

## MULTICHANNEL OPTOACOUSTIC SPECTROSCOPY OF THE ATMOSPHERE ON HF-LASER LINES

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*This paper presents results of using a multichannel optoacoustic method for investigation into the absorption on the HF-laser lines in the atmosphere. The potentialities of this method for detection of trace gases in the atmosphere are shown by the example of  $N_2O$  and  $CH_4$ . Measured absorption cross section of water molecules on laser lines are presented.*

The use of HF (DF) lasers for monitoring of the atmosphere is considered to be promising from the fact that there is a great number of lines in their output spectrum,<sup>1</sup> and because the majority of the impurities, which are important (from the standpoint of monitoring), absorb the radiation of these lasers.<sup>2</sup> Small width of their output spectrum ( $\sim 0.01 \text{ cm}^{-1}$ ) as compared to the widths of the characteristic absorption lines of gaseous impurities in the atmosphere ( $\sim 0.1 \text{ cm}^{-1}$ ) as well as stable frequency of laser oscillation render their radiation standard for the selective detection of the molecular impurities absorbing this radiation. In Refs. 1 and 3 we used optoacoustic (OA) technique for measuring the absorption cross sections of various gaseous impurities in the air on HF-laser lines. It was demonstrated that for the simple substances under study the absorption cross sections on the different HF-laser lines can differ from each other by several orders. It makes it possible (e.g., using the technique worked out in Ref. 4) to perform an optimal choice of the spectral channels for detection of a specific substance.

The present article is devoted to the elaboration of the multichannel OA technique for investigating the absorption on the HF-laser lines in the air. In doing so we performed all measurements directly in the atmospheric air without the OA cells as in Refs. 5 and 6. Such measurements are less sensitive. However, their advantages are, first of all, a simplicity of the technical design of analyzer and also the lack of influence of the cell walls on the composition of an analyzed gas. Besides, it is very important that there is no background OA signal from the cell windows in this case. Moreover, the multichannel analyzer without a cell allows one to perform measurements without sampling, under rapid temporal variations of the atmospheric parameters in the real atmosphere. The last fact in its turn allows one to take efficiently suitable steps.

As the experimental setup we used a 6-channel OA analyzer of the atmospheric air based on the pulsed chemical HF laser, whose output spectrum consists of about 30 individual vibrational-rotational lines within the spectral range from 2.7 to 3.4  $\mu\text{m}$ . The output energy on each individual line is less than 0.1 J for 1- $\mu\text{s}$  pulse. Diagram of the OA analyzer is shown in Fig. 1.

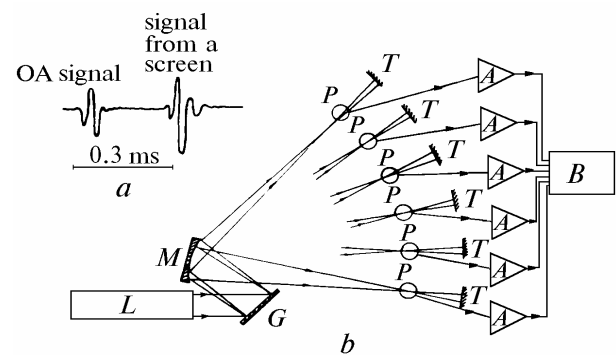


FIG. 1. Oscillograph trace of the OA signal recorded with a microphone (a) and diagram of the OA analyzer (b): *L* is the laser, *G* is the diffractive grating, *M* is the mirror, *P* are the microphones, *T* are the targets, *A* are the amplifiers, and *B* is a storage unit.

The spectrum of lasing was obtained by means of a diffraction grating *G* and a spherical mirror *M*. Near the focal plane of the mirror the microphones *P* were placed. They recorded a sound pulse appearing in the air in absorbing the laser radiation. The diameters of the radiation beams were about 0.5 cm in the area of the microphone location, and the distance from beam axis to a microphone was 2 cm. In order to exclude the influence of the signals from nearby lines, we used the screens (they are not shown in Fig. 1). The targets *T* were placed at a distance of about 10 cm from the microphones. The sound signal, appearing in interacting the laser radiation with target was used as a measure of the output energy on the corresponding line. The amplitude of the sound signal from the target was proportional to the output energy within almost 10% accuracy. The signals from the microphones were reinforced in the amplifier unit *A* and recorded in the storage unit *B*.

The capsules of MKÉ-210 microphones were used as detectors of the sound signal, recording was performed by means of S8-9 oscillographs. A characteristic oscillograph trace of the sound signal detected with a microphone is presented in Fig. 1a. The form of the OA signal is close to a calculated one in Ref. 7.

The whole of recording part of the setup was placed in a separate chamber (the chamber volume was approximately  $10 \text{ m}^3$ ), hence, it allowed us to mix the air with various gaseous impurities.

The experiments were performed with the laboratory air at temperature  $T = 294 \text{ K}$  and relative humidity of 40 % (it approximately corresponds to the  $\text{H}_2\text{O}$  molecules number density of  $2.5 \cdot 10^{17} \text{ cm}^{-3}$ ). Under these conditions water is the main (more than 98 %) absorbing impurity in the atmosphere on the HF-laser lines.

We carried out several sets of experiments, each set consisted of 3–4 measurements. A portion of the microphones was moved between the experimental sets to detect the sound signals for other laser lines. As a result, the measurements were performed on 13 lines of the HF-laser radiation. Generally, the difference between measured values of the OA signals did not exceed 20 % from one experiment to another. It may be concluded that under the conditions of weak absorption the value of the absorption coefficient is proportional to the ratio of OA signal from the atmosphere to a signal from the target (ratio of the amplitude of the first pulse to the amplitude of the second one, as shown in Fig. 1a).

Obtained coefficients of the atmospheric absorption in relative units are presented in Fig. 2 by the vertical columns. Under the conditions of constant temperature and humidity the values of the absorption coefficients are proportional to the absorption cross sections of the  $\text{H}_2\text{O}$  molecules. Thus, the relative absorption coefficients, obtained on different lines of the HF-laser radiation, can be attributed to the absorption cross sections of the  $\text{H}_2\text{O}$  molecules in the atmosphere.

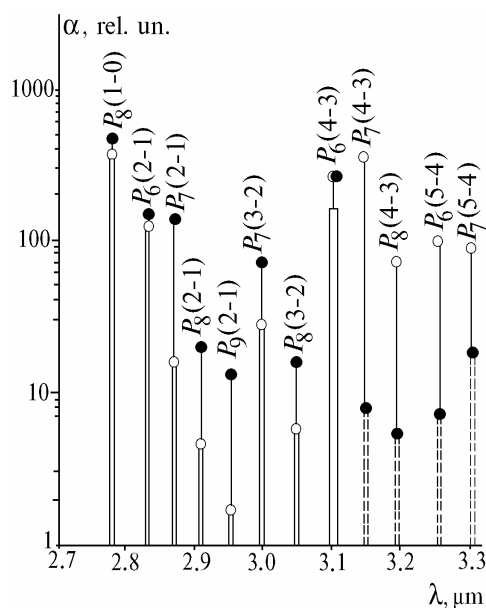


FIG. 2. Spectral behavior of the atmospheric absorption coefficient; vertical columns represent the data of experiments with air, closed circles correspond to the air +  $\text{N}_2\text{O}$  experiments, and open circles correspond to the air +  $\text{CH}_4$  experiments.

The absorption cross sections of the  $\text{H}_2\text{O}$  molecules in the atmosphere have been previously measured on a number of HF-laser lines in Refs. 9–12. The best agreement (the spread is less than 16 %) of the absorption cross sections measured in Refs. 9–12 and those presented here is observed

for line  $\text{P}_6(2-1)$  (see Table I). In this connection, we decided to calculate the absolute values of the absorption cross section basing on the results of relative measurements and the absolute data obtained on this line. The absolute values of the absorption cross sections of the  $\text{H}_2\text{O}$  molecules in the atmosphere calculated in that way are presented in Table I. Comparison of the results obtained in our experiments with results presented by other authors demonstrates their satisfactory agreement.

TABLE I.

Line	Wavenumber $\text{cm}^{-1}$ (Ref. 13)	Absorption cross sections, $\sigma \cdot 10^{21} \text{ cm}^2$				
		This paper	Ref. 9	Ref. 11	Ref. 10	Ref. 12
$\text{P}_8(1-0)$	3593.705	2.9			2.86	
$\text{P}_6(2-1)$	3531.170	1.03	1.01	0.98	1.19	0.95
$\text{P}_7(2-1)$	3483.653	0.14	0.5	0.32	0.18	0.14
$\text{P}_8(2-1)$	3434.993	0.041		0.13	0.034	0.02
$\text{P}_9(2-1)$	3385.250	0.016				
$\text{P}_7(3-2)$	3327.508	0.24				
$\text{P}_8(3-2)$	3280.576	0.05				
$\text{P}_9(3-2)$	3232.570	0.85				
$\text{P}_6(4-3)$	3219.426	1.45				
$\text{P}_7(4-3)$	3175.224	<0.10				
$\text{P}_8(4-3)$	3129.949	<0.06				
$\text{P}_6(5-4)$	3068.880	<0.09				
$\text{P}_7(5-4)$	3026.272	<0.2				

It should be noted that for a number of laser lines the absorption cross sections form insignificant values. For instance, the absorption cross section for the line  $\text{P}_9(2-1)$  under normal atmospheric conditions (50 % humidity) corresponds to the absorption coefficient less than  $0.5 \text{ km}^{-1}$ . Such lines of the radiation can be used for remote monitoring and, in particular, in solving the problems of location and remote determination of the background concentration of water molecules in the atmosphere as well as for determination of the aerosol formations from their backscattering spectra. The situation becomes all the more favourable under winter conditions, when absolute humidity of the atmosphere is much lower than in summer.

In a number of model experiments we added small quantities of the gaseous impurities to the atmospheric air. Nitrogen dioxide ( $\text{N}_2\text{O}$ ) and network gas consisting of methane ( $\text{CH}_4$ ) to the extent of more than 97% were chosen for this purpose. The number density of the added gases amounted to approximately  $10^{17} \text{ cm}^{-3}$ . The absorption coefficients obtained under these conditions on different lines of the radiation are presented in Fig. 2. One can see that small impurity additions change significantly the spectral behavior of the atmospheric absorption. The absorption in the spectral range from 2.85 to 3.00  $\mu\text{m}$  is more typical for  $\text{N}_2\text{O}$ . For the chosen number density the nitrogen dioxide absorbs HF-laser radiation approximately 10 times stronger than atmospheric air. For  $\text{CH}_4$  the spectral range from 3.15 to 3.3  $\mu\text{m}$  is the most informative one. In this range methane absorbs at least 30 times stronger than atmospheric air. The estimations made following the technique proposed in Ref. 4 with using the data from Ref. 1 demonstrate that sensitivity of the  $\text{N}_2\text{O}$  molecules detection on  $\text{P}_9(2-1)$  line is about  $2.5 \cdot 10^{15} \text{ cm}^{-3}$ ,

whereas this value for the CH<sub>4</sub> molecules on P<sub>7</sub>(4-3) line is approximately 8·10<sup>14</sup> cm<sup>-3</sup>. The values obtained agree very good with the experimental results.

Our experiments demonstrate that the proposed multichannel optoacoustic technique allows one to identify efficiently gaseous impurities in the air. Because of the high level of the background signal from water vapor in the spectral range of the HF-laser output, sensitivity of the technique (in it's using) allows one to analyze the atmosphere only at rather high concentrations of impurities, e.g., at the places of their emission into the atmosphere. The potentialities of the technique with respect to its sensitivity and possibility to detect other impurities can be essentially extended with using the multifrequency DF, CO, and CO<sub>2</sub> lasers. There are no fundamental limits for this. The estimations show that multichannel OA setup based on DF laser makes it possible to detect such substances as N<sub>2</sub>O, SO<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> at the level of concentration close to their background content in the atmosphere.

It should be noted in conclusion that the main interfering factor in the spectral range of minimum atmospheric absorption in our experiments was parasitic noise of the room (noise of the devices). The control of the noise level can be realized by employing the resonant amplifiers as well as by removing the analyzer microphone unit from the source of the noise. All these steps will lead to the substantial increase in the sensitivity of the technique. Besides, measurements at the lower temperatures (decrease in concentration of the hydrogen molecules in the atmosphere) will also improve the sensitivity of the technique.

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