Kinetics versus Thermodynamics

The Coexistence of Two Different Methane Hydrate Phases under Moderate Pressure and Temperature Conditions: Kinetic versus Thermodynamic Products[**]

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Clathrate hydrates are nonstoichiometric crystalline icelike solids comprising a three-dimensional framework in which water molecules are hydrogen-bonded so as to form well-defined cavities that contain gas molecules. The empty framework is unstable with respect to ice but is stabilized by a minimum degree of occupancy of the cavities.

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There are three known gas hydrate structures capable of holding light hydrocarbons (Table 1): structure I, structure II and structure H. Small guests such as Ar, Kr, O_2, and N_2 form structure II hydrates with both large and small cages being filled. Slightly larger guests such as methane, CO_2 and ethane form structure I hydrates, with partial filling of the small cavity, and larger molecules such as propane and isobutane form structure II hydrates with the small cavities being empty. Even larger molecules such as neohexane form structure H hydrates in the presence of an aiding gas such as methane. However, when more than one guest is present, the relationship between structure and size is not straightforward, as guests that individually form structure I hydrates sometimes together form structure II hydrates when present in certain proportions. This was documented many years ago for the guest pairs H_2S/CH_3Br, H_2S/CH_3CHF_2, H_2S/COS, and more recently for ethane/methane.[1]

Table 1: Number of cavies per unit cell for the different gas hydrate structures.[8]

Structure			Cavities		
	5^{12}	$5^{12}6^{2}$	$5^{12}6^{4}$	$4^{3}5^{6}6^{3}$	$5^{12}6^{8}$
Structure I	2	6	–	–	–
Structure II	16	–	8	–	–
Structure H	3	–	–	2	1

Guests such as methane and carbon dioxide are not known to form structure II hydrates under moderate pressure and temperature conditions ($P \leq 100$ MPa and $T \leq +20$ °C), either individually or in combination, and it is generally accepted that structure I hydrate is the thermodynamically stable phase for these guests. Hence, natural gas hydrate as well as synthetic methane hydrate—grown under conditions close to those in nature—are known to be structure I.

Although all theoretical and experimental considerations lead to the conclusion that the formation of structure II methane hydrate is unlikely under conditions encountered in nature, in this study it is shown that the coexistence of structure I and structure II methane hydrate is possible under moderate conditions. Herein, we present the results of Raman spectroscopic investigations on methane hydrate, synthesised in a pressure range between 3.0 MPa and 9.0 MPa and at temperatures between +1.5 °C and +12 °C. Euhedral crystals of methane hydrate were grown under conditions close to the dissociation curve at constant pressure and temperature in a small pressure cell with a window suitable for optical and Raman observation. Figure 1 shows a microscopic photograph of the crystals.

Analysis of the crystals by Raman spectroscopy gave some rather unexpected results. It is known that the vibrational frequency of a C–H symmetric stretch for methane can be correlated with the size of the cage—vibrational frequencies for small cavities are shifted to higher frequencies than those for methane molecules in large cavities according to the Pimentel–Charles "tight-cage–loose-cage model" as recently elaborated by Subramanian and Sloan.[3,4] Since the ratios of large to small cavities for structure I and structure II hydrates are 3:1 and 1:2, respectively, the relative peak areas in the experimental spectra should be good indicators of the structure. It turns out that the ratio of the Raman bands for most of the crystals is close to 3:1 (Figure 2a), thus indicating the presence of structure I, as expected for methane hydrate. Nevertheless, the Raman spectra of a few crystals (Figure 2b) give spectra with peak intensities 1:2, indicating the presence of structure II hydrate.

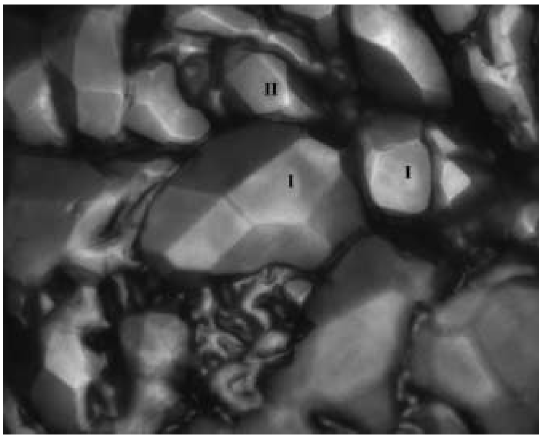

Figure 1. Coexistence of structure I (s I) and structure II (s II) methane hydrates. The width of the photographed area is 420 μm.

Raman spectra of encaged CH_4 similar to those in Figure 2b have been published by Subramanian and Sloan for mixed methane/hydrocarbon structure II hydrates.[4]

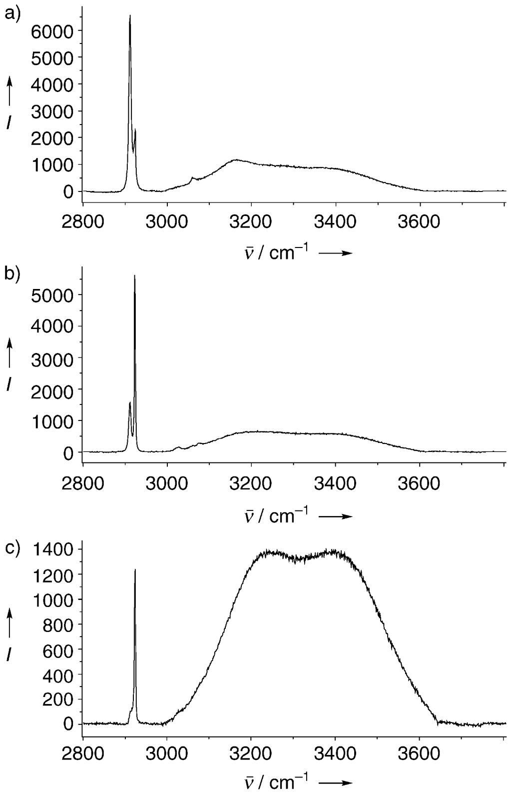

Figure 2. Raman spectra of structure I and structure II hydrates. *I* is intensity, arbitrary units.

Raman spectra for pure structure II methane hydrate have also been described by Chou et al., for samples that were converted from structure I hydrate by applying high pressure (> 100 MPa), and these also look similar to the spectrum shown in Figure 2c.[5] Chou and co-workers verified their results evincing the presence of structure II methane hydrate with X-ray diffraction data. Our Raman spectra of the CH_4 bands prove that there are at least two different phases of methane hydrate that coexist in a pressure range between 3 MPa and 9 MPa and a temperature range of between 1.5 °C and 12 °C. The two different Raman spectra for the structure II methane hydrate are probably caused by different degrees of saturation of the large cages with methane. We want to point out that the experimental setup permits a selective analysis of the separate phases. This is described in more detail in the Experimental Section.

It is clear that structure II methane hydrate is less stable than structure I methane hydrate under these conditions: if the conditions are changed, for instance, to lower temperature at constant pressure, or to higher pressure at constant temperature, the structure II crystals transform. First the crystals become less well-defined and develop characteristic micrometer-sized specks. A rounding of the crystals, reminiscent of a melting process, is followed by a transformation into a fine-grained hydrate mass. These processes are documented in Figure 3a–e. This exothermic transformation process—beginning with the structure II crystals—induces a recrystallization of the entire hydrate phase until a new steady state is reached. All of the hydrate phase has a fine-grained texture before new well-defined crystals start to grow again.

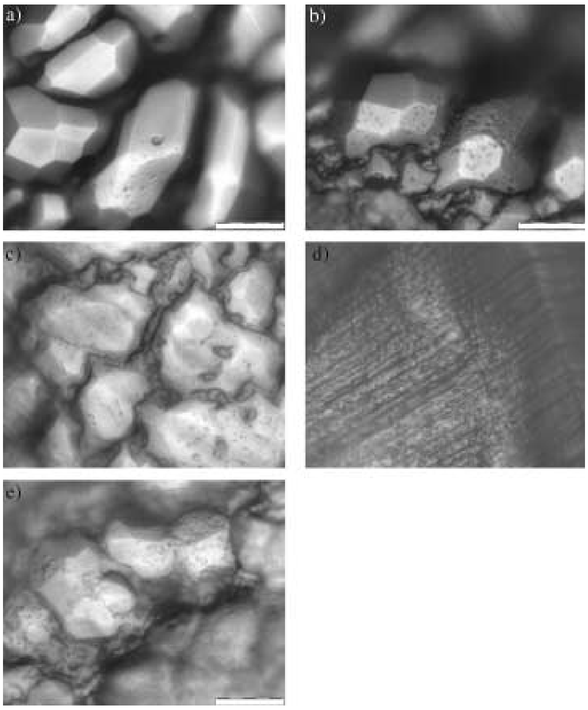

Figure 3. Transformation of structure II into structure I methane hydrates. The width of the photographed area is 420 μm, the length of the bars in a,b,e) are 100 μm.

Raman spectroscopic measurements (shown in Figure 4a–d) on these hydrates during the change in morphology show a loss of the structure II character: the intensity of the methane band at 2904 cm^{-1} (large cavities) increases, while the intensity of the methane band at 2916 cm^{-1} (small cavities) decreases. Finally, structure II methane hydrate can no longer be detected by Raman spectroscopy.

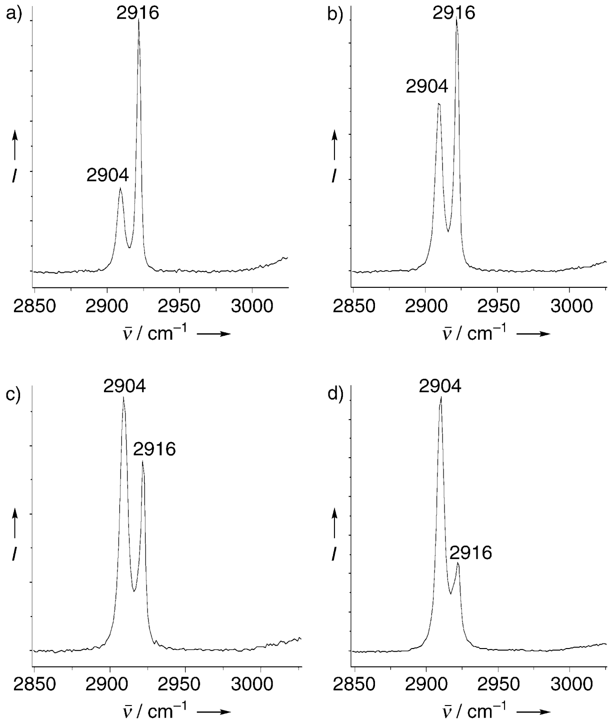

Figure 4. Raman spectra of the transformation of structure II methane hydrates into structure I methane hydrates.

Up to now the reason for the formation of structure II methane hydrate under the conditions mentioned above is unexplained. Subramanian and Sloan observed in their real-time-monitoring Raman spectra the transformation of dissolved CH_4 to CH_4 in the large and small cages of structure I methane hydrate.[6] In the initial stages of hydrate formation the ratio of large cages to small cages was 0.5, which corresponds well with ratio of large cages to small cages of structure II clathrate hydrates. Subramanian and Sloan assumed that the formation of the large cavity is the rate-limiting factor in the formation of structure I methane hydrate. The time dependency of the occupancy ratio does change with time, which is consistent with a slow transformation of structure II into structure I and it is almost complete after 5000 s. Staykova et al. observed the transient formation of structure II CO_2 hydrates during the growth of pure CO_2 hydrates on grains of ice.[7] The ^{129}Xe NMR experiments of Moudrakovski et al., who determined the cage-occupancy ratio as a function of time during the early stages of formation and growth of hydrate, also observed a predominance of small cages at an earlier part of the reaction, thus indicating a major role for the small cavities.[8] We also note that a structure II hydrate of Xe, prepared from structure II THF hydrate, proved to be quite fragile, as it is converted into more stable hydrates within minutes.[9] In these various studies the presence of large numbers of guest molecules in small cages at early stages of the hydrate growth process suggests that structure II hydrate may be the kinetically favored structure as it contains the small cage as the major building block for the structure II framework.

In summary, Raman spectroscopic investigations of the formation of synthetic methane hydrate show some remarkable features: methane hydrate crystals of very different composition have been identified. Raman spectra showing cage occupancy ratios for methane in large and small cavities were either 3:1 or 1:2, respectively, for different crystals. These in situ measurements were made in a pressure cell at temperatures between −15 °C and +15 °C and at a pressures ranging from 3.0 to 9.0 MPa. The observation of structure I and structure II hydrates under conditions where only structure I hydrate should be stable, suggests that the initial product is determined by kinetics, with structure II hydrate appearing as a metastable phase. The state of coexistence as well as the transformation of the kinetic product to the thermodynamically stable structure I of methane hydrate was documented by microscopic visual observation as well as Raman spectroscopy.

Experimental Section

The main component of the experimental setup was a pressure cell (Figure 5), which can be used in a temperature range between −27 °C and +80 °C. The temperature of the sample cell was controlled by a thermostat and the temperature was determined with a precision of ±0.1 °C. The applicable pressure range was between 0.1 and 10.0 MPa. A pressure controller was used to adjust the sample pressure with a precision of 2 % relative pressure. The small sample volume (0.393 cm^3) and the all-around cooling of the sample prevented interference from temperature gradients. With a gas flow rate of 1 mL min^{-1}, it took 17 s for the incoming gas flow to pass the cell body and to enter the void space of the cell; this time is sufficient to allow the gas to attain the cell temperature. The presence of a quartz window permitted the analysis of the phases by Raman Spectroscopy, and allowed the observation and recording of microscopic photodocumentation of formation and decomposition processes. It is worth noting that this experimental setup permits one to focus a laser beam on a precise point, for example, the surface of a hydrate crystal, and to have a precise definition of the analyzed volume thus assuring that only the selected segment is analyzed.

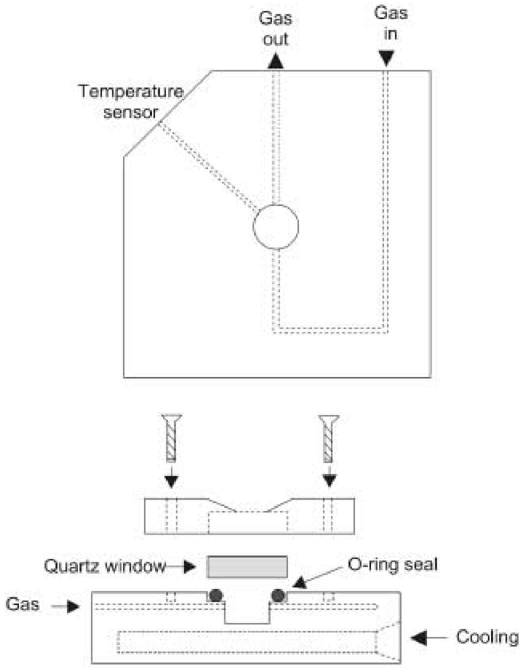

Figure 5. Sketch of the pressure cell.

The experiments were carried out by using the following procedure: pure degassed water (150 μL) was placed in the sample cell. The cell was carefully sealed and flushed with the appropriate gas before pressurization. The system was cooled down as rapidly as possible until hydrates were formed. The system was then warmed at a constant pressure to melt most of the hydrate. When only a few crystals remained, the temperature was lowered to 0.3 °C and the euhedral crystals of gas hydrate grew under steady-state conditions.

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