Instrumental Cross Calibration for Compositional Determination of Methane + Ethane Hydrates Using Raman and NMR Spectroscopy

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Direct hydrate compositional measurements have been performed for various feed mixtures of methane and ethane using Raman and NMR spectroscopy. Previous work has shown that Raman spectroscopy can be used to quantify the distribution of methane in hydrate cages. However, if one or more other gases are present in the hydrate (e.g. ethane, carbon dioxide, etc.), the gas distribution/composition in the hydrate cage is only determined qualitatively with Raman. The lack of quantitative compositional determination in multi-guest hydrate systems is due to changes in the Raman polarization cross section. Because NMR spectroscopy is inherently quantitative, measurements of a hydrate sample using both techniques was used to determine the change in the Raman cross section as a function of the second gas composition. In the pure methane hydrate system, the Raman cross section is approximately equal for methane in both cage types. The results for the binary hydrate systems indicate that the addition of the second guest changes the Raman cross section of methane in the cages disproportionably. This change could be attributed to guest-guest interactions in the hydrate system, often assumed to be negligible.