SPECTROPHOTOMETRIC COMPLEX FOR MEASURING ABSORPTION OF LASER RADIATION BY MOLECULAR GASES IN THE IR, VISIBLE, AND UV REGIONS

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In this paper we present a description of a spectrophotometer complex based on a multipass 110–m–*length gas chamber aimed at studying energy losses of laser radiation of IR, visible, and UV regions in molecular gas media and in air. We also discuss key aspects of a technique for measuring absorption coefficients. Measurements of the absorption of an Nd:YAG laser emission by air at the fundamental frequency and its second and fourth harmonics are presented.*

Spectrophotometric techniques for measuring absorption coefficients of a medium use a comparison of a light flux incident on an absorption medium to that passed through it. The value of the absorption coefficient κ_ν itself is normally determined according to the Bouguer law. Sensitivity of a spectrophotometric technique depends on the optical thickness of an absorption layer $D = \kappa_\nu L$, where L is the geometrical length of a light path in the medium, and on the capability of a recording system to record small intensity changes. In the case of using frequency tunable lasers emitting a narrow emission line whose width $\delta\nu$ satisfies the condition $\delta\nu \ll \gamma$, where γ is the half–width of the absorption line of the gas under study, the spectral resolution of a spectrophotometric technique is limited either by the width of a laser emission line or by the step of frequency tuning. The mean advantage of a spectrophotometric technique is its capability of measuring absolute values of the absorption coefficients with a very high accuracy $\Delta\kappa_\nu/\kappa_\nu \le 0.01$ (see Ref. 1).

When studying such weakly absorbing gases as air and its components in the near IR, visible, and UV regions the use of a spectrophotometric technique requires multipass absorption cells (MPC) that could provide path lengths from several hundred meters to several kilometers. In spite of many technical problems arising at creation and use of such cells[2] they enable one not only to accurately measure absorption coefficients of gases under controlled conditions but also to study the variation of characteristics of laser emission due to its interaction with the medium, when the conditions of propagation can be varied in a preset way, what cannot be reached with atmospheric paths in field conditions.

In this paper we describe a spectrophotometric complex based on a 110–m–length multipass cell intended for studying energy losses of laser radiation in model gas media and in air.

This experimental complex is equipped with high–power solid–state lasers like Nd:YAG lasers, medium glass lasers, alexandrite and ruby lasers with frequency converters of nonlinear crystals and stimulated Raman cells.

In addition to solid–state lasers the complex is equipped with metal–vapor, dye, and gas lasers. Such a set of laser sources makes it possible to study transmission of different gas media in many regions of IR, visible, and UV ranges interesting for many applications. Some results of studies of gas media carried out using this complex are presented in Refs. 3–6. In this paper we consider some aspects of a technique (the experimental results are also discussed) for measuring absorption of radiation of Nd:YAG and neodimium glass lasers at their fundamental frequencies and second and fourth harmonics.

EXPERIMENTAL SETUP AND MEASUREMENT TECHNIQUE

Block diagram of a laser spectrophotometer is shown in Fig. 1.

The multipass gas absorption cell is made of a cylindric tube of a stainless steel, its inner diameter is 0.7 m and the length is 112 m. At both ends of the tube there are two bulges of 1.4 m in diameter where systems of mirrors are mounted. The ends of the cell are closed with covers which have changeable windows for input and output of sounding laser radiation. Along the tube there are several fittings for inserting temperature, humidity, and pressure sensors. There are also several valves for pumping gases out and in. The central portion of the tube rests rigidly on one of nine bearings. Eight other supporting points are on the roller bearings. The concrete basements of bearings rest on sand pads. Optical tables that bear the alignment blocks of mirrors are mounted on heavy concrete basements. Air tightness of the connection of the alignment blocks with the tube is provided with sylphon bellows. The alignment of mirrors can be monitored remotely with electric servodrives making it possible to rotate mirrors within the angular range $\mp 5°$. In addition, the platform bearing the mirror objectives can be rotated around two mutually perpendicular axes with $\mp 3°$ near its central position. Evacuation of the cell is done in two stages. At the first stage the pumping of the cell out is performed by a rotary water cycling pump RMK–4 down to a pressure of 60 mm Hg. Further evacuation of the cell is done with five vacuum pumps NVZ–20 down to a pressure of $5 \cdot 10^{-3}$ mm Hg. The pressure inside the cell is measured with the mercury and oil gangers, with vacuum gangers of MED, VDG, and VIT–2 types distributed along the tube.

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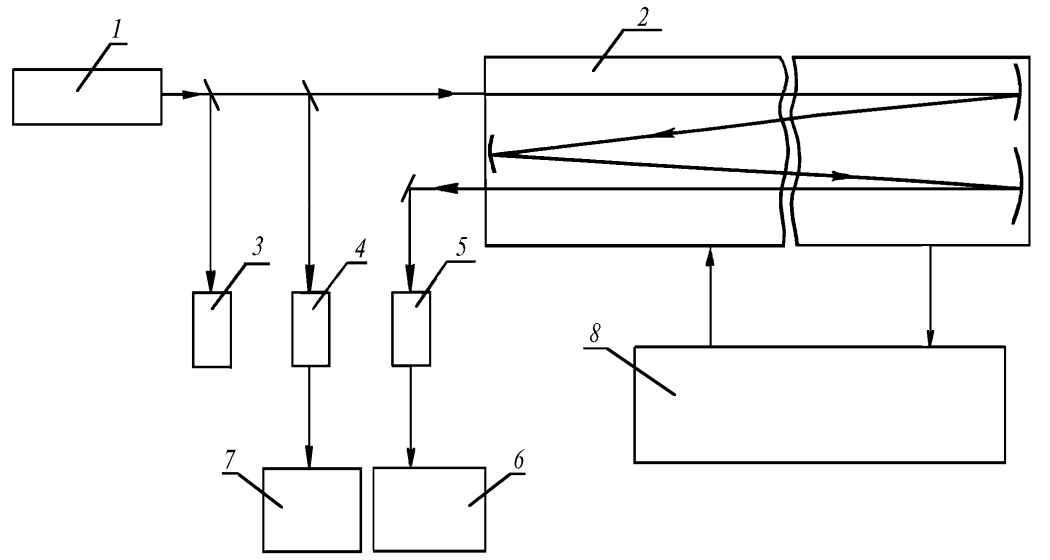

FIG. 1. Block diagram of the laser spectrophotometer: 1) laser, 2) multipass gas absorption cell, 3) wavelength meter, 4 and 5) photodetectors, 6 and 7) digital voltmeters, and 8) system for preparing and control of gas mixtures.

Filling the cell with water vapor is performed by evaporation of distilled water from a special vaporizer at both ends of the tube. Filling the tube with buffer gases is performed from bottles filled with technical gases via a gas–drying station BOV–05M.

In order to provide the studies at temperatures from 288 to 350 K and for modeling inhomogeneous paths there are 11 thermal sections along the tube. Each section has two subsections. Through the pipes of a cooling subsection water at temperature 285 K circulates, and through the pipes of a heating subsection hot water at temperature 360 K circulates.

The cell is equipped with a three–mirror optical system invented by Barskaya,[7] composed of a rectangular shaped (300 by 400 mm) collective mirror and two round mirror objectives 150 mm in diameter. In addition, we have constructed and tested in experiments with visible radiation a six–mirror matrix optical system by Chernin and Barskaya.[8]

TABLE I. The spectrophotometric system specifications.

Spectral range, nm	235–270, 350–800 1045–1075, 2090, 2650 1936, 5300, 10600
Spectral resolution, cm^{-1}	10^{-3}–10^{-2}
Specifications of the multipass gas cell:	
length, m	112
diameter, m	0.7
volume, m^3	45
pressure range, mm Hg	$5 \cdot 10^{-3}$–10^3
temperature, K	288–360
total length of the optical path, m	110–10000
Error in detection of centers line, nm	10^{-3}–10^{-4}
Transmission measurement error, %	0.5–1

The lengths of optical paths in the multipass cell that can be arranged in this cell can be found in the table of the spectrophotometric complex specifications. In the cases when cw or high–repetition rate lasers ($f \geq 1$ kHz) are used in measurements the intensities of reference (at the input of the cell) and sounding radiation are detected and measured using lock–in amplifiers.[3] In the case of short laser pulses delivered at low repetition frequency the signals from photodetectors are first time expanded and then measured with pulse voltmeters. Thus, for example, to measure intensity of pulses of neodimium glass lasers (pulse duration $\tau \sim 50$ ns) of Nd:YAG lasers ($\tau \approx 2$ ns) delivering pulses at a repetition frequency below 50 Hz we used an F–32 vacuum photoelectric cell. Output electric pulses from this detector were then expanded to $\tau = 15$ μs using integrating circuits and recorded with V4–17 pulse voltmeters.

Transmission of a gas under study is determined by the following formula:

$$T = \frac{J_\nu^{\text{out}} / J_\nu^{\text{in}}}{J_{0\nu}^{\text{out}} / J_{0\nu}^{\text{in}}}, \qquad (1)$$

where superscripts out and in denote light intensity at the output and input of the tube, respectively. Subsript 0 denotes these same intensities when the chamber is completely pumped out.

Then, using thus measured value T_ν we find the absorption coefficient κ_ν from the Bouguer law. The error in spectrophotometric measurements of κ_ν at low intensities of sounding radiation J, when nonlinear effects can be neglected, and assuming the absolute errors of the J^{in} and J^{out} measurements to be the same, can be estimated as

$$\frac{\mathrm{d}\,\kappa_\nu}{\kappa_\nu} = \frac{1}{\kappa_\nu L}\left(1 + \frac{J_\nu^{\text{in}}}{J_\nu^{\text{out}}}\right)\frac{\mathrm{d}\,J_\nu^{\text{in}}}{J_\nu^{\text{in}}}, \qquad (2)$$

where L is the length of optical path in the MPS. Minimum value of $\mathrm{d}\kappa_\nu/\kappa_\nu = 3.6(\mathrm{d}J_\nu^{\text{in}}/J_\nu^{\text{in}})$ is reached at $D_\nu = \kappa_\nu L = 1.3$ (see Ref. 1).

In spectral measurements performed with a spectrophotometer of a fixed length minimum in $\Delta\kappa_\nu/\kappa_\nu$ will be reached only at single frequency, when $\kappa_\nu L = 1.3$. When this condition is satisfied at a line center, the value $\Delta\kappa_\nu/\kappa_\nu$ depends on the frequency shift and on the shape of an absorption line under study. In the case of the Lorentzian contour this dependence is as follows:

$$\frac{\Delta k_\nu}{k_\nu} = \frac{\Omega^2 + 1}{k_0 L}\left[1 + \exp\left(\frac{k_0 L}{\Omega^2 + 1}\right)\right]\frac{\Delta J_{in}}{J_{in}} + \frac{2\Omega^2}{1 + \Omega^2}\frac{\delta\Omega}{\Omega}, \quad (3)$$

where $\Omega = (\nu - \nu_0)/\gamma$.

The error in κ_ν due to inaccurate determination of the line frequency that contributes to the total relative error of a line contour measurement is taken into account by the term $2\Omega^2/(1 + \Omega^2)$. The value $\delta\Omega/\Omega$ can be as low as 0.01 when measuring the wavelength with an IDV–2 or "Spectron" wavelength meters, or with a Fabry–Perot etalon having 5 cm spacing. Dependence of $\Delta\kappa_\nu/\kappa_\nu$ value on Ω is shown in Fig. 2 for $D = 1.3$, $\Delta J^{in}/J^{in} = 0.02$, and for spectral resolution of the wavelength meter ~10^{-3} cm^{-1}.

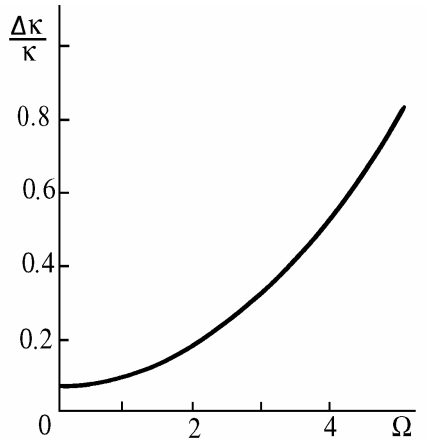

FIG. 2. Dependence of relative error in measurements of the absorption coefficient on the frequency detuning from an absorption line center.

A laser system used in the below–discussed measurements involved an Nd:YAG laser, a medium glass laser, laser amplifiers and frequency converters of the radiation at $\lambda = 1.06$ μm into the second and fourth harmonics. Let us now give a brief description of some blocks of the laser system.

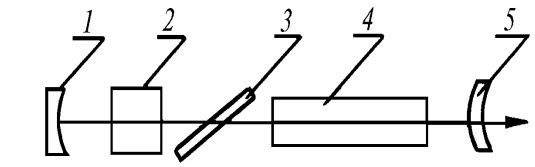

FIG. 3. Optical arrangement of an Nd:YAG laser: 1) concave mirror, 2) passive Q–switch, 3) polarizer, 4) active element, and 5) convex mirror.

An Nd:YAG laser (see Fig. 3) consists of a telescopic unstable resonator with the magnification factor of 2.2, an active element 60 mm long and 6.3 mm in diameter of an Nd:YAG crystal, a polariser (a glass plate installed at the Brewster angle), and a passive Q–switch of a LiF crystal doped with F_2^- color centers. The radius of curvature of the concave mirror is 50 cm and 22.5 cm of the convex one. The convex mirror is a spot (2.8 mm in diameter) of dielectric coating with 35% reflectivity on the convex surface of a preliminary coated backing 20 mm in diameter. Pumping of the active element is performed by a flash lamp INP–5/60A–1 in a standard quantron made of a quartz monoblock.

This laser delivers bell–shaped pulses of (2.2ý0.2) ns duration, at half maximum, with the spectral width of the emission not exceeding 0.05 cm^{-1}. Pulse energy at the fundamental frequency reaches 0.1 s, and the angular beamwidth is less than 05 mrad.

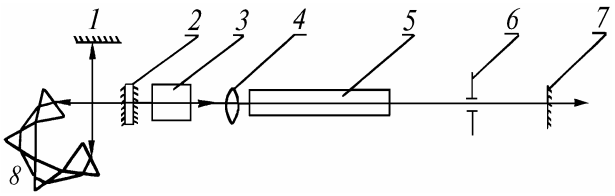

FIG. 4. Optical arrangement of a neodimium glass laser: 1 and 7) resonator mirrors, 2) Fabry–Perot etalon, 3) passive Q–switch, 4) lens, 5) active element, 6) diaphragm, and 8) block of dispersion prisms.

The neodimium glass laser system consists of a master oscillator with a dispersion resonator (see Fig. 4) and a double–pass amplifier. The cavity of the master oscillator is formed by two plane mirrors with the reflectivity 99.5 and 55%. The length of the cavity is 120 cm. A lens of 200 cm focal length installed at 80 cm from the output mirror provides selection of the fundamental transverse mode of the resonator. A preliminary spectral selection of the emission spectrum is performed with a block of four prisms optically arranged so that the condition of minimum deflection angle is satisfied simultaneously with the requirement of reflection at the Brewster angle. This enabled us to minimize the energy losses in the block of prisms. The Fabry–Perot etalon made of a plane parallel plate of K–8 glass, both sides coated, makes the laser emission spectrum narrower and is used to continuously tune the emission wavelength. The reflection coefficient of coatings is 50%. Rough wavelength tuning is performed by rotating the rear hundred per cent mirror while the Fabry–Perot etalon is used for continuous tuning. Width of the output emission spectrum in this case does not exceed $5\cdot10^{-3}$ cm^{-1}. An active element of the neodimium glass GLS–24 (its diameter is 4 mm and length is 80 mm) is pumped with a flash lamp of IFP–800 type in the quantron of a quartz monoblock. A crystal of LiF with F_2^- color centers is used as a Q–switch in this laser. The initial transmission of the Q–switch is 80%.

The output energy of the laser beam is mainly limited by the damage threshold of the Fabry–Perot etalon coatings and is about 0.02 J. Using an amplifier with the active element of neodimium glass 8 mm in diameter and 120 mm long we reach a ten times increase of the output pulse energy. Pumping of this element is performed by a flash–lamp of the IFP–1200 type within a two–ellipsoid quanton. In order to avoid (or to suppress) the feedback between the laser and amplifier we use a LiF crystal with F_2^- color centers having the initial transmission 30%.

Frequency conversion of the radiation at 1.06 μm to its second harmonic is performed with a commercially available frequency converter MCh–105. Synchronous matching of this converter is tuned by varying its temperature, at maximum the conversion efficiency reaches 40%. Because of a long time required for temperature tuning on the conversion efficiency maximum the use of the MCh–105 converter in a frequency tunable laser is too problematic. For this reason in measurements with the neodimium glass laser we use a KTP crystal where the synchronous matching is done by the crystal rotation. The efficiency of the frequency conversion of radiation with the above parameters reaches 60%.

Conversion into the fourth harmonic of the fundamental frequency is performed with a KDP crystal, whose efficiency is about 5%.

MEASUREMENT RESULTS

Measurements of the absorption of an Nd:YAG laser radiation at the fundamental frequency and its second harmonic by air have been carried out at a relatively short path (1320 m) and under total pressure of air about 760 mm Hg and partial pressure of water vapor about 10 mm Hg. Under these conditions we reached about $5 \cdot 10^{-8}$ cm^{-1} threshold sensitivity to absorption of the whole system. This sensitivity did not allow us to measure absorption coefficient values κ_ν at 1.06 and 0.53 μm wavelengths. Of course, we can state that in this case $\kappa_\nu L$ is below $5 \cdot 10^{-8}$ cm^{-1}, and this estimate well agrees with the calculational and measurement results from Ref. 9.

As to the fourth harmonic, it is noticeably absorbed by water vapor. Measured cross sections of the absorption are $(4.9 \mp 0.1) \cdot 10^{-23}$ cm^2. This value agrees with the value of H_2O absorption coefficient measured in Ref. 10 using an absorption spectrometer with nonlaser light source. The spectral resolution of this spectrometer was 3.3 cm^{-1} and the relative error of measurements $\Delta\kappa_\nu/\kappa_\nu \sim 0.25$. It should be noted that measurements carried out in Ref. 10 did not reveal any fine structure in the absorption spectrum of H_2O and that no assumptions on the origin of H_2O–molecules continuous absorption in the region 270–330 nm has been formulated in the paper.

In order to try to relate the nonselective character[10] of water vapor absorption in this region to the spectral resolution of measurement devices we have carried out measurements of the absorption of a narrow band tunable radiation at the fourth harmonic of a neodimium glass laser emission. Measurement results obtained under the 750 mm Hg total pressure and 9.9 mm Hg partial pressure of water vapor are shown in Fig. 5. The width of the emission line (at the fourth harmonic) did not exceed 0.02 cm^{-1} (or 0.14 Pm) and the step of frequency tuning was from 0.02 to 0.05 cm^{-1}. The mean value of the absorption coefficient we measured in the region 263–268 nm was $(1.83 \mp 0.12)\ 10^{-5}$ cm^{-1}. This value well agrees with the results obtained using the fourth harmonic of an Nd:YAG laser (λ = 266 nm) and reduced to conditions of our experiments.

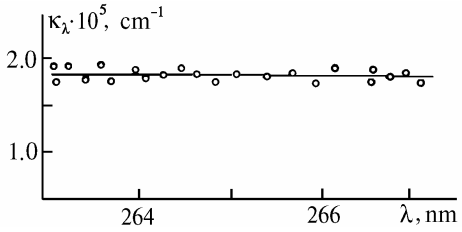

FIG. 5. Dependence of absorptivity on radiation wavelength.

One can easily see from Fig. 5 that we also failed to reveal any fine structure of the water vapor absorption spectrum in this region, though the spectral resolution in our measurements was hundred times higher than of measurements in Ref. 10. We think that this can be explained by much higher density of spectral lines of H_2O molecules in this spectral region caused by transitions from either highly excited vibrational states or from the electron–vibrational states.[11]

Thus the mean distance between neighboring sprectral lines can occur to be smaller or comparable with their half–widths, therefore, it can vary from 0.01 to 0.1 cm^{-1}. If one takes into account that in the UV region the half–widths of spectral lines, at 300 K temperature are about 0.054 cm^{-1} and can be broadened due to collisions, then it becomes clear that the observed nonselectivity of the absorption can be caused by the overlapping spectral lines.

Nevertheless we think that in order to elucidate the origin of nonselective light absorption by H_2O molecules in the region from 270 to 330 nm, and, in particular, to verify the hypothesis of author of Ref. 10 on the origin of this continuum due to earlier unknown electron–vibrational absorption band some additional investigations are needed. It is advisable, from our view point, to study in more detail the absorption spectra of pure water vapor and of its mixtures with air at different temperatures and pressures. It would also be useful to estimate contributions from transitions from highly excited vibrational–rotational states electron–vibrational bands into the absorption of light by H_2O molecules in this spectral interval.

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