Supporting Information

Selective trapping of CO_2 gas and cage occupancy in CO_2-N_2 and CO_2-CO mixed gas hydrates.

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Samples preparation

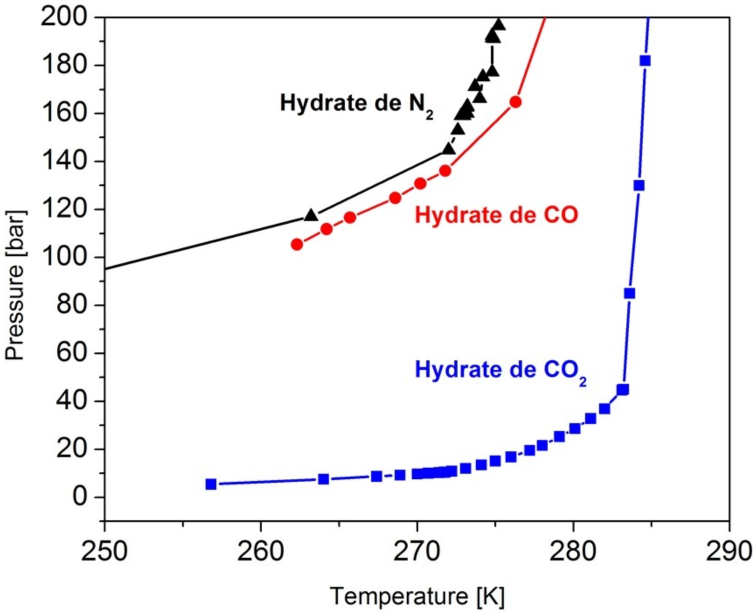

Figure S1: Phase diagram of pure CO, CO_2 and N_2 hydrates.[1-9]

For neutron diffraction experiments, the sample was formed using a powder (grain size typically of the order of 100-200 µm) of deuterium oxide ice (99.9 % D) and applying a gas pressure (purity > 99.997%) of 20 bar of CO_2, CO_2-CO or CO_2-N_2 during 3 days. The initial gas mixture compositions were 25 %, 50 % and 80 % of CO_2 in CO_2-N_2 hydrate and 25 %, 50 % and 75 % of CO_2 in CO_2-CO hydrate. The sample pressures were controlled by a PM High Pressure pump (Top Industrie, Vaux-le-Penil, France) which can contain 100 cm^3 of gas up to 500 bars. The cell temperature was maintained at 260 K (± 5 K) with a thermal bath, to ensure the formation within the thermodynamic stability region (Figure S1). For *in situ* Raman microspectroscopy, Milli-Q water was injected inside the optical cell and the temperature was controlled by using a modified temperature stage (Linkam Scientific Instruments Ltd., UK). First, the hexagonal ice has been formed at *ca*. 240K and then the temperature was raised to 270 K (± 0.1 K). Finally, 25 bar of CO-CO_2 or CO_2-N_2 gas mixture was applied with the high pressure pump on the formed hexagonal ice. The initial gas mixture compositions were 25 %, 50 % and 80 % of CO_2 in CO_2-N_2 hydrate and 30 %, 40%, 50 %, 65% and 75 % of CO_2 in CO_2-CO hydrate. In addition, one sample consisting of 90 % of CO and 10 % of CO_2 have been prepared from liquid water at 25 bar. Then, the sample was cooled until 245 K (± 0.1 K) and finally, the temperature was maintained at 270 K (± 0.1 K).

Gas mixtures were done using pure gas of CO, CO_2 and N_2 (purity > 99.997%) and two syringe pumps. Each volume and pressure is measured helping with PM HP pump and the second pump is used to store the first gas used for the mixture. Successive pressurization/depressurization were applied for homogenizing the gas mixtures. Calibration curves have been done to correlate the evolution of the Raman intensity I_{CO2}/I_{N2} and I_{CO2}/I_{CO} ratio with the initial gas concentration of the mixtures $[CO_2]/[N_2]$ and $[CO_2]/[CO]$, respectively (Figure 3).

Neutron diffraction

The experiments have been performed at Laboratoire Léon Brillouin (CEA-Saclay) using the cold neutron two-axis powder diffractometer G 4-1. Measurements were done with a wavelength of 2.428 Å. Due to a better instrumental resolution at low scattering angle 2θ, the angular range 2θ < 60° has been considered. The samples have been cold transferred into the cryostat. The pattern-matching of the powder diffractogram has been performed with the Le Bail algorithm[10] and the FullProf program from the FullProf suite[11].

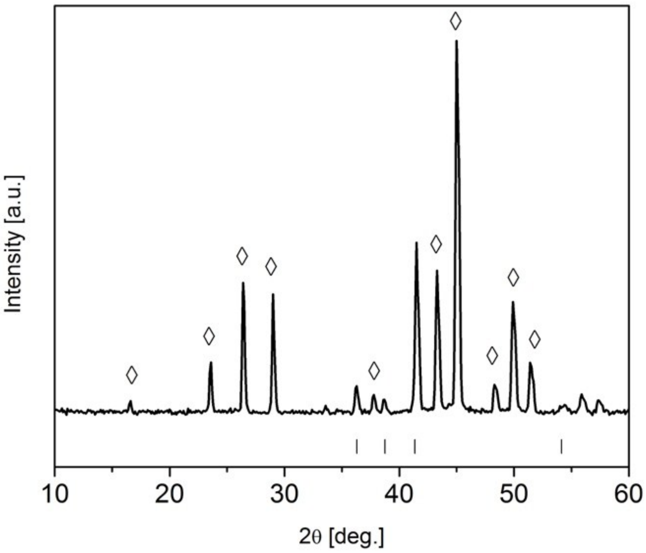

Figure S2: Neutron diffractogram (100 K and 1 bar) of the carbon dioxide hydrate formed for 3 days at 25 bar and 255K. The vertical lines and the diamonds represent the Bragg peaks of the Ih ice (blue) and SI hydrate, respectively.

Mixed CO_2-N_2 and CO_2-CO hydrates have been prepared with various gas mixtures compositions and stored at liquid nitrogen temperature. Diffractograms have been recorded after various duration of cold storage to probe the time evolution of the formed CO_2-CO hydrates. As shown in Fig. S3, the formed mixed hydrates are all of type SI (except for the gas mixture CO_2-CO of 25/75, no hydrate is formed; see manuscript for details) and no time evolution is observed whatever the mixed hydrate is.

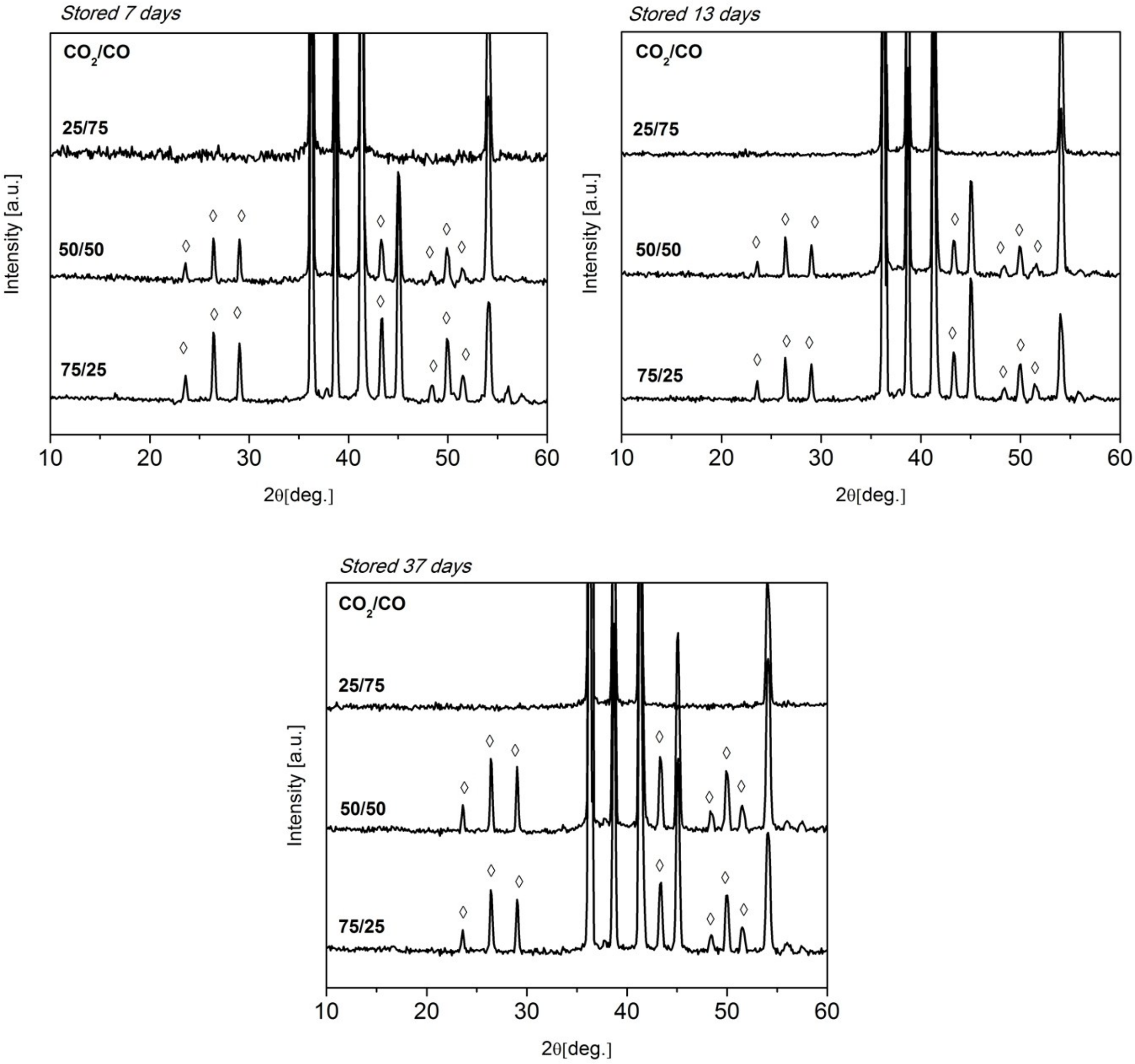

Figure S3: Neutron diffractogram (100 K and 1 bar) of the mixed CO_2-CO hydrate formed for 3 days at 25 bar and 260K and for various storing time in liquid nitrogen as indicated on the figure. Diamonds represent the Bragg peaks of the SI structure. The gas mixture composition used to form the mixed hydrate from ice is indicated on the figure. No SII Bragg peaks are observed, so that the formed SI structures are thermodynamically stable whatever the gas composition is.

Raman spectra

The spectra were recorded with a Labram HR microspectrometer (Horiba Jobin Yvon, Villeneuve d'Ascq, France) using a 514 nm wavelength laser as excitation source. A 50X objective permitted us to focus the incident laser beam and to collect the Raman scattering. The Raman scattering was dispersed by a holographic grating of 2400 lines/mm (high resolution) and analysed by a Peltier-cooled CCD detector (Andor, Belfast,UK). Thus, the intensity of different wavelengths of the spectrum can be measured with a spectral resolution of 0.8 cm^{-1} (Full Width at Half-Maximum). The wavenumber calibration of the spectrometrer was done using the 520.7 cm^{-1} mode of a silicon sample and the neon source excitation at 2348.4 cm^{-1}. For the *in-situ* experiments, the sample temperatures were maintained at the desired value (± 0.1 K) during the acquisition by using a lab-modified temperature controlled stage (Linkam Scientific Instruments Ltd., UK), including a home-made high-pressure optical cell equipped with a 2 mm thick sapphire optical window. The sample pressures were controlled by the PM High Pressure pump. All spectra were collected for typically 30 min.

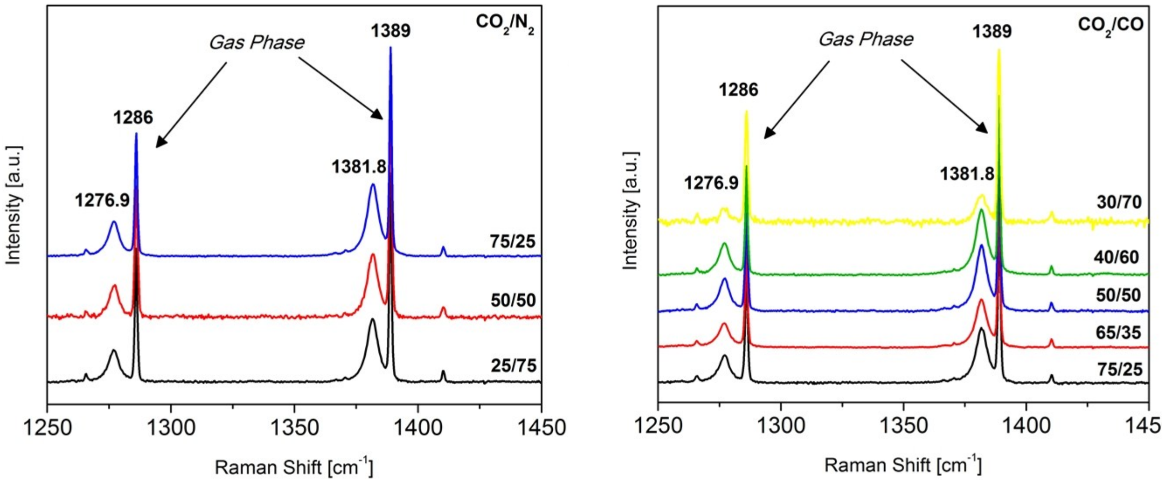

Figure S4: Raman signatures of the Fermi resonance of CO_2 in gas phase and hydrate phase in CO_2-N_2 (left) and CO-CO_2 (right) hydrates.

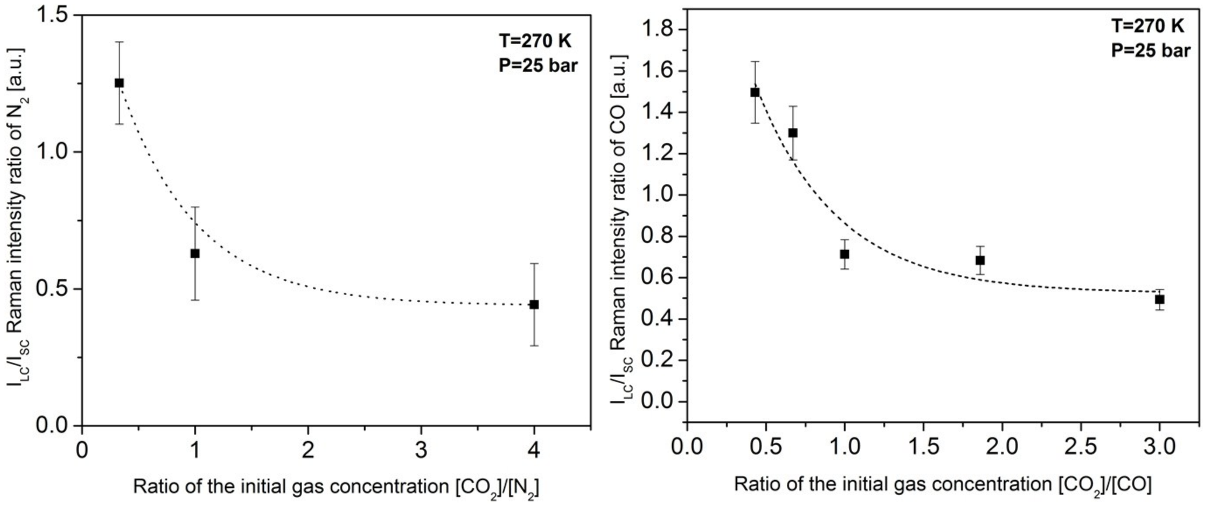

Figure S5: Evolution of the cage occupancy I_{LC}/I_{SC} ratio with the initial gas concentration for CO_2-N_2 mixed hydrate (left hand) and CO_2-CO mixed hydrate (right hand). The dotted lines are guides to the eyes obtained with simple exponential decaying functions.

The occupancy of the cage can be estimated on the basis of the ratio $I(v_1)/I(v_2) = I_{LC}/I_{SC}$, which can be expressed as:

$$\frac{I_{LC}}{I_{SC}} = \frac{n_{LC}\theta_{LC}}{n_{SC}\theta_{SC}}\left(\frac{\alpha_{LC}}{\alpha_{SC}}\right)^2 \tag{1}$$

where θ_{LC} and θ_{SC} are the occupancy in LC and in SC, respectively. n_{LC} and n_{SC} are the number of LC and SC in the hydrate structure, respectively. The scattering cross sections (i.e. the polarisability variation due to the stretching mode) of nitrogen or carbon monoxide in LC and in SC (α_{LC} and α_{SC}, respectively) are assumed to be similar. Such an assumption has been validated in the isosteric SI carbon monoxide hydrate[12] or in the SI methane hydrate.[13,14] Thus, in the SI structure, the ratio is simply given by:

$$\frac{I_{LC}}{I_{SC}} = \frac{3\theta_{LC}}{\theta_{SC}} \tag{2}$$

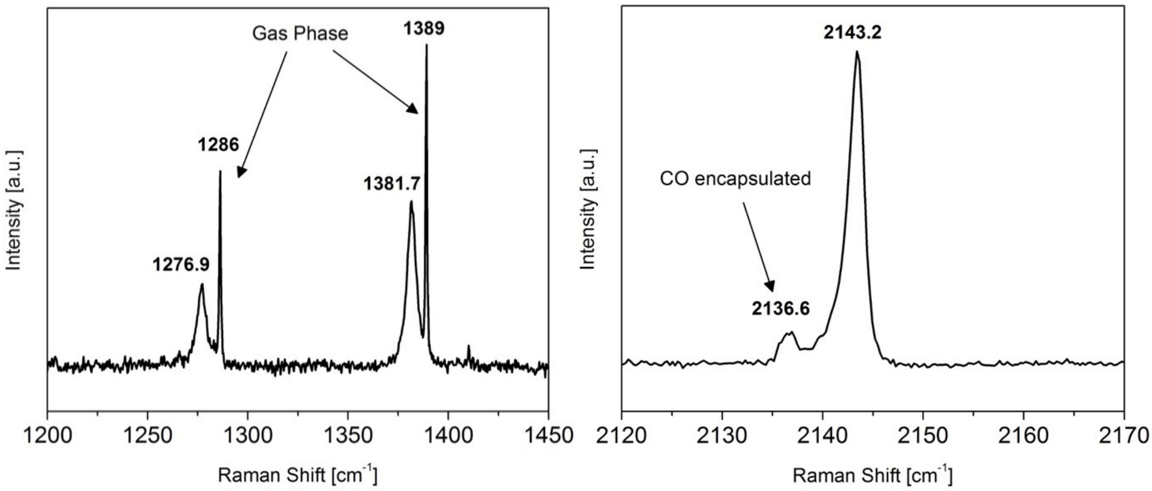

Figure S6: Raman signatures of the CO_2 Fermi resonance (left) and of the CO stretching mode (right) in the CO-CO_2 (90/10) gas mixture and in the CO-CO_2 mixed hydrate formed from liquid water pressurized at 25 bar and cooled at 270K.

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