

SPECTROSCOPY OF AMBIENT MEDIUM

Effect of Helium on the Raman Spectrum of Methane in the 2500–3300 cm⁻¹ Range

A. S. Tanichev^{a,*}, D. V. Petrov^{a,b}, I. I. Matrosova^a, and K. K. Sharybkina^a

^a Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch, Russian Academy of Sciences,
Tomsk, 634055 Russia

^b National Research Tomsk State University, Tomsk, 634050 Russia

*e-mail: tanichev_aleksandr@mail.ru

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Abstract—The peak positions and halfwidths of the Q -branch of the ν_1 band and the ratios of intensities of the Q -branches of ν_3 and $2\nu_2$ bands of methane are measured in a methane–helium mixture at different pressures and concentrations. An empirical model is developed for estimation of the He concentration in a methane-containing medium from measurements of the above parameters. The error in the He concentration is found to be less than 1% when using the ν_1 band halfwidth. The paths of improvement of this technique and enhancement of its accuracy are considered.

Keywords: methane, helium, Raman spectroscopy, gas analysis

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INTRODUCTION

The appearance of small solid-state lasers with high output power and highly sensitive multichannel photodetectors has allowed the active development of gas analysis based on Raman spectroscopy (RS) in recent decades [1–8]. One of the areas where RS is very promising is the analysis of the composition of natural gas (NG). This is due to a number of advantages of RS over gas chromatography, which is currently the basic technique for measuring the NG composition, such as absence of consumables, high speed, and the capability of controlling all molecular components with a single device.

One of the NG components is helium (He); its concentration can attain 7% [9]. Since He is in an atomic state in NG, it does not have a Raman spectrum; therefore, its content cannot be measured using the classical approach based on the spectral line intensity. This disadvantage of RS gas analyzers restricts their potential. However, according to the data by Pieroni [10], a He medium significantly affects the spectral characteristics of the Q -branch of the ν_1 band of methane (CH₄) due to the line mixing effect. This band is the strongest in the Raman spectrum of CH₄ and, therefore, the most preferred in the RS analysis of methane-containing media [11–14]. We believe that the effects of changes in the spectral characteristics of its unresolved Q -branch [10] can be used as the basis for a technique for determining the He concentration in NG. Hence, the aim of this work is to estimate the prospects of this approach in the study of the Raman

spectra of CH₄–He mixtures with different concentrations and under different pressures.

EXPERIMENTAL

An experimental setup was assembled for the study, which allowed recording Raman spectra with a resolution of up to 0.5 cm⁻¹. A solid-state single-mode SLN-532-5000 (Cnilaser, China) laser was used as a source of monochromatic radiation, providing an output power of 5 W at a wavelength of 532.094 nm in the continuous mode (the lasing line halfwidth <10 fm). The scattered light was collected at an angle of 90° to the laser beam propagation direction. The spectra were recorded with an MDR-23 diffraction monochromator (the focal length is 600 mm and the relative aperture is 1 : 6) equipped with a Hamamatsu S10141 CCD array (2048 × 512 pixels). When using diffraction gratings 1200 and 2400 lines/mm, the widths of the simultaneously recorded ranges were 750 and 250 cm⁻¹, respectively. The wavenumber calibration of the spectrometer was performed using the wavenumber shifts of lines the ν_3 CH₄ band given in [15].

Using the diffraction grating with 2400 lines/mm, the Raman spectra of CH₄–He mixtures with He concentrations of 13 and 25% under pressures of 10, 20, 30, 40, and 50 atm were recorded at the experimental setup. The spectral resolution was 0.5 cm⁻¹, and a simultaneously recorded range was 2800–3050 cm⁻¹. A similar set of spectra was recorded (in a CH₄–He

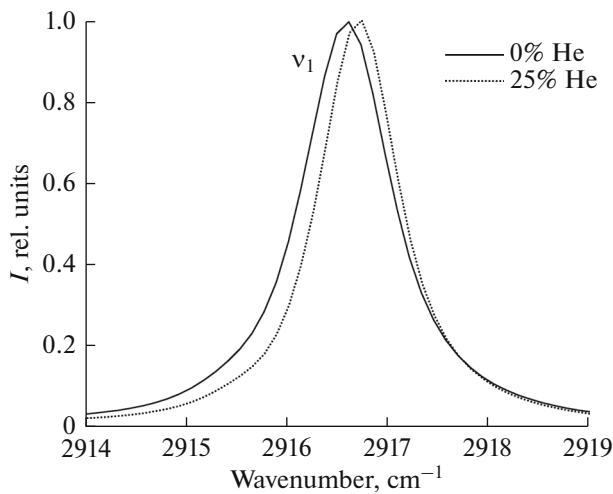


Fig. 1. Normalized Raman spectra of CH₄ in the 2914–2919 cm⁻¹ range at a pressure of 50 atm and different He concentrations in the mixture.

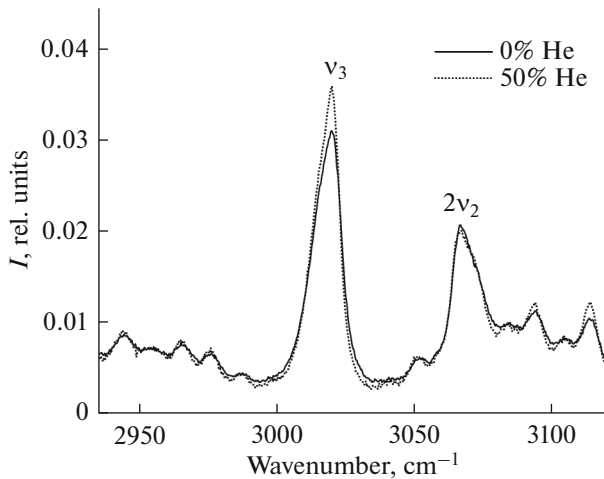


Fig. 2. Raman spectra of CH₄ normalized to the integral intensity at a pressure of 50 atm and different He concentrations in the mixture.

mixture with a He concentration of 50%) using the diffraction grating with 1200 lines/mm with a spectral resolution of ~ 1 cm⁻¹ and a simultaneously recorded range 2550–3300 cm⁻¹. The set of experimental data with a lower resolution was obtained with the aim of widening the simultaneously recorded spectral range to estimate the redistribution of intensities between the ν_1 (2917 cm⁻¹), $2\nu_2$ (3067 cm⁻¹), and $2\nu_4$ (2587 cm⁻¹) bands, which are in the Fermi resonance [16].

Thus, the positions of the maxima and halfwidths of the Q -branches of the CH₄ ν_1 band were determined from the first set of spectra, and the intensities of the Q -branches of the ν_3 and $2\nu_2$, $2\nu_4$ and ν_1 bands, from the second set. The purity of each gas used was

>99.99%. The temperature was close to 300 K during the measurements. The recording time was 100 s for each spectrum.

DISCUSSION OF RESULTS

The resulting spectra show a shift toward lower wavenumbers and a broadening of the Q -branch of the ν_1 band with an increase in the pressure, which were previously noted in [14, 17, 18]. It is also clearly seen that an increase in the He concentration in a mixture with CH₄ under equivalent pressures leads to weaker broadening and to the shift of the profile toward higher wavenumbers (Fig. 1).

In addition to these effects, we paid attention to the ratio of the peak intensities of the Q -branches of the ν_3 (3020 cm⁻¹) and $2\nu_2$ (3067 cm⁻¹) bands. It was suggested earlier [19, 20] to use that ratio for contactless estimation of the pressure of methane-containing inclusions in minerals. The ratio changes for two reasons. First, the peak intensity of the Q -branch of the ν_3 band decreases with an increase in the line widths. Second, the relative intensity of the $2\nu_2$ band of CH₄ depends on the environment [17, 21]. Most likely, this is due to a change in the conditions of interaction of the $2\nu_2$ and ν_1 bands due to the Fermi resonance.

The analysis of the spectra showed an increase in the ratio $I(\nu_3)/I(2\nu_2)$ with the He concentration at a fixed pressure (Fig. 2). In turn, the analysis of the ratio $I(2\nu_4)/I(\nu_1)$, which depends on the CH₄ conditions, according to [17, 21], showed its variation within the measurement error at different He concentrations.

Figure 3 shows the measured positions of the maximum and halfwidth of the Q -branch of the ν_1 band, as well as the intensity ratio $I(\nu_3)/I(2\nu_2)$ under various pressures and mixture concentrations. It is seen that the He medium affects the changes in each parameter measured; as for the position and halfwidth of the Q -branch of the ν_1 band, the higher the pressure, the stronger this effect.

Let us consider an algorithm for solving the inverse problem, that is, estimation of the He concentration in a CH₄–He mixture. The analysis of the dependences of measured parameters of helium on the He content in the mixture (at a fixed pressure) showed that they can be approximately described by a linear function

$$X = A + BC_{\text{He}}, \quad (1)$$

where X is the position of maximum of the Q -branch of the ν_1 band $\omega(\nu_1)$ or its halfwidth at a half maximum $\Gamma(\nu_1)$, or the ratio of the peak intensities $I(\nu_3)/I(2\nu_2)$; C_{He} is the He concentration in the mixture [0...1]; A and B are the factors which depend on the pressure, and they are different for each parameter.

Let us consider the technique for calculation of A and B . According to Fig. 3, the dependences of each parameter on the pressure P in pure CH₄ (factor A) are

nonlinear and can be approximately described by the second-order polynomials

$$X = aP^2 + bP + c. \quad (2)$$

Considering Eq. (2), Eq. (1) can be written as

$$X = aP^2 + bP + c + (dP^2 + eP + f)C_{\text{He}}, \quad (3)$$

where a , b , c , d , e , and f are the coefficients of the polynomial which is a function of two variables (mixture pressure and He concentration). The coefficients for $\omega(\nu_1)$, $\Gamma(\nu_1)$, and $I(\nu_3)/I(2\nu_2)$ were determined by approximation of corresponding experimental data by polynomial (3). The values found are tabulated. Thus, knowing the mixture pressure and measuring any of the parameters $\omega(\nu_1)$, $\Gamma(\nu_1)$, or $I(\nu_3)/I(2\nu_2)$, the He concentration in a mixture with CH_4 can be found using Eq. (3).

Let us estimate the error of this technique. By analyzing the set of spectra recorded under the same conditions, it was found that the measured position of the maximum and halfwidth of the ν_1 band are within ± 0.02 and $\pm 0.002 \text{ cm}^{-1}$, respectively. When the pressure changes in the range under study, these errors change negligibly. The error in the ratio $I(\nu_3)/I(2\nu_2)$ decreases as the pressure increases due to an improvement of the signal-to-noise ratio. In our case, the error is $\sim 2\%$ at $P = 10 \text{ atm}$ and $\sim 0.7\%$ at $P = 50 \text{ atm}$. Taking into account the errors in the position of the maximum and halfwidth and the dependences shown in Fig. 3, we have determined the errors in measuring the He concentration in a mixture with CH_4 with the use of each parameter (Fig. 4). The results indicate an increase in the accuracy with the pressure; the use of halfwidths is preferred. This is explained by the minimal measurement error for this parameter and by the fact that its dependence on He concentration is the closest to linear. In our case, the error in the He concentration was $\sim 0.9\%$ at $P = 50 \text{ atm}$.

We believe that the technique for estimating the He concentration in a binary mixture with CH_4 presented in this work can be used for NG, since CH_4 is its dominant component. In this case, in addition to the pressure, it is necessary to know the concentration of the molecular components of NG and similar dependences of the effect of each component on a parameter measured in the CH_4 spectrum (the position of the maximum of the Q -branch of the ν_1 band, its half-

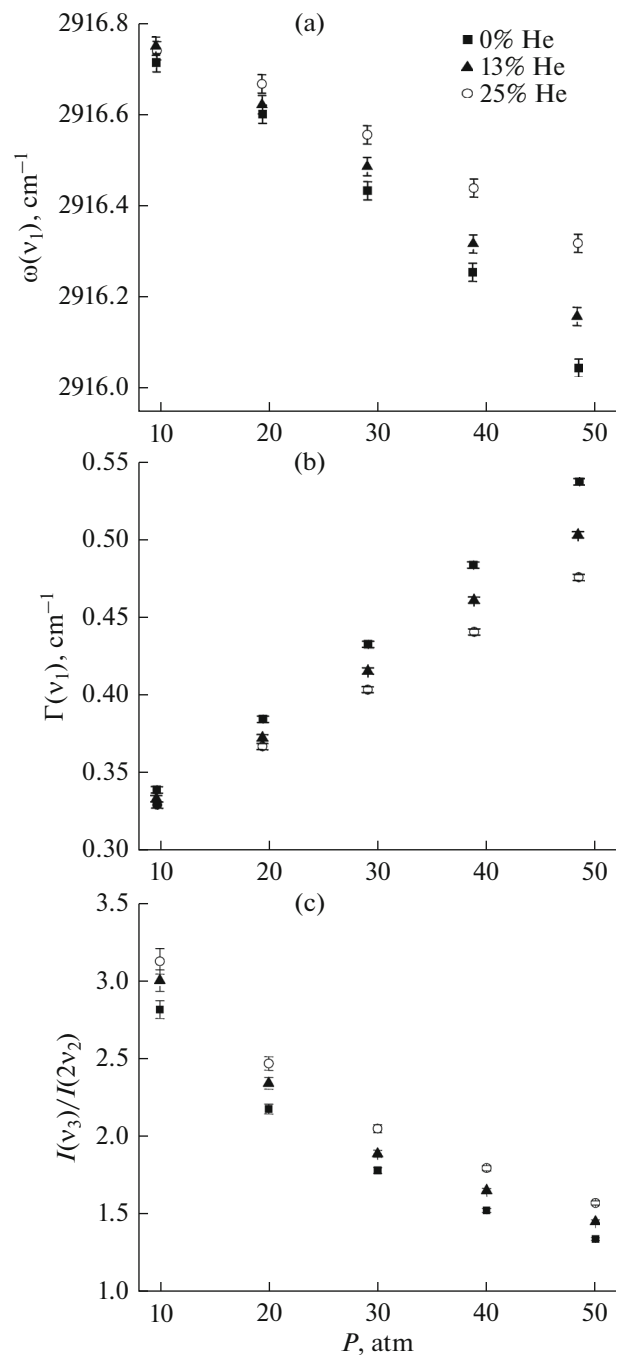


Fig. 3. (a) Position of the maximum and (b) halfwidth of the Q -branch of the ν_1 band; (c) ratio of the peak intensities of the ν_3 and $2\nu_2$ bands of CH_4 versus pressure at different He concentrations.

Table 1. Coefficients of polynomial (3) for calculation of the position of maximum of the Q -branch of the ν_1 band, its halfwidth, and the intensity ratio $I(\nu_3)/I(2\nu_2)$

X	a	b	c	d	e	f
$\omega(\nu_1)$	-1.11×10^{-4}	-0.0114	2916.860	1.479×10^{-4}	0.016	-0.061
$\Gamma(\nu_1)$	1.35×10^{-5}	0.0044	0.293	-1.744×10^{-5}	-0.0044	0.016
$I(\nu_3)/I(2\nu_2)$	9.81×10^{-4}	0.0970	3.770	-3.625×10^{-4}	0.021	0.295

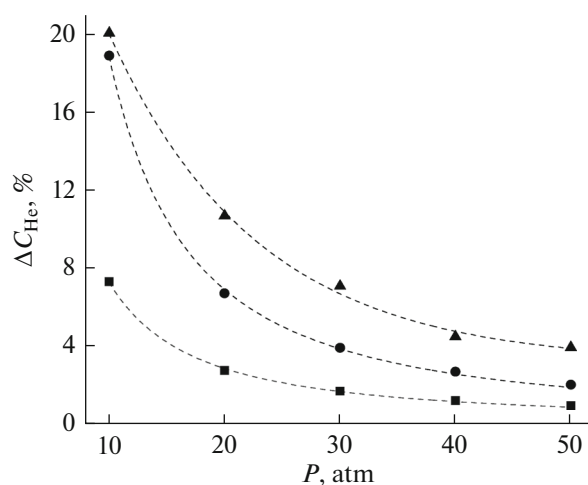


Fig. 4. The error in the He concentration in a mixture with CH_4 calculated from the position of the maximum $\omega(v_1)$ (dots), halfwidth $\Gamma(v_1)$ (squares), and the ratio of peak intensities $I(v_3)/I(2v_2)$ (triangles) versus pressure.

width, or the intensity ratio $I(v_3)/I(2v_2)$). Thus, the technique for Raman spectroscopy measurement of the content of molecular compounds is quite well developed today [6–8]. This in future will allow estimation of the He content in NG using a Raman spectrometer.

CONCLUSIONS

The study performed allowed us to ascertain the possibility of estimating the He concentration in a CH_4 –He mixture from the known mixture pressure and the measured position of the maximum of the Q -branch of the v_1 band of CH_4 or its halfwidth, or the ratio of peak intensities $I(v_3)/I(2v_2)$. The accuracy of the technique suggested increases with the pressure. The minimal error in the He concentration was $\sim 0.9\%$ in the case of measuring the halfwidth of the Q -branch of the v_1 band at $P = 50$ atm. We believe that this technique can be applied to measure the He concentration in natural gas in the future.

It should be noted that the measurement accuracy of the spectral parameters of the Q -branch of the v_1 band can be significantly improved when using a spectrometer with a higher dispersion. In turn, recording of spectra with a higher signal-to-noise ratio is to improve the accuracy of the technique which is based on measurements of the intensity ratio due to the use of a longer spectrum recording time, a photodetector with less noise, or a faster spectrometer. We believe that the measurement accuracy of the He concentration in a mixture with CH_4 or natural gas can also be increased by simultaneous accounting for all measured parameters by means of modern algorithms for data processing, such as machine learning and neural networks.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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