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Laser device for dynamics studies of optical absorption and fluorescence signals

A laser device for the determination of absorption as well as of emission signals suitable in the time range from 10^{-4} to 10^{-8} s and spectral range from 250 to 700 nm is described. Some applications of this arrangement to the investigation of physical and chemical properties of liquids and gases are discussed.

1. Introduction

In 1950, G. PORTER [1] proposed a new method for the study of absorption transitions permitting the direct measurement of spectral characteristics and, moreover, of the changes in time of absorption signals from solids, liquids and gases. This method had recourse to two synchronized light pulses: one pulse, of high intensity, caused the excitation of the sample, whereas the second one, of low intensity, but conveying a wide range of frequencies, served as analyzing beam.

Porter applied flash lamps as sources of the two pulses. The long time of the exciting pulse duration (of the order of μs) restricted the use of the method to the study of transitions with rather slow changes in population of the electronic states (with time constants of tens and hundreds of μs).

The range of applicability of the method increased radically owing to the achievements of laser physics [2, 3]. Lasers, which can produce practically monochromatic, collinear light beams with a power of hundreds of MW and pulse durations of the order of nano- and picoseconds, proved to be excellent sources of exciting radiation. WINDSOR and NOVAK [4], and PORTER and TOPP [5], were the first to apply pulse lasers in systems of the kind considered here.

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This paper contains the description of a measuring system, built by research workers of the Institutes of Physics and Chemistry of Adam Mickiewicz University of Poznań.

2. Construction of the system

Fig. 1 shows a block diagram of the device. The excitation beam is generated by a ruby laser, Q-switched passively by means of a solution of cryptocyanine in methanol. The ruby rod, of length 150 mm and diameter 7.5 mm, optically pumped with a G 422 xenon flash lamp, made by Pressler (GDR), is placed in a chamber cooled with water at about 15°C. The optical resonator consists of two dielectric mirrors of 0 and 50 % transmission for $\lambda = 694$ nm, respectively. In giant operation regime the laser yielded light flashes of the energy of about 0.5 J and a duration half-time of 30 ns (average power 15 MW). On traversing the filter F_1, which absorbs all wavelengths shorter than the laser wavelength, the beam is incident on a KDP frequency doubler crystal. The filter F_2 absorbs wavelengths longer than the second harmonic of the fundamental laser signal. A beam of wavelength 347 nm with the energy of 20 mJ in the pulse focused by means of the cylindrical lens S_5 is incident on the sample P. The beam splitter B_8 directs a part of the light to the photoelectric energy meter E, the signal of which is automatically recorded at EZ-10. An analyzing beam vertical to exciting beam ($\lambda = 347$ nm) is incident on the
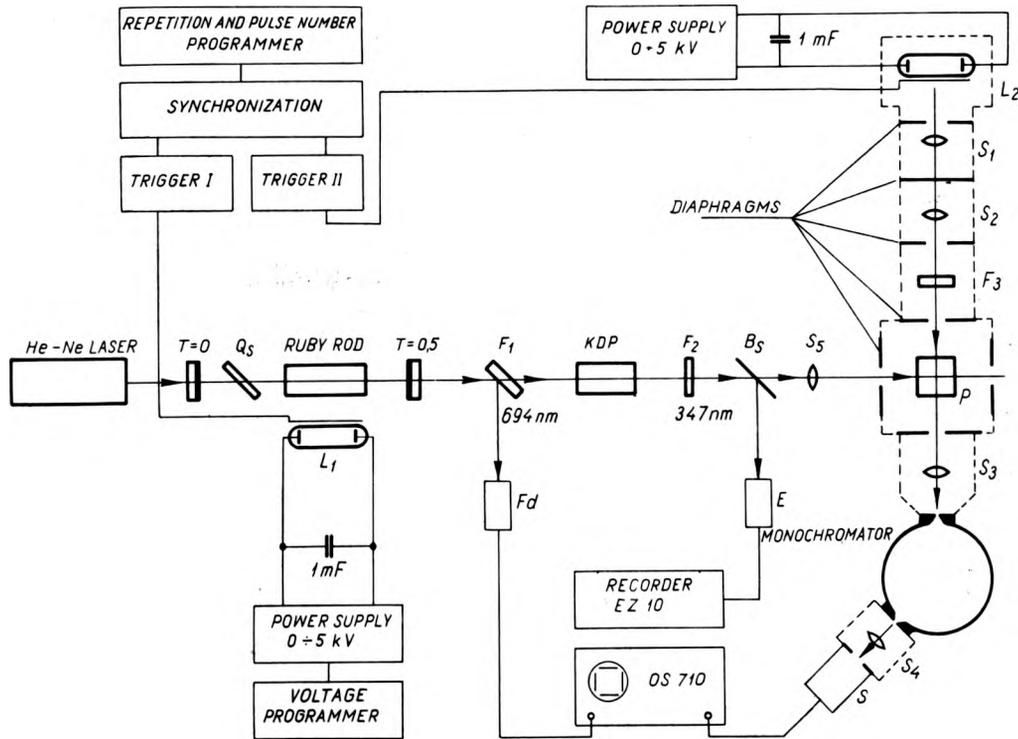
Fig. 1. Optico-electronic scheme of the measuring system: F_1, F_2, F_3 — filters, S_1, S_2, S_4 — spherical quartz lenses, S_3, S_5 — cylindrical quartz lenses, Q_s — passive Q-switch, Bs — beam splitter, L_1 — G-422 flash lamp pumping ruby rod, L_2 — analyzing light source, P — sample, E — photoelectric energy meter, S — photoelectric probe with photomultiplier, Fd — photoelectric probe with FDWCZ photodiode

sample from the flash lamp L filled with xenon under relatively high pressure (150 m T), providing for a continuous spectrum of the radiation emitted. The total energy emitted by the lamp L in a single flash is of the order of 3000 J, but only a small fraction in the form of a parallel beam, collimated by the system of lenses and diaphragms, reaches the sample. In order to reduce distortions in the signal from light noise (background), the analyzing part of the system (including the sample) is placed within a closed, blackened shield. While passing through the sample, the analyzing beam is focused by means of a cylindrical quartz lens S_3 on the slit of a prismatic C. Zeiss (Jena) monochromator, or COBRABiD M-3 double monochromator. The detection system S (having a characteristic pulse rise time of 10 ns), the essential element of which is a 1P28 or M12FQS35 photomultiplier, enables to study the time characteristics of the light signal with wavelength selected by the monochromator from the entire spectrum of the analyzing beam. The signal from the probe S is recorded with a photographic camera on the screen of an OS-710 oscilloscope (band width frequency 150 MHz). The time base of the oscilloscope is triggered

by the signal of a FDWCz (high-frequency) photodiode made by the Naukowo-Produkcyjne Centrum Półprzewodników (Scientific Manufacturing Centre for Semiconductors) in Warsaw. The photodiode makes it moreover possible to study shape of the exciting pulses at a short rise time of the device (2.4 ns).

The setup shown in fig. 1 is also well adapted to fluorescence studies. In this application the flash lamp is switched off and the probe S measures the fluorescence signal directly. The spectral characteristics of the elements of this system permit the study of absorption and fluorescence signals throughout the wavelength range from 250 to 700 nm.

The low-power He-Ne laser shown in fig. 1 defines the optical axis and serves for the accurate adjustment of the various elements. The device is operated a simply owing to an automatic system of programming and of stabilization of the voltage of the condensers supplying the flash lamp of the laser and the time control circuits. The latter makes it possible to choose the repetition time and number of flashes in each series, and enables the experimenter to concentrate exclusively on the measurements.

3. Applications of the device

Essential features of the device are: universality, and applicability to a wide range of physical and physico-chemical fields of study. The most typical examples of its applications are the following:

— Studies of the absorption spectra of the electronic excited states with a short lifetime arising in $S_1 \to S_n$ and $T_1 \to T_n$ transitions, where $n = 2, 3, 4 \ldots$. Such spectra can be obtained not only for the molecules but also for charge-transfer, exciplex, excimer and radical-ion complexes, etc [6, 7, 8].

— Measurements of the lifetimes of the electronic and vibrational excited states in the range 10^{-3}–10^{-8} s [9, 10].

— Assignment of the excited electronic level responsible for the photochemical and photophysical processes [11, 12].

— Determinations of the quantum yield of intersystem-crossing as well as determinations of the rate constants of such processes [13, 14].

— Studies of the vibrational relaxational mechanism within excited electronics levels [15, 16].

— Studies of the dynamics of ultra-fast processes, e.g. initial stages of photosynthesis [17, 18].

— Studies of intermolecular energy transfer processes [19, 20].

Results of test absorption and fluorescence measurements, carried out with the described system, have been reported at the VIIth Quantum Electronics and Nonlinear Optics Conference EKON, Poznań [21].

The essential parameters of the device decisive for its value are: the duration time of the exciting flash, the excitation radiation power, and the high rate of operation of the recording system. Hitherto described setups for laser flash photolysis generally involve pulsed analyzing sources with times of the order of microseconds. The device described above presents the advantage of a longer time duration of the analyzing lamp at a radiation intensity maintained constant for times to 10^{-3} s. This extends the range of its applicability to regions in which classical (non-laser) flash photolysis is usually applied [1].

Further work on the device will be aimed at shortening the flash time of the laser and at shaping the pulse by electro-optical method.

When using a fast 1P 28 (RCA) photomultiplier, it is possible to shorten the over-all rise time of the signal to 2.5 ns.

Лазерное устройство для изучения оптической динамики абсорбции и флуоресцентных сигналов

Описывается лазерное устройство для определения абсорбционных и эмиссионных сигналов, пригодных в диапазоне времени от 10^{-4} до 10^{-8} и для спектрального диапазона от 250 до 700 нм. Обсуждены некоторые применения этого устройства для исследований физических и химических свойств жидкостей и газов.

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