JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2002; **33**: 160–164
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jrs.813

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How to determine the pressure of a methane-containing gas mixture by means of two weak Raman bands, ν_3 and $2\nu_2$†

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Received 28 August 2001; Accepted 17 October 2001

Raman spectra of a pure CH_4 sample, two CH_4–C_2H_6 mixtures and a CH_4–N_2 mixture were obtained as a function of pressure at pressures up to 39.6 MPa_A (MPa absolute). These spectra are presented in the region 3120–2980 cm^{-1}. A clear pressure dependence of the area ratio between two weak methane bands, ν_3 (asymmetric C–H stretching) and $2\nu_2$ (overtone of the asymmetric C–H bending), is observed; the methane ν_3 band intensity is lowered relative to the methane $2\nu_2$ as the pressure is raised. The intensity ratios between these two bands, $I(\nu_3)/I(2\nu_2)$, were determined and plotted as a function of pressure. Surprisingly it is observed that the ratio at a fixed pressure is independent of the composition and thereby of the surroundings in which the methane molecule is vibrating. A model function to predict the pressure is given. From a practical point of view, the present results could be useful for determining directly the total pressure in methane mixtures the composition of which is not known.

INTRODUCTION

It is well documented that the methane ν_1 (symmetric C–H stretching) band in the Raman spectrum of a pure methane sample moves to lower wavenumber positions as the pressure is raised.[1] It is also known that this methane ν_1 band shift is affected by the presence of other gases in the sample, indicating that the methane molecular vibrations are influenced by the surroundings.[2–5] It was concluded in the literature that a determination of the total pressure in a methane mixture should be possible from the methane ν_1 wavenumber shift, provided that the relative composition of the methane mixture was known. Many more mixtures of different concentrations, however, have to be investigated before the method can be used in a reliable way for the determination of the pressure of the mixture. Other methods to determine pressures of methane mixtures with known composition have been investigated, e.g. a method based on the broadening of the linewidth of the methane ν_1 band as a function of pressure in CH_4–N_2 mixtures.[2,3] Also, a method has been described to determine the total pressure of CH_4–CO_2 mixtures, based on the area ratio between the methane ν_1 band and the CO_2 $2\nu_2$ band.[4] All the above-mentioned methods have in common that they are based on the very intense methane ν_1 Raman band.

In our previous work on analysis of natural gas samples, we expanded the Raman spectra to study bands other than the methane ν_1 band. In the expanded spectra (the C–H stretching region, 3150–2850 cm^{-1}, Fig. 3 in Ref. 6), a pressure dependence between two methane band areas became obvious. The methane ν_3 band area (at ~3020 cm^{-1}) lost intensity relative to the methane $2\nu_2$ band (at ~3070 cm^{-1}) as the pressure was raised. This paper reports a further study of that observation. The overall purpose of the study was to investigate the possibility, by means of the intensity ratio $I(\nu_3)/I(2\nu_2)$, to extract directly the total pressure of a methane mixture of unknown composition.

EXPERIMENTAL

Chemicals

The gases used were methane (99.995%), ethane (99.95%) and nitrogen (99.995%) from Hede Nielsen A/S. Three mixtures were prepared, two methane–ethane mixtures [mole fractions of CH_4, $X(CH_4) = 0.85$ and $X(CH_4) = 0.49$] and one methane–nitrogen mixture [$X(CH_4) = 0.47$].

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†Dedicated to the memory of the late Professor Murray Brooker, of Memorial University, Newfoundland, Canada.
Contract/grant sponsor: IVC-SEP.
Contract/grant sponsor: DONG A/S.
Contract/grant sponsor: Nordic Energy Research Program.
Contract/grant sponsor: Danish Technical Research Council.

High-pressure cells

Two different cells were used: a so-called tube cell and a so-called titanium cell. The tube cell was developed[6] for totally representative Raman measurements of natural gas, being constructed of stainless-steel fittings (Swagelok) and a sapphire tube of high purity. It was tested up to 15.0 MPa_A, and it was found to be perfectly tight. Reduced pressures were achieved by letting gas out of a valve. The design and construction of the cell are described in detail in Ref. 6. The titanium cell, used in the high-pressure measurement (39.6 MPa_A), was made from titanium metal and flat sapphire windows. With this cell it was possible to reach the pressure of a gas sample by manually moving a piston in the cell chamber. The titanium cell has been described in detail in Ref. 7.

Raman spectroscopy

The measurements were performed by use of a Dilor XY spectrometer equipped with a nitrogen-cooled CCD detector (1024×256 pixels). The excitation source was an argon ion laser (514.53 nm_{air}, ~200 mW, vertically polarized). The samples were placed in the macroscopic positions and the collection geometry was 90° when the sapphire tube cell was used and 180° when the titanium cell was used. Rayleigh filtration was performed by use of a Super Plus holographic notch filter from Kaiser Optical Systems (Ann Arbor, MI, USA). All spectra were obtained at room temperature (22 °C) by use of a spectrograph with a grating of 1800 grooves mm^{-1}.

RESULTS AND DISCUSSION

Raman spectra of pure methane are presented in Fig. 1(A) in the pressure range 7.9–0.2 MPa_A. A vertical dotted line has been drawn at the $2\nu_2$ wavenumber position to guide the eyes. It is clearly seen that the ν_3 band intensity increases relative to the $2\nu_2$ band as the pressure is lowered. It can also be seen that the ν_3 wavenumber position decreases with increasing pressure. The $2\nu_2$ band position, however, seems to be fairly constant at ~3070 cm^{-1}. In addition to the vibrational transition ν_3 and the overtone $2\nu_2$ it is also possible to observe rotational–vibrational transitions belonging to ν_3.

The band intensities, $I(\nu_3)$ and $I(2\nu_2)$, were measured as the height over an estimated background level [only the Q-branch of ν_3 contributes to the $I(\nu_3)$, whereas the extended rotation–vibration branches do not]. From this the intensity ratios, $I(\nu_3)/I(2\nu_2)$, were calculated as a function of pressure. A plot of the results is presented in Fig. 2 (diamonds); the points follow a decreasing curve towards higher pressures with decreasing slope. It is important to determine the intensity ratio also at pressures below 0.2 MPa_A where the curve is most steep.

The curve levels off at higher pressures and seems to reach a constant value. The Raman spectrum of a pure methane sample contained in the titanium cell at a pressure

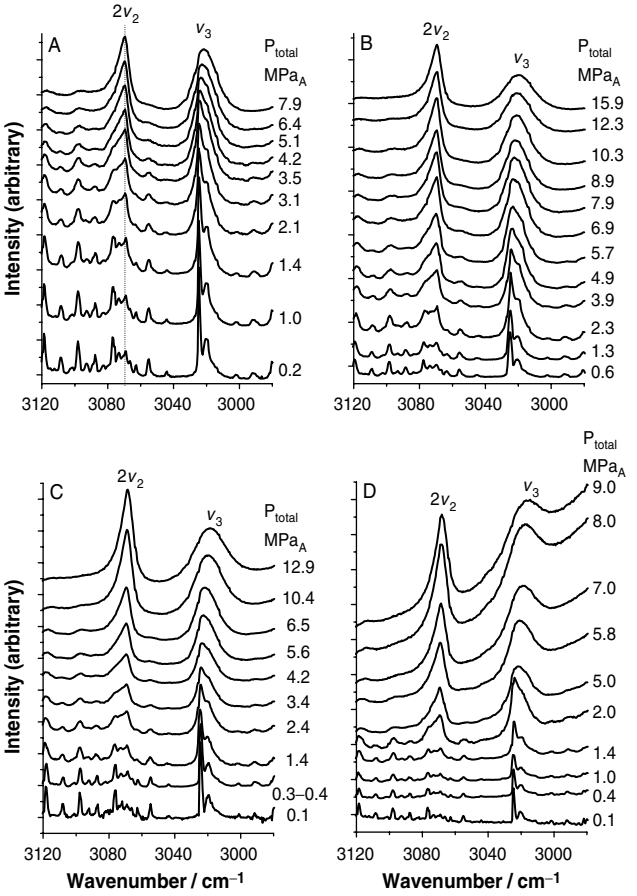

Figure 1. Raman spectra obtained at different pressures of (A) pure methane, (B) a methane–nitrogen mixture [$X(CH_4) = 0.47$], (C) an ethane–methane mixture [$X(CH_4) = 0.85$] and (D) a nearly equimolar methane–ethane mixture [$X(CH_4) = 0.49$].

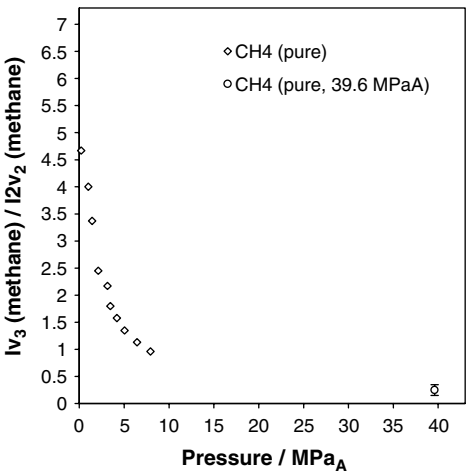

Figure 2. Intensity ratio $I(\nu_3)/I(2\nu_2)$ as a function of total pressure for the pure methane sample. Pressure range: 7.9–0.2 MPa_A.

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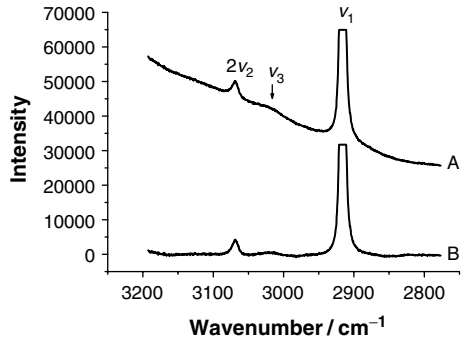

Figure 3. Raman spectrum of a pure methane sample contained in the titanium cell at a pressure of 39.6 MPa_A.

of 39.6 MPa_A is shown in Fig. 3 (curve A). Even for a short integration time, the spectrum was very intense owing to the high pressure (i.e. high gas concentration). A fluorescence background was observed at higher wavenumbers, probably due to the sapphire windows. Using Microcal Origin software[8] a baseline was estimated and subtracted from the spectrum. This corrected spectrum is also shown in Fig. 3 (curve B). Owing to the broadness of the methane ν_3 band (because of the high pressure), it is difficult to measure the intensity precisely. The intensity ratio point is shown in Fig. 2 (circle), including an estimation of the error bar.

Raman spectra of the methane–nitrogen mixture [$X(CH_4) = 0.47$] are presented in Fig. 1(B) and those of methane–ethane mixtures [$X(CH_4) = 0.85$ and 0.49] in Fig. 1(C) and (D), respectively. The same trend in the pressure dependence can be observed. The Raman spectra of the nearly equimolar methane–ethane mixture [$X(CH_4) = 0.49$] are of particular interest, because at low to moderate pressures it allowed us to determine the intensity (height) of the methane ν_3 band with fairly good precision. Figure 4 shows the Raman spectrum of the high ethane containing mixture at 7.0 MPa_A in the 3150–2800 cm^{-1} region. As can be seen, the ethane $2\nu_{11}$ band is very intense (saturated) in comparison to the weak methane $2\nu_2$ and ν_3 bands, owing

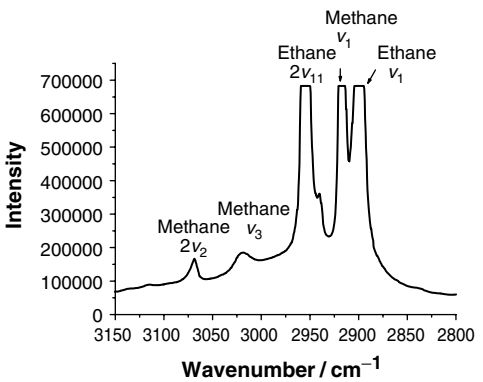

Figure 4. Raman spectrum of the equimolar methane–ethane mixture obtained at 7.0 MPa_A.

to the high ethane content. Furthermore, the linewidth of the ethane $2\nu_{11}$ band increased as the pressure was raised (as for the methane ν_1 band), resulting in increasing overlap between the ethane $2\nu_{11}$ and the methane ν_3 bands. Thus, for the mixtures with low or zero ethane content it was possible to measure the intensity ratio more precisely. All intensity ratios obtained as a function of pressure are shown in Fig. 5, plot I, including the points shown in Fig. 2 for pure methane (all data points are listed in Table 1). Intensity ratios for the Raman spectra of natural gas samples from Ref. 6 are also included. As can be seen, all the available intensity ratio data follow the same curve as for pure methane. We conclude that the intensity ratio $I(\nu_3)/I(2\nu_2)$ at a given pressure seems to be independent of the surroundings in which the methane molecules are vibrating.

To investigate whether the curve was an exponential one, we plotted the data on a logarithmic scale (Fig. 5, plot II). The points do not follow a straight line, and it is concluded that the curve is not an exponential one.

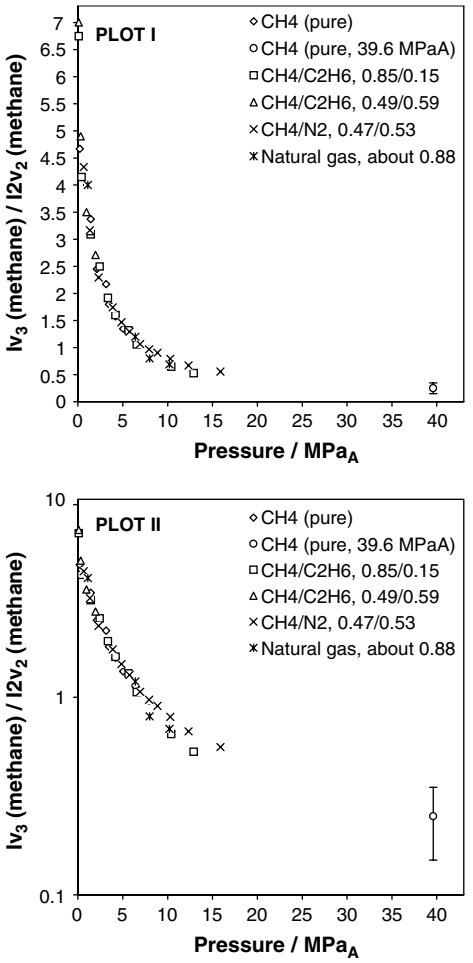

Figure 5. Intensity ratio $I(\nu_3)/I(2\nu_2)$ as a function of total pressure for pure methane and the three methane mixtures. The plot also includes intensity ratios for natural gas samples from Ref. 6. Plot I, normal scale; plot II, logarithmic scale.

Table 1. Intensity ratio $I(\nu_3)/I(2\nu_2)$ as a function of measured pressure and predicted pressure

Gas	$I(\nu_3)/I(2\nu_2)$	$P_{measured}$ (MPa_A)	$P_{predicted}$ (MPa_A)
Pure CH_4	0.25	39.6	37.5
	0.96	7.9	8.0
	1.13	6.4	6.5
	1.35	5.1	5.0
	1.58	4.2	4.0
	1.80	3.5	3.2
	2.17	3.1	2.3
	2.45	2.1	1.8
	3.37	1.4	0.8
	4.00	1.0	0.4
	4.67	0.2	0.2
CH_4–C_2H_6, $X(CH_4) = 0.85$	0.53	12.9	16.4
	0.65	10.4	12.9
	1.06	6.5	7.0
	1.32	5.6	5.2
	1.6	4.2	3.9
	1.92	3.4	2.9
	2.5	2.4	1.8
	3.09	1.4	1.1
	4.15	0.3	0.4
	6.75	0.1	0.0
CH_4–C_2H_6, $X(CH_4) = 0.49$	2.71	2.0	1.5
	3.15	1.4	1.0
	3.5	1.0	0.8
	4.9	0.4	0.1
	7.00	0.1	0.0
CH_4–N_2, $X(CH_4) = 0.47$	0.56	15.9	15.4
	0.67	12.3	12.5
	0.79	10.3	10.2
	0.90	8.9	8.7
	0.97	7.9	7.9
	1.06	6.9	7.0
	1.29	5.7	5.4
	1.47	4.9	4.5
	1.74	3.9	3.4
	2.29	2.3	2.1
	3.17	1.3	1.0
	4.33	0.6	0.3
Natural gas, $X(CH_4) \approx 0.88$	0.69	10.2	12.0
	0.80	8.0	10.0
	1.2	6.4	6.0
	4	1.1	0.5

By means of plot I it is relatively simple to read the pressure as soon as the intensity ratio has been determined. It would be desirable, however, to have a function for predicting the pressure. Such a function is given in Eqn (1). It

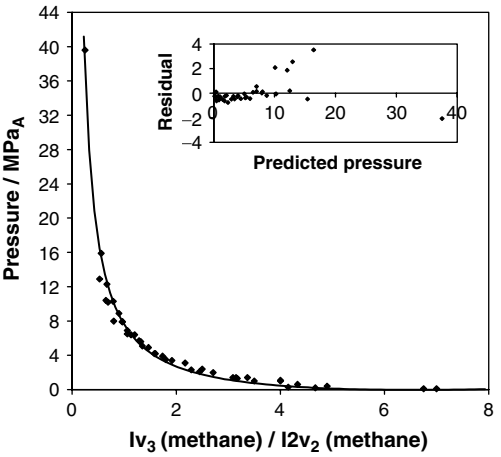

Figure 6. Gas pressure as a function of determined intensity ratio, $I(\nu_3)/I(2\nu_2)$. The model function Eqn (1) (solid line) is also included in the plot and so is the residual plot. The inset shows ε (the pressure predicted by the model minus the actual measured pressure) as a function of predicted pressure.

was estimated by fitting to the experimental data, as shown in Fig. 6, which also includes (inset) a residual plot of ε ($p_{predicted} - p_{measured}$) as a function of the intensity ratio (the predicted and measured pressures are given in Table 1). As can be seen from this plot, the residuals are low at pressures below 10 MPa_A.

$$p_{predicted} = \left[0.1 \cdot \frac{I(\nu_3)}{I(2\nu_2)}\right]^{-1} + \left[0.1 \cdot \frac{I(\nu_3)}{I(2\nu_2)}\right] + \left[0.1 \cdot \frac{I(\nu_3)}{I(2\nu_2)}\right]^{3} - 2.5 \quad (1)$$

CONCLUSION

The intensity ratio between two methane bands, $I(\nu_3)/I(2\nu_2)$, was obtained as a function of the total pressure in pure methane, in two methane–ethane mixtures, in a methane–nitrogen mixture and in natural gas samples. The intensity ratios obtained were found to depend on the pressure but to be independent of the composition and thereby independent of the surroundings in which the methane molecules vibrate. By means of these two bands, therefore, it seems to be possible to determine pressures in methane mixtures by Raman spectroscopy. The composition need not be known or determined. The plot of the intensity ratio as a function of the total pressure was shown not to be an exponential curve. A polynomial model [Eqn (1)] was found to fit the experimental data fairly well, especially at pressures below 10 MPa_A. In ethane-rich gases such as the equimolar methane–ethane mixture problems arise with increasing pressure because of broadening of the ethane $2\nu_{11}$ band obscuring the methane ν_3 band. For the intensity method to be of use to determine the pressure with high

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precision in ethane-rich methane gas mixtures, a way to resolve the methane ν_3 band from the ethane $2\nu_{11}$ band has to be developed. So far our intensity method should be useful for direct and remote determinations of the total pressure in certain methane gas mixtures which cannot otherwise be measured, e.g. gas/fluid inclusions in rocks. Application of the intensity ratio method has been demonstrated in Ref. 9.

Acknowledgments

P. V. Andersen and T. T. Dang, Department of Chemical Engineering, IVC-SEP, DTU are thanked for technical support. T. Lindgren and S. Dalsager, DONG A/S, and S. I. Andersen, IVC-SEP, Department of Chemical Engineering, DTU are thanked for stimulating discussions. IVC-SEP, DONG A/S, the Nordic Energy Research Program and the Danish Technical Research Council supported this work.

REFERENCES

1. Fabre D, Couty R. *C. R. Acad. Sci., Sér. II* 1986; **303**: 1305.
2. Fabre D, Oksengorn B. *Appl. Spectrosc.* 1992; **46**: 468.
3. Seitz JC, Pasteris JD, Chou I-M. *Am. J. Sci.* 1993; **293**: 297.
4. Seitz JC, Pasteris JD, Chou I-M. *Am. J. Sci.* 1996; **296**: 577.
5. Brunsgaard Hansen S, Berg RW, Stenby EH. *Appl. Spectrosc.* 2001; **55**: 745.
6. Brunsgaard Hansen S, Berg RW, Stenby EH. *Appl. Spectrosc.* 2001; **55**: 55.
7. Brunsgaard Hansen S. PhD. Thesis, Technical University of Denmark, Lyngby, 2000.
8. *Microcal Origin, Version 6*. Microcal Software, Northampton, MA, 1999.
9. http://www.kemi.dtu.dk/~ajo/rolf/nyest/sld001.htm.