

## **Supporting information**

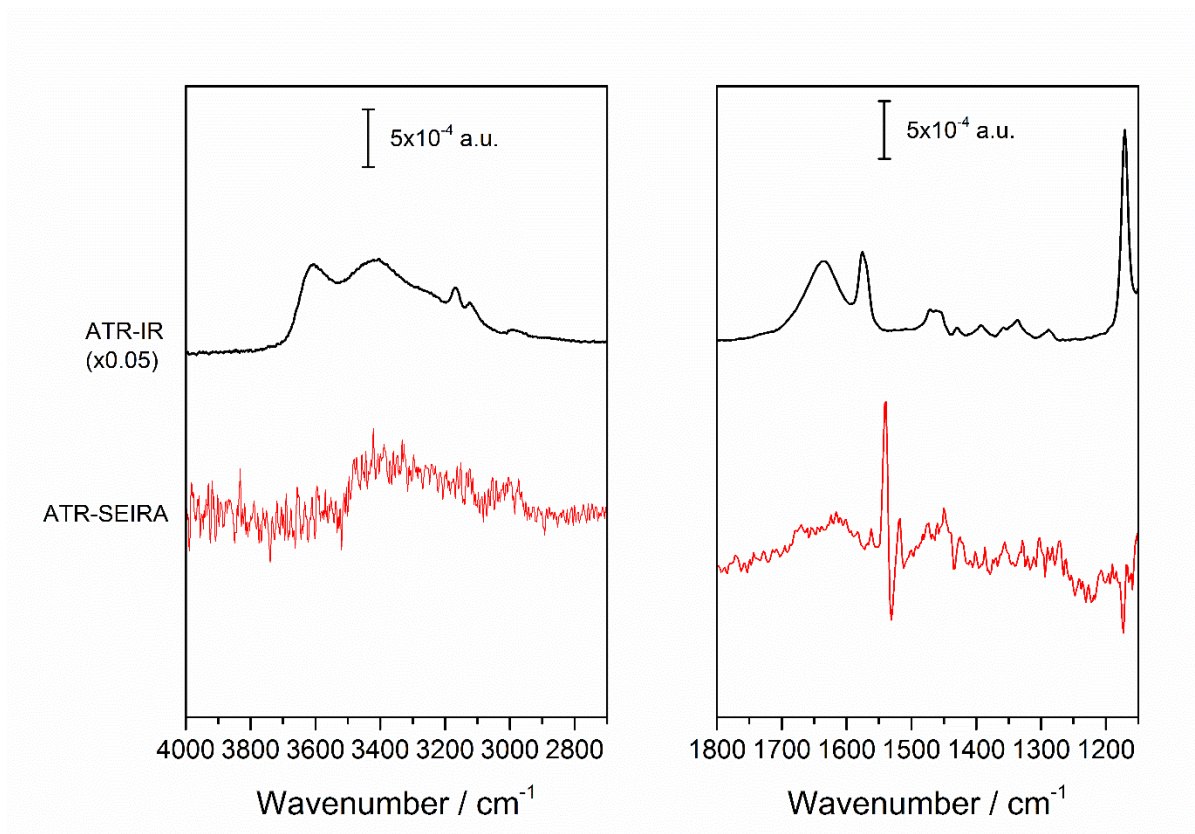
### **In-situ monitoring using ATR-SEIRAS of the electrocatalytic reduction of CO<sub>2</sub> on Au in an ionic liquid / water mixture**

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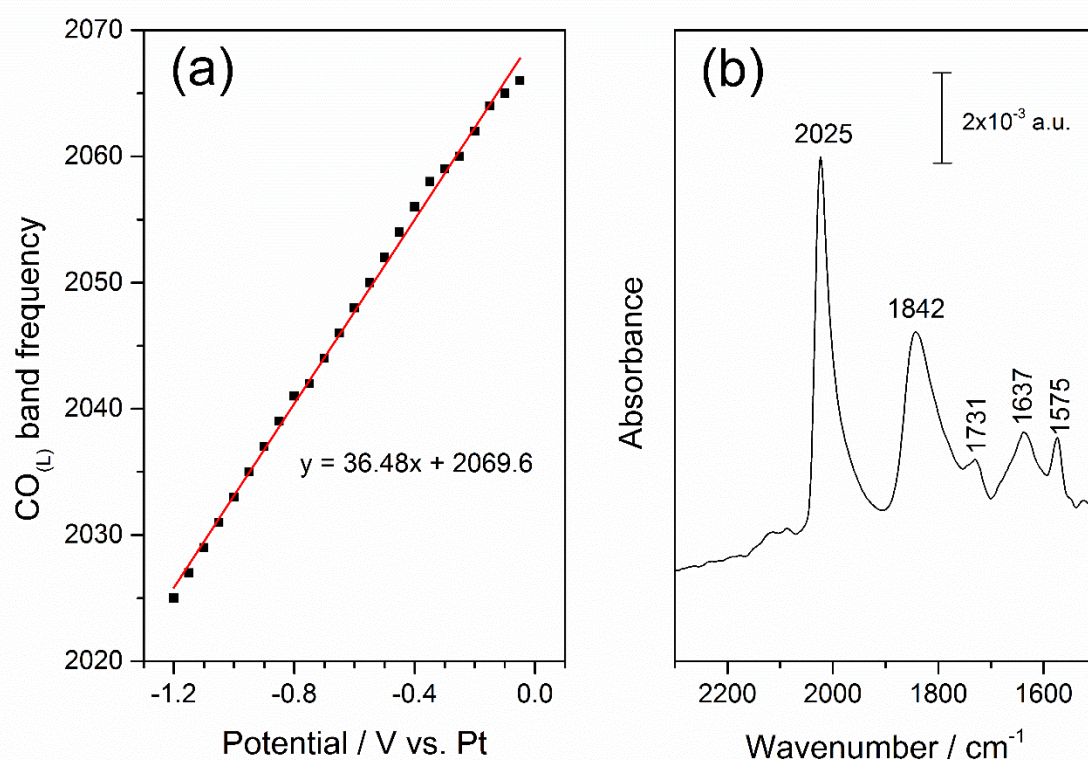
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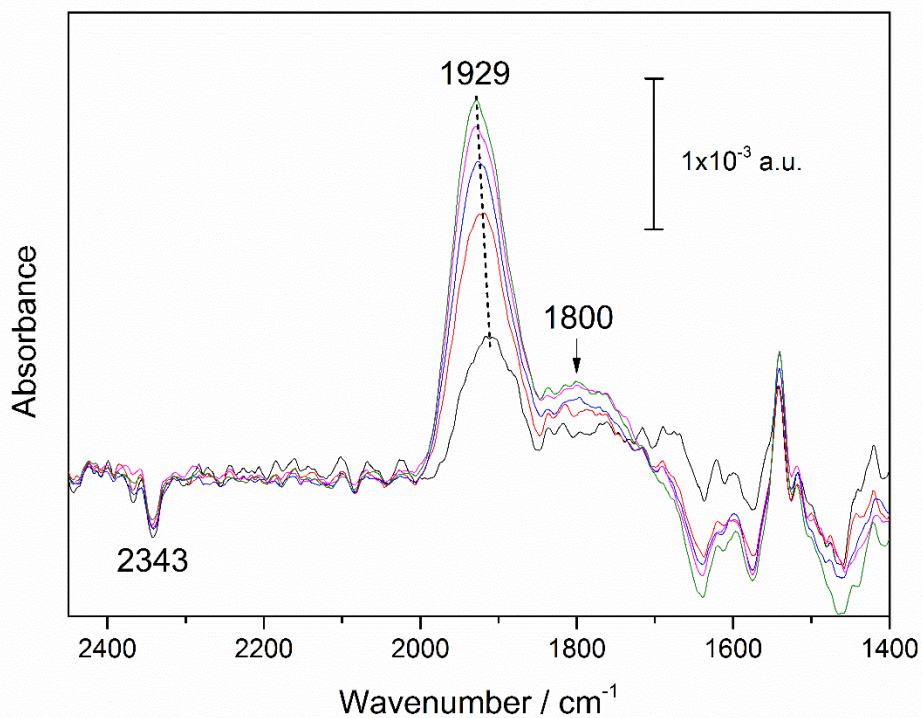
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**Figure S1.** ATR infrared spectrum (black line) of the [EMIM]BF<sub>4</sub> / H<sub>2</sub>O mixture (18% mol / mol), and ATR-SEIRA spectrum of the Au-electrolyte interface (red line) collected at -1.20 V in N<sub>2</sub>-purged [EMIM]BF<sub>4</sub> / H<sub>2</sub>O mixture (18% mol / mol), using the spectrum recorded at -0.60 V as reference. For the sake of clarity, the spectra have been split into two sections, covering the spectral ranges between 4000 and 2700 cm<sup>-1</sup> (a) and between 1800 and 1100 cm<sup>-1</sup> (b).



**Figure S2.** (a) Potential dependence of the frequency of  $\text{CO}_L$  on Pt; (b) ATR-SEIRA spectrum for Pt at  $-1.20$  V vs. Pt in CO-saturated  $[\text{EMIM}]\text{BF}_4 / \text{H}_2\text{O}$  (18% mol/mol). The spectrum recorded in the absence of CO at  $-0.60$  V was used as reference.



**Figure S3.** ATR-SEIRA spectra for Au after a potential step from  $-0.60$  V to  $-1.30$  V vs. Pt in  $\text{CO}_2$ -saturated  $[\text{EMIM}]\text{BF}_4 / \text{H}_2\text{O}$  (18% mol/mol), collected immediately after the potential step (black), and after 7 minutes (red), 13 minutes (blue), 18 minutes (pink), and 23 minutes (green). The spectrum recorded at  $-0.60$  V in  $\text{CO}_2$ -saturated electrolyte was used as reference.