Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Effects of water on low-overpotential CO_2 reduction in ionic liquid studied by sum-frequency generation spectroscopy

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1. Electrochemical cell preparation: Ag and ionic liquid-water electrolyte

The polycrystalline Ag working electrode (99.999% Accumet Materials Co.) was mechanically polished until a mirror-like surface was achieved. We polished it with successively finer Al_2O_3 lapping films (Mark V Laboratory), ranging from 12 to 1 µm grades, followed with 0.3 and 0.05 µm Al_2O_3 paste (Buehler). Then the electrode was sonicated twice for 10 minutes and rinsed extensively with ultrapure Milli-Q water to remove the Al_2O_3 paste. The electrode was dipped in H_2SO_4 for 5 s, then again sonicated and rinsed with Mili-Q water. An ultrapure water drop was placed on the electrode surface to keep it free from contaminants during electrochemical cell assembly. The reference electrode was Ag/AgCl with 3M saturated KCl from BASi Inc. The counter electrode was a Pt wire that was H_2 flame-annealed, washed with Mili-Q water and electrochemically polished (0.1 M H_2SO_4, 50 cycles from -0.2 V to -1.5 V at 50 mV/s with Ar bubbling).

The electrolyte solution of either 0.3, 45 or 77 mol % of water was composed by ionic liquid EMIM-BF_4 (98% Sigma-Aldrich) and 18.5 MΩ·cm Milli-Q water (Millipore). From now on, we will use room temperature ionic liquid (RTIL) to refer to EMIM-BF_4. This RTIL is hydroscopic; it picks up water from the environment. The lowest concentration of water was the RTIL UHP-Ar without further purification. We carried out a Karl-Fischer titration (KFT) of the Ar-purged EMIM-BF4, determining 0.3 mol% of water[1]. The subsequent concentrations of 45 % and 77 % by mol of water were obtained by adding the corresponding mass of water to the RTIL (±1 mg). The electrolyte was UHP Ar-bubbled for at least 45 min before each experiment, to remove the oxygen. For the CO_2 reduction experiments, CO_2 was bubbled for at least 1 hour (ca. 1 atm), but during the SFG-CV scans the CO_2 was stopped to avoid producing bubbles in the optical path.

The spectroelectrochemical cell was depicted in Fig. 2. All parts, except the CaF_2 window (Crystran Ltd.), were washed with detergent and water and sonicated for 15 minutes. They were rinsed with deionized water and sonicated with acetone for 15 minutes. Then they were again rinsed with deionized water, cleaned for at least 12 h with concentrated H_2SO_4 and Nochromix (Fisher), and finally boiled in

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ultra-pure water (Mili-Q, 18.2 MΩ) three times and dried in clean air. This cell is an updated version of the precious design which allows us to control the thin-layer electrolyte (TLE) with micrometer precision (±1 µm). Its total volume was 2.5 ml, 8 times less than the previously cell.

2. Meniscus versus *in situ* cyclic voltagrams

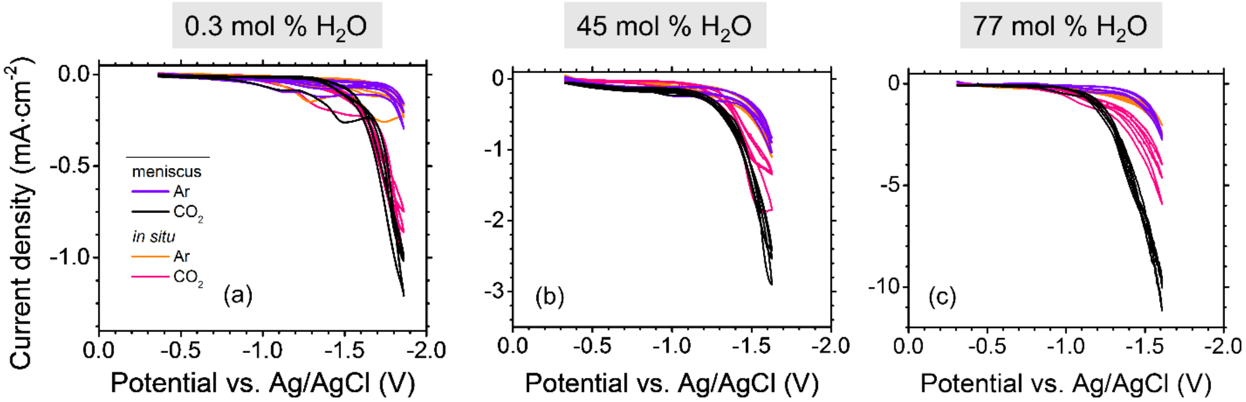

Figure S1. Comparison of the *meniscus* and the *in situ* CV for the Ar- or CO_2- saturated electrolytes.

The cyclic voltammetry (CV) experiments were performed *in situ* during the sum frequency experiments and *ex situ* in the meniscus configuration. We believe the *ex situ* measurements are more representative of the SFG experiments since both probe only the flat face of the working electrode. Figure S1 comparative results with the Ar- or CO_2- saturated 0.3 mol%, 45 mol% and 77 mol % of water. The key parameter we derived from the CV data is the threshold potential for CO_2 reduction. This threshold varied little between the two measurements, *in situ* and meniscus. The cell potential was corrected from the different electrolytes as described below.

3. Ag/AgCl reference electrode calibration in ionic liquid-water mixtures

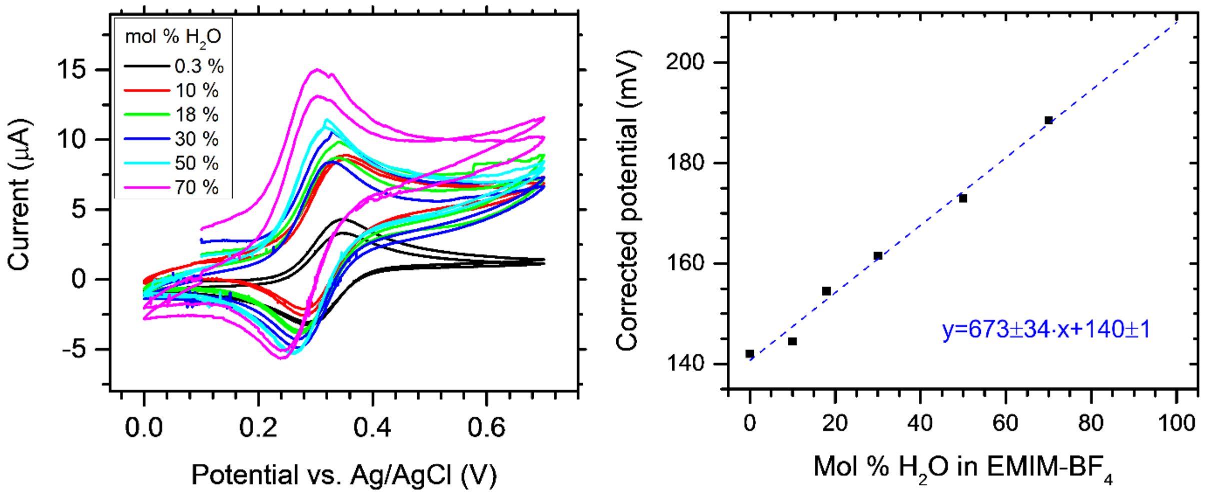

Figure S2. Left, cathodic and anodic waves of the Fc/Fc$^+$ couple in water-RTIL electrolyte. Right, corrected potential versus mol % of water RTIL mixture.

The reference electrode (RE) was Ag/AgCl in 3M saturated KCl (MF-2021 BASi, Inc.). Ferrocene (Fc) was used as an internal reference electrode as previously described[1-3]. The ferrocene/ferrocenium (Fc/Fc$^+$) redox couple (2.5 mM) in 0.1M tetrabutylammonium perchlorate (TBPA) in acetonitrile (ACN) is well known, and the redox potential in this system was compared to the potential using the water- RTIL mixtures[1, 3]. Pt and Ag were used as working and counter electrodes, respectively. The sweep rate was 5 mV s^{-1}, and all the concentrations were UHP Ar purged for at least 30 min prior to the cyclic voltammetry measurements. First, the average potentials at the peak for the TBPA/ACN was determined at 461 mV versus Ag/AgCl. Previous studies reported similar values for the Fc/Fc$^+$ couple in TBPA/ACN vs Ag/AgCl of 410 mV,[4] and 450 mV[5]. Then, the averaged peak ($E_{1/2}$) for the Fc/Fc$^+$ was measured for different mol % of water in RTIL vs Ag/AgCl (Left Fig. S2) obtaining values from 322 to 273 mV from lowest to highest water concentration. We found a linear relation between the correction potential and the amount of water in the electrolyte; obtaining a gradient of 673±34 μV/mol fraction of water and an offset of 140 ± 1 mV (Right Fig. S2). Using this linear fit, the corrected potential for 0.3, 45 and 77 mol % of water was 139, 171 and 191 mV, respectively.

4. Water-RTIL Ag interface (Potential dependent NR SFG)

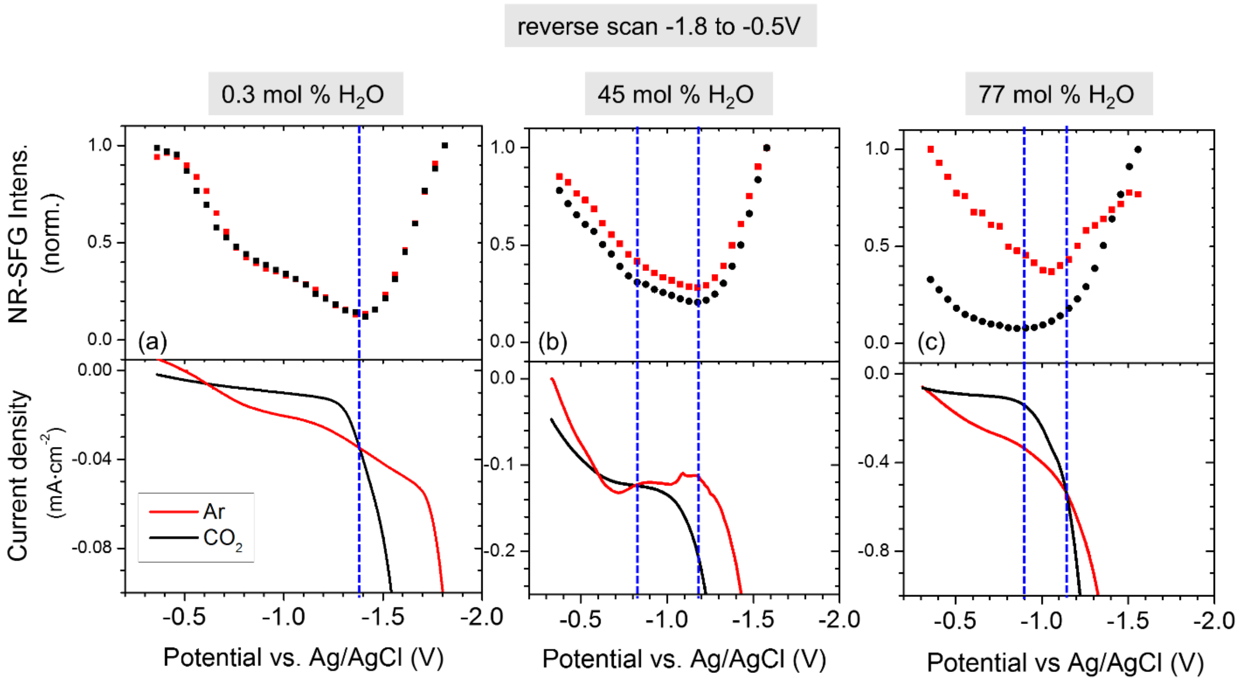

Figure S3. Top, NR SFG integrated signal versus potential in the reverse scan for the second cycle. Bottom, meniscus CV. Refer to results section for further explanation.

5. Comparison of the potential dependent NR SFG for different water concentration

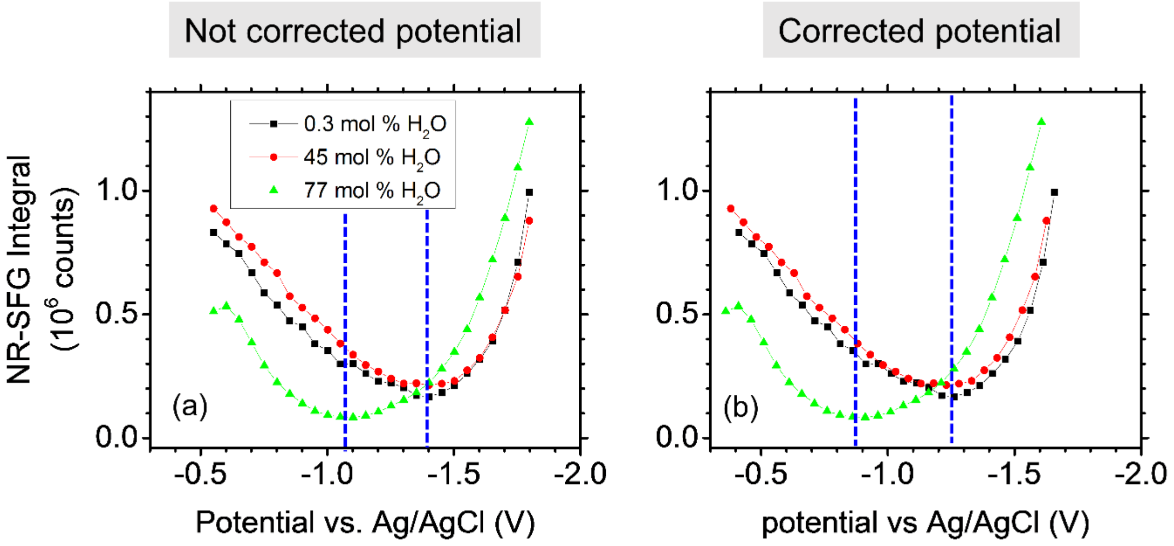

Figure S4. Potential-dependent NR SFG integral for the three water concentrations studied in RTIL. Left, the potential was not corrected. Right, the potential was corrected by the method described in section 3.

6. Infrared absorption spectra of the electrolyte water-RTIL mixture

Figure S5 shows the infrared absorption spectra of 25 µm thick layer of CO_2- saturated electrolyte for the different water concentrations in RTIL. An intense transition at 2343±1 cm^{-1} (FWHM 8 cm^{-1}) corresponds with the asymmetric stretch of the CO_2 weakly associate with the RTIL[6-9]. As the water concentration increased, this peak decreased by 0.04 with the mol % of water (See inset in Fig. S5).

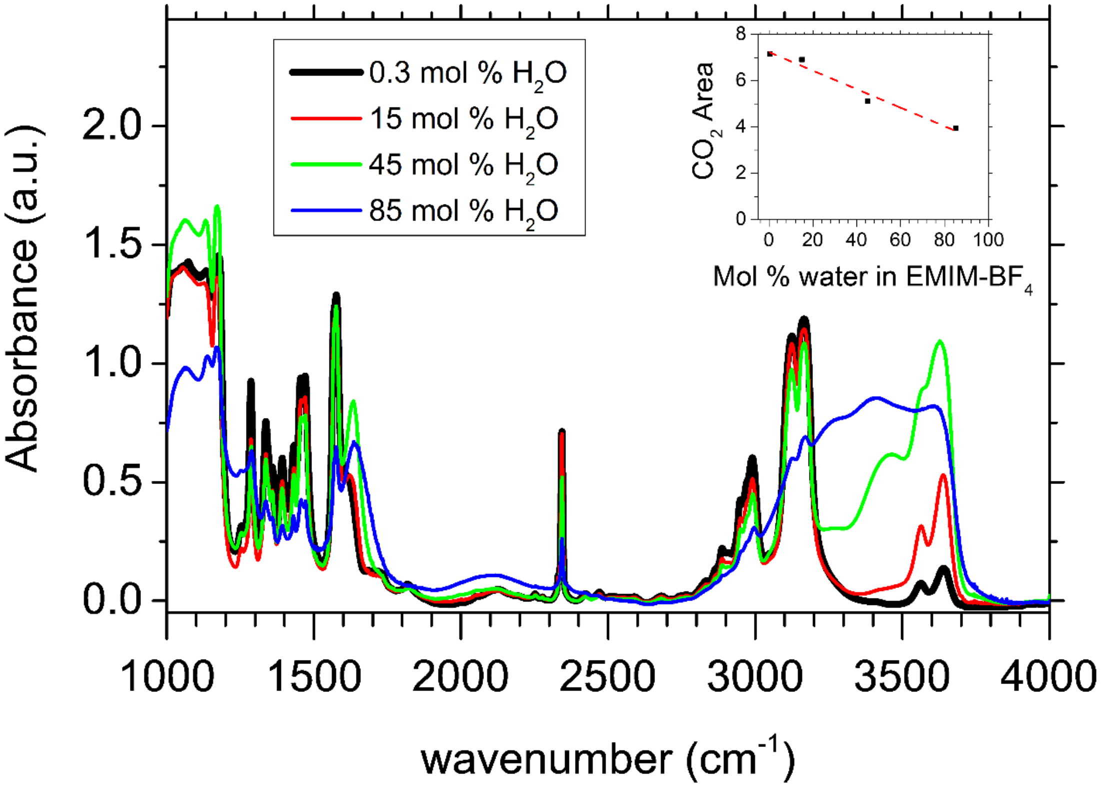

Figure S5. Infrared absorbance spectrum of 25 µm of CO_2-saturated RTIL water mixture electrolyte. Inset, CO_2 peak area versus water concentration in EMIM-BF_4.

7. Potential-dependent phantom transitions in SFG: CO_2 and EMIM$^+$ IR modes

In order to elucidate the EMIM$^+$ structural transition that mediated the CO_2 electroreduction on Ag, the IR wavelength was centered at 2343 cm^{-1}, 1500 cm^{-1} or 1250 cm^{-1}; where the CO_2 and the EMIM$^+$ vibrational modes are found. According to the literature [10, 11], these bands are attributed to the following vibrational modes: the CO_2 asymmetric stretch at 2343 cm^{-1} and for the EMIM$^+$: the in-plane ring stretch at 1575 cm^{-1}, the HCH symmetric bending at 1438cm^{-1}, the in-plane ring asymmetric stretch at 1230 cm^{-1} and the ring symmetric stretch at 1198 cm^{-1}.

Figure S6 shows the RES SFG spectra at the different IR-tuned frequencies, when the potential of the cell was scanned at more cathodic potentials, from -0.3 to -1.85 V. The overall main observation from these spectra is the potential-dependency of the RES SFG signal. Neither a frequency shift nor the appearance of other frequency mode different than the IR transitions, which are also observed in the FTIR spectra from the same electrolyte (see Fig. S7), were found. Figure S8 shows the normalized RES SFG height from different vibrational modes showed in Fig. S6. The potential dependence of these curves showed the same behavior than what we observed in the NR SFG potential dependent curves in Fig. 4. Therefore, those spectra are considered phantom transition produced by the IR-distorted pulse [12].

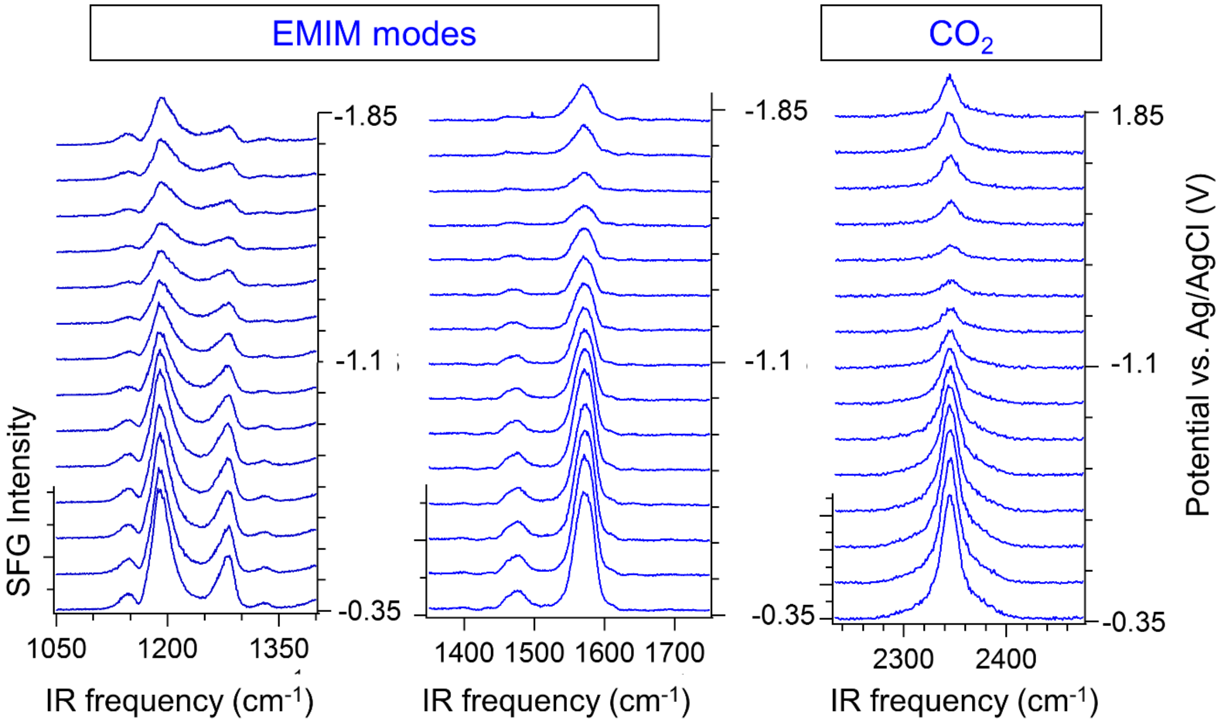

Figure S6. EMIM$^+$ and CO_2 RES SFG spectra scanned at more cathodic potentials, produced by the IR absorption from the bulk electrolyte that distorts the IR pulse.

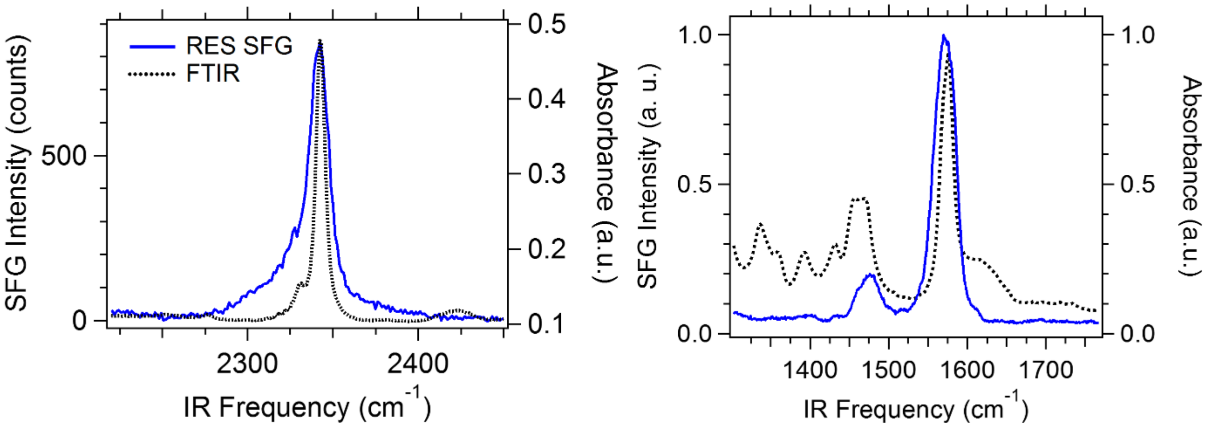

Figure S7. Comparison of the RES SFG spectra (blue solid line) from the RTIL-Ag interface overlaid with the FTIR spectra of 25 μm electrolyte of CO_2 saturated $EMIM^+$ (black dashed line). Left, CO_2 asymmetric stretch. Right, the $EMIM^+$ modes.

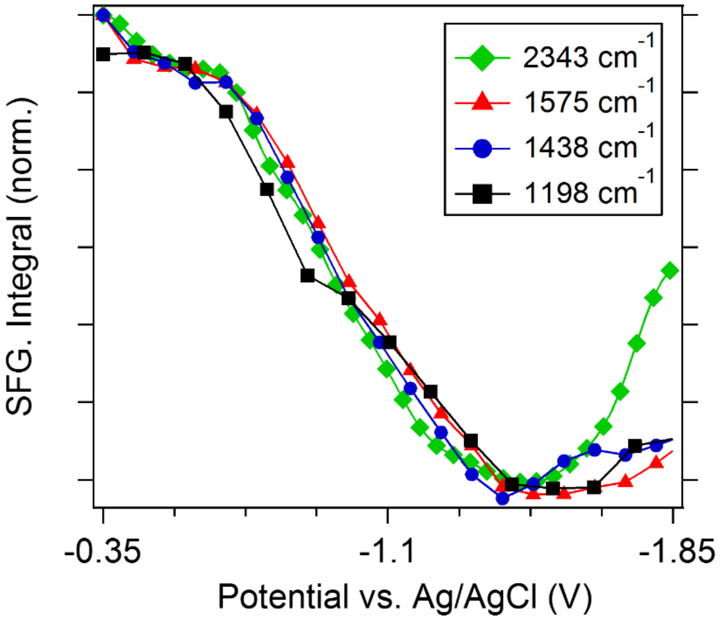

Figure S8. Potential dependent RES SFG integrated signal, normalized, for the different vibrational modes of the electrolyte: CO_2 dissolved in the RTIL and the $EMIM^+$ modes.

8. Time-dependent SFG spectra

Figure S9 shows the SFG spectra at different IR-Visible delay times from the CO_2 saturated RTIL on Ag. The IR center wavelength was set to 1250 cm^{-1}, 1500 cm^{-1} or 2343 cm^{-1} (from left to right in Fig. S9) to be resonant with the vibrational modes from the $EMIM^+$ and the CO_2; as described in the previous section. The IR-VIS delay is applied to suppress the nonresonant signal produced by the Ag electrode. The SFG spectra at 0 fs IR-VIS delay contains the interference between the NR-SFG and the RES-SFG signals, which in this case corresponds with the phantom transitions produced by the bulk electrolyte. The "dips" observed at the time-zero SFG spectra (dotted line) flip into peaks in the VIS-delayed SFG spectra (solid line). The phase flip depends on the vibrational dephasing of the modes and the time delay used for the measurement [13].

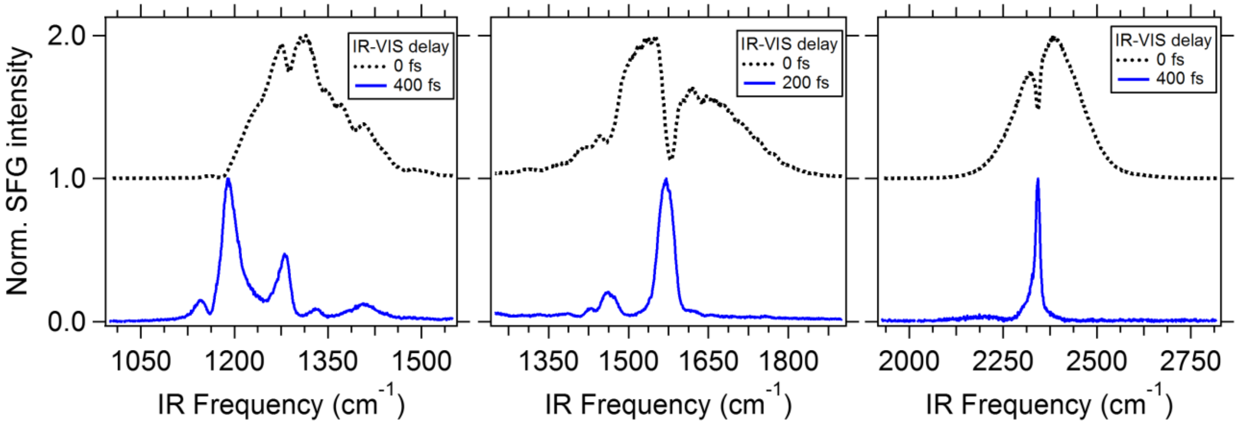

Figure S9. SFG spectra at different IR-Visible delay times: 0 fs (dotted blue line) and 200 or 400 fs (solid blue line) from the CO_2 saturated RTIL on Ag. The IR center wavelength was set to 1250 cm^{-1}, 1500 cm^{-1} or 2343 cm^{-1} respectively, from left to right.

9. Potential-dependent NR-SFG from 0.5 M K_2CO_3 in water on Ag

To probe the effect of the electrolyte in the potential-dependent NR SFG integrated signal on Ag electrode, we have monitored the NR SFG spectra from 0.5 M K_2CO_3 in water on Ag during 2 CV cycles at 5 mV/s. The IR pulse is centered at 1920 cm^{-1} where there is only a broader water absorption from the electrolyte, less than 20% of the intensity. We observed the NR SFG integral follows a linear potential dependency and how the electrolyte influences the shape NR SFG integrated signal, and it is also different than the potential-dependent NR SFG integrated signal from the RTIL-Ag interface.

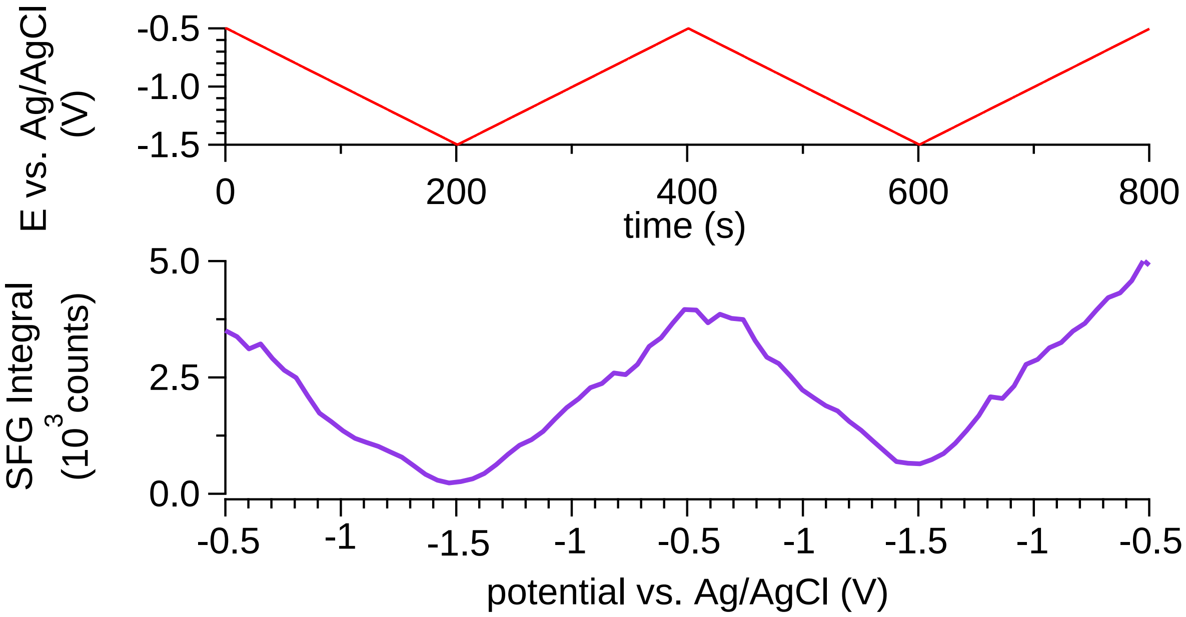

Figure S10. Top, potential applied to the cell versus time. Bottom, potential-dependent NR-SFG integrated signal of 0.5 M K_2CO_3 in water on Ag. Cyclic voltammetry at 5 mV/s, 2 cycles.

References

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