

Supplementary data

Why is the CO₂-CS₂ non-ideality larger than in CO₂-CCl₄? A Raman scattering study

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Experimental conditions

The polarised I_{VV} and depolarised I_{HV} Raman spectra were recorded on a LabRam HR8000 spectrometer with a back-scattering geometry. The spectral domain of the CO_2 Fermi dyad was measured using a Spectra Physics laser (Kr^+ 752.5 nm) and a 1800 lines/mm grating giving 0.5 cm^{-1} spectral resolution, whereas the spectral resolution was 3.8 cm^{-1} for the spectral domains of ν_2 mode of CO_2 and ν_2 mode of CS_2 and that between the CO_2 Fermi dyad (Ar^+ laser, 514 nm with a 600 lines/mm grating). The spectra have been corrected of the finite effect of the spectral resolution according to the Tanabe's correcting method ¹. The pressure bench and the Raman cell equipped with fused silica windows previously described ² to work in the 0.1 to 8.0 MPa pressure range at $T=313 \text{ K}$ was used. The cell was initially filled with the organic liquid (CS_2 or CCl_4 , Aldrich, purity > 99%) and then super critical CO_2 (Air Liquide, purity 99.995%) was added under pressure. The incident laser beam always impinged on the dense phase of the binary mixture which was continuously stirred. All the spectra have been recorded after an equilibration time greater than one hour and accumulated during times ranging from 4 to 16 minutes. The composition of the dense phase of the two systems has been interpolated from reported P-x-T data ³.

The window of the cell give a faint polarised feature at about 470 cm^{-1} which is not affected, at constant temperature, by the pressure variation (up to 8 MPa) and has been used here as an internal standard for intensity calibration of the bending mode of CS_2 (see Figure SI1).

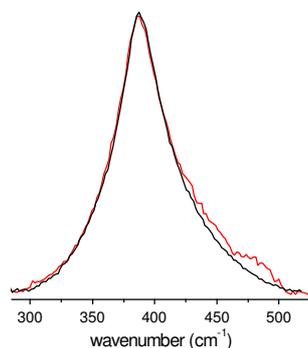


Figure SI1. Comparison of the polarised profiles of the ν_2 mode of pure CS_2 measured with the laser impinging directly on the liquid (black) and in the high pressure cell (red) at 293K.

Raman scattering intensity being arbitrary, we have scaled these profiles using as an intensity standard the window contribution which is not affected, at constant temperature, by the modest pressure variation in our experiments (up to 8 MPa) (Figure SI2).

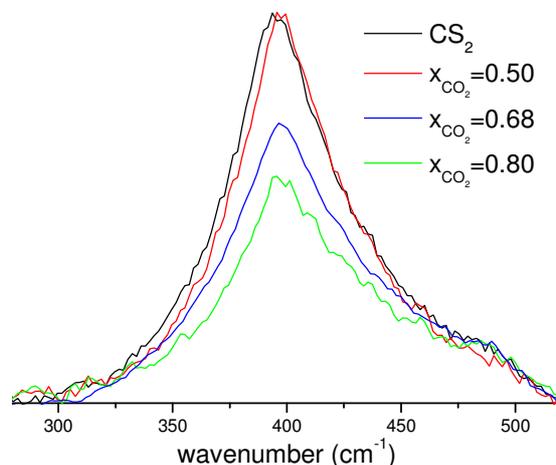


Figure SI2. Evolution with the CO₂ concentration of the polarised profiles of the ν_2 mode of CS₂ at 313 K. The spectra have been scaled to the faint polarised feature situated at about 470 cm⁻¹ which is not affected at constant temperature by the variation of pressure (up to 8 MPa),

The polarised profiles have been corrected from the scattering contribution due to the windows of the cell. Without this correction the polarised profiles were already superposable in the concentration domain from the pure CS₂ to the equimolar dilution in carbon dioxide. This correction allowed to show that even for more diluted mixture ($x_{\text{CO}_2}=0.70$) the bandshape was yet preserved (see Figure 5).

- (1) Tanabe, K.; Hiraishi, J. *J. Raman Spectrosc.* **1982**, *12*, 274.
- (2) Besnard, M.; Cabaço, M. I.; Danten, Y. *J. Phys. Chem. A* **2009**, *113*, 184.
- (3) Carvalho, P. J.; Ferreira, A. R.; Oliveira, M. B.; Besnard, M.; Cabaço, M. I.; Coutinho, J. A. P. *J. Chem. Eng. Data* **2011**, *56*, 2786.