Supporting Information:

Presolvated electron reactivity towards CO_2, N_2O in the water

Sergey A. Denisov[*] and Mehran Mostafavi

Insitute de Chimie Physique UMR 8000, CNRS/Université Paris-Saclay, Bâtiment 349, Orsay, 91405, France

E-mail: sergey.denisov@universite-paris-saclay.fr

Phone: +33169156171. Fax: +33169156188

Pressurized optical cell

The schematic representation of the experimental layout is presented in Figure SS1. The system consists of a closed water loop. The circulation of solutions, to guarantee refreshment of solution in measurement volume, was achieved using home made pump driven by electromagnets. The principle of action follows the sequence: 1) the current is applied to the electromagnets (1 and 2), working in the opposite direction: electromagnet 1 is pushing, while 2 is pulling the permanent magnets fixed on the piston; 2) once the piston is displaced, the current in electromagnets is reversed, and the piston goes down. The flow of solution during reverse movement of the piston is not affected since the lock-balls are released, letting the solution flow through the six holes in the piston.
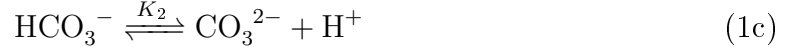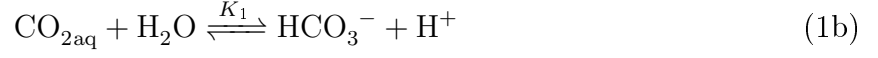
The spectroscopic cell fracture test with Ar guaranteed the safe pressure to operate below $75\,\mathrm{bar}$ with $1\,\mathrm{mm}$ input window and $5\,\mathrm{mm}$ output one, respectively. The pressure was controlled by a gas pressure regulator (0-100 bar, Swagelok) directly attached to a gas cylinder.

Once the pressure of the gas was applied using (valve 3), the equilibration for 30 minutes were undertaken. To intensify a gas exchange, a bubble of gas was formed over the water to increase the surface area for an exchange. Each measurement with a different pressure was conducted with a freshwater volume ($1.5\,\mathrm{mL}$) pumped into the cell.

The filling of the closed water circuit was accomplished by a peristaltic pump (valve 1, 2); after that, the system was isolated and pressurized to a given pressure.

H^+ and carbonate ions concentration calculation

Based on CO_2 water chemistry (eq. 1a) it is possible to calculate (eq. 2a) the pH of CO_2 water solution at different CO_2 pressures (Figure S2A), the fraction of carbonates and $CO_{2\mathrm{aq}}$ (Figure S2B).

$$CO_{2g} \xrightleftharpoons{K_H} CO_{2aq} \tag{1a}$$

$$CO_{2aq} + H_2O \xrightleftharpoons{K_1} HCO_3^- + H^+ \tag{1b}$$

$$HCO_3^- \xrightleftharpoons{K_2} CO_3{}^{2-} + H^+ \tag{1c}$$

$$[OH^-] = \frac{K_W}{[H^+]} \tag{2a}$$

$K_W = 10^{-14}$

$$[HCO_3^-] = \frac{K_1[H_2CO_3]}{[H^+]} \tag{2b}$$

$$[CO_3{}^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]} \tag{2c}$$

Substituting for $[HCO_3^-]$

$$[CO_3{}^{2-}] = \frac{K_1K_2[H_2CO_3]}{[H^+]^2} \tag{2d}$$

The rewritten electrical neutrality expression $[H^+]=[OH-] + [HCO_3^-] + 2\,[CO_3{}^{2-}]$ in terms of $[H^+]$:

$$[H^+] = \frac{K_W}{[H^+]} + \frac{K_1[H_2CO_3]}{[H^+]} + 2\frac{K_1K_2[H_2CO_3]}{[H^+]^2} \tag{2e}$$

rearanging and sustituting $[H^+]=x$ and $[H_2CO_3]=k_H P_{CO_2}$ gives:

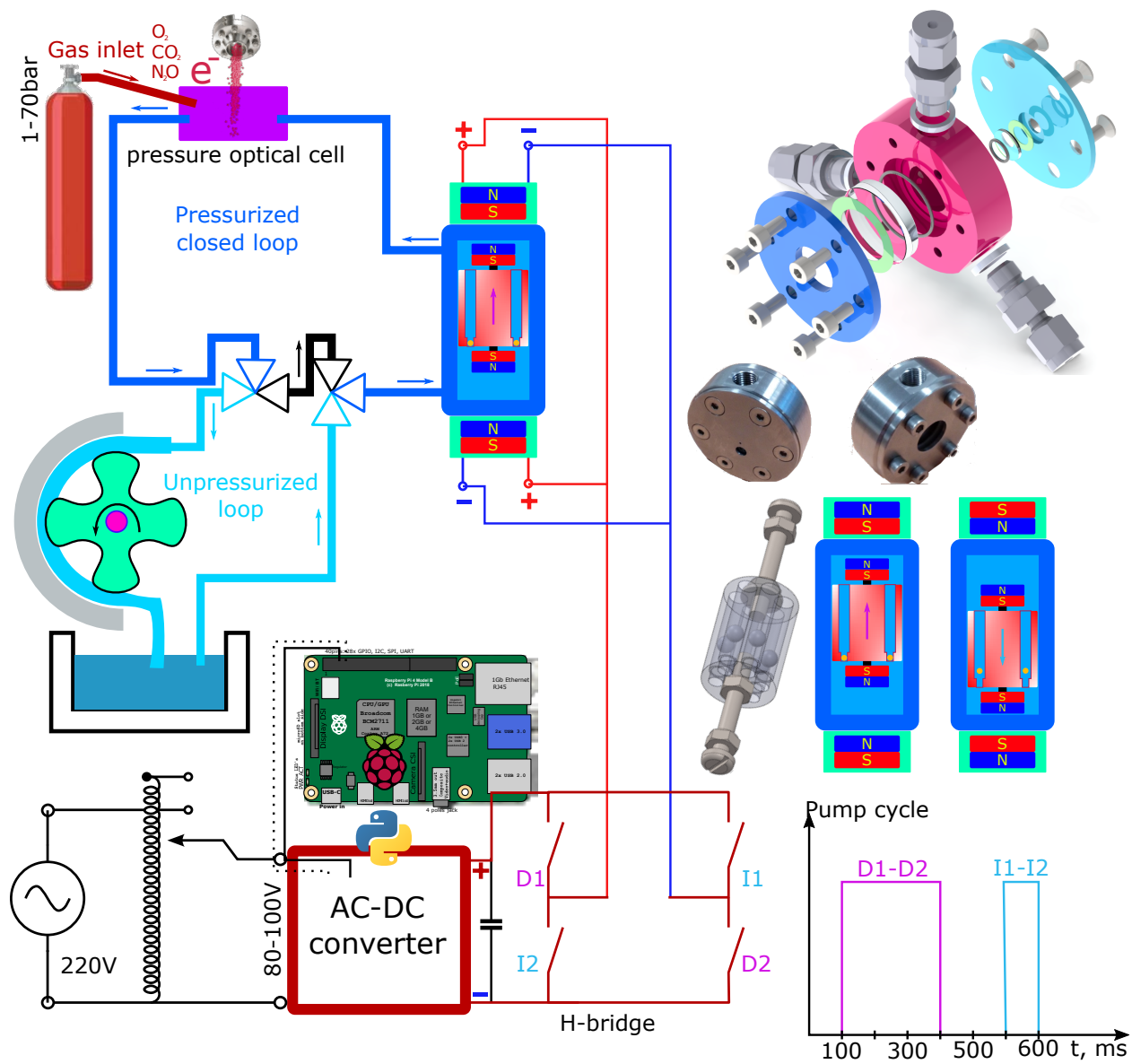$$x^3 - x \cdot (K_W + K_1 K_H P_{CO_2}) - 2K_1 K_2 K_H P_{CO_2} = 0 \tag{2f}$$

Figure S1: The schematic representation of the experiment, including the pressurized cell blueprint and its 3D model.
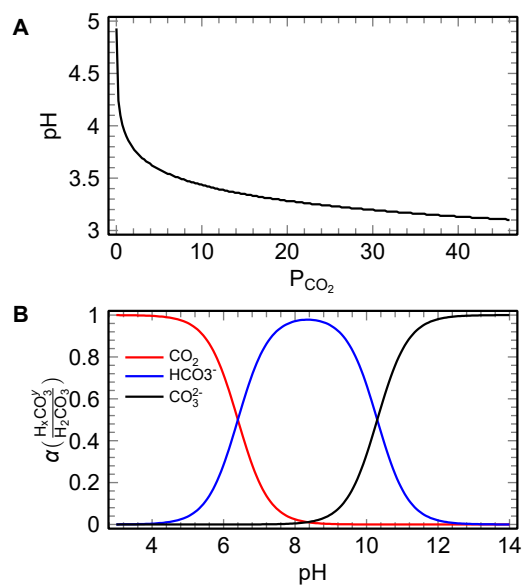
Figure S2: Calculated parameters (eq. 2): A. pH of a solution as a function of CO_2 pressure, B. the fraction of different forms of carbonates in the water-CO_2 solution $1\,atm$ of CO_2.