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CALCULATED SPECTRA OF HYDROCARBON COMPONENTS OF NATURAL GAS

The paper presents the calculated spectra of hydrocarbon components of a natural gas (NG), and they are compared with the experimental results. The results of experimental studies of NG show that the region of stretching vibrations of hydrocarbon C-H bonds, despite the very high level of the Raman signal, is of little use for the quantitative and qualitative analysis. This is due to the fact that the structure of the bands in this region of the spectrum is very complex, and the methane bands with its suppressing content in NG dominate here. The spectra of weak bands of heavy hydrocarbons against the background of very intense bands of methane are almost not revealed. In full, it is difficult to take all the details into account, as can be seen from the previous one. Therefore, we paid a special attention to the determination of the molecular components of NG such as methane (CH₄), ethane (C₂H₆), propane (C₃H₈), and butane (C₄H₁₀), by calculating the C-H vibrations and determining the spectral region, where they are located. The results of calculations confirm that the frequencies of C-H vibrations of heavy hydrocarbons (ethane, propane, and butane) do lie in the spectral range of 2500–3500 cm⁻¹ of combinational frequencies.

Keywords: natural gas, methane, ethane, propane, butane, Raman spectra.

1. Introduction

Vibrational spectroscopy of infrared absorption (IR) and Raman scattering (RS) is used for analytical purposes, the determination of the molecular structure, identification of substances, and qualitative and quantitative analyses of their mixtures. Vibrational spectra give us a number of significant features closely related to the molecular structure of substances. Vibrational Raman spectra are especially informative in this respect. This is due to certain features of Raman spectroscopy. However, extracting

this information is a very difficult problem. Experimental and theoretical studies of the problem (still far from being completed) can be useful in solving specific problems of determining the molecular structure, spectroscopic constants, and electrical properties of molecules [1–3].

To determine the content of accompanying gases and liquids in hydrocarbons and the composition of NG, various physicochemical methods are used, among which the most accurate and reliable is the vibrational Raman spectroscopy.

Recently, the interest has arisen in studying the spectra of Raman scattering of NG, according to published data. The study of the spectra of substances in the gaseous state continues [4, 5], but there is

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Table 1. Composition of a low-sulfur-containing natural gas (NG) in deposits of the Kashkadarya region

Name of deposit	Composition (% of volume)							
	H ₂ S	CO ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂₊	N ₂
Zevarda II	0.05	4.41	89.82	3.86	0.89	0.38	0.26	0.33
Zevarda III	0.05	4.46	88.85	4.42	1.11	0.46	0.30	0.35
Pamuk	0.05	3.98	90.11	3.92	0.88	0.36	0.28	0.42
Alan	0.05	4.31	90.09	3.76	0.81	0.32	0.25	0.41
Kukdumalak	0.06	4.14	90.44	3.61	0.80	0.34	0.28	0.33

Table 2. Percentage and uncertainties of various components in the natural gas, obtained by gas chromatography

Components	Chemical formula	Chromatograph, (Kashkadarya)	Chromatograph, (Russia, Tomsk)
Methane	CH ₄	95.170 ± 0.05	92.260 ± 0.15
Ethane	C ₂ H ₆	2.263 ± 0.17	3.450 ± 0.14
Propane	C ₃ H ₈	0.236 ± 0.11	1.260 ± 0.08
n-Butane	n-C ₄ H ₁₀	0.144 ± 0.04	0.224 ± 0.014
Isobutene	iso-C ₄ H ₁₀	0.085 ± 0.011	0.192 ± 0.012
n-Pentane	n-C ₅ H ₁₂	0.033 ± 0.005	0.040 ± 0.003
Isopentane	iso-C ₅ H ₁₂	0.041 ± 0.02	0.047 ± 0.003
Nitrogen	N ₂	0.842 ± 0.07	1.934 ± 0.08
Oxygen	O ₂	0.047 ± 0.003	0.008 ± 0.002
Carbon dioxide	CO ₂	1.100 ± 0.03	0.540 ± 0.03
Hydrogen	H ₂	0.003 ± 0.001	0.004 ± 0.001
Helium	He	0.016 ± 0.001	0.018 ± 0.002
Higher hydrocarbons		0.020 ± 0.001	0.023 ± 0.001

no data on methane and other hydrocarbons and its gas mixtures in a wide range of pressures and temperatures. In the scientific literature, articles appeared that confirm the conclusions made by us earlier [6]. Theoretical studies in this field only qualitatively explain the phenomena, but the quantitative data of the theory and experiment vary greatly.

One of the main tasks facing gas companies is to determine the molecular composition of NG and gas mixtures that are close to it. This is because the composition of NG can vary significantly depending on the field. In particular, the fraction of methane in NG can fluctuate in the range from 99.2% to 63.7% for various deposits [7]. For example, in the Kashkadarya region, the composition of a low-sulfur-containing natural gas for various deposits is given in Table 1 [8].

Enterprises engaged in its extraction, transportation, and processing need gas control devices. At

present, gas chromatography are usually used at these enterprises to determine the component composition of NG, its moisture content, density, and calorificity. Table 2 gives the chromatographic data on the composition of NG in the Kashkadarya region [8] and in Russia (Tomsk) [5].

The merits of this method of chromatography include the high sensitivity and relative ease of maintenance and information processing [4].

The disadvantages of chromatography are the following: the long duration of the analysis and the resulting inability to control the dynamic changes in the gas parameters when working in the duct; the need for the operator to be present during the measurements, because some functions of a chromatograph are difficult to be automatized; insufficient presentation of the sample and reliability of the analysis due to the fact that it is difficult to introduce an

analogous gas into a chromatograph without changing its thermo-physical parameters and phase state and, hence, the percentage of gas components; and impossibility to determine immediately the complete composition of NG. For a complete analysis, several different types of detectors have to be used, but the contents of some components (for example, water, hydrogen sulfide) have to be determined by other methods of analysis.

The determination of the composition of NG by the Raman scattering method is largely devoid of such drawbacks, in particular: the analysis time of a natural gas sample is from 10 minutes to 20–30 seconds, depending on the version of the recording system and the chosen analysis technique. When using a multichannel recording system, the intensities of the spectral lines of all gas components are measured almost simultaneously during a short time interval, which allows the dynamic changes in the concentrations of each component to be correctly monitored. The process of analysis can be fully automated, and the control over the work and the transfer of the obtained data can be carried out from the central control panel of the dispatcher through ordinary communication lines or departmental communication systems. The method makes it possible to conduct the analysis for those values of the thermo-physical parameters of NG that the gas has in the main pipe. There are no fundamental limitations on these parameters. It is possible to determine the component composition in a constant gas flow. The method makes it possible to determine the concentration of all components of NG at once, with the exception of inert gases, whose concentration is insignificant.

2. Experimental and Calculated Results

The Raman spectra of NG in the range 500–3500 cm^{-1} of combinational frequencies under normal conditions (295 K) are studied. The results of studies show that the region of stretching vibrations of C-H hydrocarbon bonds, despite the very high level of the Raman signal, is of little use for the quantitative and qualitative analyses. This is due to the fact that the structure of the bands in this region of the spectrum is very complex, and the methane bands with its suppressing content in NG dominate here [4, 5, 9]. The spectra of weak bands of heavy hydrocarbons against

the background of very intense bands of methane are almost not revealed. Therefore, it is difficult to consider all the details.

It is possible to clarify some details of intermolecular interactions through non-empirical calculations. Such calculations should clarify some details of the interaction of molecules, give information on which changes in comparison with an isolated molecule should be expected, when two molecules or a molecule interact with an atom of an inert gas. In these cases, it is possible to determine the lengths of bonds and their variation, change in the charge distribution, magnitude of the dipole moment of the aggregates, and frequencies of vibrations of the atoms in molecules during the aggregation, as well as the wave numbers of the bands and their depolarization coefficients.

Therefore, we paid a special attention to the determination of the following molecular components in NG: methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}), by calculating the frequencies of C–H vibrations and determining the spectral region, in which they are located.

In this connection, we have obtained optimized structures of a CH_4 monomer and interacting two CH_4 molecules (Fig. 1).

We calculated the frequencies of C–H vibrations of pure ethane under conditions of an isolated ethane molecule, C–H vibrations of pure propane under the conditions of an isolated propane molecule, and C–H vibrations of pure butane under the conditions of an isolated butane molecule (Figs. 2–4).

The calculations were performed on the basis of the Gaussian 98 W program in the Hartree–Fock approximation with a basic set of Gaussian functions RHF 6–31G (d, p) [10].

The results of calculations are as follows. For a monomeric methane molecule, the calculations gave the same length of all C–H bonds – 1.084 Å. The charges of all hydrogen atoms also turned out to be the same +0.1146, while the charge of the carbon atom is –0.4585 (in units of electron charge). The frequency of the fully symmetric vibration is 3168.8 cm^{-1} . In the Gaussian 98W RHF 6–31G (d, p) approximation, the calculated frequencies differ from the experimental ones: for stretching vibrations by ~10–15%, for deformation vibrations by ~30%. To match the experiment, we should enter a scaling factor, which is defined as $Sf = \frac{\nu_{\text{exp}}}{\nu_{\text{calc}}}$. For the

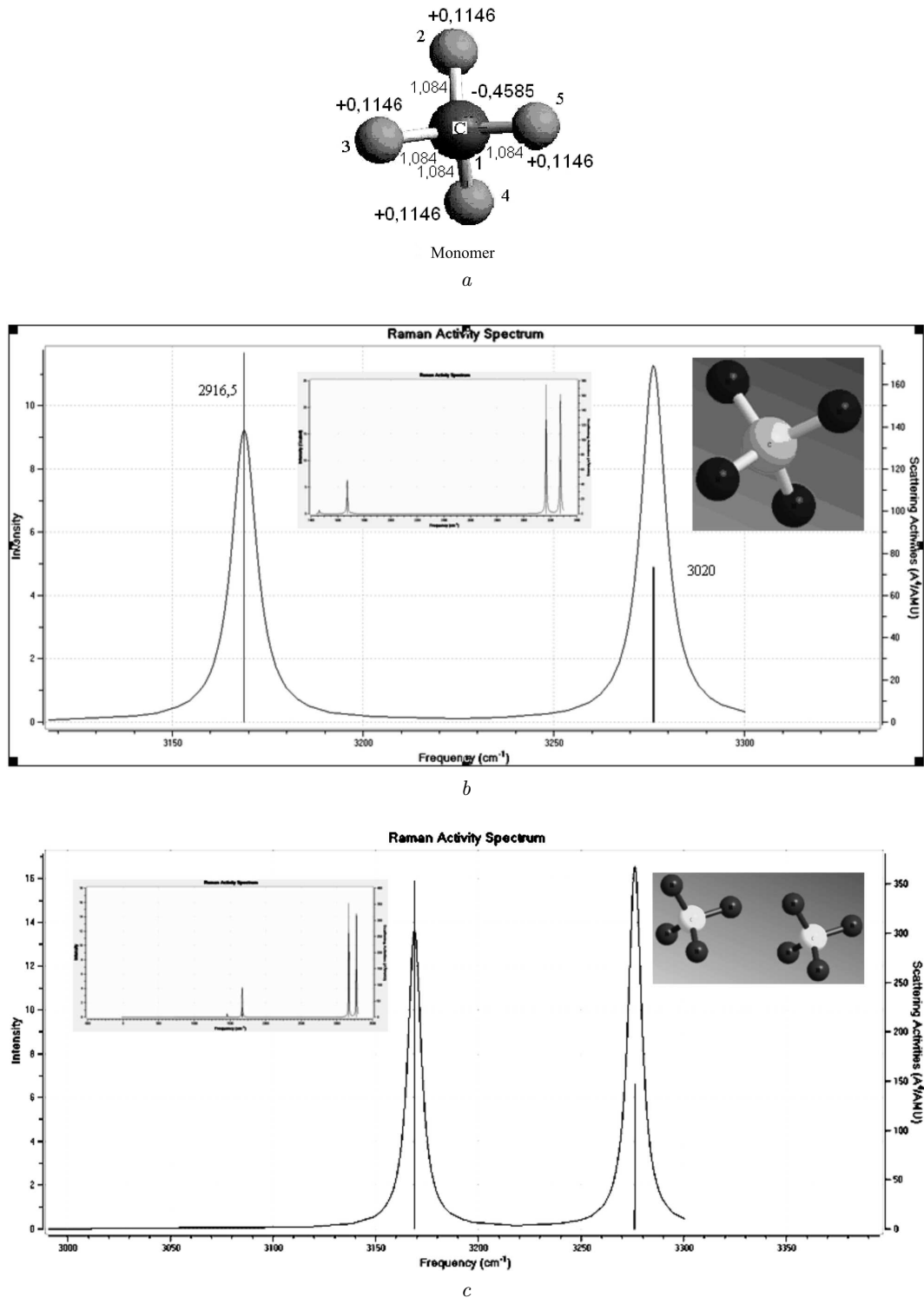


Fig. 1. Methane monomer structure (a), calculated Raman spectra of isolated methane molecules (b) and calculated Raman spectra for a methane dimer (c)

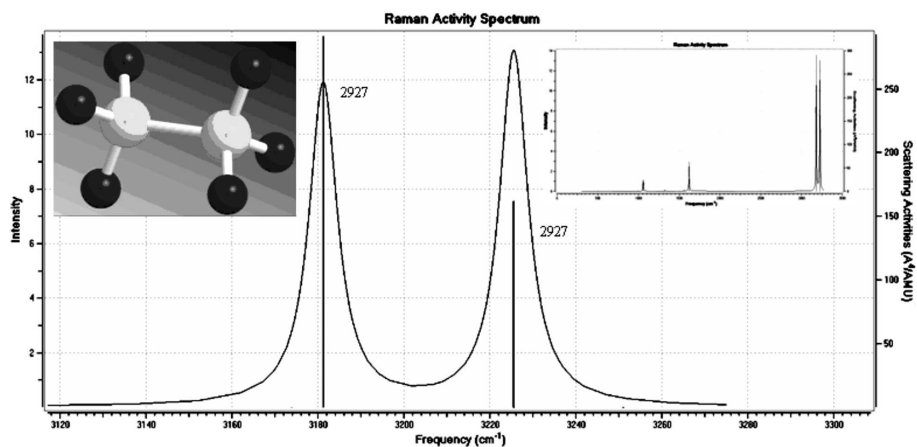


Fig. 2. Calculated Raman spectra of C–H vibrations of pure ethane under the conditions of an isolated ethane molecule

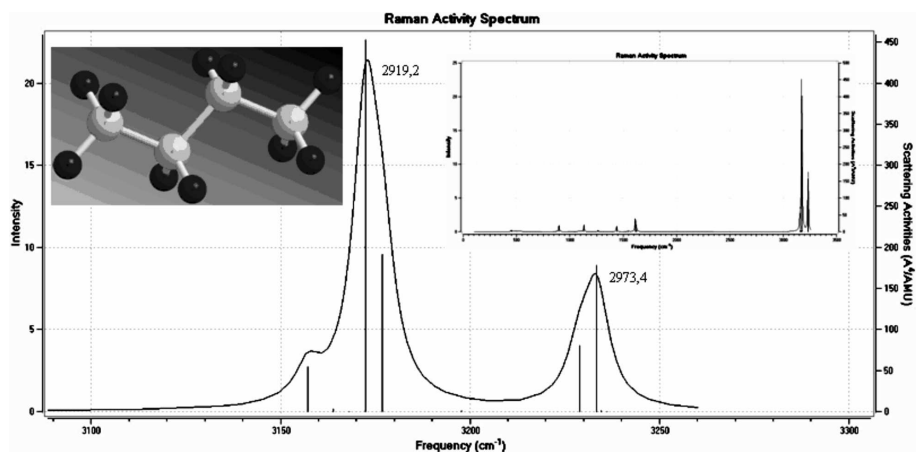


Fig. 3. Calculated Raman spectra of C–H vibrations of pure propane under conditions of an isolated propane molecule

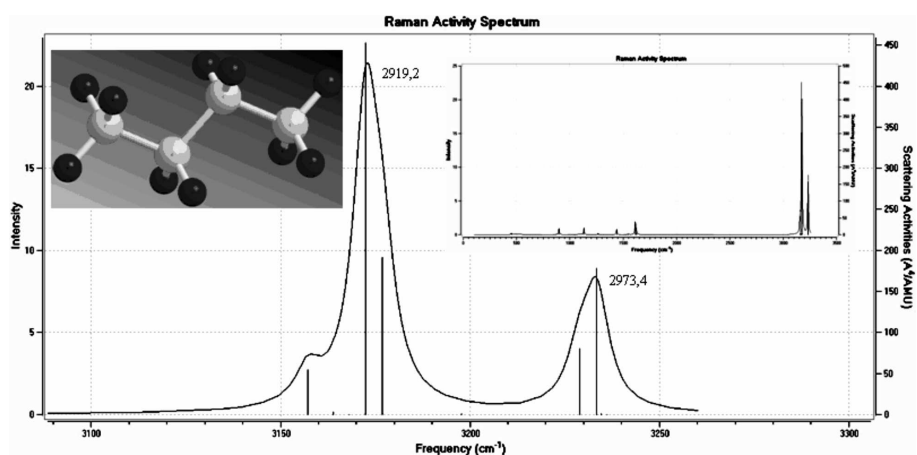


Fig. 4. Calculated Raman spectra of C–H vibrations of pure butane under the conditions of an isolated butane molecule

case of methane ($S_f = \frac{2916.5}{3168.8} = 0.92$, S_f – scaled factor, 2916.5 – the experimental frequency, 3168.8 – calculated value). The band contains only an isotropic part, so the depolarization coefficient is zero. The dipole moment, as it should be assumed, is zero.

3. Conclusion

The results of calculations confirm that the frequencies of C–H vibration of heavy hydrocarbons (ethane, propane, and butane) do lie in the spectral range of 2500–3500 cm^{-1} of combinational frequencies. The most intense Raman spectrum is observed in the region of combinational frequencies 2500–3500 cm^{-1} , where the system of vibrational bands is located [9]. The obtained results are in a good agreement with our previous calculations [9, 11, 12] and with results of other authors, who investigated low-molecular hydrocarbons [13, 14]. In this complex system of bands, a very intense Q-branch of the vibrational band $\nu_1(A_1)$ of methane with a frequency $\nu_1 = 2916.5 \text{ cm}^{-1}$ is singled out. The band $\nu_1(A_1)$ in the Raman spectrum of methane is the first band of the RS, the rotational structure of which has been resolved earlier [11, 12]. However, most of the experimental and theoretical studies are related to the triply degenerate IR bands, which have been studied for many years.

The results of theoretical and experimental studies show that carrying out the quantitative and qualitative analyses to determine the molecular components of NG, as well as the content of associated gases and liquids in low-molecular hydrocarbons, requires studies from the lower-frequency part of the Raman spectrum, in which the vibrational bands of the C–C bonds of hydrocarbon components of the natural gas are located.

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РОЗРАХОВАНІ СПЕКТРИ ВУГЛЕВОДНІВ,
ЩО ВХОДЯТЬ ДО СКЛАДУ ПРИРОДНОГО ГАЗУ

Резюме

У статті представлені розраховані спектри вуглеводнів, що входять до складу природного газу, та їх порівняння з ек-

периментальними даними. Результати експериментальних досліджень природного газу показують, що область валентних коливань зв'язків С–Н вуглеводнів, незважаючи на дуже високий рівень сигналу комбінаційного розсіяння, є мало корисною для кількісного та якісного аналізу. Це зумовлено тим фактом, що структура смуг у цій спектральній області дуже складна. Крім того, в даному інтервалі частот домінують смуги метану, який є основною складовою природного газу. Слабкі смуги важких вуглеводнів майже неможливо розрізнити на фоні дуже інтенсивних смуг ме-

тану. У зв'язку з цим дуже складно врахувати всі деталі. Таким чином, ми приділили особливу увагу визначенню молекулярних компонент природного газу – метану (CH_4), етану (C_2H_6), пропану (C_3H_8) і бутану (C_4H_{10}) шляхом розрахунку частот їх С–Н коливань і визначення, в якій спектральній області вони розташовані. Результати розрахунків показують, що, дійсно, частоти С–Н коливань важких вуглеводнів (етан, пропан і бутан) розташовані в спектральній області $2500\text{--}3500\text{ см}^{-1}$ спектра комбінаційного розсіяння світла.