LONG–PATH ABSORPTION IR–LASER–BASED GAS ANALYZER OF THE ATMOSPHERE WITH A DIFFERENCE FREQUENCY GENERATOR

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In this paper we present a description of the laser gas analyzer operating within the spectral range from 2.7 *to* 4.5 μm *with the resolution of* 0.2 cm^{-1}. *The gas analyzer is comprised of IR laser generator, transceiving system, control system, and horizontal path* 0.1–1 km *long equipped with mirror reflector. The continuous wavelengths tuning has been performed by mixing second harmonic of* Nd^{3+}:YAG *laser radiation with the radiation from a sinchronously pumped dye laser in a nonlinear optical crystal (KDP). The concentration sensitivity of the gas analyzer is at the level of* 0.1 ppm *(for methane on a* 100 m *long path). By way of example the path measurements of absorption spectra of methane and water vapor demonstrate the possibility of analyzing the minor atmospheric constituents at the background level of concentration with the use of the instrumentation proposed.*

1. INTRODUCTION

Carbon dioxide and methane are the main atmospheric gases responsible for the greenhouse effect. Their total contribution to the greenhouse effect is as much as 70%, 20% of which is accounted for by the methane. Russia has associated with the UNO Convection on limitations on the greenhouse gases release which provides the control over the emission of greenhouse gases, first of all, CO$_2$ and light hydrocarbons. In this connection, the development of instrumentation for the control and detection of sources of these gases is an urgent problem. Such instrumentation would allow the control at the level of individual industrial enterprises, gas storages, etc. to be exerted by means of measuring the CO$_2$ and CH$_4$ concentration under the same conditions in the surface layer of the atmosphere along horizontal paths several kilometers long.

One of the most sensitive laser methods for detecting gaseous atmospheric pollutants, which allows the determination of absolute concentration of a pollutant, is the DIAL method,[1] based on double frequency sensing. When constructing efficient and universal, with respect to gases to be detected, DIAL systems, preferential are continuously tunable sources of sounding radiation.[2] At present, practically the unique possibility to obtain a continuously tunable radiation with the energy sufficient for remote sensing in the 3–5 μm wavelength range is the use of nonlinear frequency conversion in parametric light generators (PLGs) and generators of difference frequency (GDFs).

In the systems with typical characteristics of photoreceiving device (InSb, $\Delta\lambda = 3{-}5$ μm, $D^* = 10^{10}{-}10^{11}$ cm·Hz$^{1/2}$·W^{-1}) and size of receiving optics ($d = 0.3{-}0.5$ m) the energy of radiation needed to record a signal from paths several kilometers long should be 0.1 mJ for a long–path absorption gas analyzer, whereas for lidar measurements (backscattering from atmospheric aerosol) it should be about 0.1 J. To provide the maximum concentration sensitivity of a gas analyzer, the linewidth of sounding radiation should be comparable with the absorption linewidth of the majority of atmospheric gases, i.e. about 0.1 cm^{-1}.

If the nomenclature of atmospheric pollutants to be detected is reduced to a set of polyatomic gases with wide absorption bands (10–100 cm^{-1}), then it is possible to use the broadband radiation of PLG with power sufficient for sensing both along a path and in the lidar mode.

When PLG is used, the radiation linewidth can be decreased from 10 to 0.1 cm^{-1} by introducing dispersion elements (diffraction grating, Fabry–Perot (FP) etalon) into the resonator but with simultaneous decrease in energy by more than an order of magnitude.[3] As a rule, the record spectral characteristics are achieved at simultaneous decrease in the mean power or narrowing the tuning range. Thus, in Ref. 4 the linewidth of the radiation from GDF being equal to $5\cdot10^{-4}$ cm^{-1} was obtained at the output power of 1 μW in the tuning range 1 cm^{-1} wide that is insufficient for a long–path absorption gas analyzer of the atmospheric trace gases.

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In this paper we describe a laser gas analyzer operating in the spectral range of 2.7–4.5 μm, where the strong characteristic absorption lines of methane and other light hydrocarbons – alkanes, CO_2, as well as of such atmospheric gases as H_2CO, HCl, SO_2 lie, and present the results of path measurements.

2. OPTICAL ARRANGEMENT OF THE IR EMITTER

Analysis of characteristics of the existing GDFs[5–10] has shown that for creation of a small–size, easily producible, long–path absorption gas analyzer the most suitable is the scheme of frequency mixing of radiation of the second harmonic of a repetitevely pulsed Nd^{3+}:YAG laser and that of a sinchronously pumped dye laser in nonlinear KDP–crystal[10] (NC). Optical scheme of a tunable source of IR radiation – GDF – is shown in Fig. 1.

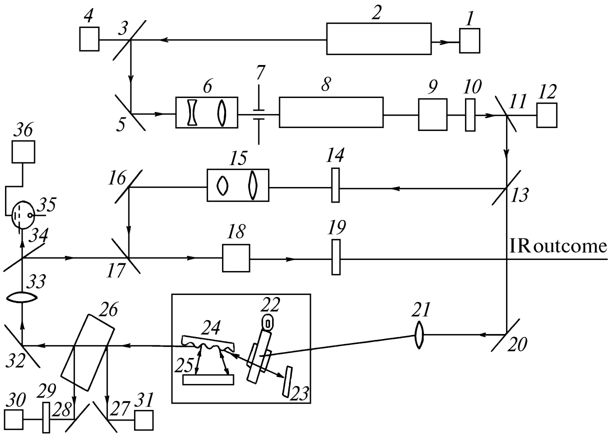

FIG. 1. Optical arrangement of a tunable generator of IR radiation.

Master oscillator *2*, operating in a single–mode regime, was assembled on the basis of a quantron with Nd^{3+}:YAG active element 3 mm in diameter and 65 mm long. Q switching is done using a passive Q–switch of Cr^{+3}:YAG crystal with the initial transmittance $T = 0.1$. For effective selection of TEM_{00}–mode, a diaphragm was introduced into the resonator. Radiation from the master oscillator had vertical polarization and energy of 15–20 mJ, the mean value of which was measured with IMO–2N *1*. With the help of the beam–folding mirrors *3* and *5*, the radiation was directed to the telescope *6*, where it was expanded up to the diameter of 5 mm, and through the diaphragm *7* 4 mm in diameter it enters the optical amplifier *8* (d= 8 mm and l = 100 mm). On amplification, the energy per pulse reaches 120–150 mJ at a pulse repetition frequency of 2 Hz.

Conversion into the second harmonic occured in a KDP–crystal *9* with 20% efficiency and, having passed through the filter *10*, cutting out the radiation with λ = 1.06 μm, the second harmonic (SH) radiation is directed with the mirror *11* onto the splitting plate *13*. On reflection from the plate *13*, the beam (65%), having passed through the $\lambda/2$ phase plate *14*, is narrowed with a telescope *15* and directed with the beam–folding *16* and dichroic *17* mirrors onto the KDP–crystal *18* of GDF. The beam diameter on the front side of the KDP–crystal is 1.5 mm.

The SH radiation, passed through the splitting plate *13* (35%), pumps a tunable dye laser (DL). Pumping radiation, having passed the mirror *20*, is focused with the lens *21* onto the cell *22* of DL. The cavity is formed of the mirrors *23*, *25*, and a diffraction grating*4* (2400 *2* grooves/mm) operating in the almost grazing incidence mode within the first diffraction order. The frequency tuning of DL is performed by rotating the mirror *25* using special scanning drive. Radiation escapes the cavity via the zeroth diffraction order. The tuning range of DL is 0.625–0.645 μm with phenalemine–160 used as a dye, 0.62–0.66 μm with rhodamine B, and 0.54–0.635 μm with rhodamine 6G.

Radiation from DL (energy per pulse about 3–4 mJ) is directed with the beam–folding mirrors *32* and *34* through the dichroic mirror *17* in line with the SH radiation onto the GDF *18*. The lens *33* focuses the DL radiation into the spot 5 mm in diameter on the front side of KDP–crystal. Difference–frequency radiation passed through the filter *19*, cutting out the radiation at λ=1.06, 0.53 μm, and λ_{DL}. The tuning range of IR radiation (using the above dyes) is 2.7–4.5 μm.

In tuning, for relative measurements of the wavelength λ_{DL}, a portion of DL radiation is diverted with the element *26* and the mirror *28* onto a Fabry–Perot etalon *29* with the free dispersion range of 1.5 cm^{-1}. Having passed through it, the radiation is recorded with a photoreceiver *30*. The reference radiation is diverted with the mirror *27* onto the similar photoreceiver *31*. Initially the DL radiation wavelength was referred using the method of photogalvanic spectroscopy.[11] To this end, a portion of DL radiation is directed to the neon thyratron *35*, and the signal is picked off at its loading resistance *36*.

3. FUNCTIONAL DIAGRAM OF THE LASER GAS ANALYZER AND ITS SOFTWARE

Functional block diagram of the gas analyzer is shown in Fig. 2. External triggering of the laser is done from a generator at a frequency of 2 Hz. IR beam, entered the path through the telescope *4* and reflected from the mirror target *7*, is then focused with the lens *8* onto a PbSe photoreceiver *F3*. For spectral calibration of sounding radiation wavelength, the optical cell *6* 0.5 m long was installed in the path of the beam. The design of the bleeding system *5* allowed a pressure of "reference" gas in the cell to be measured within the limits from 10^{-3} to 760 Torr. Portions of radiation before and after the cell are directed onto the photoreceivers $F1$ and $F2$ (made of PbSe), the former served to control the energy per laser pulse, and the latter one to measure it after passing through a "reference" gas. The photoreceivers $F1$, $F2$, and $F3$ are equipped with broadband amplifiers, matched in dynamic range with the inputs of CAMAC compatible ADCs.

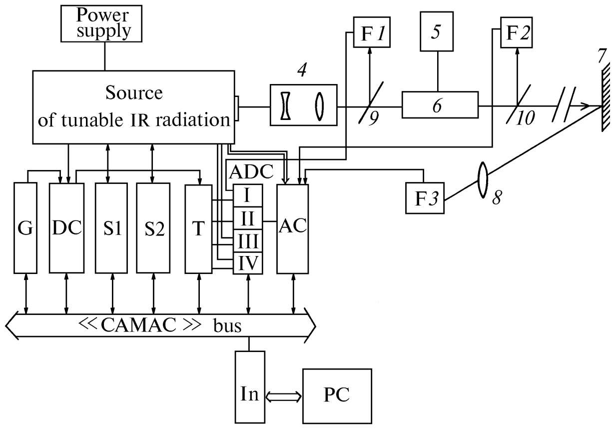

FIG. 2. Functional scheme of the long–path absorption laser computer–aided gas analyzer.

Recording and control units of a CAMAC system were connected with the host computer (IBM PC/AT–286) through the interface CAMAC–PC (In). The recording system is turned on by the synchropulse (SP), which comes from either the IR emitter or the pulse generator (G) (in the mode of measuring ADC pedestals) through a digital commutator (DC) to a timer (T). The latter generated four strobing pulses, variable in duration and lag, for reading the signal amplitude out the corresponding photoreceivers. The duration of strobing pulses can be varied from 50 ns to 2 μs. The signals from the photoreceivers through the analog commutator (CA) come to the four 12–bit ADCs, assembled on the basis of microcircuits of "charge–code" transformers and having the following characteristics: dynamic range $3\cdot10^3$ readouts, pedestal level 150 readouts, mean fluctuations of pedestals 1.5 readouts, sensitivity to charge of 1 pC per readout, time of digitizing no more than 100 μs.

The gas analyzer automation program provides the following modes of the device operation: I –adjustment, II – clamping to the operating spectral range, III – precise calibration by IR absorption spectrum of a reference gas, and IV – path measurements.

In the mode I, signals from photoreceivers (*4*, *12*, *31* in Fig. 1 and *F1* in Fig. 2) are recorded for energy control of IR radiation, master oscillator, second harmonic, and DL. Recorded in the mode II are signals from photoreceivers (*30* and *31* in Fig. 1) for interferogram recording and an amplified signal from thyratron. In the modes III and IV, signals from photoreceivers (*30* and *31* in Fig. 1) and signals from IR photoreceivers *F1* (A_0) and *F2* (A_1) or *F3* (A_1) (in path measurements) are recorded simultaneously. In all modes, the program operates in the interactive mode. The program provided both automated and interactive control over the scanning of IR radiation frequency (with the control of its current value from the DL radiation interferogram), recording, accumulation, and displaying of the experimental spectra.

The tuning of DL radiation wavelength and angular synchronism of GDF by rotating the KDP–crystal is made by stepping motors (S1 and S2 in Fig. 2), which are controlled with the help of CAMAC modules according to computer program.

4. EXPERIMENTAL RESULTS. GAS ANALYZER CALIBRATION

Initially, to clamp the operating wavelength range, the DL radiation wavelength is measured by the method of photogalvanic spectroscopy,[11] then the difference frequency of emitted IR radiation is calculated. A more precise frequency calibration is done by measuring the absorption spectrum of a reference gas (methane) in an optical cell with the length $L = 0.5$ m and clamping to experimental spectral data.[12] In so doing, the accuracy of the set of IR radiation wavelength in the tuning band is 0.02 cm^{-1}.

Shown in Fig. 3 are the portion of the reference gas, methane, absorption spectrum in the region of *P*–, *Q*–, and *R*–branches, that agrees well with the calculated spectrum. Shown in the fragment is the recorded profile of *R*(0) line, used for determining spectral linewidth of GDF radiation. The spectral linewidth of IR radiation from the spectrometer, found from the analysis of the line profile recorded, is 0.2 cm^{-1}.

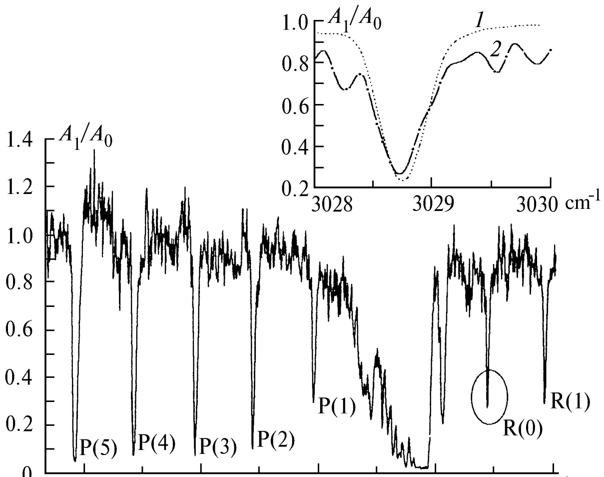

FIG. 3. A portion of the methane transmission spectrum recorded at total pressure of 75 Torr, CH_4 *partial pressure of* 5 Torr, $t = 17$°C, $L = 0.5$ m. *Shown in the fragment is the region enclosed in a circle, demonstrating the profile of absorption* $R(0)$ *line: calculational results for* $\gamma = 0.2$ cm^{-1} (*1*) *and experiment* (*2*).

5. PATH MEASUREMENTS

Once the gas analyzer is calibrated under laboratory conditions, the path measurements of air absorption in the surface layer can be conducted. The path makes up the horizontal segment of $2L = 25–200$ m length equipped with a mirror reflector. The measurements have been conducted at 2 km from the Shchelkovo underground natural gas storage (Moscow region). The pathlength was chosen to be convenient for adjustment, whereas the reserve in sensitivity of the gas analyzer allowed the measurements to be conducted along a path $2L = 1–2$ km. The adjustment of the path was made with the use of Nd^{+3}:YAG second harmonic radiation, emitted by the gas analyzer in line with sounding IR radiation.

Atmospheric transmission microwindows, optimal for path measurements of the absorption spectrum of a given constituent in the real atmosphere, were determined by the criterion of nonoverlapping with absorption lines of other constituents by calculating the transmission spectrum of the path using spectral line parameters data base HITRAN–92. In particular, when measuring the CH_4 spectra at the background level, the main interfering effect is from water vapor absorption. So, shown in Fig. 4 (upper curve) is a portion of the transmission spectra calculated for the horizontal path of $2L = 150$ m length, at air temperature of 17°C, relative humidity of 70%, and methane concentration of 3 ppm. This spectral region, 2925–2950 cm^{-1}, was chosen because here H_2O and CH_4 absorption lines are overlapped moderately, whereas at $\nu > 2960$ cm^{-1}, CH_4 absorption lines, belonging to P–branch, fall within the range of a very strong H_2O absorption. (We are planning to present a more detailed analysis of the atmospheric transmission microwindows, optimal for CH_4 spectrum recording, in a separate paper).

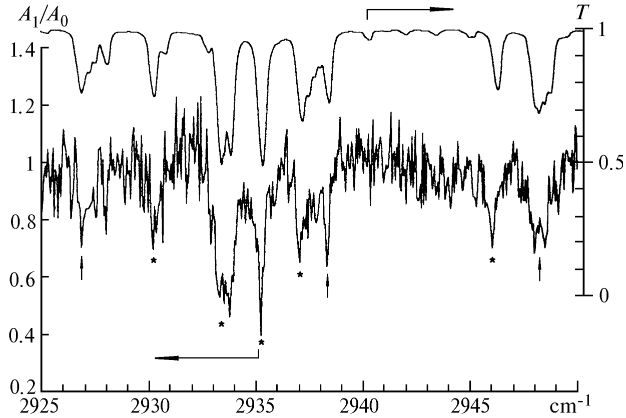

FIG. 4. Fragment of the absorption spectrum calculated for the atmospheric path of $2L = 150$ m, $\gamma = 0.2$ cm^{-1}, $C_{CH_4} = 3$ ppm, $C_{H_2O} = 70\%$, $t = 17.2$°C *(upper curve) and recorded along an atmospheric path of* $2L = 150$ m *(lower curve). Marked by arrows are the methane absorption lines, and by asterisks – the water vapor absorption lines.*

Also shown in Fig. 4 is a fragment of the transmission spectrum, experimentally recorded for a path of $2L = 150$ m (lower curve). Comparing the curves, one can see a good agreement between the experimental and calculated spectra. The measurements conducted gave the value of 3 ppm for the methane concentration in the atmosphere, that exceeds the background value for the troposphere, equal to 1.4 ppm. This difference is likely connected with the path position near the underground gas storage, being the source of CH_4 emission into the atmosphere.

It is interesting to assess the laser gas analyzer capability to detect not only H_2O and CH_4 in air, but other atmospheric constituents, first of all, those which possess broad molecular absorption bands in the range of its radiation wavelength tuning. Absorption cross section of light hydrocarbons – alkanes C_nH_{2n+2} increases with n in the region of 3.4 μm. In this connection, in spite of a sharp broadening of the absorption bands for $n \geq 3$, the concentration sensitivity of the gas analyzer is likely to hold high in path measurements of hydrocarbons heavier than methane as well.

Thus, shown in Fig. 5 is a portion of absorption spectrum of a propane and butane mixture (C_3H_8:C_4H_{10} = 1:1) in a cell ($L = 0.5$ m) at a pressure of 0.2 Torr, that corresponds to the concentration of 1.3 ppm in air for a 100 m long path. The maximum of the absorption band lies in the region of strong water vapor absorption, that is why the path measurements of hydrocarbon concentrations have low accuracy here. The region about $\lambda \approx 3.4$ μm is preferable for sensing, because H_2O absorption here is weak, whereas the absorption by hydrocarbons remains to be sufficiently strong. It can be seen from the spectrum that, in the case of a DIAL technique with the sensing wavelengths of 3.3 and 3.4 μm, the absorption cross section ratio is more than 10^3, that provides the concentration sensitivity of 0.01 ppm for a 1 km long path.

FIG. 5. Fragment of the transmission spectrum of C_3H_8:C_4H_{10} = 1:1 *mixture recorded at total pressure of* 0.2 Torr, $t = 17$°C, $L = 0.5$ m.

CONCLUSIONS

1. The computer–aided laser spectrometer with spectral resolution of 0.2 cm^{-1} tunable in the range of 2.7–4.5 μm and having concentration sensitivity (at the methane $P(6)$–$P(8)$ lines and a path of $2L = 150$ m) not worse than 1 ppm has been developed.

2. On example of path measurements of CH_4 and H_2O absorption spectra, the feasibility has been demonstrated to conduct the laser gas analysis of atmospheric constituents at the background level as well as the monitoring of gaseous emissions of industrial enterprises into the atmosphere.

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