DOI 10.1007/s10812-018-0659-8
Journal of Applied Spectroscopy, Vol. 85, No. 3, July, 2018 (Russian Original Vol. 85, No. 3, May–June, 2018)

RAMAN SPECTRUM OF GASEOUS PROPANE IN METHANE

D. V. Petrov UDC 535.375.56

Pressure effects on the Raman spectrum of gaseous propane in methane are investigated. It is found that propane Raman bands located in the range 2700–3100 cm^{-1} *shift to lower frequencies although Raman bands in the range 300–1600 cm*$^{-1}$ *change negligibly as the density of the medium containing the analyzed propane increases.*

Keywords: *Raman spectroscopy, propane, methane, natural gas.*

Introduction. Analysis of natural gas compositions using Raman spectroscopy is currently a rapidly developing area [1–8] because Raman gas analyzers do not require consumables and frequent calibrations like gas chromatographs, the most common instruments for analyzing multicomponent hydrocarbon gas mixtures, and are capable of monitoring quickly and simultaneously all molecular components at concentrations above the detection limit of the apparatus.

Natural gas is known to be a mixture of methane, ethane, propane, butanes, etc. and small amounts of inorganic compounds such as N_2, H_2, and CO_2. In turn, methane is the dominant component of natural gas. According to the literature [9–11], the medium temperature, pressure, and composition affect noticeably the Raman spectra of methane. These features should be taken into account for Raman analysis of natural gas. Raman spectra of analyzed molecules in methane also change according to Raman spectra of N_2 [12, 13], CO_2 [12, 14], and ethane [15, 16]. Propane in addition to these molecules is also a principal component of natural gas. However, experimental studies of changes in its Raman spectrum under various conditions are limited to a single report on the effect of high pressure (up to 40 GPa) on its phase transitions [17]. Therefore, the effect of the environment in which the gaseous propane is located on its Raman spectrum is a critical task.

Experimental. Raman spectra of pure gaseous propane at a pressure of 7 atm, its mixtures with methane (72, 88, and 96%) at 25 atm, and pure methane at 25 atm were recorded. These pressures were chosen because trunk pipelines contain natural gas at pressures >25 atm. Its composition should be determined at a fixed pressure of 25 atm if a sampling Raman gas analyzer is used by lowering the pressure of the gas within the cuvette to guarantee identical conditions for the natural-gas components at the time of the measurements. The pressure at which the Raman spectrum of pure propane was recorded was selected because propane starts to transition from the gas to the liquid state at room temperature and pressures >7 atm.

The Raman spectrometer with a 90° arrangement for collecting scattered radiation that was used previously [5, 6] was used in the present work. Collimated exciting radiation of diameter ~3 mm was generated by a solid-state diode laser with output power 2 W at 532 nm and was directed into a gas cuvette (~10 cm^3 volume). Scattered radiation was collected using a pair of identical objective lenses with relative aperture $f/1.8$ and focal length 50 mm. The collected radiation was spread into a spectrum using a specialized MKR-2 spectrometer with input relative aperture $f/1.8$. Spectra were recorded using a Hamamatsu S10141 CCD-array (2048 × 256 pixels) with Peltier cooling to -10°C operating as a linear CCD because of vertical binning. This array at input slit width 40 μm and diffraction grating 1600 lines/mm provided a resolution of ~6 cm^{-1} with 1.8 cm^{-1}/pixel dispersion and simultaneous recording of the spectral range 200–3800 cm^{-1}. The spectrometer frequency was calibrated using the emission spectrum of a Ne lamp [18].

The pressure of the studied gas mixtures was monitored by a manometer with an uncertainty of <0.02 atm. The gases were >99.9% pure. The exposure time for each spectrum was 300 s. The gas cuvette was thermostatted at 300 ± 1 K.

Results and Discussion. Let us examine the Raman spectrum of propane (Fig. 1). A large part of the fundamental vibrational bands was situated in the range 300–1600 cm^{-1} [19] (Fig. 1a). The strongest band in this range ν_8 (868 cm^{-1})

---

[*] To whom correspondence should be addressed.

Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch, Russian Academy of Sciences, 10/3 Akademicheskii Ave., Tomsk, 634055 Russia; email: dmvitpetrov@gmail.com; National Research Tomsk State University, Tomsk, Russia. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 85, No. 3, pp. 359–363, May–June, 2018. Original article submitted December 27, 2017.

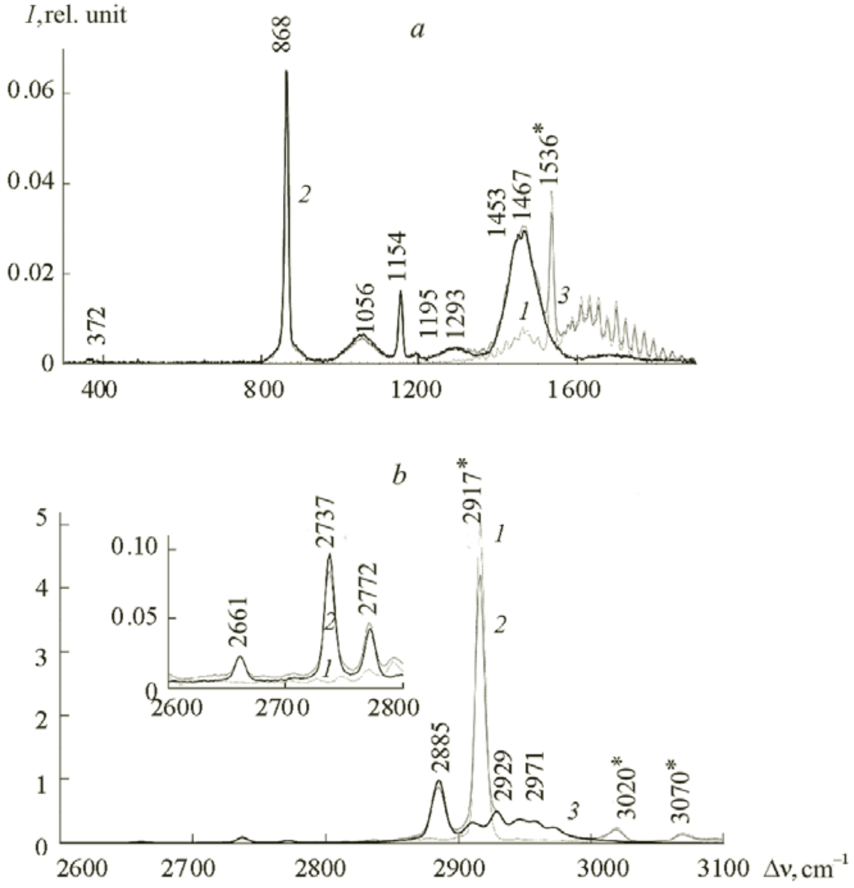

Fig. 1. Raman spectra of methane (1), propane (2), and their mixture (3) in the ranges 300–1900 (a) and 2600–3100 cm^{-1} (b); *frequency shifts of methane bands are indicated.

corresponded to C–C stretching vibrations. Bands due to CH_3 rocking vibrations ν_{20}, ν_7, ν_{25}, and ν_{12} with maxima at 1056, 1154, 1195, and 1293 cm^{-1}, respectively, were located nearby. According to the literature [19], bands ν_{11}, ν_5, and ν_4 for CH_3 (ν_5 and ν_{11}) and CH_2 bending vibrations (ν_4) formed a broad band at 1400–1550 cm^{-1}. However, only two maxima at frequencies 1453 (ν_5) and 1467 cm^{-1} (ν_4) could be identified in our instance and in previous work [20]. Band ν_9 (372 cm^{-1}) corresponding to C–C–C bending vibrations appeared in the low-frequency range. Moreover, propane showed the strongest bands in the range 2850–3050 cm^{-1} (Fig. 1b). This spectral range contained bands corresponding to CH_2 (ν_1, 2971 cm^{-1}) and CH_3 symmetric stretching vibrations (ν_3, 2885), CH_3 antisymmetric stretching vibrations (ν_2, 2958), and a Fermi resonance triplet $2\nu_{11}$:$2\nu_5$:$2\nu_4$ with maxima at 2911, 2929, and 2946 cm^{-1} that was collocated with them. Another triplet with maxima at 2661, 2737, and 2772 cm^{-1} that was most probably due to coupling of combination modes $\nu_4 + \nu_{25}$ and $\nu_5 + \nu_{12}$ with overtone $2\nu_6$ was found in the range 2600–2800 cm^{-1} (these bands will be mentioned further according to their frequencies).

The obtained propane Raman spectra were processed by approximating relatively narrow and well-resolved bands as Gaussians in order to evaluate their positional changes under various conditions. The mean-square deviation of this approximation was ≤ 0.1 cm^{-1}, which allowed the band position to be determined to an accuracy of up to 0.1 cm^{-1}. The bands at 868, 1154, 2661, 2737, 2771, and 2885 cm^{-1} were analyzed using this procedure. It is noteworthy that the Raman spectrum of pure methane was subtracted from the spectra of the propane–methane mixtures during processing for better extraction of information about the characteristics of these bands. The propane Raman spectra had traces of methane band ν_1 (2917 cm^{-1}), a broadened band ν_3 (3020), and intensity changes of the $2\nu_2$ band (3070) because the methane Raman spectrum obtained from the subtraction procedure changed for this mixture [11]. However, these peculiarities did not affect the estimated positions of the analyzed propane bands.

Table 1 indicates that the propane Raman spectrum in the mixture (4% C_3H_8 + 96% CH_4) at 25 atm was rather close to that of pure propane at 7 atm. However, the bands at 2737, 2771, and 2885 cm^{-1} shifted to lower frequencies by ~0.3 cm^{-1}

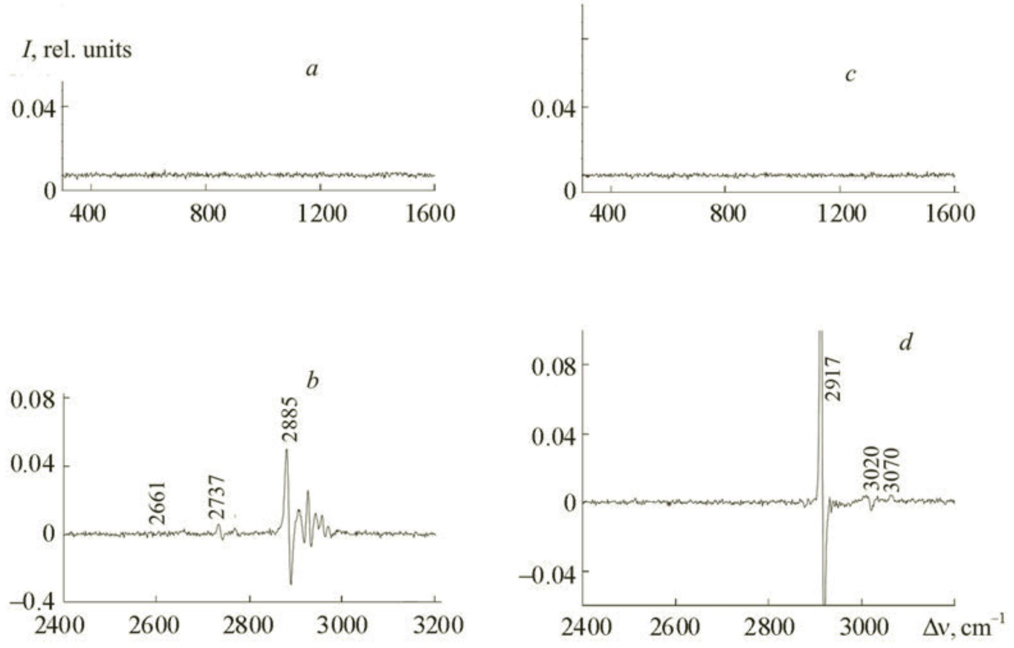

Fig. 2. Difference Raman spectra [C_3H_8 (7 atm) – C_3H_8 (1 atm)] (a, b) and [(4% C_3H_8 + 96% CH_4) (25 atm) – CH_4 (25 atm) – C_3H_8 (7 atm)] (c, d) in the ranges 300–1600 and 2400–3200 cm^{-1}.

TABLE 1. Frequency Shifts of Propane Raman Bands under Various Conditions

P, atm	Gas composition	Δν, cm^{-1}					
7	100% C_3H_8	867.7	1154.3	2660.8	2737.1	2771.5	2885.1
25	4% C_3H_8 + 96% CH_4	867.7	1154.3	2660.7	2737.1	2771.5	2885.1
25	12% C_3H_8 + 88% CH_4	867.7	1154.2	2660.7	2737.0	2771.4	2885.0
25	28% C_3H_8 + 72% CH_4	867.7	1154.2	2660.7	2736.9	2771.2	2884.8

if the propane concentration in the mixture was increased from 4 to 28%. In turn, the positions of the bands at 868, 1154, and 2661 cm^{-1} were practically unchanged. This band behavior was most probably due to the fact that they represented different types of vibrations. Analogous shifts of CH stretching bands and overtones in Fermi resonance with them occurred if the medium density was increased [11, 16]. The positions of bands corresponding to C–C stretching vibrations and CH bending vibrations experienced negligibly small shifts [9, 16].

The aforementioned bands were analyzed to confirm this by recording a series of Raman spectra of pure propane at pressures 1–7 atm in steps of 1 atm. Table 2 indicates that the bands at 2737, 2771, and 2885 cm^{-1} shifted to higher frequencies by ~0.4 cm^{-1} if the pressure was reduced. The frequency of the band at 2661 cm^{-1} tended to increase slightly (~0.2 cm^{-1}) although the shift was within experimental uncertainty. In turn, the positions of the bands at 868 and 1154 cm^{-1} changed insignificantly. Thus, the observed trends with the changes of medium density were the same as in the studied mixtures with methane. It was concluded based on the results that an optimum base Raman spectrum of propane as appropriate pressure could be chosen for quantitative analysis of any mixture of propane in methane by deconvoluting the Raman spectrum of the mixture into Raman spectra of the separate molecules.

Figures 2a and 2b show different Raman spectra of propane at pressures of 7 and 1 atm to confirm that the results were correct. No visible changes occurred in the range 300–1600 cm^{-1} although bands in the range 2400–3200 cm^{-1} shifted. It is also noteworthy that the positions of all propane bands in the range 2850–3050 cm^{-1} shifted (toward higher frequencies).

TABLE 2. Frequency Shifts of Propane* Raman Bands at Various Pressures

P, atm	$\Delta\nu$, cm^{-1}					
7	867.7	1154.3	2660.8	2737.1	2771.5	2885.1
6	867.7	1154.3	2660.9	2737.2	2771.6	2885.2
5	867.7	1154.4	2660.9	2737.3	2771.7	2885.2
4	867.7	1154.4	2660.9	2737.4	2771.8	2885.3
3	867.7	1154.4	2660.9	2737.4	2771.8	2885.4
2	867.7	1154.4	2660.9	2737.5	2771.8	2885.4
1	867.7	1154.4	2660.9	2737.6	2771.9	2885.5

*Gas composition 100% C_3H_8.

The triplet with maxima at 2911, 2929, and 2946 cm^{-1} strengthened slightly if the pressure was increased. Analogous intensity redistributions among methane Fermi-resonance bands were noted during studies of methane Raman spectra [9, 11]. Figure 2c and 2d demonstrate the result of subtracting the Raman spectra of propane at a pressure of 7 atm and methane at 25 atm from that of the mixture (4% C_3H_8 + 96% CH_4). It can be seen that the propane Raman spectrum was completely compensated. The discrepancy was determined by the change of the methane Raman spectrum in the presence of propane that was reported before [11].

Conclusions. It was found that the spectral characteristics of separate gaseous propane Raman bands changed depending on the analytical conditions. In particular, Raman bands in the range 2700–3100 cm^{-1} shifted in methane with different propane concentrations and varying pressure. The intensities of the triplet bands with maxima at 2911, 2929, and 2946 cm^{-1} also changed relative to the strongest Raman spectral band of propane ν_3 (2885 cm^{-1}), with which they were in Fermi resonance. In turn, the characteristics of bands in the range 300–1600 cm^{-1}, which corresponded to C–C stretching and CH_3 bending vibrations, changed insignificantly. An optimal basis Raman spectrum of propane at the corresponding pressure could be selected for any composition for quantitative analysis of the composition of a mixture of propane in methane by deconvoluting its Raman spectrum into the Raman spectra of the separate molecules. The results were useful for Raman gas analysis of natural gas and other fuel gases containing propane.

Acknowledgment. The work was sponsored by the Russian Foundation for Basic Research (Project No. 16-32-60111 mol_a_dk).

REFERENCES

1. J. Kiefer, T. Seeger, S. Steuer, S. Schorsch, M. C. Weikl, and A. Leipertz, *Meas. Sci. Technol.*, **19**, No. 8, 085408 (2008).
2. S. C. Eichmann, J. Kiefer, J. Benz, T. Kempf, A. Leipertz, and T. Seeger, *Meas. Sci. Technol.*, **25**, No. 7, 075503 (2014).
3. M. Hippler, *Anal. Chem.*, **87**, 7803–7809 (2015).
4. M. P. Buric, K. P. Chen, J. Falk, and S. D. Woodruff, *Appl. Opt.*, **48**, No. 22, 4424–4429 (2009).
5. M. A. Buldakov, I. I. Matrosov, B. V. Korolev, D. V. Petrov, and A. A. Tikhomirov, *Zh. Prikl. Spektrosk.*, **80**, No. 1, 128–132 (2013) [M. A. Buldakov, I. I. Matrosov, B. V. Korolev, D. V. Petrov, and A. A. Tikhomirov, *J. Appl. Spectrosc.*, **80**, No. 1, 124–128 (2013)].
6. D. V. Petrov and I. I. Matrosov, *Appl. Spectrosc.*, **70**, No. 10, 1770–1776 (2016).
7. R. Sharma, S. Poonacha, A. Bekal, S. Vartak, A. Weling, V. Tilak, and C. Mitra, *Opt. Eng.*, **55**, No. 10, 104103 (2016).
8. T. Wlodek, S. Kuczynski, R. Smulski, and K. Polanski, *AGH Drilling, Oil, Gas*, **33**, No. 3, 619–627 (2016).
9. D. V. Petrov, *J. Raman Spectrosc.*, **48**, No. 11, 1426–1431 (2017).
10. D. V. Petrov, *Zh. Prikl. Spektrosk.*, **84**, No. 3, 399–403 (2017) [D. V. Petrov, *J. Appl. Spectrosc.*, **84**, No. 3, 420–424 (2017)].
11. D. V. Petrov, *Spectrochim. Acta, Part A*, **191**, 573–578 (2018).
12. D. V. Petrov, I. I. Matrosov, D. O. Sedinkin, and A. R. Zaripov, *Opt. Spektrosk.*, **124**, No. 1, 12–15 (2018) [D. V. Petrov, I. I. Matrosov, D. O. Sedinkin, and A. R. Zaripov, *Opt. Spectrosc.*, **124**, No. 1, 8–12 (2018)].
13. J. C. Seitz, J. D. Pasteris, and I. M. Chou, *Am. J. Sci.*, **293**, No. 4, 297–321 (1993).
14. J. C. Seitz, J. D. Pasteris, and I. M. Chou, *Am. J. Sci.*, **296**, No. 6, 577–600 (1996).

15. S. B. Hansen, R. W. Berg, and E. H. Stenby, *Appl. Spectrosc.*, **55**, No. 6, 745–749 (2001).
16. D. V. Petrov, *J. Raman Spectrosc.*, **49** (2018); doi: 10.1002/jrs.5326.
17. D. Kudryavtsev, A. Serovaiskii, E. Mukhina, A. Kolesnikov, B. Gasharova, V. Kutcherov, and L. Dubrovinsky, *J. Phys. Chem.*, **121**, No. 32, 6004–6011 (2017).
18. D. V. Petrov, I. I. Matrosov, D. O. Sedinkin, and A. R. Zaripov, *Proc. SPIE Int. Soc. Opt. Eng.*, **10466**, 1046606 (2017).
19. T. Shimanouchi, *Tables of Vibrational Molecular Frequencies*, National Bureau of Standards (U.S.) (1972).
20. K. M. Gough, W. F. Murphy, T. Stroyer-Hansen, and E. Norby Svendsen, *J. Chem. Phys.*, **87**, No. 6, 3341–3346 (1987).