Raman spectroscopic investigations of CO_2/C_3H_8 binary mixed hydrate: an insight into the hydrate structure and cage occupancies

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Recently, the microscopic instruments, such as Raman Spectroscopy, helped researchers to measure directly the properties and molecular aspects of clathrate hydrates. Based on our last work by reviewing different techniques to measure hydrate composition[1], it was revealed that the thermodynamic simulations had the best accordance with the experimental data obtained by the microscopic tools, like Raman spectroscopy. This suggests that using these direct measurement techniques might help to get closer to reality, and adjust model parameters.

Therefore, we studied CO_2/C_3H_8 mixed hydrate *via* vibrational Raman spectroscopy in order to provide qualitative information about the hydrate structure. This work was conducted in cooperation with the Institute of Molecular Sciences at University of Bordeaux (ISM). I would like to gratefully acknowledge the funding received from GdR2026 CNRS "Hydrates de Gaz" through this collaborative work between ISM Bordeaux and Mines Saint-Etienne. I am also very grateful to Professor Arnaud Desmedt (and his team) for his active involvement and constructive scientific suggestions and discussions which improved effectively this work.

Raman spectra were recorded with a confocal micro-Raman spectrometer LabRAM HR Evolution (Horiba Jobin Yvon, Villeneuve d'Ascq, France) using a 532 nm radiation from a diode pumped solid state laser. The incident laser beam was focused onto the sample through a microscope with a 50× objective (NA = 0.45, Olympus) allowing the sample to be probed with a micrometric spatial resolution. Scattered light was dispersed by 1800 grooves/mm holographic grating system and collected in the backscattered geometry with a CCD detector. A set of experiments on Raman spectroscopic investigations of simple CO_2 and C_3H_8 hydrates as well as CO_2/C_3H_8 mixed hydrate at isobaric conditions was conducted. The results were then discussed by considering the Raman shifts of guest molecules in gas phase, hydrate phase as well as in the mixture.

Typically, pure CO_2 and pure C_3H_8 form sI and sII, respectively. The CO_2/C_3H_8 mixed hydrate is theoretically supposed to form sII. However, the results of mixed hydrate revealed that the hydrate structure as well as cage occupancies could depend on vapor composition. Consequently, the hydrate composition may change significantly according to the operational conditions. In fact, double-peaks of C-C and C-H stretch vibrations of propane were observed which was different from the spectroscopic results of pure propane.

These investigations helped us to explain why hydrate composition of this mixture significantly changed during our experiments at Mines Saint-Etienne.

[1]*Maghsoodloo Babakhani S. et al. Fluid Phase Equilibria 472 (2018): 22-38*