

# A Raman technique applicable for the analysis of the working principle of promoters and inhibitors of gas hydrate formation

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We report a Raman technique applicable for the *in situ* analysis of the development of hydrogen bonds in the liquid water-rich phase just before the onset of gas hydrate formation. Herewith, the phase transition as well as the working principle of hydrate formation inhibitors and promoters can be analyzed. © 2015 The Authors. *Journal of Raman Spectroscopy* published by John Wiley & Sons Ltd.

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## Introduction

Gas hydrates are solid networks of cavities, whose framework is formed of hydrogen bonded water molecules.<sup>[1]</sup> In typical hydrates, most cavities house one guest molecule – the so-called hydrate former – e.g. small hydrocarbons,<sup>[2]</sup> noble gases,<sup>[3]</sup> fluorinated compounds, or small ether molecules.<sup>[4]</sup> With respect to the energy and environmental sectors, gas hydrates can be considered as boon and bane at once

- Boon as (1) huge amounts of methane hydrates stored in the sea sediments and permafrost deposits represent a potential source of natural gas,<sup>[5,6]</sup> (2) because of the high overall density of the compound hosted in the cavities, hydrates can act as storage medium for gases during transportation, e.g. of hydrocarbons or hydrogen, and (3) they may be utilized for the 'ultimate' disposal of environmentally problematic gases such as carbon dioxide (CO<sub>2</sub>).<sup>[7,8]</sup>
- But on the other hand, they are bane as the undesired formation of gas hydrates in oil and gas pipelines is sometimes responsible for pipeline blockage. The annual costs for chemicals added as hydrate formation 'inhibitors' are in the range of hundreds of millions of US\$, not comprising the convey stop and drill time loss due to hydrate pipe blockage.<sup>[9,10]</sup>

Summarizing, there are processes, such as gas transportation, gas storage, or carbon capture, that profit from the promotion of the hydrate formation mechanism, while for others, such as gas or oil conveying or reservoir drilling, the inhibition of hydrate formation has to be assured for the prevention of pipe blockage.

Irrespective of whether the hydrate formation should be promoted or inhibited, the system must be influenced at early times, meaning before the formation of a continuous solid hydrate phase. Hydrate formation is promoted or inhibited by the addition of respective chemicals into the liquid water-rich phase.

Thermodynamic inhibitors or promoters are designed to influence the system already before first hydrate nuclei are formed and thus shift the pressure and/or temperature at which the phase

transition to hydrates occurs. In contrast, 'kinetic' and 'anti-agglomerate' inhibitors are designed to mainly influence the growth or the agglomeration of the already formed hydrate nuclei or pre-stages of these clathrates and thus retard the formation of a continuous solid hydrate phase and with this keep the already formed hydrate particles dispersed in the liquid phase.<sup>[9]</sup>

Most probably because of the complex nature of water, the formation mechanisms of hydrates (kinetics, metastability, and formation of different kinds of cavities) as well as the mechanisms promoting or inhibiting the formation of hydrates are not fully understood.<sup>[11]</sup> Spectroscopic approaches have provided some insights into the hydrate formation mechanisms and into the generation of different kinds of cavities on a microscopic level.<sup>[12–15]</sup> The mentioned studies have two things in common. Firstly, mainly the gas hydrates themselves have been analyzed and not the liquid water-rich phase. Secondly, the focus of the spectral investigations into hydrates has been placed on the hydrogen former (mostly methane), but not on the water molecules, which form the cavities. Few other studies are known that put more emphasis onto the role of the water molecules – not in the liquid water-rich-phase – but in the solid gas hydrate phase.<sup>[16–18]</sup>

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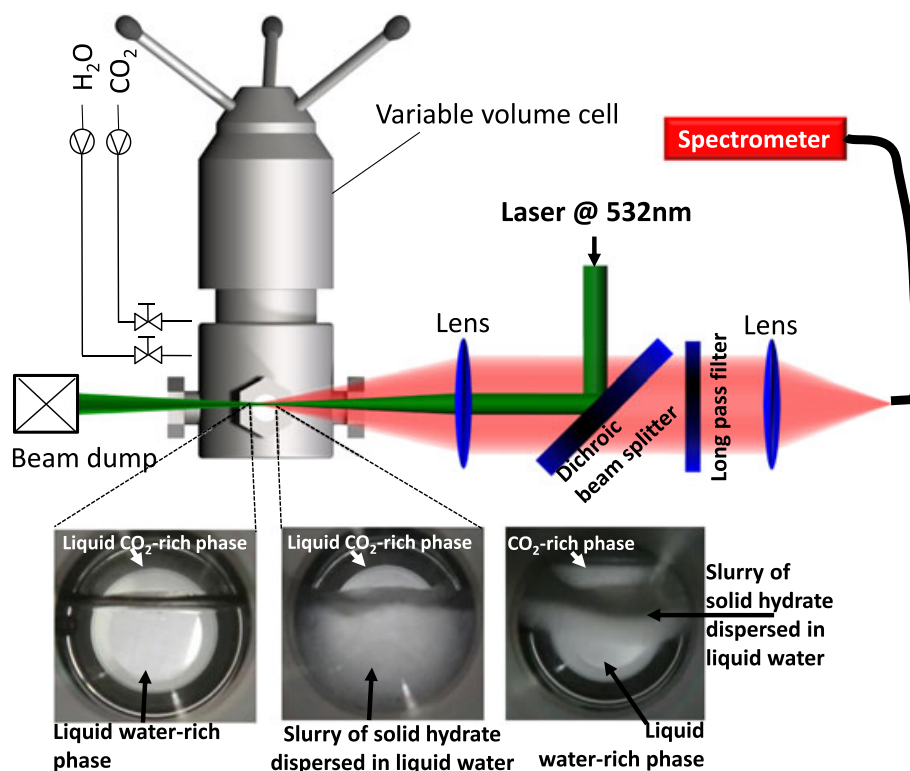
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Our work has been motivated by the facts that firstly, the addition of salt to water at ambient conditions may significantly influence the development of the hydrogen bonds in the aqueous system,<sup>[19]</sup> and secondly, various salts are known to act as thermodynamic hydrate formation inhibitors.<sup>[20]</sup> Therefore, we here demonstrate a Raman-based methodology for the analysis of the development of hydrogen bonds in the liquid water-rich phase before and after the onset of hydrate formation. It can provide information about how promoting or inhibiting chemicals affect the development of hydrogen bonds in the water-rich phase before the hydrate formation takes place. From this, an understanding of the working mechanisms of the promoters and inhibitors can be developed, which will make a tailor-made production of promoter and inhibitor chemicals possible. The understanding and optimization of inhibiting and promoting strategies will not only have a huge impact on energy and environmental sciences but is also important from an economical point of view as well, especially that the inhibition of hydrate formation requires huge financial effort. Additionally, this technique may be helpful in understanding the existence of the so-called 'memory effect', which is related to a different, faster formation of gas hydrates from solutions that have experienced a previous presence of hydrates.<sup>[21,22]</sup> Previous experimental *in situ* investigations required laborious methods such as neutron scattering.<sup>[23]</sup>

## Experimental setup

Figure 1 shows a sketch of the experimental setup used for the investigation into the development of the hydrogen bonds of the water molecules during the formation mechanisms of CO<sub>2</sub> hydrates. It comprises the high-pressure variable-volume view cell with accessories required to control the conditions inside the

chamber and the self-developed Raman sensor required for the remote *in situ* analysis of the development of hydrogen bonds. The identical view cell and Raman sensor have already been used before, also for the analysis of the development of hydrogen bonds but in the context of CO<sub>2</sub>-based surfactant-free micro emulsion-like systems.<sup>[24]</sup> Once water and CO<sub>2</sub> have been fed into the chamber at the desired pressure of 4 MPa, the fluids are isobarically cooled from room temperature to 278 K and remain at this temperature until the formation of hydrate is observed visually. Cooling is realized by circulating coolant from a thermostat through the double-walled jacket of the chamber. Isobaric conditions are realized by keeping the CO<sub>2</sub> pump, which is controlled at 4 MPa, and the chamber connected. A magnetic 'fish' positioned at the bottom of the chamber continuously agitates the liquid water-rich phase and thus assures a good mass transport between the liquid water-rich phase at the bottom of the chamber and the liquid CO<sub>2</sub>-rich phase on top. Once the hydrate formation starts, a hydrate film is formed at the meniscus between the two liquid phases. The film soon is torn down in flakes by the agitation process, which distributes the flakes throughout the liquid water-rich phase, as it is shown in the middle photograph of Fig. 1. A movie is provided in the Supporting Information showing how the hydrate is formed. We call this newly formed two-phase mixture 'slurry' as it is composed of solid hydrate particles distributed in a water-rich liquid phase. If the agitation of the liquid water-rich phase is switched off soon after the start of the hydrate formation, the hydrate flakes accumulate in the slurry phase in between the liquid water-rich phase (bottom) and the liquid CO<sub>2</sub>-rich phase (top), as it can be seen in the right photograph of Fig. 1. The slurry phase is an additional barrier for mass transfer and interrupts the rapid formation of further hydrate. The Raman sensor probes the Raman spectra temporally resolved



**Figure 1.** Sketch of the experimental setup comprising the Raman sensor with signal detection in backscattering direction and the high-pressure variable-volume view cell with accessories.

from the liquid water-rich phase, the slurry, or the liquid CO<sub>2</sub>-rich phase in a backscattering arrangement. Individual Raman spectra are recorded in direct sequence with an integration time of 1 s each.

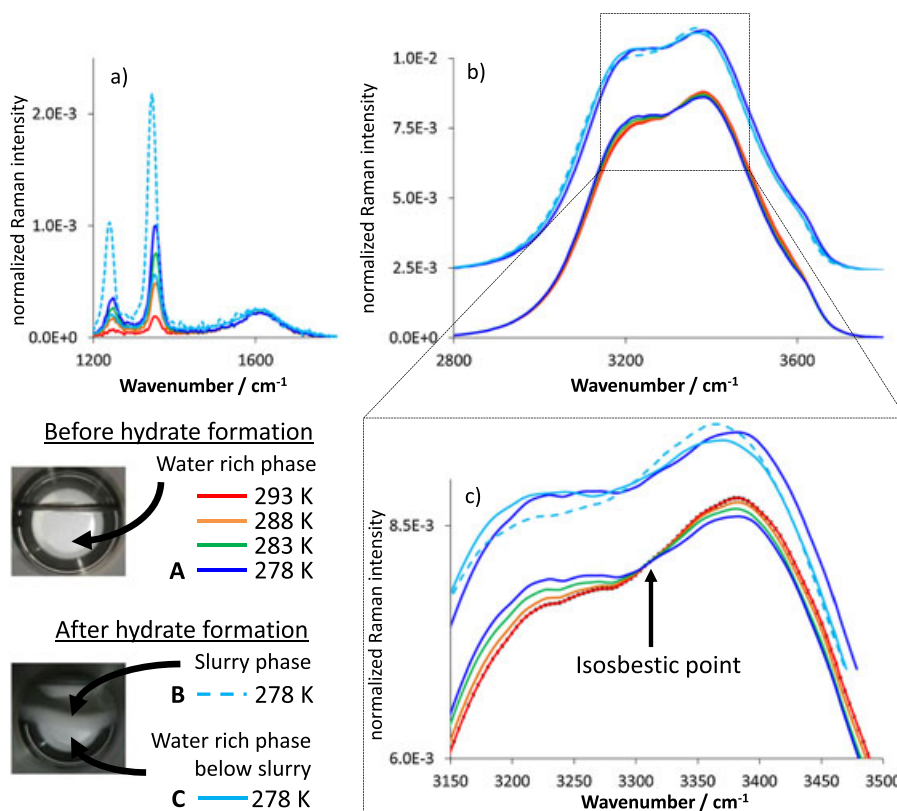
## Results

Figure 2 shows – as solid colored lines – the single Raman spectra of the liquid water-rich phase during the cooling period and before hydrate formation at four different temperatures. Additionally, Raman spectra are provided from the slurry phase as broken light blue line (mean of 100 single spectra due to low signals from the slurry) as well as from the liquid water-rich phase (single spectrum) remaining after hydrate formation under the slurry as solid light blue line, and labeled with letters B and C, respectively. All spectra shown in Fig. 2 are normalized to the area under the OH stretch vibration, which is depicted in the upper right part (b) of the figure. The upper left part (a) shows the spectral region comprising the CO<sub>2</sub> dyad and the OH bend vibration of water. The lower part (c) shows a magnification of the spectral region between 3100 and 3500 cm<sup>-1</sup>. Herein, in order to exemplarily demonstrate the high reproducibility of the spectra acquired, the standard deviation of 100 single spectra for the measurements made at 293 K (red solid line) is provided as black error bars. The relative standard deviation of the measurements is below 2% and almost falls within the width of the red line.

Considering solely the spectra taken from the liquid water-rich phase before the hydrate formation (red, orange, green, and dark blue spectra) two things become obvious as follows:

- The CO<sub>2</sub> dyads grow with decreasing temperature. This is due to the solubility of CO<sub>2</sub> in water, which increases with decreasing temperature.
- The signature of the OH stretch vibration is a function of temperature. While the shoulder left of the isosbestic point increases, the shoulder right of the isosbestic point decreases with decreasing temperature. This behavior is due to a shift of an equilibrium of water molecules in states attributable to a strong development of hydrogen bonds (left of the isosbestic point) and states attributable to a looser development of hydrogen bonds (right of the isosbestic point),<sup>[25–28]</sup> and has frequently been exploited for the measurement of temperature.<sup>[29–32]</sup> The influence of the dissolved CO<sub>2</sub> onto the development of the hydrogen bonds is significantly less pronounced as found in different sets of experiments in our lab and therefore is neglected here compared with the influence of the temperature.

Therefore, the analysis of the areas left and right of the isosbestic point of the OH stretch vibration of water in general can indicate how any action in the system, which might be a temperature variation, a pressure variation, or the addition of any chemical, influences the development of hydrogen bonds in the liquid phase. This straightforward strategy can make accessible how hydrate inhibiting or promoting chemicals affect the development of the hydrogen bonds in the liquid phase before the start of hydrate formation. This is crucial as during the transition from the liquid to the hydrate phase, a framework of hydrogen bonded water molecules



**Figure 2.** Raman spectra of the liquid water-rich phase at different temperatures before the onset of hydrate formation (solid lines), of the slurry phase composed of hydrate and liquid water after the onset of the hydrate formation at 278 K (broken light blue line), and of the liquid water-rich phase below the slurry phase (solid light blue line) at 278 K and at 4 MPa. Subpart (a) shows the spectral region between 1200 and 1800 cm<sup>-1</sup>, subpart (b) shows the spectral region between 2800 and 3800 cm<sup>-1</sup>, and subpart (c) shows a magnification between the wavenumbers 3150 and 3500 cm<sup>-1</sup>. Exemplary error bars provided for the spectrum at 293 K represent the standard deviation computed from 100 single spectra. The spectra for 278 K in subparts (b) and (c) have been shifted for a clearer presentation.

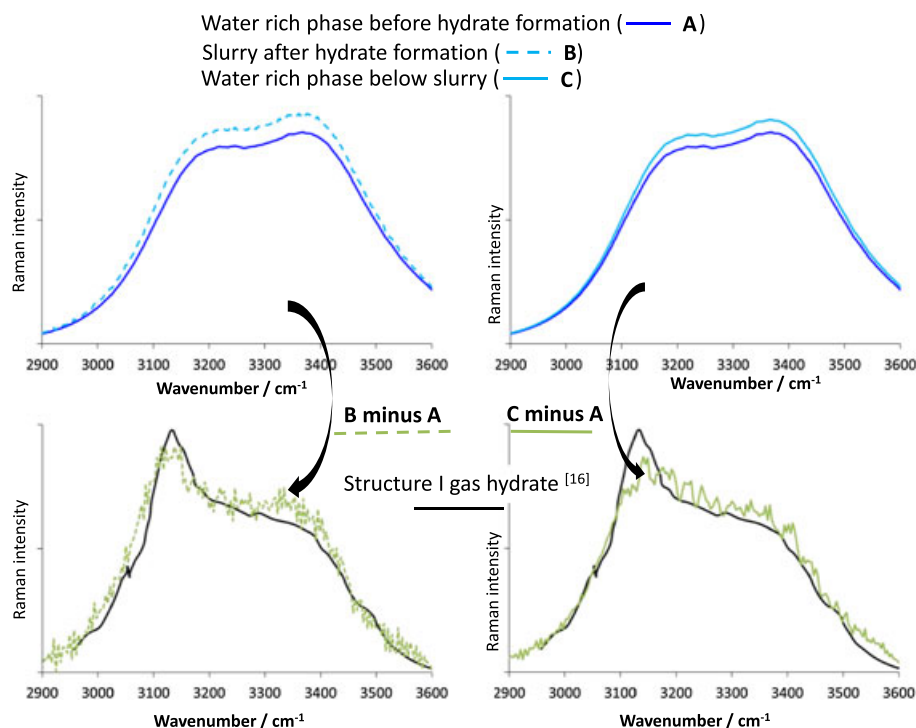
is formed.<sup>[1]</sup> Even if the Raman spectrum of the chemicals added to the liquid water-rich phase spectrally overlaps with the OH stretch vibration of water, the OH stretch vibration Raman signature of solely the water can be isolated from the interfering rest using deconvolution methods as described by Schuster *et al.*<sup>[33]</sup> and already applied during the investigation into the development of hydrogen bonds in micro emulsion-like systems.<sup>[24]</sup>

In the further progress, we compare the Raman spectra taken from the liquid water-rich phase before the hydrate formation (A in Fig. 2, dark blue solid line), the slurry (B in Fig. 2, light blue broken line), and the liquid water-rich phase after hydrate formation (C in Fig. 2, light blue solid line), all corresponding to 278 K and 4 MPa. Four things should be realized as follows:

- The CO<sub>2</sub> dyad Raman signal of the slurry (B in Fig. 2) exceeds the one of the liquid water-rich phase before hydrate formation (A in Fig. 2). This indicates that the hydrate, which is formed at the interface between the liquid water-rich phase and the liquid CO<sub>2</sub>-rich phase, contains much more CO<sub>2</sub> than the liquid water-rich phase before the hydrate formation.
- The CO<sub>2</sub> dyad Raman signal of the liquid water-rich phase after hydrate formation (C in Fig. 2) is smaller than that of the liquid water-rich phase before hydrate formation (A in Fig. 2). This indicates that the solubility of CO<sub>2</sub> in the liquid water-rich phase is reduced in the presence of a coexisting hydrate phase.<sup>[2]</sup>
- The signatures of the OH stretch vibration of the liquid water-rich phase after (C in Fig. 2) and before (A in Fig. 2) hydrate formation are different, although temperature and pressure are identical. This indicates that the overall characteristics of hydrogen bonds in both cases are different. Figure 3 will clarify this.
- The signatures of the OH stretch vibration of the liquid water-rich phase before hydrate formation (A in Fig. 2) and

of the slurry (B in Fig. 2) are rather similar although the characteristics of hydrogen bonds in the solid hydrate form should be very different (much stronger) to those in the liquid water-rich phase. This indicates that the majority of the slurry is still a water-rich liquid, and only the minority is solid hydrate. Figure 3 will clarify this, too.

Figure 3 compares in the lower part the Raman spectrum of the OH stretch vibration of pure hydrate structure I (black solid line), which has been extracted from Schicks *et al.*,<sup>[16]</sup> with the Raman spectra (green lines), we computed for the solid hydrate from the acquired Raman spectra A, B, and C. For the isolation of the spectral contribution of solely the hydrate phase (green spectra), we subtracted a weighted Raman spectrum of pure liquid water (spectrum A) from spectra C and B, which contain Raman contributions of liquid water and of solid hydrate. Good agreement between the structure I hydrate spectrum (black solid line) and the computed spectra 'B – A' and 'C – A' (green lines) was found for weighting spectrum A with respect to the intensity of the band with 0.917 and 0.943, respectively. In other words, by this subtraction, we were able to specifically remove the Raman signal contributions of solely the liquid water (A in Fig. 3) and thus isolated the Raman signal contributions originating from only the solid hydrate (green spectra) dispersed either in the slurry (B in Fig. 3) or in the liquid water-rich phase below the slurry (C in Fig. 3). Obviously, the two green spectra are similar to structure I gas hydrate and therefore indicate the presence of structure I hydrate in both cases. Of course, we expected to see that the difference between the OH stretch vibration of the slurry phase (B in Figs 2 and 3) and the liquid water-rich phase before hydrate formation (A in Figs 2 and 3) is due to the presence of structure I hydrate. But we did not expect to see that also the difference between the OH stretch vibration of the two



**Figure 3.** Comparison of the Raman spectra of a pure structure I hydrate phase taken from Schicks *et al.*<sup>[16]</sup> (black solid lines) and the Raman spectra of solely the hydrate phase (green lines) dispersed in the slurry (broken green line, B minus A) or in the liquid water-rich phase below the slurry (solid green line, C minus A). The Raman signal of liquid water has been removed from the Raman spectra taken from the slurry (broken light blue line, B) or from the liquid water-rich phase below the slurry (solid light blue line, C) by subtracting a Raman spectrum of the water-rich phase before hydrate formation (solid dark blue line, A).

liquid water-rich phases once before (A in Figs 2 and 3) and once after (C in Figs 2 and 3) the formation of gas hydrates is obviously due to the presence of a macroscopically not visible residue of hydrate structure I particles. It has to be emphasized here that the liquid water-rich phase after hydrate formation looked absolutely transparent. The detectability of hydrates in macroscopically transparent and still liquid phases has an implication of utmost importance for the investigations of the working principle of 'kinetic' or 'anti-agglomerate' hydrate inhibitors, too, as they are especially designed to keep systems flowing as a liquid, which already contain hydrate nuclei, particles, or pre-stages of them. These inhibitors do not really inhibit the hydrate formation but keep the hydrate nuclei and particles – once they are formed – dispersed in the still conveyable liquid phase and by this prevent pipelines from blockage. On the basis of the difference of spectra from macroscopically homogeneous liquid water-rich systems containing and not containing hydrates, information can be extracted about which 'kinetic' or 'anti-agglomerate' inhibitors are more suitable for purposes of flow assurance than others.

## Conclusions

In conclusion, the Raman-based *in situ* and remote analysis of the OH stretch vibration of water from the liquid water-rich phase before and after the hydrate formation, the slurry phase, and the solid hydrate phase provides a promising strategy toward a comprehensive understanding of the mechanisms of hydrate formation and the inhibition or promotion of this mechanisms by the addition of chemicals to the liquid water-rich phase. Additionally, even the efficiency of 'kinetic' or 'anti-agglomerate' inhibitors can be analyzed, which do on purpose not affect the development of hydrogen bonds before hydrate formation, as the approach presented here may provide information on the presence of small hydrate particles that are hindered from further growth or agglomeration. As huge amounts of methane are stored in hydrates and as flow assurance in pipelines and during drilling down to oil or gas reservoirs consumes huge financial efforts, comprehensive investigations into the working mechanisms of inhibiting and promoting chemicals are required from an environmental as well as from an economical point of view.

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