Raman Spectroscopic Studies of Natural Gas

"The Raman spectroscopic studies of natural gas" is a part of Susanne Brunsgaard Hansens Ph.D. project "The Application of Raman Spectroscopy for Analysis of Multi-Component Systems".

Supervisors
Rolf W. Berg, Department of Chemistry, DTU and Erling H. Stenby, Engineering Research Centre, IVC-SEP, Department of Chemical Engineering, DTU.

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Development of a high pressure measuring cell for natural gas

A system for obtaining Raman spectra of gases at high pressures has been constructed. In order to secure that a natural gas sample is totally representative, we have developed a gas-measuring cell suitable for measurements at high pressures, built up by stainless steel fittings (Swagelok) and a sapphire tube. Perfect tightness has been demonstrated up to 15.0 MPa_A. The cell has been successfully used for obtaining Raman spectra of natural gas at high pressures. A picture of the so-called “Sapphire tube cell” is shown below.

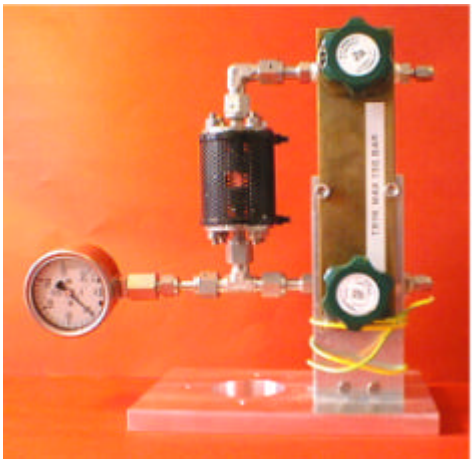


Photo showing the sapphire tube cell.

Raman spectroscopic studies of natural gas

Three different natural gas samples delivered by DONG A/S were analysed with success:

(1) from the Nybro Gas Treatment Plant, raw (10.2 MPa_A)
(2) from the same plant downstream of pressure regulation and filtration (8.0 MPa_A)
(3) from the Ll. Torup Gas Storage Facility, cavern TO7 (6.4 MPa_A).

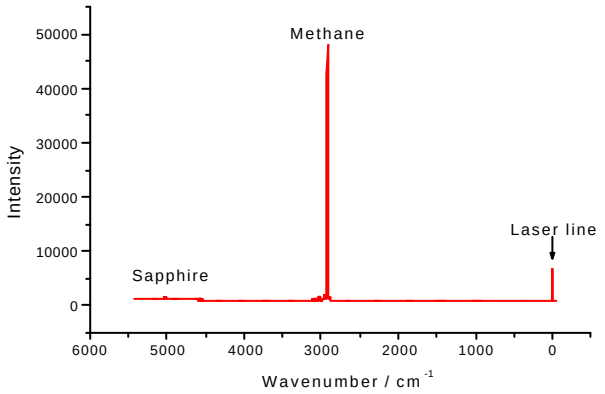
Qualitative analysis

The Raman spectrum of the natural gas sample taken from Ll. Torup Gas Storage Facility is shown in Fig. 1. Two small peaks arising from the sapphire (Cr^{3+}) tube are seen at about 5000 cm^{-1}. The methane content in a typical Danish natural gas sample is about 88 % in accordance with the observation that the symmetric CH_4 stretching band ($\acute{\imath}_1$) at ~2917 cm^{-1} is the most intense one in the spectrum. In fact the band is so intense that it overwhelms other information in the spectrum. Thus, the spectrum has been expanded and divided into four sections so it is possible to see bands from other components in the gas (Fig. 2, upper red curve). Polarised spectra of the sample were also obtained (Fig. 2, red curves, indicated as pol VV and pol VH) as a help when interpret the bands. The blue curve is the spectrum of the filtered natural gas sample from Nybro and the green curves are the spectra of the raw natural gas sample obtained at a high pressure (10.2 MPa_A and at a lower pressure (1.1 MPa_A).

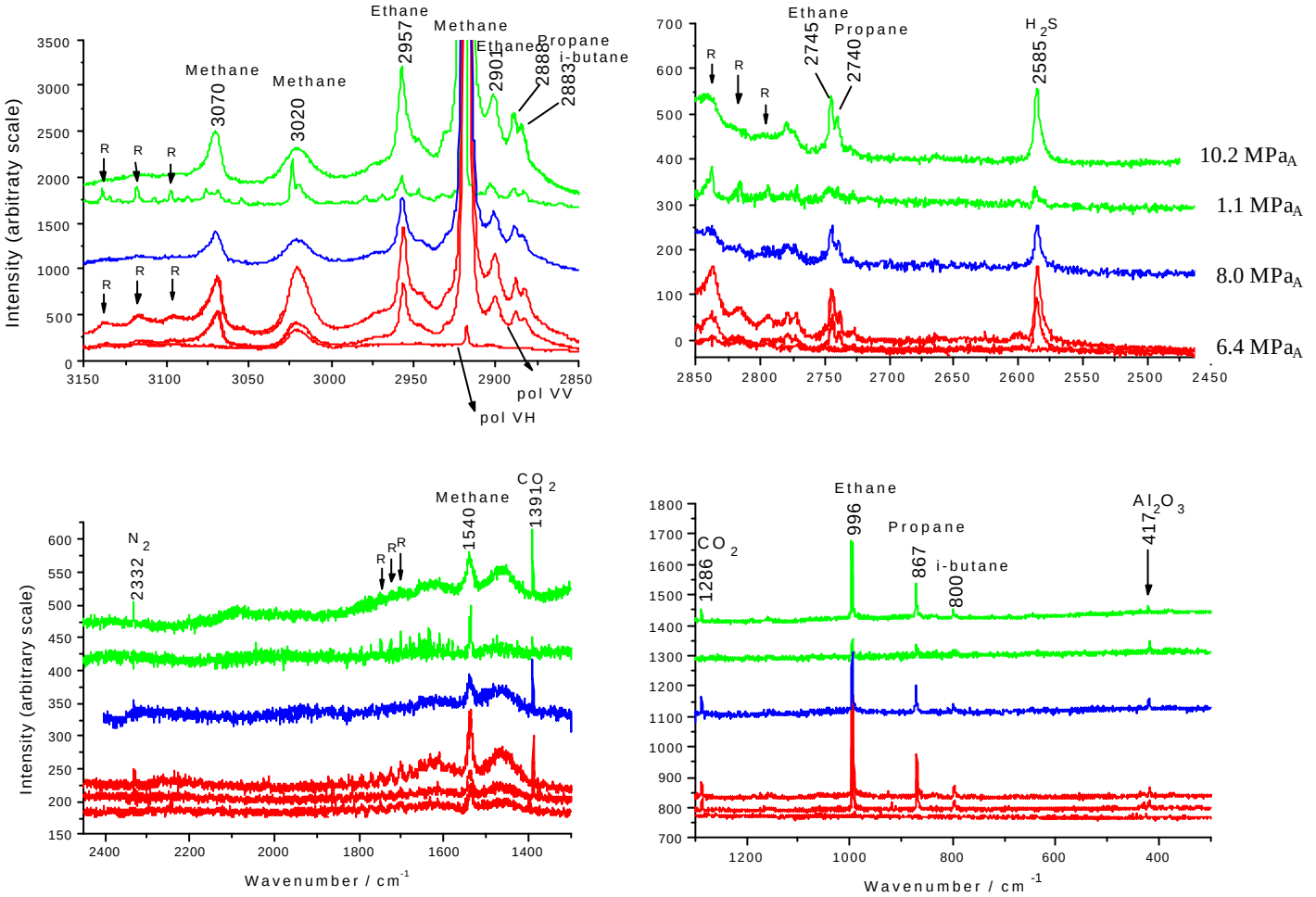
By comparing the spectra one concludes that it is the same component to be seen in all of them.

Detected organic compounds: The methane $\acute{\imath}_3$ (C-H asymmetric stretching) band and the methane $\acute{\imath}_2$ (asymmetric stretching) is observed at ~2920 cm^{-1} and ~1540 cm^{-1} respectively. Both of these bands are depolarised. In addition to the vibrational transitions it is also possible to observe rotational-vibrational transitions for these two depolarised bands (indicated with arrows in Fig. 2). Besides methane it was also possible to detect methane, ethane, propane and i-butane. The observed band at ~3070 has previously been observed in the Raman spectra of CH_4-rich inclusions and it was assigned to C-H stretching in olefin hydrocarbons and to higher hydrocarbons. The band has, however, been observed in the spectrum of pure methane. Thus, the correct assignment must be that it is the overtone of the methane $\acute{\imath}_2$ band at ~1534 cm^{-1}.

Detected inorganic compounds: Besides the organic compounds it was also possible to detect N_2 and CO_2. Most surprisingly was it, however, that it is possible to detect **hydrogen sulphide** at ~2585 cm^{-1}, despite of the fact that it is only present in natural gas in quite low concentrations. The content is low, typically 1-3 mg / Nm^3, because of desulphurisation off shore.



The Raman spectrum of a natural gas sample from Nybro (10.2 MPa_A) contained in the sapphire tube cell.



The Raman spectra of three natural gas samples (contained in the sapphire tube cell) from red) Ll. Torup (6.4 MPa_A), upper curve: no polarizer, lower curves: VV and VH polarization; blue) Nybro, downstream of pressure regulation and filtration (8.0 MPa_A); green) Nybro, raw (10.2 MPa_A) and the same sample at a lower pressure (1.1 MPa_A).

Publications

The design and construction of the sapphire tube cell & the Raman spectra of the natural gas samples are described in details in the following publication:

S. Brunsgaard Hansen, R. W. Berg and E. H. Stenby, “High Pressure Measuring Cell for Raman Spectroscopic Studies of Natural Gas”, Appl. Spectrosc. 55(1), xx (2001).

Contact

Susanne Brunsgaard Hansen, sbh@kemi.dtu.dk
Rolf W. Berg, rwb@kemi.dtu.dk