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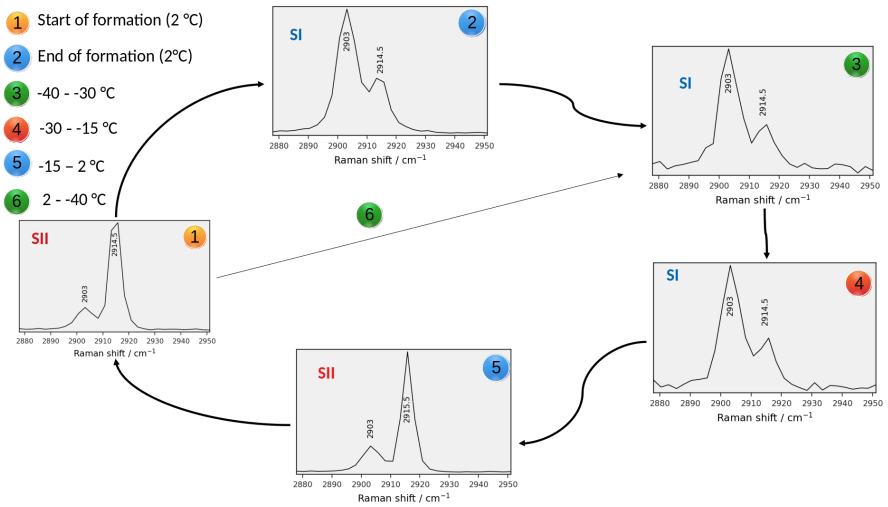
Ahmed Omran[a]
A.H. Ait Blal, Valentin Valtchev*
Normandie Université, ENSICAEN, UNICAEN, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France

omran@ensicaen.fr

Climate-Resilient Technologies: Adapting Methane Hydrate Transformations to Moderate Thermodynamic Conditions

Crystalline clathrate hydrates represent solid materials characterized by a distinctive framework structure, wherein hydrogen-bonded water molecules form well-defined cavities capable of accommodating gas molecules. Notably, the formation of methane hydrates with structure II (sII) is not observed within moderate temperature and pressure ranges (P ≤ 100 MPa and T ≤ +20 °C). Instead, the dominant and thermodynamically stable phase is structure I (sI) hydrate. Consequently, both natural gas hydrate and synthetic methane hydrate, cultivated to simulate natural conditions, predominantly exhibit the sI structure.
In this study, we present the outcomes of Raman spectroscopic investigations aimed at manipulating the transformation of methane hydrates under a constant low pressure of 2.7 MPa and within a temperature range of +2 to -40 °C. Considering that the ratios of large to small cavities in structure I and structure II hydrates are 3:1 and 1:2, respectively, the relative peak areas observed in the experimental spectra serve as reliable indicators of the hydrate structure. Raman spectroscopic investigations coupled with multivariate curve resolution - alternating least squares (MCR-ALS) method investigated hydrate formation at 10 MPa and 275.2 K. The results showed that sII was formed earlier as a kinetic product, followed by a mixed sI-sII phase, which is finally transformed into the thermodynamically stable sI. Such a result indicates that forming $5^{12}6^2$ cavity is the rate-limiting step for hydrate formation and agrees well with previous investigations [1]. Upon reducing the temperature gradually to -40 °C, sI remains the dominant phase.
Interestingly, a phase transformation to a dominant stable sII structure was found when the temperature increased gradually from -15 °C to +2 °C, which is reported for the first time at those very moderate thermodynamic conditions. The sII two remained intact for 3 days, indicating relatively high stability of the structure. SII could be reverted to sI again by direct cooling to -40 °C. Such results have important implications related to such important issues as the energy storage, climate change, geotechnical engineering, and material science development in general.



References

[1] Schicks, Judith M., and John A. Ripmeester, Angewandte Chemie International Edition, 43 (2004) 3310 –3313.