

## SPECTROSCOPY OF ATOMS AND MOLECULES

# Raman Spectra of Nitrogen, Carbon Dioxide, and Hydrogen in a Methane Environment

D. V. Petrov<sup>a,b,\*</sup>, I. I. Matrosov<sup>a</sup>, D. O. Sedinkin<sup>a</sup>, and A. R. Zaripov<sup>a</sup>

<sup>a</sup> Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch, Russian Academy of Sciences,  
Tomsk, 634055 Russia

<sup>b</sup> Tomsk State University, Tomsk, 634050 Russia

\*e-mail: Dpetrov@imces.ru

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**Abstract**—Changes in the Raman spectra of N<sub>2</sub>, H<sub>2</sub>, and CO<sub>2</sub> are studied in the range of 200–3800 cm<sup>−1</sup> depending on the concentration of surrounding CH<sub>4</sub> molecules at a fixed medium pressure of 25 atm and temperature of 300 K. It has been found that changes in the spectral characteristics of purely rotational H<sub>2</sub> lines in a CH<sub>4</sub> medium are negligible, while the Q-branches of the  $\nu_1/2\nu_2$  Fermi dyad in CO<sub>2</sub> become narrower and wavenumbers of its high-frequency component and  $\nu_1$  band of N<sub>2</sub> decrease. In addition, under these conditions, the ratio of intensities of the CO<sub>2</sub> Fermi dyad Q-branch varies in proportion to the concentration of surrounding molecules of CH<sub>4</sub>. The obtained data will be used in diagnosing the composition of natural gas using Raman spectroscopy.

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## INTRODUCTION

Natural gas (NG) is a multicomponent gas mixture widely used as an ecologically pure fuel and raw for the chemical industry. In addition to CH<sub>4</sub> the fraction of which can reach ~95%, the NG composition includes CH<sub>4</sub> homologues (C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub>H<sub>12</sub> etc.), as well as nonhydrocarbon compounds (as a rule, N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>). The content of these components in NG is different for different occurrences; as a consequence, its caloric and chemical value can considerably vary. In connection with this, determining the composition of NG is of great importance both for gas buyers and for gas suppliers.

Currently, the method of NG composition diagnostics on the basis of Raman spectroscopy is actively developed [1–8]. This method has such advantages as the possibility to carry out rapid analysis, absence of consumable materials, and the simultaneous monitoring of all molecular medium components whose concentration exceeds the sensitivity threshold of the equipment.

Currently, in spite of the relatively low level of informative signals, the experimentally verified limit sensitivity of the Raman gas analysis in diagnosing the NG is 0.002% [1]. In turn, to increase the accuracy of this method, one needs data on changes in Raman spectra of main NG components depending on conditions they are placed under directly within the ana-

lyzed NG sample. Earlier, we have established that the Raman spectrum of the main NG component—methane (including the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $2\nu_2$ , and  $2\nu_4$  bands)—rather strongly depends on temperature [9] and pressure [10]. Based on this, it was concluded that, to increase the validity of Raman gas analysis, the latter should be carried out at fixed values of these parameters. Since NG is subjected in main pipelines to a pressure of not less than 25 atm, it is appropriate to determine its composition with a sample Raman gas analyzer at a pressure of 25 atm so as to reliably provide identical conditions the NG components are placed under. In turn, the optimum temperature from the viewpoint of technical implementation is ~300 K.

The next step in this direction is the determination of the CH<sub>4</sub> (as a dominating NG component) effect on the Raman spectra of other NG components under the abovementioned conditions. In spite of the fact that the literature presents data concerning the CH<sub>4</sub> effect on fundamental bands of N<sub>2</sub> [11, 12], CO<sub>2</sub> [13], and C<sub>2</sub>H<sub>6</sub> [14] under pressures of up to 3000 atm, the required information cannot be obtained from them in view of large ranges in the obtained values at low pressures (<25 atm).

In this regard, this work is devoted to studying the CH<sub>4</sub> effect of main nonhydrocarbon NG components (N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>) on Raman spectra at a pressure of 25 atm and temperature of 300 K.

## EXPERIMENTAL

The investigations were carried out using an experimental setup based on the Raman spectrometer used earlier in [1]. Collimated exciting radiation with a diameter of  $\sim 3$  mm was generated by a solid-state diode-pumping laser (SDL-532-2000) with an output power of 2 W at a wavelength of 532 nm and directed into a gas cell with a volume of  $\sim 10$  cm<sup>3</sup>. The scattered radiation was collected in the direction perpendicular to the direction of laser-radiation propagation using a pair of identical lenses with a relative aperture of  $f/1.8$  and focal distance of 50 mm. The spectral decomposition of the collected radiation was carried out using an MKR-2 specialized spectral device with an input relative aperture of  $f/1.8$ . The spectra were recorded using a Hamamatsu S10141 CCD matrix ( $2048 \times 256$  pixels) with Peltier cooling to  $-10^\circ\text{C}$ . The matrix operated in the regime of a CCD array due to vertical binning of charges. Using the entrance slit with a width of  $40\ \mu\text{m}$  and diffraction grating of 1600 grooves/mm, the matrix ensured a resolution of  $\sim 6\ \text{cm}^{-1}$  at a dispersion of  $1.8\ \text{cm}^{-1}/\text{pix}$  and simultaneous recording of the spectral range of  $200\text{--}3800\ \text{cm}^{-1}$ . The wavenumbers calibration of the spectrometer was carried out by the radiation spectrum of a neon lamp [10].

On this equipment, Raman spectra of  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2$ , as well as of their mixtures with different concentrations of  $\text{CH}_4$  (20, 40, 60, 80, and 96%), were recorded. The required pressure (25 atm) of the gaseous media under study was monitored by a manometer with an error of  $<0.02$  atm. The purity of the used gases was  $>99.9\%$ . The exposure time for each spectrum was 300 s, and the gas cell was thermostabilized at  $300 \pm 1$  K.

## RESULTS AND DISCUSSION

Figure 1 presents normalized Raman spectra of  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2$ . In the spectral range under study,  $\text{N}_2$  has only one fundamental vibrational-rotational band  $\nu_1$  with a forbidden Q-branch, the maximum of which was observed at  $2328.72\ \text{cm}^{-1}$ . The  $\text{CO}_2$  spectrum in this range is a Fermi dyad, which is a result of the interaction between the  $\nu_1$  band and  $2\nu_2$  overtone [15, 16]. Since the observed Q-branches cannot be uniquely associated with the corresponding vibrations in this case, we below mention them as a low-frequency  $\nu^{(-)}$  ( $1284.72\ \text{cm}^{-1}$ ) and high-frequency  $\nu^{(+)}$  ( $1388.01\ \text{cm}^{-1}$ ) components of the Fermi dyad  $\nu_1/2\nu_2$ . In turn, the Raman spectrum of hydrogen is presented in this range only by pure rotational lines:  $S_0$  ( $354.82\ \text{cm}^{-1}$ ),  $S_1$  ( $587.40\ \text{cm}^{-1}$ ),  $S_2$  ( $815.01\ \text{cm}^{-1}$ ), and  $S_3$  ( $1034.86\ \text{cm}^{-1}$ ). Note that the procedure of calculating the NG is carried out in the range of  $200\text{--}2600\ \text{cm}^{-1}$  [17] and, in this regard, the  $\text{H}_2$  vibrational-rotational

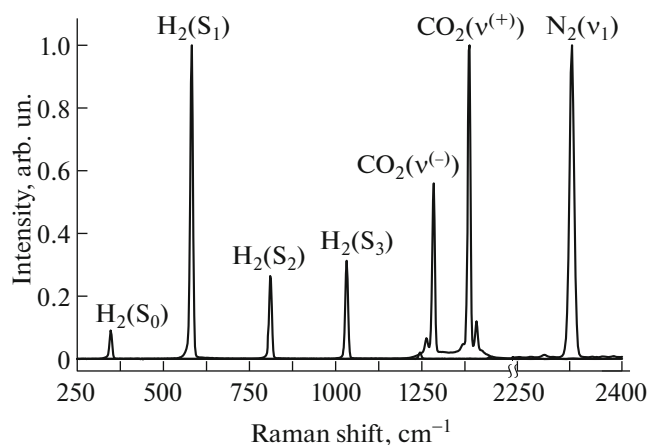


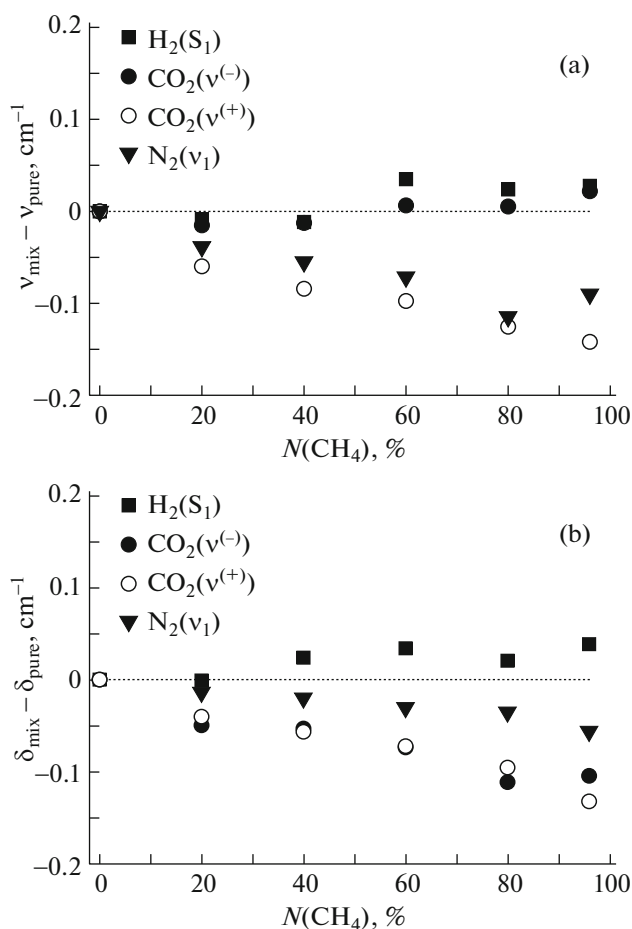
Fig. 1. Raman spectra of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{CO}_2$  in the spectral range of  $250\text{--}2400\ \text{cm}^{-1}$ .

band of  $\nu_1$  having a wavenumber of  $4156\ \text{cm}^{-1}$  is not of practical interest in this context.

In the course of the work, wavenumbers and half-widths (widths at half-maximum) of the abovementioned Q-branches ( $\text{N}_2(\nu_1)$ ,  $\text{CO}_2(\nu^{(-)})$ , and  $\text{CO}_2(\nu^{(+)})$ ) and four pure rotational lines of  $\text{H}_2$  were studied depending on the concentration of surrounding  $\text{CH}_4$  molecules. To increase the accuracy, they were approximated by the Gaussian profile. In this case, the root-mean-square deviation did not exceed  $\sim 0.06\ \text{cm}^{-1}$ . In the course of the investigation, it was found that  $\text{CH}_4$  had a similar effect on all  $\text{H}_2$  lines. In this regard, the obtained results (Fig. 2) present data only for the most intense line  $S_1$  ( $587.40\ \text{cm}^{-1}$ ). It is also necessary to note that the analysis of spectra of  $\text{CO}_2$  in a mixture with  $\text{CH}_4$  was preceded by the procedure of subtracting the pure  $\text{CH}_4$  spectrum from them in view of the overlapping of  $\text{CO}_2$  bands with the wing of the  $\text{CH}_4\ \nu_2$  band ( $1536\ \text{cm}^{-1}$ ).

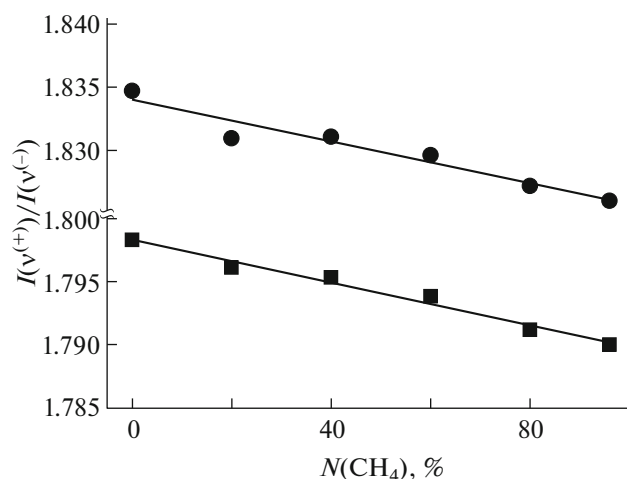
According to the obtained data, the position of the Q-branch of  $\text{N}_2(\nu_1)$  is shifted to the region of low wavenumbers shifts by  $\sim 0.10\ \text{cm}^{-1}$  with an increase in the  $\text{CH}_4$  concentration from 0 to 96%. Under similar conditions, Q-branches of the  $\text{CO}_2$  Fermi dyad behave differently: the wavenumber of high-frequency component  $\nu^{(+)}$  decreases by  $\sim 0.15\ \text{cm}^{-1}$ , and the position of low-frequency component  $\nu^{(-)}$  remains almost unchanged (within the measurement accuracy). In turn, the effect of the  $\text{CH}_4$  environment on positions of  $\text{H}_2$  rotational lines under these conditions was negligibly small.

As for changes in half-widths of the analyzed lines and Q-branches, one can note the following. The most noticeable effect is exerted by  $\text{CH}_4$  on



**Fig. 2.** Variation in (a) wavenumbers and (b) half-widths of Q-branches of N<sub>2</sub> and CO<sub>2</sub>, as well as of pure rotational lines of H<sub>2</sub> depending on the concentration of surrounding CH<sub>4</sub> molecules.

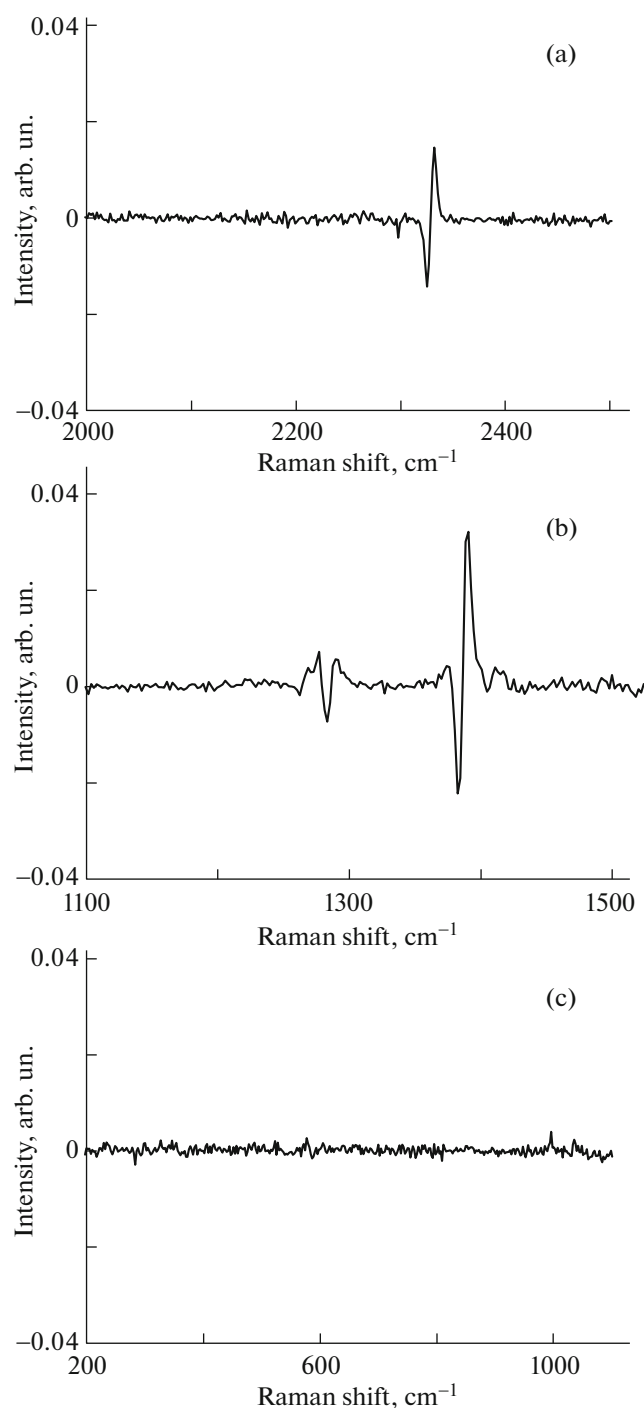
Q-branches of CO<sub>2</sub>, which is reflected in their narrowing by  $\sim 0.1 \text{ cm}^{-1}$ . Here, it should be noted that, in contrast to changes in wavenumbers, the change in their half-widths is identical. The Q-branch of N<sub>2</sub> under these conditions is also subjected to narrowing but by a lesser value ( $\sim 0.06 \text{ cm}^{-1}$ ). In turn, pure rotational lines of H<sub>2</sub> were broadened with an increase in the CH<sub>4</sub> concentration by  $\sim 0.04 \text{ cm}^{-1}$ . It is necessary to note that, in spite of the fact that data for N<sub>2</sub> and H<sub>2</sub> are within the measurement accuracy, all observed trends correspond to changes in the medium density. In particular, with an increase in the CH<sub>4</sub> fraction in the mixture with H<sub>2</sub>, the medium becomes denser, which results in the broadening of the H<sub>2</sub> lines; in the cases with CO<sub>2</sub> and N<sub>2</sub>, the medium becomes less dense, which leads to narrowing of their Q-branches. Since the density of CO<sub>2</sub> greatly differs from the density of CH<sub>4</sub> as compared to N<sub>2</sub>, the observed change in



**Fig. 3.** Ratio of integral (squares) and peak (circles) intensities of Q-branches of the CO<sub>2</sub> Fermi dyad depending on the concentration of surrounding CH<sub>4</sub> molecules.

half-widths of CO<sub>2</sub> Q-branches is greater. This version also finds endorsement in [11, 13, 18].

In the course of the work, effects of intensity redistribution between Q-branches of the CO<sub>2</sub> Fermi dyad and individual rotational lines of H<sub>2</sub> in the case in which these molecules were in a medium with a different CH<sub>4</sub> content were also studied. For this purpose, the intensity ratio  $I(\nu^{(+)})/I(\nu^{(-)})$  was determined from all the obtained Raman spectra of CO<sub>2</sub> and the ratios  $I(S_1)/I(S_0)$ ,  $I(S_1)/I(S_2)$ , and  $I(S_1)/I(S_3)$  were determined from the Raman spectra of H<sub>2</sub>. According to the obtained data, intensity redistributions of pure rotational H<sub>2</sub> lines due to a different environment were not observed, in turn, for Q-branches of the CO<sub>2</sub> Fermi dyad that took place (Fig. 3), both for peak intensities and for integral ones. Note that the intensities for  $\nu^{(-)}$  were integrated in the range of 1275–1295  $\text{cm}^{-1}$ ; for  $\nu^{(+)}$ , in the range of 1377–1397  $\text{cm}^{-1}$ . In turn, peak intensities were determined from Gaussian profiles approximating these Q-branches. It is seen from the obtained data presented in Fig. 3 that the ratio  $I(\nu^{(+)})/I(\nu^{(-)})$  decreases with an increase in the CH<sub>4</sub> concentration. Since the performed measurements are relative, one cannot with certainty say from the experimental data that the abovementioned effect is caused either by an increase in the intensity of low-frequency component  $\nu^{(-)}$  or by a decrease in the intensity of high-frequency component  $\nu^{(+)}$ . However, according to the mechanism of the interaction between the  $\nu_1$  and  $2\nu_2$  bands [15], the observed decrease in the distance between the Q-branches of the dyad with a decrease in the medium density (due to the decrease in the CO<sub>2</sub> concentration in the mix-



**Fig. 4.** Difference between Raman spectra of (a)  $N_2$ , (b)  $CO_2$ , and (c)  $H_2$  for pure gases and in a mixture with  $CH_4$  (96%).

ture) testifies to weakening of the Fermi resonance between these bands. Note that we observed similar effects earlier [10, 19] when studying Raman spectra of  $CH_4$  and  $CO_2$  depending on pressure.

To visually confirm the changes in Raman spectra of analyzed molecules in the  $CH_4$  environment, the

difference between normalized spectra with the  $CH_4$  concentration of 0 and 96% was obtained. It is seen from the data presented in Fig. 4 that, in spite of the relatively low resolution of the used spectrometer, shifts of the Q-branches of  $N_2$  ( $\nu_1$ ) and  $CO_2$  ( $2\nu_2$ ), as well as broadenings of both  $CO_2$  Q-branches, are clearly seen. In turn, the spectra of  $H_2$ , both in the  $CH_4$  environment and beyond it, have no significant distinctions. It follows from the residuals in difference spectra of  $N_2$  and  $CO_2$  that ignoring these features can lead to relative errors in determining concentrations of these gases at a level of several percent and mask bands of other NG components.

## CONCLUSIONS

The presented investigations of changes in Raman spectra of  $N_2$ ,  $CO_2$ , and  $H_2$  in a  $CH_4$  environment at a fixed pressure of 25 atm demonstrated the following. The wavenumber of the Q-branch of the Raman vibrational band  $\nu_1$  of  $N_2$  decreases. Q-branches of the  $\nu_1/2\nu_2$   $CO_2$  Fermi dyad are subjected to narrowing. In this process, the wavenumber of the Q-branch of high-frequency component  $\nu^{(+)}$  decreases and the shift of low-frequency component  $\nu^{(-)}$  remains unchanged. In addition, the ratio of their intensities  $I(\nu^{(+)})/I(\nu^{(-)})$  (both peak and integral ones) decreases under these conditions. Such changes in the spectra in the determination of the NG composition by decomposing its Raman spectrum into basic spectra of individual components will cause increases in measurement errors. In this regard, it is necessary to take into account these changes either by introducing corrections to the procedure of Raman-spectrum processing or by formation of basis spectra under corresponding conditions. In turn, lines of the pure rotational spectrum of  $H_2$  do not change their spectral characteristics in the  $CH_4$  medium and can be used without additional corrections.

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