

## LASER SENSING OF HIGHER HYDROCARBONS AGAINST THE METHANE BACKGROUND

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*A new express method for determining the total level of higher hydrocarbons against a background of high methane levels is reported. It is based on the sharp qualitative difference of the dependence of the absorption coefficients of methane and the higher hydrocarbons on the pressure of demonstrate the possibility of against a background which exceeds the gaseous medium examined. We demonstrate the possibility of detecting a propane concentration against a background which exceeds it by one hundred times.*

Hydrocarbons other than methane are included in the list of the most dangerous air pollutants<sup>1</sup>. Industrial emissions and motor exhaust gases are the main sources of hydrocarbon pollution. A great number of different types of hydrocarbons can be present in the air simultaneously, and they take part in photochemical reactions with nitrogen and sulphur oxides forming highly toxic smog. Some hydrocarbons have carcinogenic properties. Methane does not undergo photochemical reactions and in high concentrations is dangerous for health. Thus, the possibility of measuring the total content of hydrocarbons other than methane, which are referred to below as the higher hydrocarbons (HHC), is of great practical importance for the environment. This monitoring of HHC's must be operative and continuous to be an effective means of detecting pollution sources. Known methods of HHC determination have various drawbacks such as a long startup time, slow reaction, and the necessity of using consumable reactants.

This paper describes a new method, free of these drawbacks, that was developed to determine the HHC sum against the background of a high methane level. The method is based on the application of the sharp qualitative difference among the dependences of the absorption coefficients  $k$  for He-Ne laser radiation ( $\lambda = 3.3922 \mu\text{m}$ ) of methane and the higher hydrocarbons on the pressure  $P$  of the gaseous medium being analyzed over the range  $0-10^5$  Pa ( $k = l^{-1} \ln [I_{\text{in}}/I_{\text{out}}]$ , where  $I_{\text{in}}$  and  $I_{\text{out}}$  are the intensities of the laser radiation upon entrance to and exit from the gaseous medium, respectively, and  $l$  is the radiation path length in the medium).

As is well known, the methane absorption spectrum for  $P \leq 10^5$  Pa is resolved and the laser line  $\lambda$  is in the central part of one of the methane absorption lines ( $F2(1)P7$ ) within the interval of its Doppler width. This results in the nonlinear form of the dependence  $k_m(p)$ . The known experimental dependences of  $k_m(p)$  obtained in Refs. 3 and 4, are shown in Fig. 1. As can be seen, these dependences

differ substantially. Since such uncertainty in the knowledge of  $k_m(p)$  makes realization of this method difficult, we calculated it and measured it experimentally for dilute methane-air mixtures in order to make the dependence  $k_m(p)$  more precise. The calculations were based on superhigh-resolution spectroscopy data.<sup>5,6</sup> Following Refs. 7 and 8, the laser transition frequency  $\nu_L$  was assumed to be equal to

$$\nu_L = 2947.9121 \text{ cm}^{-1} + 0.53 \times 10^{-7} (p_L - 705) \text{ cm}^{-1} \quad (1)$$

where  $p_L$  is the pressure of the helium-neon mixture inside the laser, in Pa.

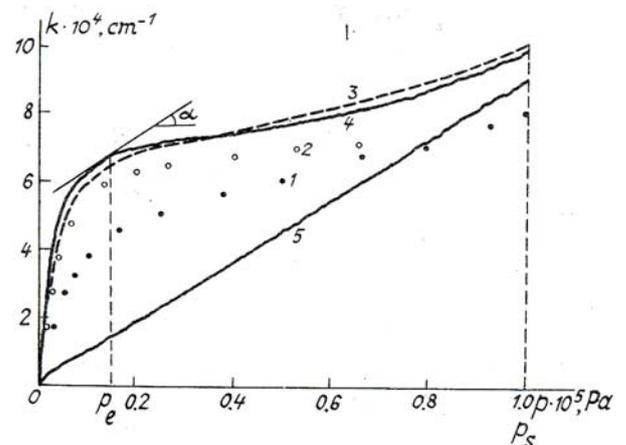


FIG. 1. Dependence of the absorption coefficients of mixtures of methane (curves 1 through 4) and propane (curve 5) with air on the total pressure of the mixture for methane and propane concentration equal to  $10^2$  ppm and radiation wavelength  $\lambda_L = 3.3922 \mu\text{m}$ : curves 1 and 2 represent the experimental data for methane in Refs. 3 and 4; curves 3 and 4 represent the calculated values and the experimental data for methane from the present paper; curve 5 represents the experimental data for propane from the present paper.

Six transition lines  $F1(1)$ ,  $E(0)$ ,  $A2(Q)$ ,  $F2(0)$ ,  $F1(0)$ , and  $F2(1)$  of the methane band P7 were taken into account in the calculations. The absorption due to the first five lines is calculated by the Lorentz theory because their detuning from  $\lambda_L$  exceeds the Doppler bandwidth of methane by many times. The absorption due to the  $F2(1)$  line was calculated by the Voigt theory. The dependence of the shift of the central frequency of the  $F2(1)$  line on the pressure  $p$  in Ref. 4 was taken into account, which is particularly important in calculating  $k_m$  within the range  $p = 5\text{--}30$  kPa.

$$\varphi^{F2(1)} = 2947.9121 \text{ cm}^{-1} - 1.02 \times 10^{-7} p \text{ cm}^{-1}, \quad (2)$$

where  $p$  is the pressure of the methane–air mixture in Pa. The dependence of  $k_m$  on  $p$  for  $p_L = 200$  Pa (the typical value of  $p_L$  for the helium–neon laser used in the analyzer described below) which we calculated is shown in Fig. 1 (curve 3).

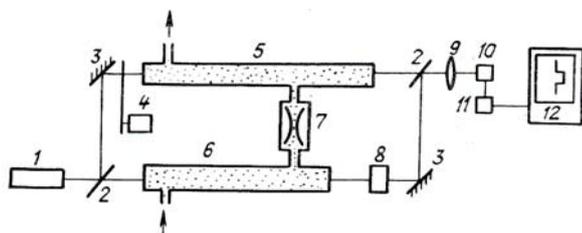


FIG. 2. Diagram of the experimental setup used to determine the dependences of the absorption coefficient of the hydrocarbon–air mixtures on the total pressure of the mixture for radiation wavelength  $\lambda_L = 3.3922 \mu\text{m}$ : 1 is the He-Ne laser; 2 is shutter; 3 is the two-way mirror; 4 is the cell filled with the hydrocarbon–air mixture; 5 is the electric pressure sensor; 6 is the lens; 7 and 8 are the photodetectors; 9 is the differential amplifier; 10 is the X–Y recorder.

We see that the calculated curve 3 lies slightly above the dependence  $k_m(p)$  obtained in Ref. 4 and substantially above the dependence  $k_m(p)$  obtained in Ref. 3. The experimental dependence of  $k_m(p)$  was obtained by means of the two-beam photometric setup shown in Fig. 2. A single-mode He-Ne laser 1 with a system for automatic tuning of the generation frequency to the center of the transition  $\lambda_L$  was used, ensuring a stability of laser output near 0.5%/hour. Photodetector 7 records a signal proportional to the radiation intensity  $I_{in}$  at the input of the cell 4 ( $l = 50$  cm), photodetector 8 records a signal proportional to  $I_{out}$ . The difference signal  $\Delta I = I_{in} - I_{out}$  is applied to Y input of the X–Y recorder 10 by means of a differential amplifier with a phase detector circuit. The sensitivity of the measuring circuit to variations of  $\Delta I/I_{in}$  corresponded to  $\Delta I/I_{in} \leq 5 \times 10^{-3}$ . Since hydrocarbon–air mixtures with concentrations of about  $10^2$  ppm were used, the portion of the laser radiation flux absorbed in the cell

4 did not exceed  $\Delta I/I_{in} < 0.1$ . This makes it possible to set  $k = \Delta I/(I_{in} \times l)$  and  $y \sim k$ . The signal from the sensor 5, proportional to the pressure  $p$  in the cavity 4, was applied to X input. The cavity was evacuated before the start of measurements and was then steadily filled over the course of 10–15 minutes with the hydrocarbon-containing mixture. During the process of filling the cell, a record was made of the pressure dependence of  $k$ . The experimentally determined pressure dependence of  $k_m$  obtained in this way is shown in Fig. 1 (curve 4). As can be seen from the figure, the experimental and calculated curves 3 and 4 agree well. These refined dependences were used to calculate the HHC level against the methane background.

Unlike methane the absorption spectra of heavier hydrocarbons in the vicinity of  $\lambda_L$  consist of a large number of lines which overlap even at small pressures and form a continuous spectrum. In this case we can expect a linear dependence of  $k(p)$ :

$$k_{\text{HHC}} = \kappa_{\text{HHC}} C_{\text{HHC}} p \quad (3)$$

where  $\kappa_{\text{HHC}}$  is a constant specific for each HHC which does not depend on  $p$ ;  $C_{\text{HHC}}$  is the relative concentration of the HHC in the sample. The linear character of the dependence of  $k_{\text{HHC}}$  on  $p$  is important for the realization of the method. The following simplified consideration will explain it. Suppose that in the vicinity of the laser line  $\lambda_L$  the absorption spectrum of the HHC is determined by a continuum of overlapping lines with the same intensity  $S$  and collision width  $\gamma_{\text{col}}$ , and distributed with constant density  $\rho$  per unit frequency interval  $\nu$ . At the laser radiation frequency  $\nu_L$  the absorption per molecule at one of the HHC lines centered at  $\nu'$  is given by

$$\kappa = \frac{2S}{\pi} \frac{\gamma_{\text{col}}}{\gamma_{\text{col}}^2 + (\nu_L - \nu')^2} \quad (4)$$

The absorption due to the line continuum extending over the region  $\nu_L \pm \Delta$  with  $\Delta \gg \gamma_{\text{col}}$  (which is the case for HHC absorption bands) can be defined as

$$\kappa_{\text{HHC}} = \int_{-\Delta}^{\Delta} \rho \kappa(\nu') d\nu' \approx \frac{2\rho S}{\pi} \int_0^{\infty} \frac{\gamma_{\text{col}} d\nu'}{\gamma_{\text{col}}^2 + (\nu_L - \nu')^2} \approx \rho S \quad (5)$$

If the dependence of  $\kappa$  as given by Eq. (4) on  $p$  is only through  $\gamma_{\text{col}}$ , then  $\kappa_{\text{HHC}}$  as given by Eq. (5) is independent of  $p$ . Hence Eq. (3) follows. In order of magnitude  $\kappa_{\text{HHC}}$  is equal to  $10\text{--}4 \sin^{-1} \text{Pa}^{-1}$  (Refs. 4, 9, and 10).

The linear character of the dependence of  $k_{\text{HHC}}$  on  $p$ , as far as we know has not been proven experimentally. Having examined the dependences  $k(p)$  (by the above method) for ethane, propane, butane, isobutane, pentane, hexane, and vapors of kerosene, petrol, and ethyl alcohol, we have in fact demonstrated the linear character of these

dependences. The experimental dependence  $k(p)$  for propane is shown in Fig. 1 (curve 5) as an illustration. We realized the following method for the analysis of the total HHC content against the methane background, based on the qualitative difference of the  $k_m(p)$  and  $k_{\text{HHC}}(p)$  dependences. Radiation from laser 1 with wavelength  $\lambda_L = 3.3922 \mu\text{m}$  (Fig. 3) enters through the input of the two-beam optical arrangement. The data which are read out at the output are proportional to the difference  $\Delta I$  of the absorption of the two laser radiation fluxes which have passed through the long S and the short cell 6. The gas sample inside the cells is maintained at different pressures in the two cells ( $p_1$  and  $p_s$ , respectively). As a result of the highly nonlinear dependence of  $k_m(p)$ , the ratio of the pressures  $p_1$  and  $p_s$  and also the ratio of the lengths of the cells  $l_1$  and  $l_s$  can be so assigned that the absorption due to methane inside both cells will be the same:

$$\frac{\Delta I}{I_{1m}} = k_m(p_s) l_s - k_m(p_1) l_1 = 0 \quad (6)$$

At the same time, the absorption due to the HHC in both cells will differ, owing to the linear character of the dependence of  $k_{\text{HHC}}$  on  $p$

$$\frac{\Delta I_{\text{HHC}}}{I_{1m}} = (p_s l_s - p_1 l_1) \kappa_{\text{HHC}} c_{\text{HHC}} \neq 0 \quad (7)$$

Thus, this optical scheme does not react to methane and allows one to determine the HHC content against its background. It is easy to find the ratios  $l_s/l_1$  and  $p_s/p_1$  for which the signal  $\Delta I_{\text{HHC}}$  will be at its maximum value, provided that Eq. (6) is satisfied. We determine  $p$  and  $I$  on the basis of  $p_1$  and  $l_s$ , which we assume to be preset. Taking Eq. (6) into account, we find from Eq. (7) that the maximum value of  $\Delta I_{\text{HHC}}$  is achieved under the condition

$$\left. \frac{\partial k_m(p)}{\partial p} \right|_{p=p_1} = \frac{k_m(p_s)}{p_s} \quad (8)$$

We can see from Fig. 1 and formula (8) that when  $p = p_g$  the slope  $\text{tg} \alpha$  of the tangent to the curve  $k_m(p)$  is equal to the slope of a straight line drawn from the origin to the point  $(p_s, k_m(p_s))$ . Choosing  $p_s = 10^5 \text{ Pa}$  as the most convenient value, we determined from Eqs. (6) and (8) that  $p_1/p_s = 0.16$  and  $l_s/l_1 = 0.61$ . Given these values of  $p_s, p_1$ , and  $l_s/l_1$ , we find from Eq. (7) that

$$\frac{\Delta I_{\text{HHC}}}{I_{1m}} \approx 0.5 \kappa_{\text{HHC}} l_1 c_{\text{HHC}} \quad (9)$$

Hence, the expression for determining  $C_{\text{HHC}}$  is as follows:

$$C_{\text{HHC}} = \frac{2 \Delta I_{\text{HHC}} / I_{1m}}{\kappa_{\text{HHC}} l_1} \quad (10)$$

The above method of total HHC content determination against a methane background was

experimentally confirmed by control analyses carried out using a setup with  $l_g = 0.9 \text{ m}$  (Fig. 3) and a certified mixture of methane and propane in the ratio  $C_m/C_{\text{HHC}} = 13$ . The experimental value of  $C_m/C_{\text{HHC}}$  obtained by the above-described method was equal to  $13 \pm 1$ , which coincides with its certified value within the limits of an 8% relative error.

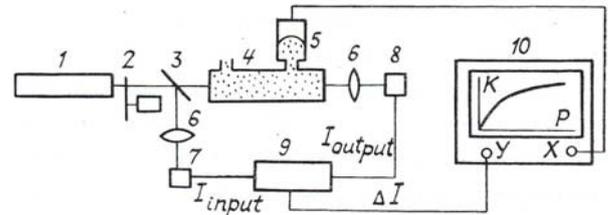


FIG. 3. Diagram of the experimental setup used to determine the total higher hydrocarbon content against the methane background: 1 is the He-Ne laser with  $\lambda_L = 3.3922 \mu\text{m}$ ; 2 is the two-way mirror; 3 is the mirror; 4 is the shutter; 5 and 6 are the cells; 7 is the pneumoresistor; 8 is the attenuator; 9 is the lens; 10 is the photodetector; 11 is the amplifier; 12 is the recording voltmeter.

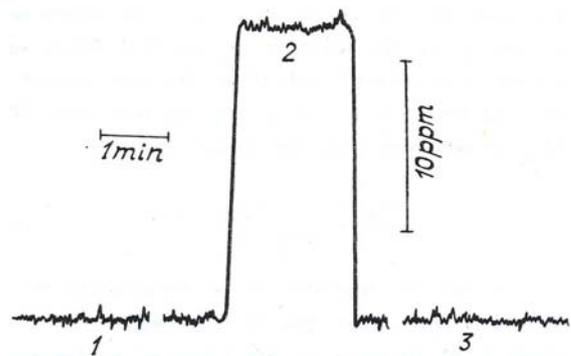


FIG. 4. Readings of the HHC sum analyzer. Curve 1 was obtained when only methane was present in the hydrocarbon-air mixture ( $C_m = 5 \times 10^2 \text{ ppm}$ ). Curve 2 was obtained for a mixture of methane and propane with air ( $C_m = 2.2 \times 10^2 \text{ ppm}$ ,  $C_{pr} = 1.7 \times 10^1 \text{ ppm}$ ). Curve 3 is the analyzer baseline.

Figure 4 shows typical analyzer records in the cases when the sample contained only methane (curve 1), a mixture of methane and propane (curve 2), and when hydrocarbons were absent in the sample (curve 3). As can be seen from Fig. 4, our analyzer concentrations near  $5 \times 10^2 \text{ ppm}$ . The sensitivity to propane is determined by the stability of the baseline of the analyzer. On the basis of the noise level observed while recording the signal and the fact that the methane signal did not exceed this noise level for  $C_m$  as high as  $5 \times 10^2 \text{ ppm}$ , we conclude that the method described here enables one to determine higher hydrocarbon concentrations in mixtures containing methane with ratios  $C_m/C_{\text{HHC}} \leq 100$ , i.e., against a background of overwhelming methane content.

## REFERENCES

1. Yu.S. Dugov, A.Yu. Belikov, G.A. D'yakova, et al., *Methods of Air Pollution Analysis* (Khimiya, Moscow, 1984).
2. Yu.N. Medyanovskii, V.A. Barykina, A.I. Firger, et al., *Instrumentation for Analytical Monitoring of the Atmosphere and of Industrial Discharges* (Kiev: VNIIP, **37** 1985).
3. B.N. Edward and D.E. Burch, *J. Opt. Soc. Amer.*, **55**, No. 2, 174 (1965).
4. A.B. Antipov, V.A. Kapitanov, Yu.N. Ponomarev, et al., *The Opto-Acoustic Method in Laser Spectroscopy of Molecular Gases* (Nauka, Novosibirsk, 1984).
5. M. Dang-Nhu, A.S. Pine, and A.G. Robiette, *J. Mol. Spectrosc.*, **77**, 57–68 (1979).
6. L.S. Rothman, *Appl. Opt.*, **20**, No. 5, 791–795 (1981).
7. I.P. Konovalov, A.I. Popov, and E.D. Protsenko, *Opt. Spectrosc.*, **33**, No. 1, 15–21 (1972).
8. N.B. Koshelyavskii, V.M. Tatarenkov, and A.N. Titov, *Kvant. Elektronika*, **3**, No. 2, 417–424 (1976).
9. D.N. Jaynes and B.H. Beam, *Appl. Opt.*, **8**, No. 8, 1741–1742 (1969).
10. V.A. Balakin, A.I. Popov, and A.V. Sadchikhin, *The Fifth All-Union Symposium on High and Super high-Resolution Molecular Spectroscopy* (Institute of Atmospheric Optics, Siberian Branch, USSR Academy of Sciences, Tomsk, 1980).