Raman spectrum of methane in nitrogen, carbon dioxide, hydrogen, ethane, and propane environments

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A B S T R A C T

Using binary CH_4 - mixtures with varied concentrations of H_2, N_2, CO_2, C_2H_6 and C_3H_8 and a fixed ambient pressure of 25 bar, the influence of the environment on spectral characteristics (Raman shift, half-width, peak intensity) of Q-branches of the ν_1, ν_2, ν_3, and $2\nu_4$ methane Raman bands are investigated. It is found that depending on the environment these bands demonstrate different changes in their Raman shifts and half-widths. It is shown that the ratios of peak intensities $I(\nu_2)/I(\nu_1)$, $I(\nu_3)/I(\nu_1)$ and $I(2\nu_4)/I(\nu_1)$ are very sensitive to the environment. The Raman shifts and half-widths of CH_4 bands are assumed to depend on the absolute concentration of molecules in the analyzed medium. The data obtained would be useful in Raman diagnostics of natural gas.

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1. Introduction

At present, Raman spectroscopy is extensively used for natural gas diagnostics [1–8]. Its major merits, compared to conventional gas chromatography, are the absence of consumable and expendable materials, fast operation, and simultaneous control over all molecular components of the medium whose content exceeds the sensitivity threshold of the equipment. Despite the relatively low intensity of Raman signals, the sensitivity of this method achieved in the present-day experiments is <0.005% [8]. In order to promote this analytical method and improve the measurement accuracy, the data on Raman spectra of the main components of natural gas changing as a function of the environment are necessary. This primarily concerns methane (CH_4), since it is the main component of natural gas where, depending on the gas field, its content can vary within 40–99% [9].

Despite the fact, that available literature contains sufficient data on changes in spectral characteristics of high intensity CH_4 Raman band ν_1 (symmetric $C-H$ stretching mode, 2917 cm^{-1}) as a function of temperature [10–13], pressure [11–16], and environment [14–17] other CH_4 Raman bands with lower intensity are more suited for natural gas diagnostics using Raman spectroscopy. In particular, the component composition of natural gas is determined within the range 200–2600 cm^{-1}, where ν_2 (doubly degenerate deformation mode, 1534 cm^{-1}) and $2\nu_4$ (overtone of deformation mode, 2587 cm^{-1}) bands are located [1,8], while ν_3 (triply degenerate asymmetric $C-H$ stretching mode, 3020 cm^{-1}) and $2\nu_2$ (overtone of deformation

mode, 3070 cm^{-1}) bands were proposed for determination of pressure of methane-containing media [18,19].

Natural gas in the main pipelines is under pressure, which can vary in the range of 25–100 bar [20,21]. According to Ref. [22] pressure exerts a significant influence on all CH_4 Raman bands located in the range of 200–3800 cm^{-1}, therefore it is expedient to carry out Raman analysis of the natural gas composition at a fixed pressure. Optimal value in this case is 25 bar, since from the technological point of view, pressure reducing in the cell of Raman gas analyzer is much easier than increasing. In this regard this study deals with the influence of the principal components of natural gas (hydrogen (H_2), nitrogen (N_2), carbon dioxide (CO_2), ethane (C_2H_6) and propane (C_3H_8)) on the ν_1, ν_2, ν_3, and $2\nu_4$ bands of the CH_4 Raman spectrum at a pressure of 25 bar.

2. Experimental

To carry out the investigations, an experimental setup based on the Raman spectrometer used earlier was designed [8,23]. Collimated exciting radiation ~3 mm in diameter from a continuous wave DPSS laser (SDL-532-2000T) with output power of 2 W at a wavelength of 532 nm was directed into a gas cell. The cell represented a hollow metal cube with volume of ~10 cm^3 having fused silica windows and intended to collect radiation scattered at an angle of 90° to the direction of propagation of the laser beam. Scattered radiation was collected and focused onto the spectrometer input slit employing two f/1.8 lens objectives (f = 50 mm). A holographic notch filter was inserted between the objectives to attenuate by 6 order of magnitude of scattered radiation at the laser wavelength. To decompose light into a spectrum, a no-moving-parts f/1.8-spectrometer MKR-2 was used with a 40-μm wide input slit that provided a simultaneous registration of Raman spectra

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in the range of $200 - 3800$ cm^{-1} with spectral resolution of 0.063 nm/-pixel which is equivalent to ~1.8 cm^{-1}/pixel in the middle of the spectral range. To register spectra, a Hamamatsu S10141 CCD matrix with Peltier cooling down to -10 °C was used. The matrix had 2048×256 active pixels with sizes 12×12 μm and was used as a linear CCD since charges were summed in columns (vertical binning was performed). For wavenumber calibration of the spectrometer, 28 lines of emission spectrum of neon were used [22].

Using the above setup, we investigated Raman spectra of pure CH$_4$ and binary gas media CH$_4$-N$_2$, CH$_4$-H$_2$, CH$_4$-CO$_2$, CH$_4$-C$_2$H$_6$, and CH$_4$-C$_3$H$_8$ with different contents of the mixture components. The concentration of CH$_4$ in the mixtures with N$_2$, H$_2$, CO$_2$, and C$_2$H$_6$ was 20%, 40%, 60%, 80% and 96%, while in the mixtures with C$_3$H$_8$ it was 72%, 88%, and 96% (due to a low pressure of saturated C$_3$H$_8$ vapors at room temperature) with the uncertainty <0.5%. The enumerated gas mixtures were prepared from pure gases (>99.9%) in a separate gas-mixing chamber, whose volume was several times greater than that of the measurement gas cell. To prepare a gas mixture with a certain component composition this chamber was filled with the desired gas and then with methane at a certain partial pressures, taking into account their compressibility factors. The total pressure of the resulting mixture inside the gas-mixing chamber was ~27 bar. Afterwards, the mixture was directed into the gas cell of the Raman spectrometer up to a pressure of 25 bar. The manometer uncertainty was <0.02%.

The time of Raman spectrum registration for every gas sample was 300 s. In order to rule out undesirable temperature effects, the gas cell temperature was stabilized at the level of 300 ± 0.5 K; moreover, the ambient room temperature in the laboratory was also maintained at this level. The investigations were performed for five days (one mixture per day) and every experimental series started with registration of the Raman spectrum of pure CH$_4$.

3. Results and Discussion

In this study, for every registered Raman spectrum Q-branches of CH$_4$ vibrational bands ν_1, ν_2, ν_3, and $2\nu_4$ were analyzed. In the case of CH$_4$-C$_2$H$_6$ and CH$_4$-C$_3$H$_8$ mixtures, exhibiting spectral band overlapping, the spectra of pure C$_2$H$_6$ and C$_3$H$_8$ were subtracted from the registered spectra of the mixture in order to form the CH$_4$ Raman spectrum, which was followed by its analysis. For a more accurate evaluation of Raman shifts and half-widths of Q-branches they were fitted by Gaussian functions. Standard deviations derived from the fitting data did not exceed 0.05 cm^{-1}.

Fig. 1 presents the estimates obtained for Raman shifts of the bands under study and Fig. 2 shows their half-widths. For the sake of better illustration of the tendency of each band to broadening or shift, the data in all of the graphs are presented in equal scales.

It has to be noted that among five Raman spectra of pure CH$_4$ obtained during five days of experiments there was a sufficiently good stability of the spectral characteristics of its Q-branches – the deviations fit within the data processing error.

According to the data given in Fig. 1, the type of surrounding molecules equally affects all Raman bands of CH$_4$, i.e., it leads to either increase or decrease in the Raman shift. At the same time, different bands exhibit different susceptibility to shifting. For instance, the Raman shift of ν_2 is practically independent of the environment, while the positions of ν_1, ν_3 and $2\nu_4$ are. The presence of H$_2$ and N$_2$ gives rise to an increase in the Raman shifts (up to $+0.3$ cm^{-1}), with H$_2$
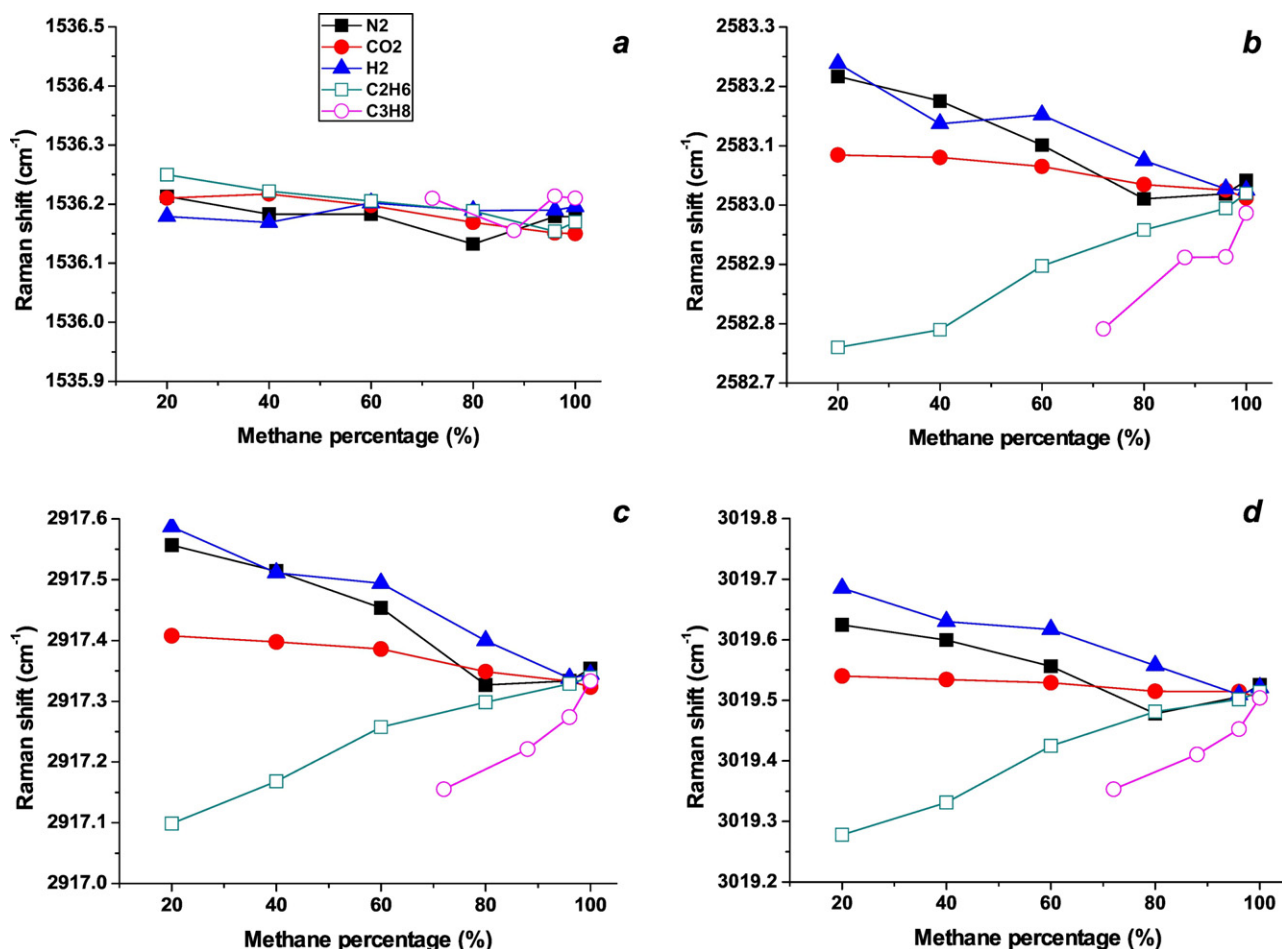

Fig. 1. Raman shifts of Q-branches of the ν_2 (*a*), $2\nu_4$ (*b*), ν_1 (*c*), ν_3 (*d*) methane Raman bands as a function of environment.