A GAS HYDRATE AUTOCLAVE SUITABLE FOR IN-SITU FIBER OPTIC INFRARED SPECTROSCOPIC STUDIES

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ABSTRACT
In the present study, fiberoptic mid-infrared (MIR) spectroscopy has been applied for establishing first evidence on these mechanisms via in-situ measurements at simulated deep-sea conditions. Therefore, a commercial gas hydrate autoclave (GHA 200, PSL Systemtechnik) was modified such that a silver halide (AgCl/AgBr) mid-infrared (MIR) transparent optical fiber could be guided through the vessel. This assembly enables growing gas hydrates at controlled conditions, while simultaneously monitoring the transition of liquid water to gas hydrate via IR evanescent field absorption spectroscopy evaluating major vibrational signatures of the involved molecular constituents. Next to continuous pressure and temperature traces, optical observations via an in-situ video camera are correlated to the spectroscopic signatures during gas hydrate formation. The collected spectra of ambient air and DI-water were compared to those collected with a custom-made pressure vessel that was successfully used during our previous studies.1

Keywords: gas hydrates, infrared spectroscopy, fiber optics, evanescent field sensing, influence of detergents

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**NOMENCLATURE**

AgBr: Silver bromide  
AgCl: Silver chloride  
CCD: charge coupled device  
d<sub>p</sub>: penetration depth of the evanescent field [µm]  
n: refractive index  
FEWS: fiber optic evanescent wave spectroscopy  
MCT: mercury cadmium telluride  
OAPM: off-axis parabolic mirror  
PTFE: polytetraflouroethylene  
λ: wavelength [µm]

**INTRODUCTION**

Fiber optic mid-infrared spectroscopy was used to study gas hydrate formation and dissociation at simulated deep-sea conditions. Therefore, a custom-made pressure chamber with a feed through for an IR transmitting AgCl/AgBr fiber was used during our previous work.\(^2-5\)

In the present study, a commercial gas hydrate autoclave (GHA200, PSL Systemtechnik) was partially replicated and modified (similar to the custom-made vessel) to make it suitable for evanescent wave MIR spectroscopy. Thus, enhanced understanding on the mechanisms of gas hydrate nucleation, growth and dissociation on a molecular level, and on the influence of detergents in these progresses is gained via the associated IR vibrational signatures.

Due to pronounced water absorption bands in the mid-IR region, fiber optic evanescent wave spectroscopy (FEWS) was applied. Due to the refractive index contrast between water and the AgCl/AgBr fiber, an exponentially decreasing standing wave, called evanescent field leaks into the adjacent medium along the surface of the fiber. The penetration depth of this wave is mainly dependent on the optical properties of the matrix surrounding the fiber, and on the wavelength of the light coupled into the waveguide. In liquid and solid media, the penetration depth amounts to approx. 0.5 - 0.8 µm. \(d_p\) may be calculated by the following equation (Equation 1)\(^6\)

\[
d_p = \frac{\lambda}{2\pi \sqrt{n_2^2 \sin^2 \theta - n_1^2}}
\]

Equation 1: Penetration depth of the evanescent field

Consequently, only a small volume within the adjacent medium is being probed, and a high sensitivity can be achieved in aqueous media in spite of the strongly absorbing vibrational excitations of the water molecules.

**EXPERIMENTAL**

A GHA 200 (PSL Systemtechnik, Germany, see figure 1) gas hydrate autoclave suitable for high-pressure conditions up to 200 bars was used. A Pt100 thermocouple, connected to a ministat 125 thermostat (Huber, Germany) was attached to control the temperature inside the vessel. The pressure was controlled via a HDA 4745 pressure transducer (Hydac Electronic GmbH, Germany). Optical access was provided by a Watec WAT-231S2 CCD-camera (Watec, Japan) through a sapphire window located in the top part of the autoclave. A stirrer below the autoclave drove a magnetic bar inside the vessel.

![Figure 1: GHA 200 gas hydrate autoclave, lower part (left side) and upper part with thermocouple (right side)](image)

In order to render the device suitable for mid-IR fiber optic measurements, the lower part of a GHA 200 gas hydrate autoclave was rebuild and modified. A fiber feed through was installed, by drilling two holes, facing each other into the steel walls. Swagelok tube fittings (SS-200-1-4BT) were fitted into the holes and sealed with PTFE tape. To install the fiber with pressure sealing through the tube fittings, cylindrical Teflon ferrules were developed, as shown in Figure 2.

For infrared spectroscopic observations, a Bruker IRcube (Bruker Optik, Ettlingen, Germany) Fourier transform IR spectrometer was used. Radiation was incident at an off-axis parabolic mirror (OAPM; A8037-295, Janos Technology, Keen, NH, USA, diameter: 50.8 mm, focal length: 25.4 mm, gold coated) reflected from a planar gold mirror mounted in front of the collimated spectrometer radiation outlet. The IR radiation was focused by the OAPM onto the polished end facet of a silver halide (AgCl/AgBr) optical fiber, and
propagated along the waveguide via total internal reflection. At the distal end of the fiber, the radiation was collimated by another OAPM (A8037-295, Janos technology), and then focused by a third OAPM onto a stirling cooled mercury-cadmium-tehlluride detector element (K 508, Infrared Associates, Stuart, FL, USA), which was connected to the IRcube via a preamplifier (MCT-1000, Infrared System Development Corp., Orlando, FL, USA) and an external detector connection module (Bruker ANA Box E550/A, Bruker Optik, Ettlingen, Germany). The detector positioner and all mounts, posts, and mounting screws were purchased from Thorlabs (Dachau, Germany) or Newport (Irvine, CA, USA). The entire set-up was mounted on a low-reflective, black anodized breadboard (24” x 18” x 1/2”, MB1824, Thorlabs), which in turn was mounted to the spectrometer by custom made anodized aluminum brackets. The fiber ends were positioned to the focal points of the parabolic mirrors with Newport FPH-DJ fiber chucks.

Table 1 gives an overview over the properties of the optical fibers used during the present studies.\(^7\) Their composition was AgCl\(_0\).3Br\(_{0.7}\); the diameter was 700 \(\mu\)m, and their length was approx. 40 cm. For comparison, spectra were taken with a custom-made gas hydrate sensor system, with a fiber feed through similar to the above explained. The spectra were collected at ambient conditions. Spectra of water were collected inside both pressure vessels, with the water exceeding the top face of the fiber for approx. one centimeter. DI-water was used.

![Figure 2: Construction drawing of Teflon ferrules and images of the fixture and fitting of the IR transmitting fiber](image)

**Table 1:** Mechanical, physical, and optical properties of the silver halide fibers applied in the present study

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific weight</td>
<td>6.39 g/cm(^3)</td>
</tr>
<tr>
<td>Melting point</td>
<td>412 °C</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>100 Mpa</td>
</tr>
<tr>
<td>Knoop hardness</td>
<td>15 kg/mm(^2)</td>
</tr>
<tr>
<td>Minimal bending radius</td>
<td>5 (\times) diameter</td>
</tr>
<tr>
<td>Transmission range</td>
<td>4 – 15 (\mu)m</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.21</td>
</tr>
<tr>
<td>Practical numerical aperture</td>
<td>0.5</td>
</tr>
<tr>
<td>Attenuation loss at 5.25 (\mu)m (CO-Laser)</td>
<td>1 - 2 dB/m</td>
</tr>
<tr>
<td>Attenuation loss at 10.6 (\mu)m (CO(_2)-Laser)</td>
<td>0.5 - 1 dB/m</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Figure 3 shows spectra of ambient air collected with the gas hydrate sensor system inside both, the modified commercial (red spectrum) and the custom-made (blue spectrum) initially used pressure chamber. Both spectra represent an average of 4000 scans at a resolution of 4 \(\text{cm}^{-1}\).

![Figure 3: Mid-IR fiber optic spectra of ambient air collected inside the modified commercial (red spectrum) and the initially used custom-made (blue spectrum) pressure vessel](image)

Both spectra look very similar. Differences in absorption intensity may be due to variances of the different silver halide fibers. Furthermore, constant compacting pressure between the silver halide fiber and the PTFE ferrules cannot be ensured when tightening the fittings. This circumstance results in spectral changes of the C-H (3000 – 2835 \(\text{cm}^{-1}\)) or C-F (1300 – 1120 \(\text{cm}^{-1}\)) absorption bands of Teflon or other synthetic materials (inside the fiber chucks) that are in contact with the fiber.
Both spectra also show the expected absorption bands of atmospheric water (3650 – 3300 cm⁻¹, 1900 – 1320 cm⁻¹, and 1000 – 600 cm⁻¹) and CO₂ (2400 – 2290 cm⁻¹).

In figure 4, spectra of water, again collected inside both pressure chambers (modified commercial autoclave, red spectrum; initially used custom-made autoclave[11], blue spectrum) are illustrated. The spectra average 4000 scans each, with a spectral resolution of 4 cm⁻¹. The red spectrum was normalized to the maximum absorption of the blue spectrum at 600 cm⁻¹.

CONCLUSIONS AND OUTLOOK

It is shown that the modified commercial gas hydrate autoclave is suitable for infrared spectroscopic gas hydrate studies. In the present work, this device was compared to a custom-made pressure vessel that was successfully used for gas hydrate studies in our previous work, and revealed concurrent performance for recording water spectra; the system is now prepared for first gas hydrate measurements.

To determine the mechanisms of gas hydrate growth and dissociation, and to study the influence of detergents on the dynamics of these processes IR spectra of a variety of dissolved detergents are currently collected. Their influence on gas hydrate growth will be determined during long-term experiments at controlled temperature and pressure conditions.

Finally, in order to simulate deep-sea conditions, experiments with artificial seawater, sediment, and surfactant-producing bacteria present inside the pressure vessel are planned.

REFERENCES


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