Double-beam laser spectrometer
of nanosecond resolution

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The paper describes the design and performance of a double-beam pulse spectrometer used for measuring, in the real time, changes in transient absorption, evolution of emission and dynamics of the ground state depletion of molecular media. The technique of digital recording and data processing at the sampling rate of 2 gigasamples/s ensures a resolution of single nanoseconds in the time interval of up to 10 μs. The spectrometer has been successfully tested in photophysical studies of the triplet states of xanthione in benzene and *n*-hexane solutions.

1. Introduction

Despite the recent development of the pico- and femtosecond methods of time resolved spectroscopy [1]—[4], the nanosecond spectroscopy of transient absorption is still a powerful and convenient tool in investigation of the properties of molecules in triplet states as well as the intra- and intermolecular processes involving photophysical and photochemical individua in triplet states [5]—[8]. The idea and applications of transient absorption measurements have been described in part in our earlier works concerning mainly the picosecond range [9], [10].

Transient absorption spectroscopy originates from the flash photolysis technique developed in order to study transient individua created in photophysical and photochemical processes. Regarding the short lifetime of the transient individua, their absorption spectra could be measured either by the method requiring their prior stabilization [11] or by the flash photolysis technique described for the first time by Norrish and Porter in the 50's [12], [13]. At the beginning the resolution of the flash photolysis method was of the order of milliseconds (2 ms), then microseconds (Niemann, Klenert [14], [15], 0.2 μs), and in the 60's its resolving power was improved to nanoseconds (Novak, Windsor [16], 30 ns). The flash photolysis method is based on the fact that an intense flash of light generates the transient individua at a concentration high enough to enable measurement of their absorption spectrum. Porter and Norrish used the photographic method of recording of the transient absorption spectra (flash spectrography) obtaining a spectrum for a given moment of time. Davidson *et al.* [17] introduced a system

employing a photoelectric detector permitting investigation of the time dependence of transient absorption spectra in a given spectral range (flash spectrophotometry). An experimental solution proposed by PORTER [18] and applied in mid-60's by HERR and PIMENTEL [19] was a combination of the two: flash spectroscopy and flash spectrophotometry systems achieved by introducing a rotating or oscillating mirror in the dispersive unit. This solution permitted studies of evolution of transient absorption spectra as a function of time and wavelength simultaneously.

Despite a variety of specific solutions all transient sbsorption spectrometers include certain functional blocks: a source of exciting light, a source of analysing light, a system providing time resolution, and a system for detection of analysing light. A source of exciting light can be flash-lamps [12], [20], or pulse lasers [16], [21] – [23], while Xe lamps with a shutter [24], flash lamps [21], [25], [26], tunable lasers (the whole spectrum point after point) [27] or nanosecond continuum [28] can be used as a source of analysing light. Also, laser-triggered breakdown sparks in gases [16], [29] as well as laser-excited fluorescence continua from scintillator dyes [30], [31] have occasionally been used for generation of broadband analysisn radiation. Time resolution can be achieved in the real time either: by using photodetector and oscilloscope (possibly with a memory) or transient digitizer, or employing the sampling technique: with the use of a gated photomultiplier [32] – [35], a boxcar as a gating and averaging device [24], or by the pump-probe method with electronically or optically introduced delay [27]. The analysing light is detected by a photomultiplier, photodiode, photodiode array (PDA), charge coupled device (CCD) or optical multichannel analyser [36].

Development of recording technology has brought digital oscilloscopes which combine a simple and clear data display of an oscilloscope with the virtues of a transient digitizer (precision, digital readout) working at a very high rate, up to 4 gigasamples per second. The possibility of averaging, statistical processing and storage of data carried out by a computer prompted new solutions for the real time measurements performed with a flash lamp as a source of white analysing light allowing investigation of the whole course of transient absorption process at a given wavelength during a single flash. This paper reports the design of a newly constructed nano/microsecond transient absorption spectrometer and results of the tests of its operation. In order to take full advantage of the experimental solution proposed, a double-beam geometry of detection was applied which permits continuous reference of each absorption curve to the zero line determined for each flash individually.

2. Design and construction of the spectrometer

The constructed two-beam transient absorption spectrometer of nanosecond resolution belongs to the group of flash spectrophotometry apparatuses although, since it employs an Nd:YAG laser as a source of exciting pulses, it should also be classified as laser spectrophotometry apparatus. The exciting pulses are generated by an optoelectronically Q-switched Nd:YAG laser (Quantel YG 571 C10 type). The

sample is excited by nanosecond (10 ns) pulses of tripled frequency ($\lambda_{ex} = 355$ nm) generated at a repetition rate of 2 Hz adjusted to the frequency of flashes from a miniature xenon lamp JFK-120 which is a source of analysing light. The light from the lamp is collimated to form a beam of about 30 mm in diameter. A diaphragm put in the path of this beam separates from it two parallel beams of 4 mm in diameter. One of these beams passes through the part of the sample subjected to the laser pulse while the other falls onto the unexcited part of the sample (Fig. 1).
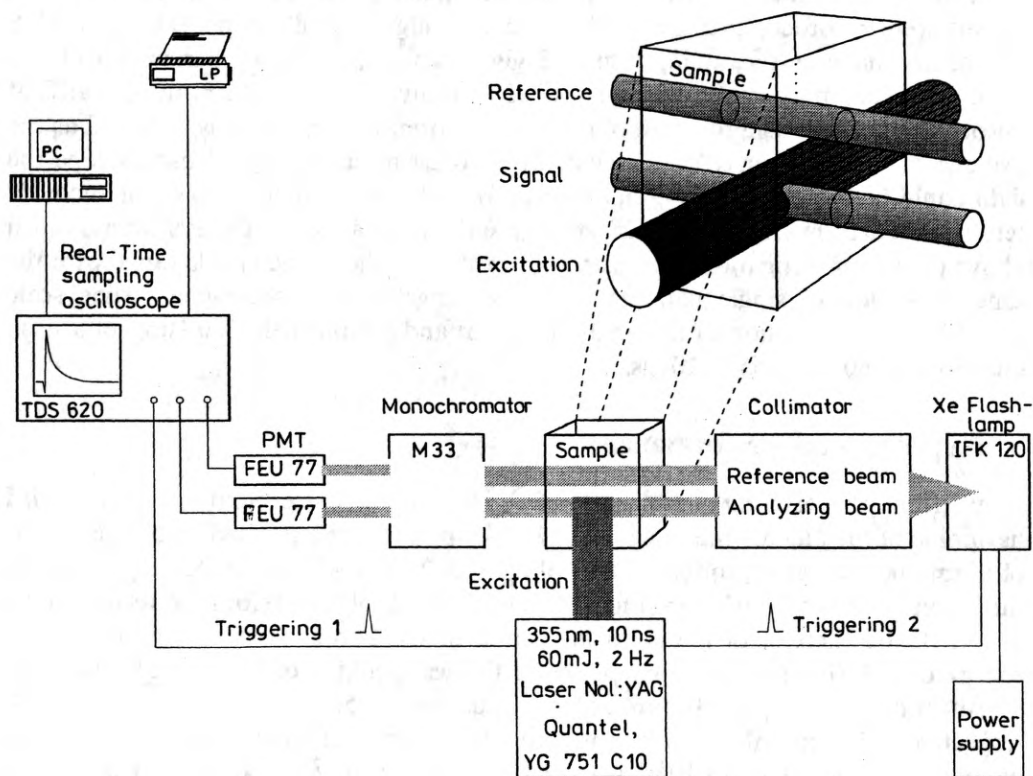

Fig. 1. Schematic diagram of the measuring system. The geometry of beams at the sample cell shown in the insert

These are the analysing and the reference beams, respectively. Such a solution ensures increased sensitivity and stability of measurement which becomes independent of the fast changes in the intensity of the analysing light and its spectral inhomogeneities. The senistivity of measurements of transmission changes in a 1 cm thick sample is $<1\%$ which corresponds to the absorbance change by $\Delta A = 0.004$. The geometry of the illuminating system has been designed in such a way as to maximize the separation between the analysing and reference beams, which finally was >20 dB. In transient absorption spectrometers the measured signal is frequently disturbed by fluorescence and scattering characterized by spherical geometry of propagation. In order to keep their effect to a minimum, two long pipe collimators were mounted behind the

sample holder. With the usual width of the monochromator slits of ~ 0.5 mm they restricted the solid angle of detection to $< 10^{-4}$ steradians. The fragment of the spectrum to be analysed, typically of a width $\Delta\lambda = 7$ nm, was selected from the range of $400 - 750$ nm by a double prism monochromator M33 (COBRABiD). The analysing and the reference beams having passed through the sample fell in parallel onto the input slit of the monochromator and left it through the output slit still as two independent beams carrying different information. Changes in the intensities of each of the beams were measured by two preselected pulse photomultipliers FEU-77. The signals were recorded, averaged and stored in a digital oscilloscope Tektronix TDS 620 of the maximum sampling rate of 2 gigasamples/s, frequency bandwidth of 500 MHz and the maximum sensitivity of 1 mV/div. A curve illustrating transient absorption changes as a function of time for a chosen wavelength was obtained as the average of 20 to 30 runs. After preliminary processing in the digital oscilloscope the data could be obtained in the graphic form from the printer and were simultaneously sent to a PC 286 microcomputer for storage and further analysis. The system described above permits investigation of transient absorption in the whole visible range with the time resolution of single nanoseconds. The range of the spectrometer time scale depends on the duration of the analysing pulse and for the JFK-120 lamp of a flash duration of 60 µs it is $\leqslant 10$ µs.

3. Experimental performance

Apart from the exciting wavelength of $\lambda_{ex} = 355$ nm corresponding to the third harmonic of the fundamental beam $\lambda = 1.064$ µm, the laser equipped with a generator of harmonics can also produce beams of $\lambda_{ex} = 532$ nm and 266 nm corresponding to the second and the fourth harmonics. The wavelength of the exciting beam is selected to match the energies of the electronic states of the sample studied. The maximum energy of individual nanosecond pulses of the wavelengths of the second, third and fourth harmonics ($\lambda_{ex} = 532$ nm, 355 nm, 266 nm) is 500 mJ, 190 mJ and 90 mJ, respectively. These values correspond to the number of quanta in an individual nanosecond pulse of 1.34×10^{18}, 3.40×10^{17} and 1.20×10^{17}, respectively. Taking into account that even for a sample of as high concentration as, *e.g.*, $c = 1 \times 10^{-2}$ mol/dm^3, the number of molecules in the irradiated volume of 2×10^{-3} cm^3 is 1.2×10^{17}, and regarding the fact that to avoid interactions of the excited molecules only a small fraction of the total number of molecules can be allowed to absorb a quantum of the exciting light, the energy of laser pulses of each of the above mentioned wavelengths is more than enough for transient absorption measurements.

Although the spectrometer has been designed for investigation of transient absorption spectra, the solutions applied permit realization of the following three types of time-resolved spectral measurements:

1. Measurements of transient absorption spectra at different moments of time, as well as rise and decay curves of absorption from the electronic states excited by the pumping pulse.

2. Emission measurements; emission spectra, the curves of phosphorescence rise

and decay. Dynamic measurements of phosphorescence are performed with a single beam (the analysing beam is blocked) and at a wavelength close to that of the maximum intensity in the emission band.

3. Ground state depletion (GSD) measurements; measurements of the recovery of absorption from the ground state after a disturbance caused by sudden excitation of a considerable number of molecules by a nanosecond laser pulse. GSD measurements are performed with two beams through analysis of changes in transmission or absorbance within one of the bands of absorption from the ground state.

These three kinds of measurements provide different information about the physical properties of the system studied. Transient absorption measurements give data on the transitions between the excited states and the dynamics of population of the excited states from which absorption transitions to the states of still higher energy can occur. Results of the emission measurements carry the information on the dynamics of population of the emitting states (usually different from those studied in absorption measurements) and on the energy of emission transitions. Ground state depletion measurements supply the information on the overall dynamics of recovery of the ground state population including the contribution of all emission and radiationless, intra- and intermolecular decay processes in the systems studied [37]. In particular, GSD signals carry the information on the
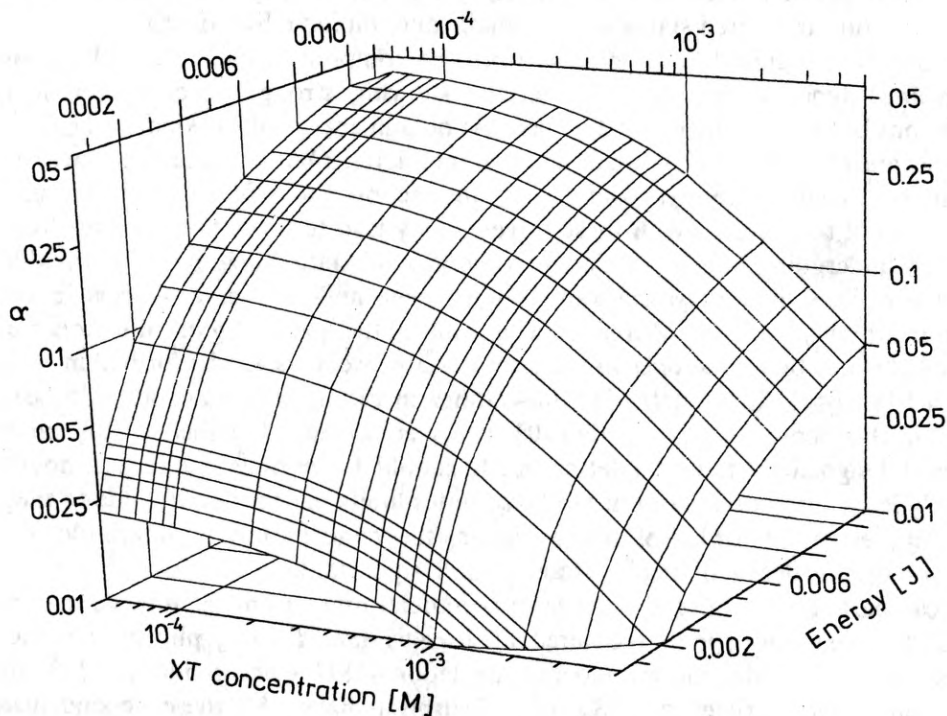

Fig. 2. Fraction of excited molecules as a function of xanthione concentration and pulse energy, calculated for $\lambda_{ex} = 355$ nm

contributions of the processes and individua which for the energy reasons are beyond the spectral range of the spectrometer.

An important experimental problem is to estimate the dependence of the fraction α of the excited molecules on the solute concentration and the energy of the exciting pulse (Fig. 2).

Because of the exponential decay of the exciting pulse intensity, in order to meet the condition of homogeneous excitation when studying samples of high optical density, the analysed excited region in the sample must be restricted to about 1 mm. Also, a strong attenuation of the analysing light from the flash lamp can be reduced by diminishing the light path in the sample to, *e.g.*, 2 mm. This would permit successfull GSD measurements even in the spectral range with relatively intense absorption bands.

4. Test measurements

The performance of the spectrometer in the three kinds of experiments described above was tested for xanthione in benzene and *n*-hexane solutions. Xanthione is a typical representative of thioketones, the compounds of easily measurable and relatively well known intramolecular properties [38]–[40]. However, the intramolecular properties of these compounds, and particularly the mechanisms of their interaction in excited states with aromatic and aliphatic hydrocarbons, are still rather poorly recognized. The solvents were the compounds characterized by the well defined types of interactions: benzene showing strong universal (physical) interactions but chemically unreactive because of high energy of its bonds [40], [41], and *n*-hexane characterized by weak physical interactions but chemically reactive, in particular susceptible to hydrogen atom abstraction [40], [42]. Intramolecular interactions of thioketones with these solvents may lead to formation of short lived individua undergoing immediate decay to the ground state. Such excited individua can be exciplexes in the system xanthione/benzene and thioketyl radicals in the system xanthione/*n*-hexane. Moreover, as a result of the quenching of thioketones in the excited states by thioketones in the ground state, excimers can be formed in both systems [43], [44]. Such effects for thioketones in the S_2 state have already been studied in the picosecond time scale [10]. The spectrometer described in this paper has been designed to study triplet states. It should be emphasized that although relatively low energy of thioketones in these states limits their reactivity, due to their long lifetimes, of an order of microseconds, the contribution of intermolecular processes to the decay of triplet states is still significant.

Decay parameters of the T_1 state have been determined from the time courses of $T_1 \rightarrow T_n$ transient absorption measured at $\lambda = 465$ nm, $T_1 \rightarrow S_0$ phosphorescence measured at $\lambda = 760$ nm and ground state depletion (GSD) measured at $\lambda = 400$ nm, at the long-wavelength edge of $S_0 \rightarrow S_2$ absorption band. All these dependences have been measured for xanthione in benzene and in *n*-hexane at 295 K. Measurements of transient absorption, phosphorescence and GSD have also been
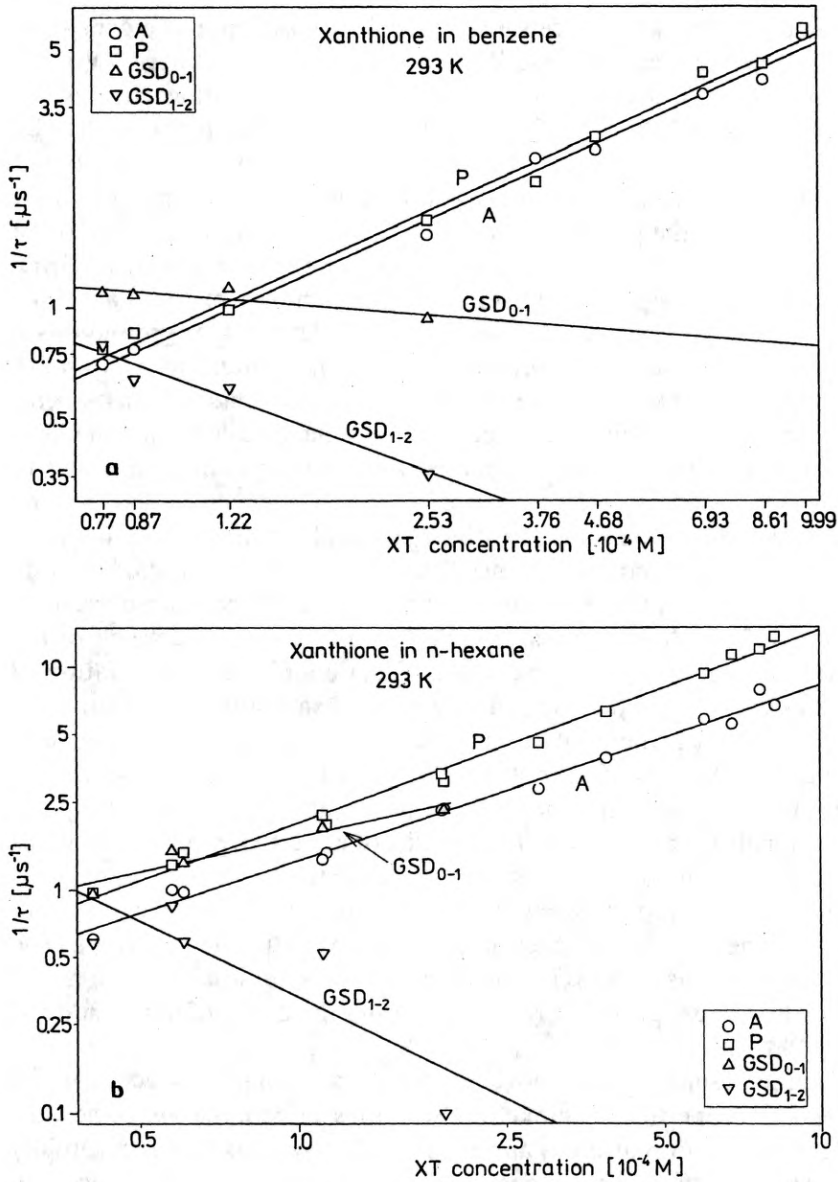
Fig. 3. Decay rate constants (inverse lifetimes) or transient absorption (A), phosphorescence (P) and ground state at depletion (GSD) signals for XT solutions in benzene (a) and *n*-hexane (b). GSD data have been determined from the single exponential fit to the initial parts (from 0 to 1 µs) of the decay curves GSD_{0-1}, and from the middle parts (from 1 to 2 µs) of these curves, GSD_{1-2}

performed as a function of xanthione concentration in both solvents studied. Figures **3a,b** present the rate constants of decay of transient absorption, phosphorescence and GSD versus xanthione concentration in benzene, C_6H_6, and *n*-hexane, C_6H_{14}. The dependences of T_1 state decay time on xanthione concentration determined

from the measurements of phosphorescence and transient absorption are consistent with earlier results [40] and can be described by the well known Stern—Volmer expressions for the concentration selfquenching. Far more interesting conclusions follow from the obtained GSD curves. Significantly different decay times implied by the beginning of the curve (from 0 to 1 µs) and its further part (from 1 to 2 µs) testify to the non-exponential character of the decay and to a decrease of its rate constant with time. At the beginning the ground state population increases mainly due to the transitions from the decaying T_1 state as indicated by close rate constants of GSD, phosphorescence P and transient absorption A in the samples of low xanthione concentration. Later, when the T_1 state is already relaxed, the ground state population increases due to a decay of another individuum different form T_1 and of a significantly longer lifetime. The contribution of this process increases with increasing xanthione concentration. Such dependences of the rate constants of GSD, phosphorescence and transient absorption on time and xanthione concentration can only be explained by assuming a formation of a triplet excimer of the lifetime significantly longer than that determined for the T_1 state of xanthione. The decay of this excimer after a few microseconds becomes the main channel of the ground state population. The dependence of the GSD rate constant on xanthione concentration is a highly complex one for quite a few reasons. The excimer forms as a result of the interaction of xanthione molecules excited to the T_1 state and the concentration of these molecules is a function of both the concentration of xanthione in solution and time. The concentration of excimer molecules decreases due to a decay to the ground state and the concentration-dependent selfquenching. Such a convoluted functional dependence of GSD signal on time and concentration, although makes its quantitative analysis difficult, permits a positive verification of the problem of contribution of the triplet excimer in the decay of excited thioketones.

This interpretation is supported by changes in the shape of the transient absorption spectra measured at different times after excitation (Figs. 4a,b). The spectra recorded 1.5 µs or 2 µs after excitation reveal changes, indicating the presence of an individuum which most probably is formed during the decay of the T_1 state of xanthione.

In conclusion, the results of the above experiments, taking into account the physical and chemical properties of thioketone solutions in benzene and *n*-hexane, provide the evidence of the formation of an excimer in the systems which essentially contribute to the triplet state decay, as postulated when considering the process of selfquenching of thioketones in the T_1 state [44].

5. Conclusions

The transient absorption spectrometer whose construction and performance are described in this work, combines the advantages of digital detection and processing with the simplicity and convenience of the real time measurements. The solution based on double-beam recording of the signal by two independent detectors has significantly increased the accuracy of measurements as it enables current moni-
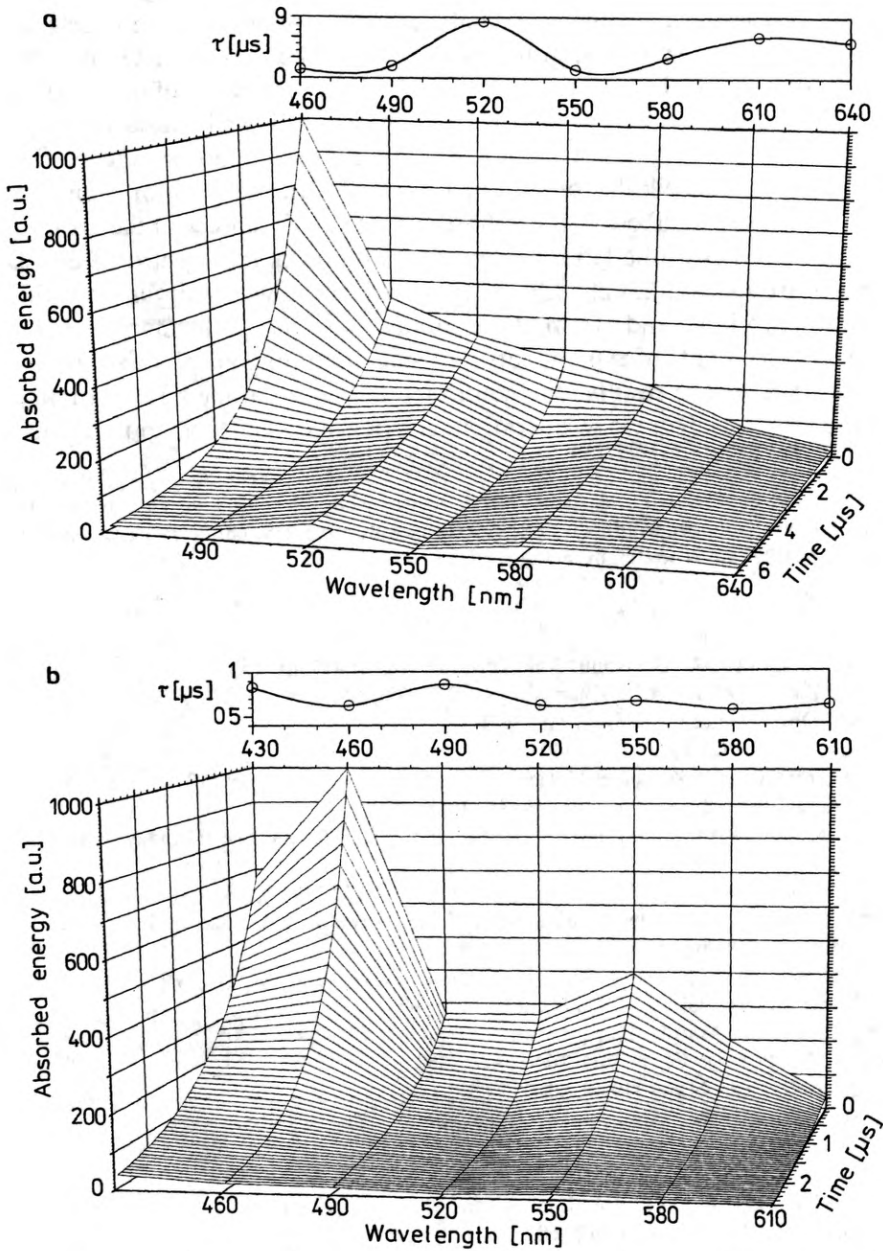
Fig. 4. Simplified time-resolved transient absorption spectra of XT in benzene (a) and in *n*-hexane (b). The upper parts present the wavelength dependence of transient absorption decay time determined by a single exponential fit to the experimental decay curve

toring of background and current reconstruction of the zero line, depending on intensity fluctuations and time changes of the light from the analysing flash lamp. The experimental solution applied permits us to restrict substantially the necessary

sample exposure to exciting and analysing light and thus minimizes the effects of photochemical decomposition of the substance studied. The spectrometer can be used to study nonstationary absorption and emission in the time scale of up to 10 μs with a time resolution of single nanoseconds. It is particularly well suited to study the properties of molecules in triplet states. A very important advantage of the proposed solution is the possibility of studying not only transient absorption but also emission (in the case described — phosphorescence) and dynamics of the ground state depletion. The studies of the latter required adaptation of the spectrometer for use of strongly absorbing samples as GSD is measured at the wavelengths from the range of strong absorption bands from the ground state. The performance of the spectrometer in all three kinds of experiments has been tested on xanthione solutions in benzene and n-hexane. The results fully confirmed a high accuracy and sensitivity of the spectrometer, proved its easy operation and a wide range of applications.

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