High-Pressure Measuring Cell for Raman Spectroscopic Studies of Natural Gas

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A system for obtaining Raman spectra of gases at high pressure has been constructed. In order to ensure that a natural gas sample is totally representative, a high-pressure gas-measuring cell has been developed, built up by stainless steel fittings and a sapphire tube. The design and construction of this cell are described. A perfect pressure seal has been demonstrated up to 15.0 MPa_A (MPa absolute). The cell has been successfully used to obtain Raman spectra of natural gas samples. Some of these spectra are presented and assigned. The most remarkable observation in the spectra is that it is possible to detect hydrogen sulfide at concentrations of 1–3 mg H_2S/Nm^3. An attempt to make a quantitative analysis of natural gas by the so-called "ratio method" is presented. In addition to this, the relative normalized differential Raman scattering cross sections for ethane and *i*-butane molecules at 8.0 MPa_A and 10.2 MPa_A have been determined.

Index Headings: **Raman spectroscopy; High-pressure cell; Natural gas.**

INTRODUCTION

Natural gas from the Danish fields in the North Sea is distributed by DONG A/S (the National Oil and Gas Company of Denmark). To ensure that the natural gas has the right quality before it is sent out via the pipeline network, the natural gas quality is measured at the Nybro Gas Treatment Plant (west coast of Jutland, Denmark) before it is transmitted or is sent to storage; e.g., in the L1. Torup Gas Storage Facility (in the north of Jutland). DONG A/S is continuously checking the quality of the gas—for example, by measuring the dew point and by analysis by gas chromatography. Previously in the literature the Raman method has been used to measure the nitrogen content in Dutch natural gas,[1] which has a high nitrogen content (~ 14%) compared to Danish gas (~ 0.4%). The intention of the present work is to investigate whether it is possible to use Raman spectroscopy as a tool to analyze the natural gas, in general, e.g., with respect to gas composition (aerosols, unwanted compounds, etc.). When performing Raman spectroscopy on virgin natural gas samples, the big hurdle often lies in the design and construction of the cell. *In situ* cells have been described in the literature for other situations.[2,3] When a natural gas sample is taken at high pressure and brought to ambient pressure, the gas will expand, which results in a drop in temperature. Heavier hydrocarbons will condense (due to the temperature drop), which will cause a change in the chemical composition in the gas phase. In the following discussion, the design of a tight, high-pressure gas-measuring cell for natural gas and the way to sample gas into the cell without condensation to ensure that the Raman measurements refer to a totally representative sample are considered.

EXPERIMENTAL

Design of the Cell. At the natural gas plants, the natural gas sampling loops connect by means of stainless steel fittings. Therefore it was decided to use fittings as the basic construction parts of the cell. A cell for Raman measurements must include a section that is transparent for the laser and Raman light. The challenge in designing the gas-measuring cell for high pressures lies in the choice and construction of this transparent section and the sealing of it to ensure integrity. A circular tube is a good choice because it can be connected to standard high-pressure fittings and sealed by means of O-rings. A quartz tube was considered at first but because of the difficulty of obtaining it in precise dimensions, with respect to diameter, we decided to use a tube of sapphire. Small amounts of impurities in the sapphire (i.e., traces of Cr^{3+} and other metal ions) cause fluorescence in the Raman experiments. Thus to avoid this phenomenon, we used sapphire with the very highest purity, delivered by ST Sanchez Technologies, France (dimensions: 39.5 ± 0.2 mm length, an outer diameter of 6.35 ± 0.01 mm, an inner diameter of 4.32 ± 0.5 mm). The common term sapphire is used because of the tradition among manufacturers of this material, even though it would be more correct to designate pure α-Al_2O_3 as corundum. Strictly speaking, sapphire is α-Al_2O_3 incorporated with Fe^{2+}, Fe^{3+}, and Ti^{4+} ions; when Cr^{3+} is incorporated in the α-Al_2O_3, the name is ruby.[4]

The layout of the final high-pressure gas measuring cell is shown schematically in Fig. 1. All fittings (Swagelok), including the two packless valves (**2a** and **2b**), have been supplied by the Danish Swagelok Company. With respect to O-rings the original viton ones in **4**, **8**, and **12** have been replaced by O-rings of nitrile rubber because even small amounts of CO_2 in natural gas were found to spoil the viton (the O-rings are indicated with "o" in the figure). Parts **5** and **8** were connected through a hole in the metal disk (**7**) and welded together. The nut (**6**) was screwed on part **4**. The metal disks were stabilized by four rods (**11**) around the tube (**10**), and surrounded by a safety metal net (**9**). To stabilize the whole cell, we inserted a brass plate (**16**); through the holes **18a** and **18b** (in the rack) it was screwed onto an aluminum block. Finally the cell was equipped with a pressure gauge (15) (WIKA bourdon manometer; measurement range: 0–25.0 MPa_R, MPa relative). The volume of the cell chamber was determined to 10.0 ± 0.5 cm^3 by

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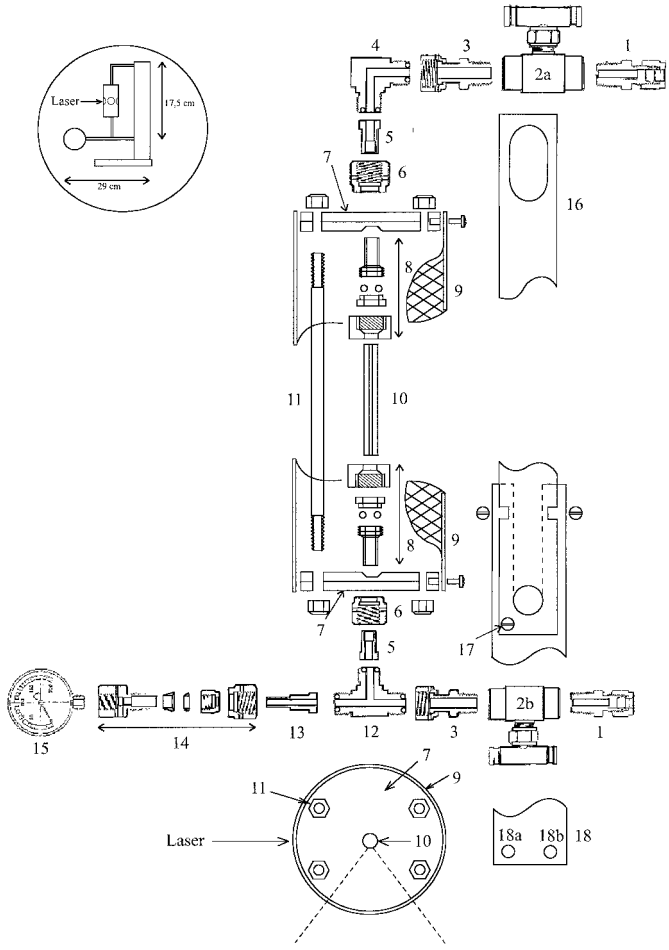

FIG. 1. Schematic illustration of the high-pressure gas-measuring cell. (**1**) Male connector (NPT) including blind plug; (**2**) packless valve; (**3**) male connector; (**4**) elbow, including two O-rings; (**5**) socket weld gland; (**6**) female nut; (**7**) metal disk; (**8**) Cajon ultra-torr adapter; (**9**) safety metal net; (**10**) sapphire tube (dimensions: 39.5 ± 0.2 mm length, an outer diameter of 6.35 ± 0.01 mm, an inner diameter of 4.32 ± 0.5 mm); (**11**) connector rod; (**12**) tee, including three O-rings; (**13**) tube adapter gland; (**14**) female connector; (**15**) WIKA pressure gauge (measure range: 0–25.0 MPa_R); (**16**) stabilizing brass plate; (**17**) screw for grounding to earth; and (**18**) rack (the cell is screwed on a aluminum block through **18a** and **18b**).

weighing the cell filled with water and without. It was tested with methane up to 15.0 MPA_A, and it was found to be perfectly leak-free for weeks.

Filling of the Cell. The cell was transported to the gas plants, either to the Nybro Gas Treatment Plant or to the L1. Torup Gas Storage Facility. At the plant, fitting **1** was connected to the DONG A/S gas sampling loop. Both valves **2a** and **2b** were opened, and the cell was flushed at a low flow. After flushing, valve **2b** was closed, and the cell was filled with natural gas to the full maximum pressure very slowly (to avoid any explosion of the sapphire tube). After filling, valve **2a** was closed, and the cell disconnected. Hereafter, the cell was transported to the Raman laboratory for Raman measurements.

Raman Spectroscopy. The Raman spectra were measured with a DILOR-XY confocal Raman spectrometer. The high-pressure gas measuring cell was placed in the macroscopic entrance position, and the collection geometry was 90°. The 514.53 nm_{air} line of an Ar-ion laser

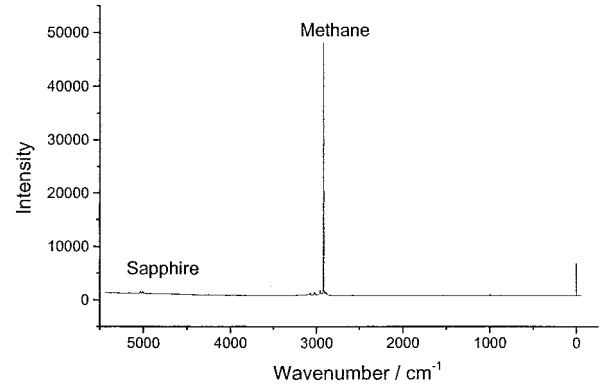

FIG. 2. The Raman spectrum of a natural gas sample at high pressure from L1. Torup Gas Storage Facility (6.4 MPa_A).

was used as the exciting source (~ 200 mW, vertically polarized). The Rayleigh filtration was done, not by use of the foremonochromator but with a super-plus holographic notch filter from Kaiser Optical Systems, Inc. (Ann Arbor, MI). All spectra were acquired by use of the spectrograph with a grating of 1800 grooves per mm. The scattered radiation was detected by a liquid nitrogen-cooled charge-coupled device (CCD) detector (1024 × 256 pixels). The I_{VV} and I_{VH} scattering configurations (V = vertical, H = horizontal) were obtained by use of a polarizer in the scattered beam. All spectra were measured at room temperature (22 °C). The spectra were calibrated by use of Ne lines to wavenumber better than ~ 5 cm^{-1} unless otherwise specified.

Chemicals. Methane of high purity, N45, i.e., 99.995% (Hede Nielsen A/S), was used. The natural gas samples were delivered by DONG A/S. The samples were taken (1) from the Nybro Gas Treatment Plant inlet (10.2 MPa_A); (2) from the same plant downstream of pressure regulation and filtration (8.0 MPa_A); and (3) from the L1. Torup Gas Storage Facility, cavern TO7 (6.4 MPa_A). For the preparation of hydrogen sulfide, the following chemicals were at hand: CaS (solid) and H_2SO_4 (6 M liquid).

RESULTS AND DISCUSSION

Qualitative Analysis. In Fig. 2 the Raman spectrum of the natural gas sample from L1. Torup Natural Gas Storage Facility is presented. The spectrum is almost without fluorescence, but shows two small peaks at about 5000 cm^{-1} (i.e., in the red end of the spectrum) arising from the sapphire tube. The composition in a typical Danish natural gas sample, measured by gas chromatography, is shown in Table I. As is seen in the table, the methane content in the typical natural gas sample is about 88%, in accordance with the observation that the C–H stretching band in methane (~ 2920 cm^{-1}) is the most intense one in the spectrum shown in Fig. 2. In fact the band is so intense that it overwhelms the other bands in the spectrum. To illustrate the spectrum more clearly, it has been divided into four sections and enlarged so bands from the other components in the gas become obvious; see Fig. 3 (the upper ***A*** curve is the spectrum shown in Fig. 2). In addition to the Raman spectrum ***A*** (upper curve) obtained with no polarizer, spectra obtained with VV and VH polarization are also presented (the two lower ***A*** curves in Fig. 3). The polarization helps the interpretation of the

TABLE I. Composition of a typical Danish natural gas sample measured by gas chromatography at the Nybro Gas Treatment Plant.

Component	mol %
Methane	87.77%
Ethane	6.45%
Propane	2.92%
n-Butane	0.58%
i-Butane	0.44%
n-Pentane	0.084%
i-Pentane	0.12%
Hexane and higher	0.068%
CO_2	1.12%
N_2	0.34%

bands. In Fig. 3, the spectra of natural gas samples from the Nybro Gas Treatment Plant (curves ***B***, filtered 8.0 MPa_A, and ***C***, raw 10.2 MPa_A) are also included in order to compare the three different gas samples. Furthermore, a spectrum of the Nybro filtered natural gas sample at lower pressure (1.1 MPa_A) is included (curves ***D***) to determine whether there are differences between high and low pressures with respect to composition (e.g., due to condensation). The lower pressure was achieved by slowly letting gas out of one valve.

In Table II the vibrational peaks of the spectra shown in Fig. 3 are listed and assigned. In addition to the pure vibrational transitions, it is also possible to observe rotational–vibrational transitions (P, Q, and R branches) for the asymmetric C–H stretching band (~ 3020 cm^{-1}) and the asymmetric deformation band (~ 1540 cm^{-1}) of methane. Arrows in Fig. 3 indicate some of these rotational–vibrational transitions. By comparing spectra ***D*** and ***C***, one can see that the intensity of the peaks increases with increasing pressure (because of the higher gas concentration). In fact there is also a shift of band position toward lower wavenumbers with increasing pressure. This wavenumber shift as a function of pressure for methane has been thoroughly investigated in the literature.[5–7] By comparing all the spectra, one concludes that the same components can be seen in all of them. The alkane molecules detected in the natural gas were methane, ethane, propane, and *i*-butane. The observed band at ~ 3070 cm^{-1} has previously been observed in the Raman spectra of CH_4-rich inclusions, and it was assigned to higher hydrocarbons[8] and to C–H stretching in olefin hydrocarbons.[9] The band has, however, been observed in the spectrum of pure methane (see below). The correct assignment, therefore, must be that it is the overtone of the methane ν_2 band at ~ 1534 cm^{-1}, which can couple to the ν_1 by Fermi resonance. ν_2 has E symmetry, and tables for group theory reveal that the direct product $E \times E$ for the T_d point group involves the total symmetry species A_1 corresponding to ν_1. This observation is in accordance with the fact that the band at ~ 3070 cm^{-1} is polarized. Aromatic molecules also have polarized bands in this region of the spectrum arising from the symmetric C–H stretching in the benzene ring. Figure 4 presents the spectrum of the natural gas samples obtained at 6.4 MPa_A (curve ***A***) in the 3110–2980 cm^{-1} region, together with the spectrum obtained of a pure methane sample (curve ***B***) contained in the high-pressure measuring cell at 6.2 MPa_A. By comparing the spectrum of the natural gas sample

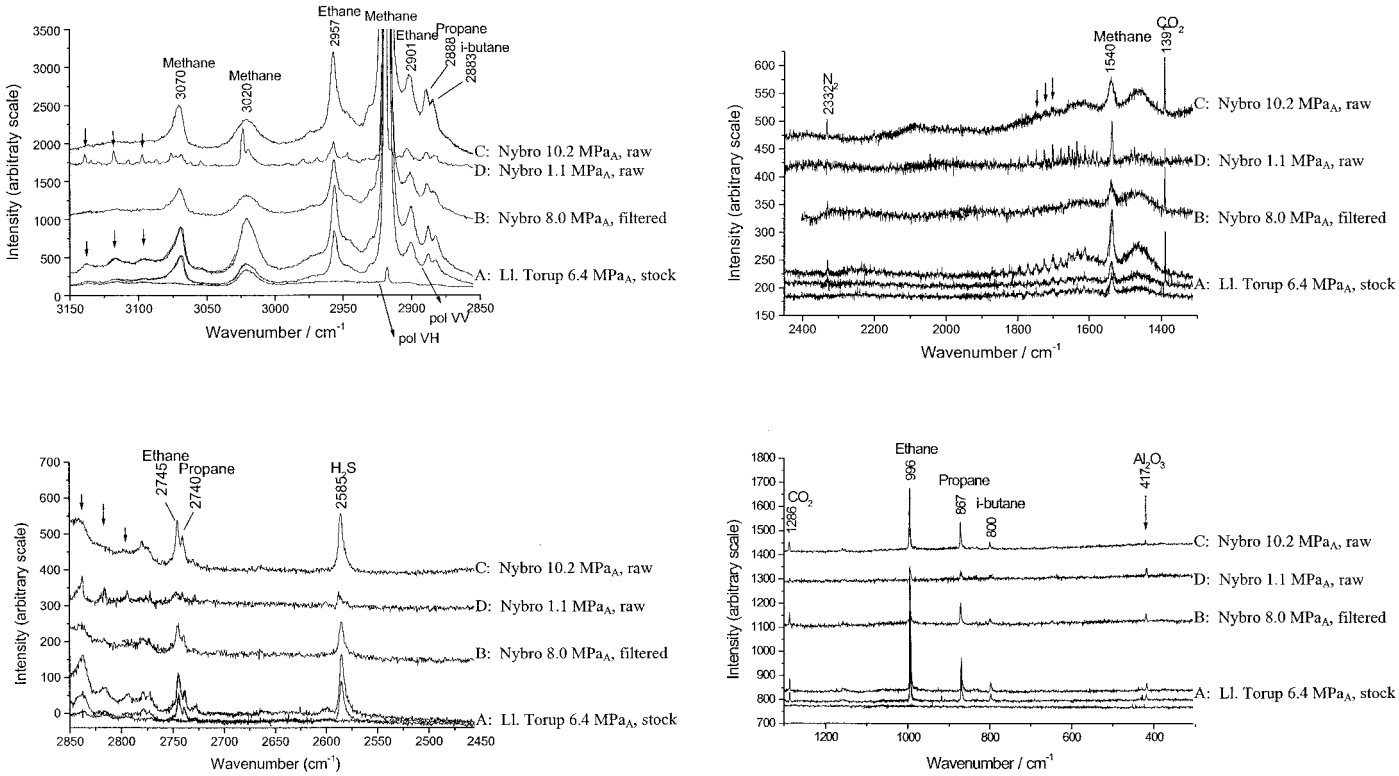

FIG. 3. The Raman spectra of the three different natural gas samples from (***A***) L1. Torup Gas Storage Facility (6.4 MPa_A), upper curve: no polarizer, lower curves: VV and VH polarization. (***B***) Nybro Gas Treatment Plant after passing through the filter (8.0 MP_A). (***C*** and ***D***) Nybro Gas Treatment Plant before passing through a filter (10.2 MPa_A and 1.1 MPa_A, respectively).

TABLE II. Wavenumbers (cm^{-1}) and assignments of bands seen from Raman spectra of natural gas. Wavenumbers in parentheses are from the literature.

Wavenumber (cm^{-1})	Assignment/component	Tentative assignment/vibration based on Refs. 16 and 24	
3070	Methane (2·1534 = 3068)[22]	Overtone ($2\nu_2$)/pol.	
3020	Methane (3020)[22]	Antisym. C–H str./depol.	
2957	Ethane (2954)[22]	Overtone ($2\nu_2$)	Fermi resonance
2918	Methane (2917)[22]	Sym. C–H str./pol.	
2901	Ethane (2896)[22]	Sym. C–H str./pol.	Fermi resonance
2887	Propane (2887)[22]	Sym. C–H_3 str./pol.	
2883	*i*-Butane (2880)[22]	Sym. C–H_3 str./pol.	
2745	Ethane (2742)[22]	Overtone ($2\nu_2$)/pol.	
2740	Propane (2739)[22]	Overtone ($2\nu_2$)/pol.	
2585	H_2S (2611, 1:2574)[11–16]	Sym. S–H str./pol.	
2332	N_2 (2335)[23]	N–N str./pol.	
1540	Methane (1534)[22]	Antisym. bend./depol.	
1391	CO_2 (1388)[22]	Sym. C–O str./pol.	Fermi resonance
1286	CO_2 (1285)[22]	Overtone ($2\nu_2$)/pol.	Fermi resonance
996	Ethane (988)[22]	C–C str./pol.	
867	Propane (867)[22]	Sym. C–C str./pol.	
800	*i*-Butane (794)[22]	Sym. C–C str./pol.	
417	Al_2O_3 (418)[18]	Al–O (lattice)	

with almost the same pressure as the methane sample (curves ***A*** and ***B***), one sees that the area ratio between the band at ~ 3070 cm^{-1} and the band at ~ 3020 cm^{-1} appears to be the same for the two samples. In fact, the area ratios have been determined by the Microcal Origin peak fitting module[10] (Gaussian function as the fitting function), and they were found to be almost the same. It is therefore concluded that the band at ~ 3020 cm^{-1} is not due to aromatics in the natural gas samples, neither in our case nor in the literature. This conclusion is in agreement with the information that aromatics (benzene, toluene, and xylene isomers) are present in the Danish natural gas only at very low concentrations (according to analysis done by gas chromatography by DONG A/S, on a level of 20–50 ppm_v).

In addition to the organic components, it was also possible to detect N_2 and CO_2. It was most surprising, however, that it is possible to detect H_2S (band at ~ 2585 cm^{-1}), which should be present in Danish natural gas only in quite low concentrations (according to DONG A/S, the concentration is typically 1–3 mg H_2S/Nm^3). H_2S is removed off shore in the North Sea before the natural gas is transmitted to the shore. According to the literature for gaseous H_2S, the ν_1 (symmetric S–H stretching) bands occur at 2611 cm^{-1}, [11–14] and the ν_3 (asymmetric S–H stretching) bands at 2627 cm^{-1}.[12,13] With a phase change from the gaseous to the liquid state, the bands of H_2S shift towards lower wavenumbers, ~ 2574 cm^{-1}.[15,16] From this result, it is concluded that the H_2S molecules are in a state near the liquid state in the natural gas at high pressure—noting that the band was found at ~ 2585 cm^{-1}. H_2S has three fundamental vibrations and all of them are Raman permitted according to the selection rules. In Fig. 5 the Raman spectrum of a H_2S gas sample made in our laboratory is presented. The gas sample was made from 5 mg CaS and sulfuric acid. The gas was collected in a bent ampoule (squared) through which the laser light was sent. The S–H stretching band envelope was observed at ~ 2617 cm^{-1}. The band center for ν_3 near 2627 cm^{-1} is not obvious (see Fig. 6), for reasons that are not known (see the discussion in Ref. 14). A reinvestigation of the gas spectrum of H_2S seems to be required. Also, according to the literature,[12,13,17] the S–H bending ν_2 should be at ~ 1183 cm^{-1}. In the Raman spectrum in Fig. 5 it is not possible to observe this vibration. The vibration has, however, been observed in a Raman spectrum at ~ 0.13

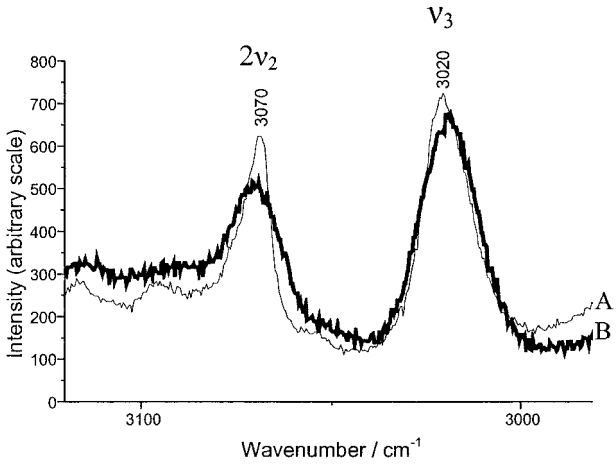

FIG. 4. A comparison between the methane bands at 3070 cm^{-1} ($2\nu_2$) and 3020 cm^{-1} (ν_3): (***A***) natural gas sample, 6.4 MPa_A, and (***B***) a pure methane sample, 6.2 MPa_A.

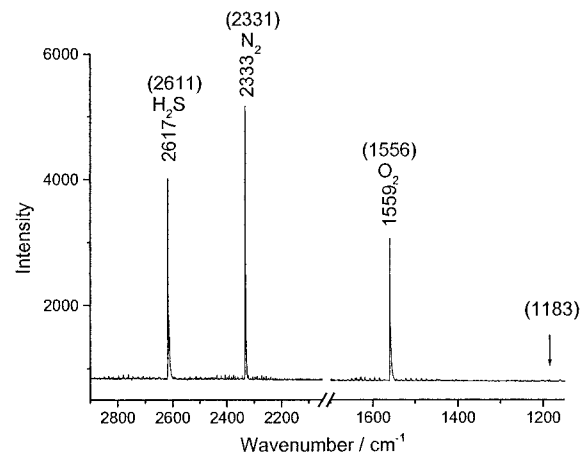

FIG. 5. The Raman spectrum of H_2S also containing N_2 and O_2.

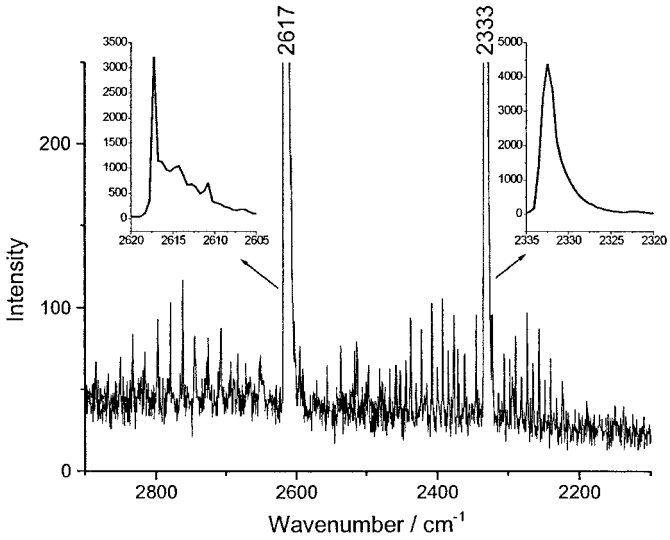

FIG. 6. The Raman spectrum of H_2S and N_2 (expanded).

MPa.[12,13] In the Raman spectrum of our H_2S (Fig. 5), N_2 and O_2 bands are observed at 2333 and 1559 cm^{-1}, respectively, probably due to N_2 and O_2 from the air adsorbed to the CaS piece.

The band at ~ 417 cm^{-1} is assigned to be a lattice vibration in sapphire. This assignment is in accordance with the literature[18] and the observation that the peak did not increase in intensity with increasing pressure.

Quantitative Analysis. The present quantitative analysis is based on the so-called ''ratio method''. The method is described in Ref. 19 for the case of two-component inclusions. In natural gas, however, there are many components, so the method was used on the assumption that the concentration of one component, here methane, is known. The irradiance, the scattering volume, the angle of collection of light, and the other experimental details are the same for all present species. By Eq. 1, which is a modified Placzek relation,[20] it is seen that it is possible to determine the mole fraction of any component in the natural gas if (1) the component shows a band in the Raman spectrum and (2) the RNDRS (relative normalized differential Raman scattering)[21] cross section for the component is known.

$$\frac{C_x}{C_{methane}} = \frac{A_{x(\nu_x)} \cdot \Sigma_{methane(\nu_1)}}{A_{methane(\nu_1)} \cdot \Sigma_{x(\nu_x)}} \qquad (1)$$

where C_x is the mole fraction of component x in the natural gas; $\Sigma x(\nu_x)$ is the RNDRS, relative to N_2, cross section for component x vibrating at wavenumber ν_x (referred to as $\sigma_{rA(\nu_A)}$ in Ref. 19); $\Sigma_{methane(\nu_1)}$ is the RNDRS for the case where ν_1 = (2917 cm^{-1}) was used, having literature values[21] of 9.1, 8.7, and 9.3, and the average (i.e., 9.03) was used in the calculations; and $A_{x(\nu_x)}$ is the area of the band at wavenumber ν_x for component x.

RNDRS cross sections, determined relative to N_2, are listed in Ref. 21. Since the cross sections have been normalized, they should be independent of the wavelengths of the exciting source. There are, however, relatively big variations between the values. The values listed for the 515 Ar-ion nm exciting wavelength were consistently used, and in the cases where there is more than one value given, the average value was used.

TABLE III. Determination of (1) mole fraction of gas components in natural gas (first part of the table) and (2) RNDRS cross sections for ethane and *i*-butane (second part of the table).

Component analyzed	x	Band ν_x/cm^{-1}	$\Sigma_{x(\nu x)}$	$A_x/A_{methane(\nu 1)}$	C_x/mol % calcd.[c]	C_x/mol % measd., GC[d]
Propane	A[a]	867	1.7[b]	0.003054	—	—
	B[a]	867	1.7[b]	0.003674	1.71	2.84
	C[a]	867	1.7[b]	0.003647	1.71	2.99
CO_2	A[a]	1285	0.78[b]	0.005734	—	—
	B[a]	1285	0.78[b]	0.001097	1.12	1.36
	C[a]	1285	0.78[b]	0.001283	1.31	0.92
CO_2	A[a]	1388	1.21[b]	0.000978	—	—
	B[a]	1388	1.21[b]	0.001496	0.98	1.36
	C[a]	1388	1.21[b]	0.001021	0.67	0.92
N_2	A[a]	2331	1[b]	0.000407	—	—
	B[a]	2331	1[b]	0.000566	0.45	0.33
	C[a]	2331	1[b]	0.000456	0.36	0.34
Ethane	A[a]	993	—	0.005938		—
	B[a]	993	0.85[c,e]	0.006783		6.34
	C[a]	993	0.88[c,f]	0.006870		6.23
i-Butane	A[a]	794	—	0.001002		—
	B[a]	794	2.02[c,e]	0.001122		0.44
	C[a]	794	1.60[c,f]	0.001005		0.50

[a] Gas samples from A: L1. Torup, stock; B: Nybro, filtered; and C: Nybro, raw.
[b] Values from literature.[21]
[c] Values calculated from this work.
[d] Gas chromatographic analysis done by DONG (the GC data for the L1. Torup sample are not known). $C_{methane}$ values for the Nybro filtered and Nybro raw natural gas samples are 87.85 and 88.16%, respectively.
[e] 8.0 MPa_A.
[f] 10.2 MPa_A.

The area of the band has been determined by the Microcal Origin peak fitting software.[10] As previously done, a Gaussian function was fitted to each band, and the area between the curve and the baseline determined. The detemined area ratios $A_x/A_{methane}$ are listed in Table III. The band areas were reproducible with a relative uncertainty ~ 5–10% (for the $A_{methane}$ areas, the likely accuracy was better than 5%). The main uncertainty source was without doubt the estimation of the position of the baseline. Table III also lists the concentrations (C_x) for propane, CO_2, and N_2 calculated by Eq. 1. By comparing these values with the concentrations measured by gas chromatography (done by DONG A/S, also included in the table), one can see that there is a very good agreement with respect to magnitude. Keeping in mind the uncertainty in the area ratios and the problems of precision with respect to the RNDRS cross sections, one cannot expect more precise results. Furthermore, all the RNDRS cross sections used in the calculations are for gases at low pressure. It is known that the RNDRS values depend somewhat on pressure;[6] for gases up to 10%, larger cross sections have been found.

An effort was also made to determine the H_2S concentrations by the ''ratio method'', but the results were very poor. Our calculations gave the values 9600 mg/Nm^3 for the Nybro filtered sample (8.0 MPa_A) and 13 100 mg/Nm^3 for the Nybro raw sample (10.2 MPa_A); but according to DONG A/S, the concentration is 1–3 mg/Nm^3. An explanation could be that, because of the two lone pairs

of electrons on sulfur, the H_2S molecule scattering cross section could be much more pressure dependent than the other molecules in the natural gas, thereby giving a relatively much more intense band in the Raman spectrum at high pressures. It appears that an investigation of this effect in the Raman spectra of H_2S and H_2S mixtures as a function of pressure needs to be done.

The RNDRS cross sections for *i*-butane are not given in Ref. 21 (and as far as the authors know, they have not been reported elsewhere). For ethane (993 cm^{-1}), the cross section has not been given for the 515 nm exciting wavelength. Since the concentrations of these two components in the natural gas samples are known, it is possible to determine cross sections by Eq. 1.

The 993 cm^{-1} band of ethane and the 794 cm^{-1} band of *i*-butane were used. Area ratios are listed in Table III (second part of the table) and so are the gas concentrations measured by gas chromatography (GC). The RNDRS cross section for *i*-butane (794 cm^{-1}) (relative to N_2) at 8.0 MPa_A was determined to be 2.02 and at 10.2 MPa_A to be 1.60. The RNDRS cross section for ethane (993 cm^{-1}) at 8.0 MPa_A (relative to N_2) was found to be 0.85 and at 10.2 MPa_A to be 0.88. The values in Ref. 21 are 1.24 (488 nm exciting wavelength) and 2.2 (364 nm exciting wavelength).

CONCLUSION

A new high-pressure gas-measuring cell has been described. The Raman spectra of different natural gas samples obtained in this cell have been presented and assigned. The heaviest alkane to be detected was *i*-butane. The band at ~ 3070 cm^{-1} has been assigned as the overtone of the ν_2 vibration in methane. It was also possible to detect N_2, CO_2, and H_2S. A quantitative analysis of two of the natural gas samples has also been described. There was agreement between this analysis and analysis done by GC, except with respect to H_2S. Further Raman studies of H_2S and H_2S mixtures need to be done with respect to both band positions and relative ν_1 band area as a function of pressure. Finally, the RNDRS cross sections for ethane at 8.0 MPa_A and 10.2 MPa_A were determined to be 0.85 and 0.88, respectively, and for *i*-butane at the same pressures to be 2.02 and 1.60. It has been shown that the cell is well suited for high-pressure measurements on natural gas.

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