REMOTE SENSING OF ATMOSPHERE, HYDROSPHERE, AND UNDERLYING SURFACE

Remote Detector of Hazardous Substances Based on a Tunable ¹³C¹⁶O₂ Laser

B. G. Ageev*, A. V. Klimkin, A. N. Kuryak, K. O. Osipov, and Yu. N. Ponomarev*****

V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, Tomsk, 634055 Russia

e-mail: ageev@asd.iao.ru **e-mail: tosha@asd.iao.ru *e-mail: yupon@iao.ru* Received January 21, 2017

Abstract—A description of the developed prototype of a remote detector of hazardous substance vapors based on a tunable ${}^{13}C^{16}\hat{O}_2$ laser is given. Results of test measurements of laser radiation transmission of organic liquid vapors (acetone, ammonia, ethanol, gasoline) are presented. The remote detection of acetone and ammonia vapors at distances up to 100 m is experimentally implemented.

Keywords: remote detection, ${}^{13}C^{16}O_2$ laser, hazardous substances **DOI:** 10.1134/S1024856017040029

INTRODUCTION

The interest in laser methods for detecting hazardous and harmful admixtures in the open atmosphere has been increasing in recent years [1]. This is conditioned by the invention of high power commercial lasers wavelength-tunable in different spectral ranges, new highly sensitive fast-operating receivers, and improvement of spectroscopic and mathematical methods for processing measurement results. The laser detectors allow the real-time solution of prime-importance problems of remote detection of hazardous substances in the atmosphere [2].

The laser methods for detection and identification of inorganic and organic compounds, including vapors of explosive materials (EM) and other hazardous substances, are based on characteristics of their electron-vibration-rotational spectra [3, 4]. The knowledge of these spectra in a wide range provides for the choice of optimal wavelengths of laser radiation sources for a particular substance.

This paper describes a laboratory prototype of the remote detector of gases and vapors of hazardous substances based on a frequency-pulse tunable ${}^{13}C^{16}O_2$ laser. The use of its lasing lines allows us to avoid the influence of absorption by atmospheric $CO₂$ [5]. In addition, intense absorption lines of a series of toxic gases and vapors of toxic substances, like NH_3 , O_3 , ClO, SO_2 , HNO_3 , and $HCOOH$ [6], and vapors of certain substitute explosives (SE), for example, peroxide compounds of triacetone triperoxide, fall in the laser generation range [7]. As a component of such SE, acetone (C_3H_6O) is used. It is released during decom-

position of such SEs, and, consequently, can be one of their markers.

The paper also presents discrete transmission spectra of vapors of certain organic liquids (ammonia, acetone, ethanol, and gasoline) measured at wavelengths of the laser used. A possibility of the remote detection of ammonia and acetone vapors in concentrations of about 200 ppm at a distance of up to 100 m is shown experimentally.

REMOTE DETECTOR OF VAPORS

When designing the prototype of the device for remote detection of substance vapors, the optical effect of radiation absorption was used, consisting in the fact that when propagating along an atmospheric path with a substance sought, the laser beam scatters on the topographic target and the scattered signal is recorded. As a base for the problem solution, we took the detector developed earlier [8] and substituted a single-frequency ${}^{13}C^{16}O_2$ laser for a tunable laser.

The block-diagram and general view of the laser path detector are shown in Figs. 1 and 2, respectively. The prototype is an autonomous setup, with a receiving-transmitting unit no larger than $1000 \times 900 \times$ 700 mm3 . Components of the receiver-transmitter are mounted (see Fig. 2) on the optical plate (THORLABS Inc., United States). The transmission section is mounted at the setup top. It consists of a ${}^{13}C^{16}O_2$ laser, integrating sphere with photoreceiver of the reference channel, collimating lens, system of mirrors, and auxiliary alignment semiconductor visible (green) laser.

Fig. 1. Schematic view of the path detector: sensing laser with power supply and control unit (*1*), collimator (*2*), receiving telescope (*3*), photoreceiver with power supply (*4*), ADC (*5*), personal computer (*6*); thermostatic system of the sensing laser (*7*), alignment laser (*8*), and supporting construction (plate) (*9*).

The receiving section, mounted at the setup bottom, consists of the telescope and photoreceiver of the measurement channel. The totally equipped setup can be set either at a stationary point or on a mobile vehicle.

As a laser source, an automated waveguide RFexcited Z-shape cavity ${}^{13}C^{16}O_2$ laser with the radiation wavelength tuning by lines of ${}^{13}C^{16}O$, *P*-branch in the 10.99–11.4 μm range (20 lasing lines) was used, designed and produced by Special Technologies Ltd., Novosibirsk [9]. The control for the laser tuning by lasing lines is conducted with a controller, which ensures turn of the cavity diffraction grating by a stepwise engine in the position corresponding to the required lasing line. The grating position is determined by the preliminary calibration. The laser consists of laser head, HF generator, and power supply. The laser construction provides for a possibility of air and liquid cooling. The maximal mean generation power at strong lines attains 5 W with water cooling and about 0.4 W in the air-cooling mode.

Along with the laser source, the transmission system of the detector includes a compact two-component tunable collimating optical system, which allows simultaneous tuning of the whole optical channel. The optics is made from spherical mirrors ensuring the radiation focusing to the required distance (50–100 m) via shifting one of the mirrors along the optical axis to \pm 5 mm.

In the reference and measurement channels, the photoreceivers were used for recording the modulated radiation within the wavelength range from 2 to $20 \mu m$. As reference, a MG-30 pyroreceiver was used (with the threshold sensitivity 10^{-9} W Hz^{1/2} inside a unit frequency band), and for the measurement channel, a liquid-nitrogen-cooled KRT photodetector (with a specific detectability of $3 \times 10^{10} \,\mathrm{W}^{-1} \,\mathrm{Hz}^{1/2} \,\mathrm{cm}$).

The receiving system is a Cassegrain system with a cooled photoreceiver. The primary mirror in the Cassegrain system has an aperture of 250 mm and is focused to 75 m.

To make the prototype operation effective, a system for automating the measurement procedure was developed: signals from photoreceivers of the refer-

Fig. 2. General view of the path detector.

ence and measurement channels are applied to the input of an external ADC board, mounted in a computer, and to an oscillograph (for testing). The radiation wavelength tuning and data recording, acquisition, and preprocessing are performed using a Lab-View program. During this, the amplitudes of photoreceiver signals are measured, averaged, and input into the computer memory. An ADC National Instruments NI PCI 6251 board is used as an instrument for measuring and digitizing amplitudes of signals from photoreceivers of both channels.

RESULTS OF TEST LABORATORY MEASUREMENTS

Before testing the prototype, a series of experiments were conducted for measuring the transmission of ${}^{13}C^{16}O_2$ laser radiation by vapors of several chemical compounds. Spectra of the saturated vapors of the following substances mixed with air were measured:

1) Ammonia ($NH₃$): liquid medical solution.

- 2) Acetone (C_3H_6O) : liquid, chemically pure.
- 3) Ethanol (C_2H_6O): liquid, rectificate.
- 4) Gasoline: liquid, routine solvent.

The choice of substances is conditioned by the following reasons: ammonia and acetone are evident indicators of substitute explosives; ethanol and gasoline, being the volatile inflammable liquids, have strong absorption lines in the range of ${}^{13}C^{16}O_2$ laser generation.

Transmission of the vapors was measured at the setup by the standard spectrophotometric scheme (Fig. 3). The transmission of the absorbing layer was calculated by the formula

$$
T = (U_{\text{out}}/U_{\text{in}})(U_{\text{0out}}/U_{\text{0in}}),
$$

where *U* are photoreceiver signals, subscripts "out" and "in" correspond to the measurement and refer-

Fig. 3. The scheme of test measurements: reference channel (I), measurement channel (II); ${}^{13}C^{16}O_2$ laser (*1*), absorption cell (*2*), beam splitter (*3*), and photoreceivers (*4* and *5*).

ence channels, respectively; "0" means the absence of the substance studied.

For recording radiation in the reference and measurement channels, pyroelectric receivers MG-30 were used.

The absorbing vapor layer was prepared in an absorption cell, which is a glass tube \varnothing 20 × 500 mm. The tube ends are covered by $BaF₂$ optical windows. The cell provided the airtightness of the inner volume. In the case of the cell filling with air, zero values of signals *U* were determined. The studied gas mixture was prepared by filling the preliminary evacuated cell with saturated vapors of a corresponding substance from a container; then, the values U_{in} and U_{out} were recorded.

Figure 4 shows the results. For the comparison, Fig. 4a shows also the results of calculation by the literature data for conditions of the experiment.

It is seen that the results agree satisfactorily. The presence of a single line in the $NH₃$ spectrum allowed us to test the scale of the laser wavelength tuning.

TECHNIQUE FOR TESTING THE PROTOTYPE

The vapor detector prototype was tested in laboratory conditions on a closed path in IOA SO RAS following the spectrophotometric scheme (Fig. 5). The prototype was adjusted to path measurements: the scatterer and modeling topographic reflector were at a distance of 77 m from the prototype; the cell with

Fig. 4. Measured transmission spectra of (a) ammonia, (b) acetone, (c) ethanol, and (d) gasoline vapors.

Fig. 5. Scheme of path measurements: ${}^{13}C^{16}O_2$ laser (*1*), scatterer (2), receiving telescope (3), measurement photoreceiver (*4*), reference photoreceiver (*5*), personal computer (*6*), cell (*7*), valves (*8*), and container with acetone or ammonia (*9*).

ammonia or acetone vapors simulating SP was at a distance of 65 m.

The procedure of the path measurements was similar to the measurements conducted at the setup earlier. In the given case, the absorption cell was a metal tube $\varnothing 68 \times 620$ mm. At the tube ends, KRS-5 optical windows (thallium bromide–thallium iodide) and pumping valves were mounted. When filling the cell with air, zero values of the photoreceiver signals were determined. An absorbing medium, a mixture of ammonia or acetone vapors with air, was prepared by blowing saturated vapors through the cell using an air compressor at a rate of 2 L/min until stabilization of the photoreceiver signal in the measurement channel; after that, the blowing was ceased and the photoreceiver signals of the reference and measurement channels were recorded again.

A fragment of the signal recorded in acetone vapors at the lasing line with a wavelength of 11.193 μm is shown in Fig. 6. The estimate of vapor concentration in the cell gave a value of \sim 263 ppm with an error of \pm 30 ppm.

Figure 7 shows the variation in the transmission recorded in the cell with ammonia vapors (\sim 200 ± 20) ppm during radiation wavelength scanning. The decrease in the gas mixture transmission is seen at $~\sim$ 1800 scanning steps, which corresponds to adjustment of the laser cavity to the *P*30 line (11.262 μm).

CONCLUSIONS

In the result of the work carried out on the base of a tunable ${}^{13}C^{16}O_2$ laser, a prototype of a laser detector of hazardous substances was designed and produced.

Laboratory experiments on the local detection of chemical compound vapors (ammonia, acetone, ethanol, gasoline) were conducted.

Acetone and ammonia vapors with concentrations of ∼200 ppm were detected in a path segment

Fig. 6. Photoreceiver signal of the measurement channel versus time recorded in acetone vapors at a wavelength of 11.193 μm.

Fig. 7. Transmission of the cell with ammonia vapors as a function of the number of scanning steps.

60 cm long at a distance up to 100 m at a signal-tonoise ratio ∼10.

The prototype can become a basis for designing remote gas analyzers of a series of toxic chemical compounds for use in industry or ecological monitoring departments.

ACKNOWLEDGMENTS

This work was performed in the framework of Project VIII.80.1.3 of the Program of Basic Research of the State Academies of Sciences.

REFERENCES

- 1. C. A. Munson, J. L. Gottfried, F. C. De Lucia, K. L. McNesby, and A. W. Miziolek, *Laser-Based Detection Methods for Explosives, Rep. N ADA474060* (US Army Research Laboratory, 2007).
- 2. J. I. Steinfeld and J. Wormhoudt, "Explosives detection: A challenge for physical chemistry," Annu. Rev. Phys. Chem. **49**, 203–232 (1998).
- 3. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A&B* (Wiley-Interscience, New York, 2008).
- 4. Sh. Sh. Nabiev, D. B. Stavrovskii, L. A. Palkina, V. L. Zbarskii, N. V. Yudin, E. N. Golubeva, V. L. Vaks,

E. G. Domracheva, E. A. Sobakinskaya, and M. B. Chernyaeva, "Spectrochemical features of certain brisant explosives in the vapor state," Atmos. Ocean. Opt. **26** (5), 377–390 (2013).

- 5. V. S. Starovoitov, S. A. Trushin, and V. V. Churakov, " $13C^{16}O_2$ -laser based photoacoustic gas analyzer of multicomponent air pollution," Zh. Prikl. Spektrosk. **66** (3), 345–350 (1999).
- 6. V. S. Starovoitov, S. A. Trushin, and V. V. Churakov, "Use of lasers on $CO₂$ isotopologues for photoacoustic monitoring of air pollution," Zh. Prikl. Spektrosk. **59** (5-6), 504–509 (1993).
- 7. A. Pal, C. D. Clark, M. Sigman, and D. K. Killinger, "Differential absorption lidar $CO₂$ laser system for remote sensing of TATP related gases," Appl. Opt. **48** (4), B145–B150 (2009).
- 8. G. V. Sakovich, A. I. Chernov, S. V. Silant'ev, A. B. Vorozhtsov, A. A. Pavlenko, E. V. Maksimenko, M. M. Makogon, A. V. Klimkin, K. Yu. Osipov, Yu. N. Ponomarev, V. A. Kapitanov, and B. G. Ageev, "Prototype of a remote detector of explosives on the basis of an isotope $SO₂$ laser," Polzunovskii Vestnik, No. 4, 38–46 (2010).
- 9. www.detectors.lc-solutions.com.

Translated by S. Ponomareva