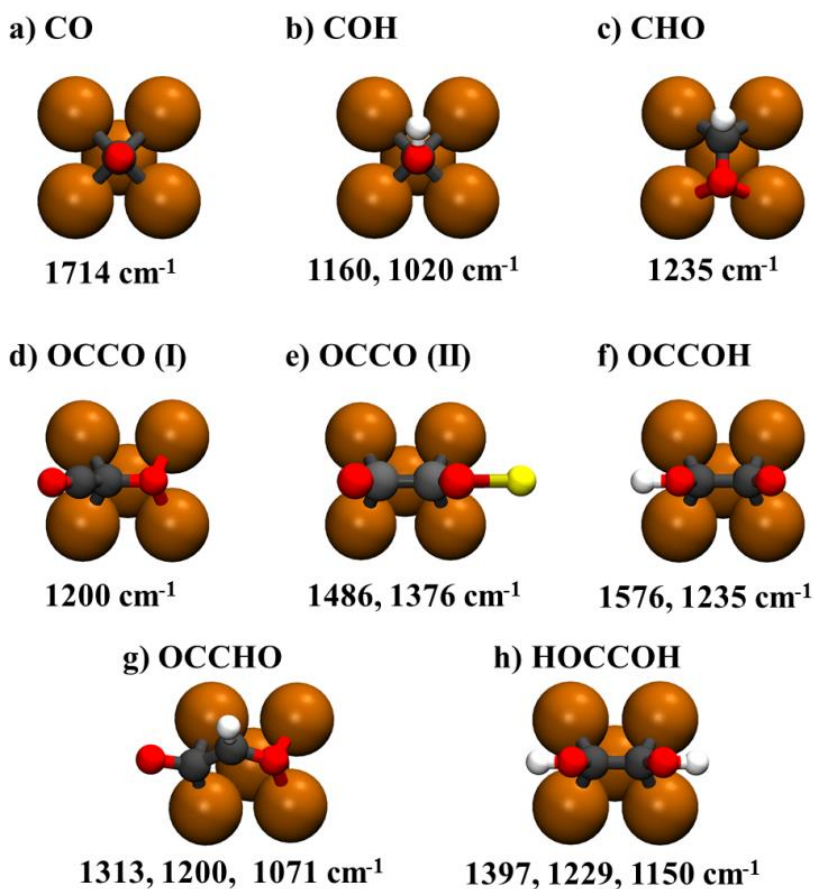
**Figure 4.2:** Potential dependent absorbance spectra for Cu (100) in the presence of a)  $^{13}\text{CO}$  (left) and with b)  $\text{D}_2\text{O}$  as electrolyte (right) in a 0.1 M LiOH solution. Reference spectrum recorded at +0.1 V vs. RHE. Highlighted bands and their corresponding frequencies are indicated with a vertical line at  $1191\text{ cm}^{-1}$  for  $^{12}\text{C-OH}$  stretching,  $1145\text{ cm}^{-1}$  for  $^{13}\text{C-OH}$  stretching and  $1584\text{ cm}^{-1}$  for  $^{12}\text{C=O}$  stretching.

From the combined results of the experiments in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , we observe two vibrational bands coming from C-containing species that are formed at low overpotentials on Cu(100) only. It is important to note that at the low overpotentials considered in our experiments, namely +0.1 to -0.15 V, no products are observed (for instance, the earliest onset potential on Cu(100) is that of  $\text{C}_2\text{H}_4$  at -0.4 V).<sup>59, 138</sup> Thus, the bands in question should, in principle, be assigned to vibrations of adsorbed intermediates of CO reduction rather than to species in solution. To verify this hypothesis, we have scrutinized the IR spectra of

various possible species in solution, including various  $C_1$  and  $C_2$  species. Transmission spectra of species in solution such as formaldehyde, formate and methanol ( $C_1$  molecules), and acetaldehyde and acetic acid ( $C_2$  molecules) were recorded, shown in Appendix III, figure AIII.2. The absence of the bands at 1191 and 1584  $\text{cm}^{-1}$  in the transmission spectra rules out the possibility that the bands observed during the reduction of CO on Cu(100) correspond to these species in solution. Although methanol has a C-OH vibration at 1195  $\text{cm}^{-1}$  in 0.1 M LiOH, the vibration at 1584  $\text{cm}^{-1}$  is absent (see Appendix III, figure AIII.2c) and its substantially negative onset potential (-0.95 V<sup>50</sup>) precludes the presence of methanol at the low overpotentials at which this work was performed (+0.1 to -0.15 V). The transmission spectra of acetaldehyde also displays a band at 1195  $\text{cm}^{-1}$ , however, this band is associated with the C-OH stretching from the methanol present in the acetaldehyde solution as a stabilizer. In addition, acetaldehyde presents other two bands at 1712 and 1666  $\text{cm}^{-1}$ . The absence of these bands in the spectra obtained during CO reduction rules out the possibility of acetaldehyde as a product. Another compound that could have vibrational frequencies close to those in Figures 1 and 2 is acetylenediol ( $\text{HO}\equiv\text{COH}$ ). Maier et al collected the infrared spectra of this double alcohol<sup>139</sup> and reported a single C-OH stretching band at 1212  $\text{cm}^{-1}$ .

Having verified that the observed bands at 1191 and 1584  $\text{cm}^{-1}$  do not correspond to species in solution, we now resort to DFT calculations to see whether a given adsorbed intermediate or a combination of them exhibit such bands. Since both  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  production from CO possess relatively early rate-limiting steps<sup>57, 140-141</sup>, we have limited our analysis to  $C_1$  and  $C_2$  species with no or a low content of hydrogen atoms (see Figure 4.3). First, consider the  $C_1$  species CHO and COH (Figure 4.3b-c), which are the two possible products of the first hydrogenation of CO. They both have bands close to the band observed during the adsorption/reduction of  $^{12}\text{CO}$  on Cu(100) at 1191  $\text{cm}^{-1}$  (Figure 4.1b, right panel), but none of them exhibit the additional vibrational band at 1584  $\text{cm}^{-1}$  (Figure 4.2, right panel). The same is true for the CO dimer (OCCO, Figure 4.3d), which presents a vibrational band at 1200  $\text{cm}^{-1}$  but

does not exhibit a band around  $1584\text{ cm}^{-1}$ . Besides, a lithiated dimer (Figure 4.3e) features two C-O stretching frequencies that are not close to either of the bands at  $1191$  and  $1584\text{ cm}^{-1}$ . Conversely, a CO dimer in which one of the oxygen atoms has been hydrogenated (OCCOH, Figure 4.3f) exhibits bands close to both experimental bands. In addition, we have calculated the vibrational signatures of a CO dimer of which one of the carbon atoms has been hydrogenated (OCCHO, Figure 4.3g). This adsorbate has vibrational bands around  $1313$ ,  $1200$ ,  $1071\text{ cm}^{-1}$  but no band close to  $1584\text{ cm}^{-1}$ . Adsorbed acetylenediol, namely a doubly hydrogenated CO dimer (HOCCOH, Figure 4.3h) was also considered in our DFT calculations. The predicted vibrational frequencies for C-OH stretching are  $1397$ ,  $1229$  and  $1150\text{ cm}^{-1}$ . We also considered a simultaneously hydrogenated and lithiated dimer (HOCCOLi) and its vibrational frequencies were found at  $1427$  and  $1246\text{ cm}^{-1}$ . Finally, a doubly lithiated dimer (LiOCCOLi) possesses C=O stretching frequencies at  $1329$  and  $1261\text{ cm}^{-1}$ .



**Figure 4.3:** Schematic structures of possible adsorbed intermediates on Cu(100) and their calculated infrared-active vibrational frequencies in the 1100-1600  $\text{cm}^{-1}$  wavenumber region. Cu, C, O, and H atoms are depicted as orange, gray, red and white spheres

Therefore, we conclude that the bands at 1191 and 1584  $\text{cm}^{-1}$  arise from C-O-H and C-O stretching vibrations and correspond, in the simplest case, to a hydrogenated dimer (OCCOH), or in general to this adsorbate in combination with other  $\text{C}_1$  and  $\text{C}_2$  adsorbates. This is in line with previous computational works showing that OCCOH is the most stable intermediate formed after the first hydrogenation of CO on Cu(100).<sup>53</sup> In Chapter 5 we performed further experiments and calculations to examine the influence of various alkaline cations on CO dimerization and their impact on the CO reduction pathway.

## **4.4 Conclusion**

In conclusion, we have shown experimentally that Cu(100) electrodes in LiOH solutions host a C-containing adsorbate at low overpotentials with vibrational bands at 1191 and 1584  $\text{cm}^{-1}$ . Based on DFT calculations of a wide variety of  $\text{C}_1$  and  $\text{C}_2$  intermediates, we ascribe these bands to the C-O-H and C=O stretching modes of a hydrogenated CO dimer (OCCOH). These results provide for the first time direct confirmation of an important hypothesis in the electrocatalysis of  $\text{CO}_2$  reduction on copper, namely that the C-C coupling to  $\text{C}_2$  species on Cu(100) takes place through a reductive dimerization step at the early stages of the reaction mechanism. The fact that the vibrational features ascribed to the CO dimer could not be observed on Cu(111) under identical conditions confirms that CO dimerization is a structure-sensitive process favored by sites with square symmetry, in agreement with previous experimental<sup>64</sup> and theoretical studies.<sup>54</sup>

