COMBINED SPECTROMETER WITH A CW DIODE LASER

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Spectrometer with cw diode laser is described which allows the transmission and absorption spectra of gaseous media to be measured simultaneously by the spectrophotometric and photoacoustic methods. These spectra of ozone mixture with argon at different partial pressures of ozone have been recorded and measured over the range of 1047.7–1048.2 cm^{-1}.

INTRODUCTION

To study the absorption spectra of ozone and its gaseous mixtures in IR region, a technique of diode laser spectrophotometry is widely used.[1] This technique allows the absorption coefficient of a substance under study to be determined by comparing intensities of sounding radiation at the input and the output of a measuring cell.

Ozone interacts actively with the surface of the measuring cell walls or other gaseous components of the mixture under study. That is why the ozone concentration in the cell ought to be controlled continuously during the measurements of the ozone spectral lines. A long–term stability of the ozone concentration in a cell cannot be attained in practice even if the measuring cells are thoroughly prepared for work with ozone what assumes the use of special materials, polish and cleaning of the inner surface of the cell, and also it passivation.

The ozone concentration is generally controled by optical methods, for example, from absorption of the mercury lamp radiation by ozone at the wavelength of 253.7 nm (Refs. 2 and 3). Such a method provides a measurement accuracy of the concentration no more than 10 % over the range of ozone pressure from 1 to 6 Torr.

If the measuring cell of a fixed length is used in a spectrophotometer then the range of measured values of the absorption coefficient k or optical thickness $D = k\,l$, where l is the cell length, is determined mainly by the photodetector dynamic range. This range is characterized by the value 10^2–10^3 (Ref. 4). Extension of the range of the absorption coefficient measurement is attained due to an increase in D that is possible when increasing the length l or using the optics providing a multipass of radiation through the gas under study.

In the spectroscopy of weakly absorptive gases the photoacoustic (PA) method is widely used.[5] This method allows the spectra of weak absorption to be recorded using single–path cells of small volume ($\varnothing \sim 1$ cm, $l \sim 5$–10 cm) for k within the range of 5–6 orders of magnitude.

The threshold sensitivity of the PA method (minimum detectable value k_{min}) can be as low as $\sim 10^{-10}$ cm^{-1} W (Ref. 6) that makes it possible to measure $k \sim 10^{-5}$ cm^{-1} even with the use of low–power diode lasers.

In this paper the results are discussed of the tests of the combined laser spectrometer operating over the range of 1040–1140 cm^{-1}, where the PA measuring cell is used also as the spectrophotometric cell simultaneously.

SPECTROMETER DESIGN AND MEASUREMENT TECHNIQUE

The spectrometer was designed and constructed at the Laboratory of Molecular and Atmospheric Spectrometry of Reims University (France) based on the diode laser spectrophotometer described in Ref. 7. The optical scheme of the spectrometer is presented in Fig. 1. The spectrometer consists of the following main elements: laser diode ($Pb_{1-x}Sn_xSe$) cooled to the temperature of 15 K *1*, an optical collimator *2*, and a chopper *3* providing the modulation frequency $f_1 = 127$ Hz. Smooth frequency tuning of the diode laser radiation is performed by changing the electric current through the diode.

Laser radiation characteristics:

region of the wavelength tuning 1040–1140 cm^{-1},
output power 40–140 μW,
generation line width $\leq 10^{-3}$ cm^{-1},
beam diameter at the collimator output 14 mm,
frequency of the amplitude modulation 15–3000 Hz,
precision of setting the modulation frequency:
0.1 Hz (over the range of 15–300 Hz),
1 Hz (over the range of 150–3000 Hz).

To control the radiation tuning, 25 % – fraction of the laser beam power is directed by a beam splitter *4* to the confocal Fabry–Perot interferometer *5* with the base of 25 cm and the free dispersion region of 0.01 cm^{-1}. The photodetector MDS 1423 (HgCdTe) *6* cooled to the temperature of the liquid nitrogen was used for recording the interferogram peaks. The main

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portion of radiation is focused to the PA cell by the lens made of BaF_2. The beam splitter *9* directs a beam potion at the cell input to another one photodetector MDS 1423 *8*. The same photodetector *10* allowed the radiation power behind the PA cell to be measured.

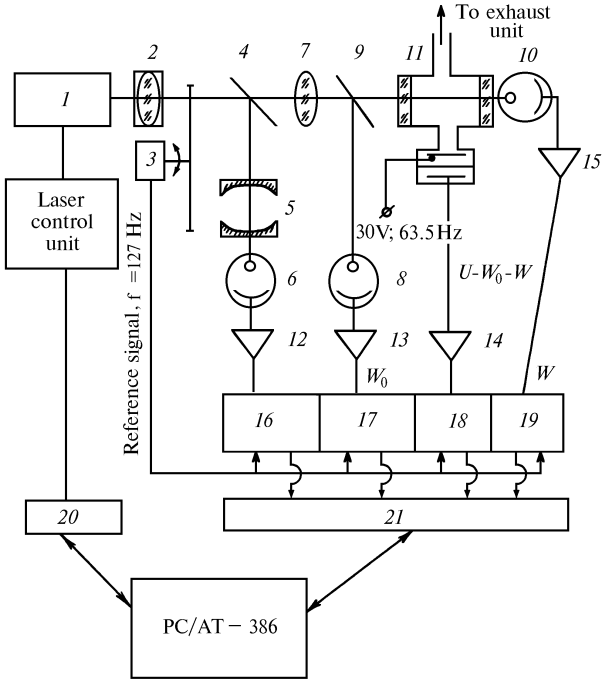

FIG. 1. Block diagram of the combined diode laser spectrometer.

To study the mixtures containing ozone, special PA detector was constructed at the Institute of Atmospheric Optics, SB RAS (Tomsk). The measurement cell of this detector is made of stainless steel and fluoroplastic, and the cell windows are made of BaF_2. The cell has a 15 mm inner diameter and 100 mm length. The windows of the cell are perpendicular to the cell optical axes. To decrease the amplitude of continuous background signal caused by an absorption of scattered radiation by the cell inner surface, the latter was thoroughly polished.

The pressure sensor (condenser microphone) was built–in into the cell wall. The design of the condenser microphone was the same as that described in Ref. 5 but differs from them only by absence of materials stimulating the transformation of ozone into oxygen. In the design of the microphone a special electrode–activator was used. It was connected with the generator of sinusoidal voltage with an amplitude of 30 V and frequency of 0.5 f_1.

The force of electrostatic attraction acting on the microphone membrane on the side of the electrode–activator stimulated the microphone oscillations at the frequency f_1. A signal amplitude at the microphone output is proportional to the force of the electrostatic attraction and square of the voltage amplitude across the electrode–activator. At the fixed values of constant polarization voltage across the microphone and amplitude of the sinusoidal voltage applied to the electrode–activator and also at the same pressure and gas composition in the cell, the amplitude signal from a microphone is a constant value too.

Introduction of an additional electrode–activator made it possible to easily control the dependence of the microphone sensitivity on the pressure or gas composition being investigated in the measurement cell. Moreover, possible change in the microphone sensitivity caused by a change in the elastic properties of the membrane (during the exploitation) could be compensated for by varying the voltage across this electrode in the way to obtain a previous value of the sensitivity. It was found that the sensitivity can be restored with an error less than 2 %.

Signals from the photodetectors *6*, *8*, and *10* and condenser microphone after amplifying them with the amplifiers *12–15* are recorded by the selective voltmeters *16–19* of the model 124A "Prinston Applied Research". From the output of the selective voltmeters the signals being measured are input through the interfaces into a personal computer together with the information about electric current through the laser diode that determines the wavelength of radiation generated. The monitor screen shows the transmission and absorption spectra (spectrum of PA signal) of a gas in the cell.

The gas mixture is prepared in a vacuum system with the elements made of a stainless steel and Pyrex. The gases O_2 ($\geq$ 99.995 %) and Ar ($\geq$ 99.998 %) produced by "Alfagas" (France) were used in the experiment. Contents of other gaseous mixtures were the following: in O_2: $H_2O \leq 5$, CO, CO_2, $CH_4 \leq 0.5$, $N_2 \leq 10$, $H_2 \leq 3$, noble gases $\leq$ 30 ppm; in Ar: H_2O, $O_2 \leq 3$, $C_xH_y \leq 1.5$, $N_2 \leq 10$ ppm.

Ozone was produced from oxygen with the use of the electric discharge technique described in Ref. 8. When cooled to the liquid nitrogen temperature more than 95 % of oxygen is transformed into ozone.

Passivation of the measuring cell is carried out by the following way. First, the cell and the vacuum system were pumped out to the pressure of 10^{-6} Torr. Then ozone was prepared in the ozoner and filled the cell and vacuum system up to the pressure of 10 Torr. Manyfold change of ozone was carried out during several days and then pumping out was repeated. The mixture of ozone and argon was prepared in the PA cell directly. First the cell was filled in by ozone ($P_{O_3} \leq 1.1$ Torr) and then argon was leak–in to the required pressure. Total pressure of the mixture in the measurement series was kept at 20 Torr. It was controlled by the capacity sensor (MKS Baratron) with the precision of 0.1 Torr.

EXPERIMENTAL RESULTS AND DISCUSSION

The absorption spectrum of ozone in the mixture with argon was recorded in the range of 1047.7–1048.2 cm^{-1} for the six values of the ozone partial

pressure between 0.06 and 1.1 Torr. The power spectra for the laser radiation absorbed by the O_3–Ar mixture under the pressure $P_{O_3} = 0.6$ Torr obtained by the spectrophotometric (curve *1*) and photoacoustic (curve *2*) methods are presented in Fig. 2. Figure 3 illustrates the absorption coefficient at the maximum of the O_3 spectral line at 1047.9763 cm^{-1} recorded by the PA method as a function of the corresponding coefficient determined under the same conditions by the spectrophotometric method. The absorption coefficients for each partial pressure of ozone are normalized to this coefficient obtained under the highest pressure of 1.1 Torr.

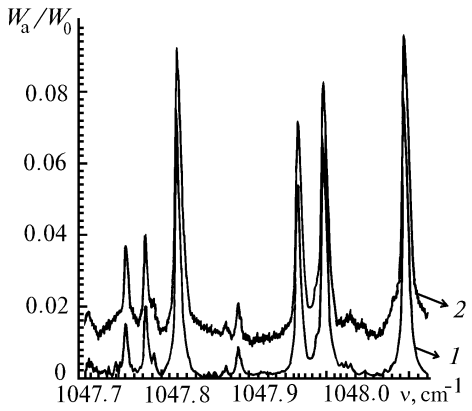

FIG. 2. The absorption spectrum of ozone in argon measured by the spectrophotometric (1) and photoacoustic (2) methods; W_0 is the power at the cell input, W_a is the power absorbed in the cell.

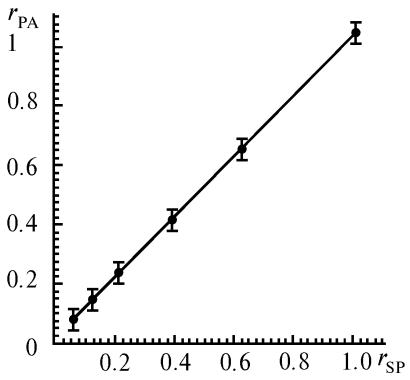

FIG. 3. Comparison of the measurement results for the absorption coefficient at the line center at different pressures of ozone obtained by the spectrophotometric (r_{SP}) and photoacoustic (r_{PA}) methods.

Figures 2 and 3 demonstrate a good agreement between the results obtained by two different methods. In Fig. 2 the ozone absorption spectrum is a little bit higher than the spectrum determined from the spectrophotometric measurements. This is caused by the background signal which is always present in PA measurements.[5]

Figure 3 shows a possibility of using PA channel of recording laser radiation energy absorbed by a gas to continuously control the ozone concentration in the cell during measurements. An additional laser emitting at a fixed frequency of radiation which is well absorbed by ozone can be used for such a control, for example, a He–Ne laser at the wavelength of 0.63 μm with radiation absorbed in the Chappuis band or cw CO_2 laser with the radiation resonance to the vibrational–rotational transitions in the ozone bands ν_1 or ν_3. Compared with the average power of the diode laser, power of He–Ne and CO_2 lasers is essentially higher. Since the sensitivity provided by the PA method is proportional to a power passing through the PA cell,[5,6] the amplitudes of PA signals at these fixed wavelengths exceed the amplitude of signals caused by absorption of the diode laser radiation. In this case the diode laser radiation is modulated at one frequency, but the additional laser radiation is modulated at different frequency.

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