AUTOMATED FLUORESCENCE LASER SPECTROMETER

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Schematic of the spectrometer is presented, and functioning of its main blocks is described. Recordings of laser emission spectrum and fluorescence spectra of water vapor and aluminum in laser plasma demonstrate the analytical capabilities of this spectrometer.

Luminescence methods of investigations are exceptionally high sensitive and give a unique possibility to study the excited states of molecules and radicals, photochemical processes, dynamics of intra- and intermolecular processes, structure and properties of molecules and compound chemical and biological objects. The fluorescence spectroscopy method is successfully used for the substance analysis for a long time.

Lasers considerably raised a potential of the method[1]: the spectral resolution and sensitivity of analysis were improved; the number of objects under study, in particular, gases increased; remote sensing of gas pollution and atmospheric parameters became feasible.

Development of facilities for *in situ* and remote laser gas analysis requires knowledge of the fluorescence spectra caused by laser radiation. The automated spectrometer being described in this paper is intended for complex measurements of excitation and emission spectra of molecules and atoms in the gas phase.

The spectrometer includes a tunable dye laser, a fluorescence cell, an MDR-6 monochromator, data processing and spectrometer control system based on a personal computer, and units of the CAMAC-VECTOR standard (Fig. 1). The spectrometer has also an IR laser for atomizing samples in condensed phase.

The dye laser system involves a master oscillator and an amplifier. The master oscillator is constructed following the scheme with the so-called grazing incidence of radiation on a diffraction grating (DG).[2] In this case the radiation is incident on the DG at an angle close to 90° that provides a high selectivity of the system. Diffracted light is incident on the mirror or the second DG in the autocollimation setup. Tuning of laser radiation wavelength is carried out by rotation of the mirror or the second DG. Such a scheme allows the spectrum width to be attained at a level of hundredth of reciprocal centimeter for the efficiency of pumping radiation conversion about 5%.

The ILTI-205 laser with the pulse power up to 5 MW at the wavelength 532 nm, pulse duration 10 ns, and repetition rate up to 25 Hz is used as a pumping source. The pumping radiation power is divided between the master oscillator and a one-passage amplifier in the proportion 1:3. Total efficiency of the pumping radiation use is about 20% for the spectrum width 0.03–0.05 cm^{-1}.

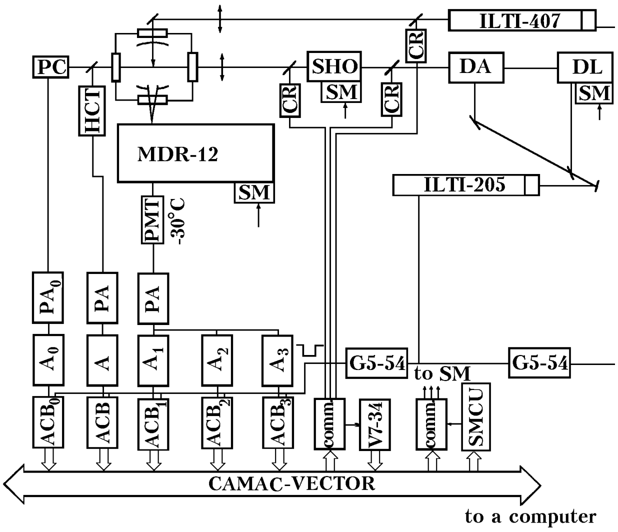

FIG. 1. Block diagram of the spectrometer: the second harmonic oscillator SHF, the dye laser DL, the dye amplifier DA, the stepper motor SR; the cavity receiver CR, the F-7 photocell PC, the hollow cathode tube HCT, the FEU-130 photomultiplier tube PMT with a cooling unit, the BUS2-94 preamplifier PA, the BUS2-97 amplifier A, the ADC BPA-01F unit ACB, the stepper motor control unit SMCU, and the commutator (comm.).

The dye laser is tuned by rotating the autocollimation DG with the micrometer screw which is rotated through the reduction gear by the SDR-711V stepper motor.

The laser radiation can be converted into radiation of UV range by frequency doubling in a KDP crystal. The crystal in a hermetically sealed package and compensator are rotated by a drive based

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on the SDR-711V stepper motor (Fig. 2*a*). Thus, angular crystal position (synchronism angle) tuning synchronously with changes in the laser wavelength preserving at the same time spatial location of UV radiation and crystal adjustment at the maximum conversion efficiency at each wavelength are provided. For a precise laser tuning to a given wavelength, the hollow cathode tubes are used.

The fluorescence gas cell is made of stainless steel. The highly effective system of collecting radiation matched the monochromator is located inside. The cell is evacuated and filled with the gas under study using the VUP-5 pump. For experiments with solid samples an atomic beam source providing the atom concentration up to 10^{13} cm^{-3} is used or atomization is carried out by radiation of the ILTI-407 laser radiation (this version is shown in Fig. 2*b*; a sample of the cylinder form is rotated by the electric motor). The cell temperature can be brought up to ~ 80°C by the built-in heaters.

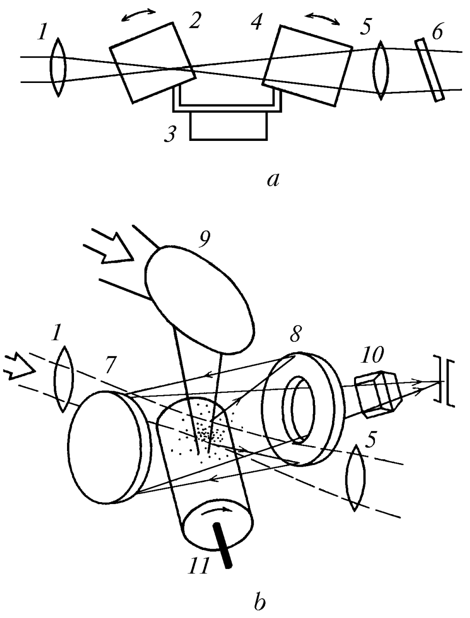

FIG. 2. The block diagram of the second harmonic generator a and the fluorometer b: focusing and collimating lenses 1 and 5, nonlinear crystal 2, the stepper motor drive 3, compensator 4, filter UVG glass 6, the mirror light collecting system 7 and 8, mirror 9, Pekhan prism 10, and a sample 11.

A large number of the signal sources and objects to be controlled, operation in real time caused the use of a combined measuring and controlling system based on a computer. Standard equipment is also used that, on the one hand, sharply decreases time for creating of the complex and, on the other hand, provides the metrological characteristics of the measurement channels. The measuring and controlling channels were unified to a certain extent that simplified an adjustment, calibration, and testing of the system, as well as its software.

The laser DG, nonlinear crystal, and monochromator are tuned by three identical stepper motors. A choice and change in motor rotation direction, setting of rotation velocity, identification of extreme positions, motor synchronization are carried out by computer. In the spectrometer a program-controlled starting of the lasers with optically coupled isolation is also realized.

The system of light signal measurement uses the charge integration method[3] and consists of BUS2-94 charge sensitive preamplifiers, BUS2-97 controlled amplifiers, and BPA-01F amplitude-to-code converters. When measuring the fluorescence signal, three parallel channels with different amplification factors are used that provides a dynamic range not less than 200 000. The intensity of the light flux is limited from below by the photodetector dark current (0.01 photon per a laser pulse), and from above by maximum amplitude of the preamplifier output signal. The amplifiers are calibrated by computer with the use of a BGA2-97 stable oscillator.

The system proposed allows the measurements to be carried out over a wide range (counting, intermediate, and current) of intensity without switching and filters. The measurement error is mainly determined by statistical nature of the signals and equals 0.2–1.3% for averaging over 20 pulses. When measuring the fluorescence temporal characteristics, a signal from the photomultiplier tube (PMT) is applied to an oscilloscope and photographed.

Power is measured by the cavity receivers PP-1. Signals from these receivers are commutated and measured by the V7-34 voltmeter.

The spectrometer operation in automatic mode under the computer control is supported by the software composed of subroutines of unit survey, information read-out from the crate line, operation with the stepper motors, plot and table output, laser starting and stop, statistical processing of measurements, rejection of fault measurements. Besides, there are service subroutines for tuning dye laser and monochromator to a given wavelength, initial installation of the system, testing and calibration of the system units, examination of the data obtained before, etc. At the beginning of the experiment an operator, in an interactive regime, inputs the tuning range of the laser or the monochromator, the number of measurements to be averaged, and also a service information for representation in the summary listing (measurement conditions, measuring system parameters, etc.). The obtained data are recorded and can be used for further analysis by the operator decision.

The spectrometer specifications are given below.

TABLE I.

Excitation spectral range, nm	1060, 530, 355, 265, 560–610, 280–305
Spectral resolution, cm^{-1}	0.01–0.03
Error of absolute measurements of excitation wavelength, pm	1
Pulse power of laser radiation, MW	0.01–10
Pulse duration, ns	8–15
Pulse repetition rate, Hz	up to 25
Spectral range of fluorescence recording, μm	0.2–1.2
Absolute measurement error of the fluorescence wavelength, nm	0.1
Pressure of gases under study, mm Hg	0.1–760
Medium temperature, K	300–450
Measurement sensitivity, cm^{-1}	10^{-13}

The spectrometer operation is illustrated in Figs. 3–5. Figure 3 shows the spectrum of the dye laser radiation. The tunable laser radiation is accompanied by the background radiation with an intensity which is smaller by a factor of 10^2–10^4 and carrying some tenths of a per cent of the output power.

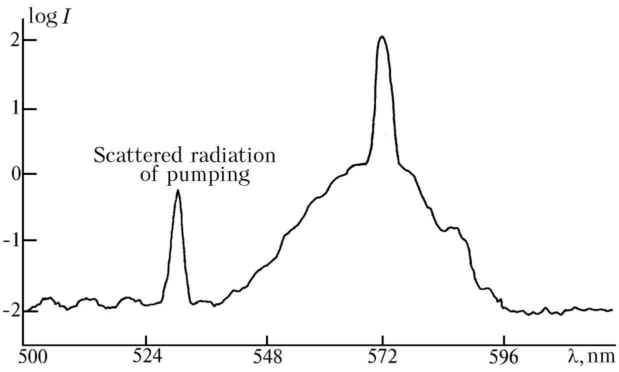

FIG. 3. Emission spectrum of the dye laser.

Figure 4 presents the fluorescence spectrum of water vapor in the band discovered in Ref. 4 at room and elevated temperatures. Radiation of the fourth harmonic of a garnet laser was used for excitation. The fluorescence intensity does not fall with temperature increase, as it is in the case of dimer nature of this band, but increases: at 20°C the cross section equals $3.1\cdot10^{-26}\,\text{cm}^2/\text{sr}$ and $4.2\cdot10^{-25}\,\text{cm}^2/\text{sr}$ at 72°C, moreover, a sharp rise of the fluorescence takes place in the region of 370 nm.

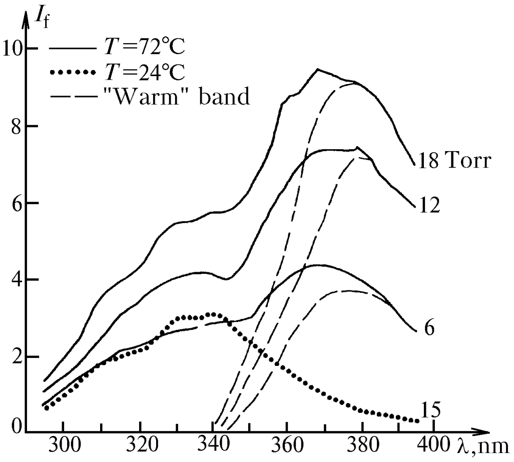

FIG. 4. Fluorescence spectrum of the water vapor.

The fine structure of the excitation spectrum was recorded (Fig. 5) when investigating the aluminum atom fluorescence in laser plasma.

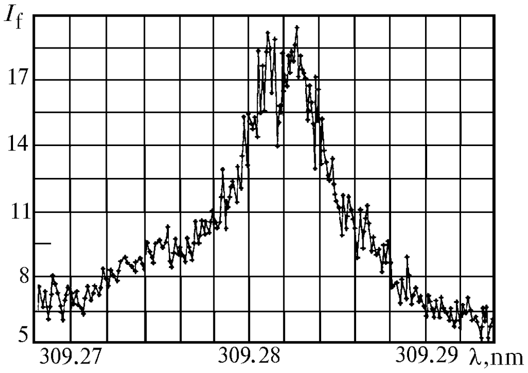

FIG. 5. Spectrum of excitation of fluorescence of the transition $3p^2\,P^0_{3/2} - 3p^2\,D_{3/2}$ *of aluminum in the laser plasma. The step of wavelength tuning is* 0.001 Ð, *the spectrum width is* 0.003 Ð.

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