Optica Applicata, Vol. XXV, No. 4, 1995

Transient absorption spectrometer for the picosecond time range

M. SZYMAŃSKI, M. BALICKI, M. BINKOWSKI, J. KUBICKI, E. PAWŁOWSKA, T. WRÓŻOWA, A. MACIEJEWSKI

Institute of Physics and Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60–780 Poznań, Poland.

A new experimental solution of a picosecond transient absorption spectrometer with a high power pulse YAG:Nd^{+3} laser, YG 571C type (Quantel), has been described and tested. The system has been designed to study photophysical and spectral properties of molecular systems. The excitation is realized with the second, third and fourth harmonics of the basic YAG:Nd^{+3} laser frequency of the maximum energies of 30, 10 and 4 mJ, respectively, the pulse width of ~15 ps (fwhm) and the repetition rate of 10 Hz. The analysing beam is the "white" light of the picosecond continuum generated by the 1064 nm beam in isopropanol. The optical delay line of 20 cm travel range permits investigation of the processes occurring in the time scale to 1.3 ns with the time step of ~3 fs. Autocorrelation measurements of two-photon fluorescence excitation were performed in the system in order to determine the instrument response function. The zero-point position was found from the $T_1 - T_n$ transient absorption measurements in benzophenone/hexane solution. The system was used to study the interaction of the excited xanthione molecules with alkanes and benzene occurring in the picosecond time scale. The sensitivity of the system permits measurements of transient absorption in a sample of a molar extinction coefficient ~500 M^{-1} cm^{-1} with the actual time resolution of ~1 ps.

1. Introduction

Molecular spectroscopy and photophysics are concerned with investigation of the mechanisms and effects of the interaction of light (in a broad sense of the word) with molecules which are usually dispersed in liquid, solid or gas matrices. Absorption of a photon by a molecule is accompanied by electronic, vibrational, or rotational transitions which can initiate a chain of radiative and radiationless inter- and intramolecular processes. These processes may include different kinds of luminescence, internal conversion, intersystem crossing, various forms of the excitation energy transfer to molecules of the same kind (self-quenching), to other molecules (quenchers) dispersed in the matrix or to the molecules of the solvent (matrix). Intermolecular interactions are, of course, bidirectional, *e.g.*, the interactions with solvent are of importance in the relaxation and thermalization processes. Thus, a direct consequence of light absorption can be, for instance, an energetic transition in a molecule which usually involves a change in its geometry and charge distribution, modes of molecular vibrations and their intensities; a photochemical reaction or formation of molecular aggregates [1].

The methods used to study photophysical systems, their properties and the processes they are involved in comprise steady state and dynamic spectroscopy, energy balance analysis and many others, both physical and chemical ones [2], [3]. Much improvement to almost all experimental methods used in molecular spectroscopy and photophysics has come about due to the application of lasers because of their unique characteristics, including monochromaticity of radiation, high power and spectral brightness, splendid stability of work and a possibility of precise tuning [4]. However, the application of lasers in dynamic studies of photophysical individua was a real breakthrough. Pico- and femtosecond laser pulses are short enough to be used in direct studies of the energy states of molecules and processes describing transtions between the states [5], [6]. Although the radiative lifetimes of molecules in excited singlet electronic states are usually long ($\sim 10^{-8}$ s), but due to intra- and intermolecular interactions the actual decay times are reduced to nano- or picoseconds. The relaxation times of the vibrational levels of molecules are usually of an order of $10^{-11}-10^{-12}$ s.

Dynamic studies in molecular spectroscopy and photophysics are performed by either emission or absorption methods [7], [8]. In both cases, they are aimed at accurate determination of lifetimes of the excited states as well as the dependence of the excited level population on time as a function of the excitation and emission wavelength. It is commonly assumed that emission measurements are experimentally easier to carry out than measurements of absorption. It is technically easier to measure even extremely weak light signals, and compare their relative intensities, than to measure very small changes in intensities of strong light beams, as it is the case in the absorption spectroscopy. On the other hand, luminescence (fluorescence or phosphorescence) can be observed in relatively few photophysical systems and takes place (with few exceptions) from the lowest excited electronic states, *i.e.*, from the first singlet (S_1) and triplet (T_1) states. Thus, it is understood that such emission brings only the information about the states from which the radiative transition takes place and about the interactions affecting the molecule behaviour in these states. So, the steady state as well as dynamic emission spectroscopies are a source of important information, but this information is available only for a limited number of systems.

Since not all molecules (photophysical systems) show luminescence emission but all absorb light, it would be natural to expect that absorption spectroscopy is more universal than emission one. However, it should be remembered that the usual absorption spectroscopy provides the information about the energy transitions from the ground state (to be more exact, from the levels populated at room temperature) and the dynamic measurements can only bring the information on the recovery of the disturbed equilibrium of the ground state population [9]–[12]. To be able to gain some information on the dynamics of excited levels, the use of transient absorption measurement technique is required.

This paper describes a spectrometer for transient absorption measurements designed and constructed for the studies of dynamics of excited states and interactions in molecular systems in the picosecond time scale. The basic charac-

teristics of the experimental setup are given and the operation of the setup is illustrated by results of chosen photophysical studies.

2. Method of transient absorption measurements

Absorption transitions take place from the energy levels occupied at a given temperature. This means that in normal conditions the transitions occur from the populated rovibrational components of the ground state. The condition for observation of absorption transitions from excited states is to generate the population of these states. A sufficiently strong short exciting pulse can induce a substantial population of an excited state and then absorption due to the transitions from this excited state to higher ones can be observed [13]–[19]. These energy transitions are schematically shown in Fig. 1. The transient absorption signal

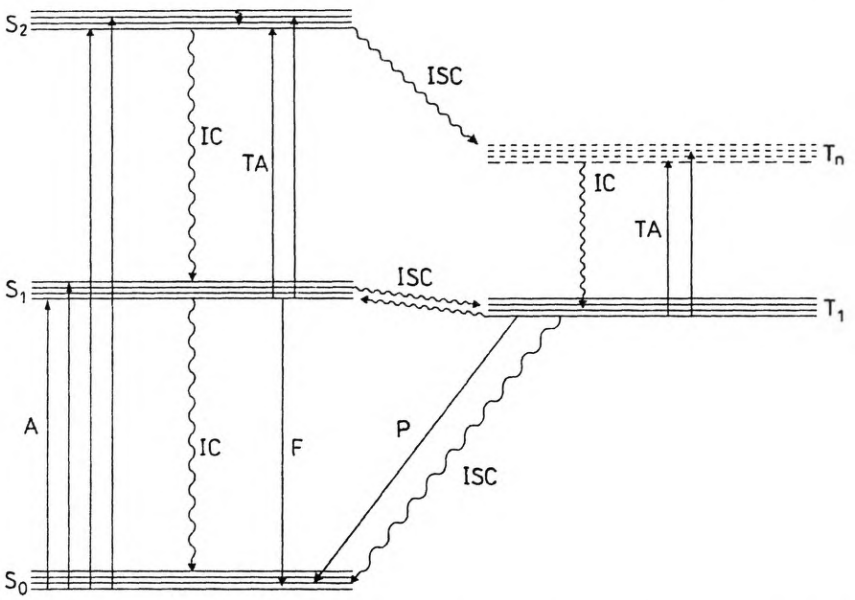

Fig. 1. Jabłoński diagram of molecular energy levels and energetic transitions: S_0, S_1, S_2 – singlet states, T_1, T_n – triplet states, A – absorption, TA – transient absorption, IC – internal conversion, ISC – intersystem crossing, F – fluorescence, P – phosphorescence

decays at a rate proportional to the population of the directly excited state which is depopulated in result of all various radiative and nonradiative processes taking place from this state. It should be noted that the shape of transient absorption rise and decay curves depends only on the dynamics of population and depopulation of the directly excited state and not on the properties of the higher excited states which are populated as a consequence of transient absorption. However, the spectrum of transient absorption depends on the states position on the energy scale. Dynamic measurements of transient absorption provide similar information on the excited

states as dynamic measurements of emission, however, the former are more universal and convenient as absorption is a common phenomenon and its effective measurement is enabled by the proper choice of external conditions while the emission decay can be rarely observed.

A precursor of the method of transient absorption measurements was the experimental technique of flash photolysis devised by NORRISH and PORTER [20] and later modified by PORTER [21]. In this technique, photofragmentation of samples was induced by a strong flash from a lamp supplied by a battery of capacitors and then absorption spectra of the fragments were analysed by an additional flash light through a spectrograph. This technique was adapted for the transient absorption spectroscopy by monochromatization of the exciting and analysing beams, introduction of a controlled delay between the exciting and analysing pulses and time-resolved recording of the absorption signal. The time course of transient absorption was analysed at first in the real time with photomultipliers and oscilloscopes or transient digitizers. When improvement in laser technology permitted construction of lasers working at repetition rates of the order of tens of Hz, the absorption spectra were recorded with systems based on boxcar integrators. These new experimental solutions were effective in the range of milli-, micro- and nanosecond time scales. When the need to study transient absorption in the pico- and subpicosecond range arose and the appropriate technology was developed, the pulse-probe method was proposed which can be applied down to femtosecond time scale. In this method, the studied phenomenon is induced by one beam (light pulse) of short duration and the effects of this pulse, decaying in time, are analysed by another beam (light pulse) directed onto the sample at a desired prefixed delay. Many experimental solutions of the pulse-probe method have been developed [16], [17], [22], [23], however, the following features have preserved their common characteristics. Each measuring point is determined by a different pair of pulses; an exciting and analysing one. When the results are averaged, a resultant point may be determined by a group of pulse pairs. The time resolution of the system depends on the performance of a variable optical delay line which ensures precise timing of the analysing pulse relative to the exciting one. The detection system reads out the time-integrated photoelectric signal as a function of the delay of the analysing beam with respect to the exciting one. No fast electronics is applied; the laser system works at a low repetition rate, of an order of tens of Hz, which permits application of high power pulse lasers as generators of exciting pulses. The system proposed in this work belongs to this category.

3. Transient absorption spectrometer

Light pulses used for excitation and analysis of a studied sample are generated by a picosecond YG 571C laser (Quantel). It works at a repetition rate of 10 Hz and comprises a generator and a YAG:Nd^{+3} amplifier. The generator is acousto-optically mode-locked and the effectiveness of mode synchronization is additionally improved by applying a solution of 9740 Eastman Kodak dye of the formula

$C_{49}H_{43}ClO_6$ in 1,2-dichloroethane in a flow cell mounted directly at the zero mirror (passive mode-locking). By changing the laser line width, trains of pulses of half widths: 20, 50, 100 or 200 ps can be generated. Single pulses are selected from these trains by a photoelectrically controlled Pockels switch. The selected pulse is then amplified in a double-pass amplifier to reach at the laser output the energy of 75 mJ in a 20 ps (fwhm) pulse of wavelength of 1064 nm. The laser is also equipped with generators of harmonics producing single pulses of 30 mJ for 532 nm, 10 mJ for 355 nm and 4 mJ for a wavelength of 266 nm; with the pulse duration decreasing from initial 20 ps with increasing order of the harmonic. Two beams are directed from the picosecond laser to the spectrometer: one made of the harmonics to be the exciting beam and the other, the basic beam, to generate a picosecond continuum which is used to analyse the state of a sample at a chosen moment. In our experiments, the exciting beam has always been the third harmonic of the fundamental laser frequency. The harmonics generators convert only part of the incident energy of the fundamental beam, while the other part is used to generate the picosecond continuum [24] in the path of the analysing beam. A diagram of the transient absorption spectrometer is shown in Fig. 2. The short-wave exciting beam is passed through a prismatic delay line and collimated on the sample by a lens of the focal length of 30 cm. A constant prefixed delay introduced by this line compensates for the differences of the optical paths in the pathways of excitation and analysis and permits suitable setting of the zero point (*i.e.*, the moment the two beams meet on the sample) on the time axis.

In the studies of transient absorption processes, a source of the probing light is a spectrally broadened laser pulse, the so-called continuum. Such a continuum can be generated in many different substances. Many gas, liquid and solid media, when a picosecond high power laser pulse passes through them, can produce spectral broadening of the pulse reaching as much as tens of thousands cm^{-1}. This is a threshold effect depending on the power density and the length of a medium in which the continuum is generated. The threshold power density of this effect is close to those of self-focusing and of Stimulated Raman Scattering, so these effects frequently accompany the generation of continuum and minimization of their contribution can significantly improve the continuum output. The greatest spectral broadening is achieved in H_2O, D_2O, quartz glass and in NaCl crystals. The use of liquids is recommended to avoid damage to the medium which might be caused by electric breakdown in solids. We studied performance of the continuum generated by the fundamental beam (1064 nm) of YG 571 C laser in liquids in short or long cells when the liquid was either flowing through the cell or stirred. Because of the destructive effect of high power and high energy laser pulses, care was taken that the distance between the cell windows and the focal point be sufficiently long. Therefore the cells we used were not shorter than 8–10 cm. The time shape of the spectrally broadened pulse was roughly the same as for the incident pulse. For generation of the continuum the following liquid media were used: water, heavy water, carbon tetrachloride, isopropanol, perfluoro-1,3-dimethylcyclohexane and cyclohexane. In the latter compound, a very strong anti-Stokes stimulated Raman scattering was

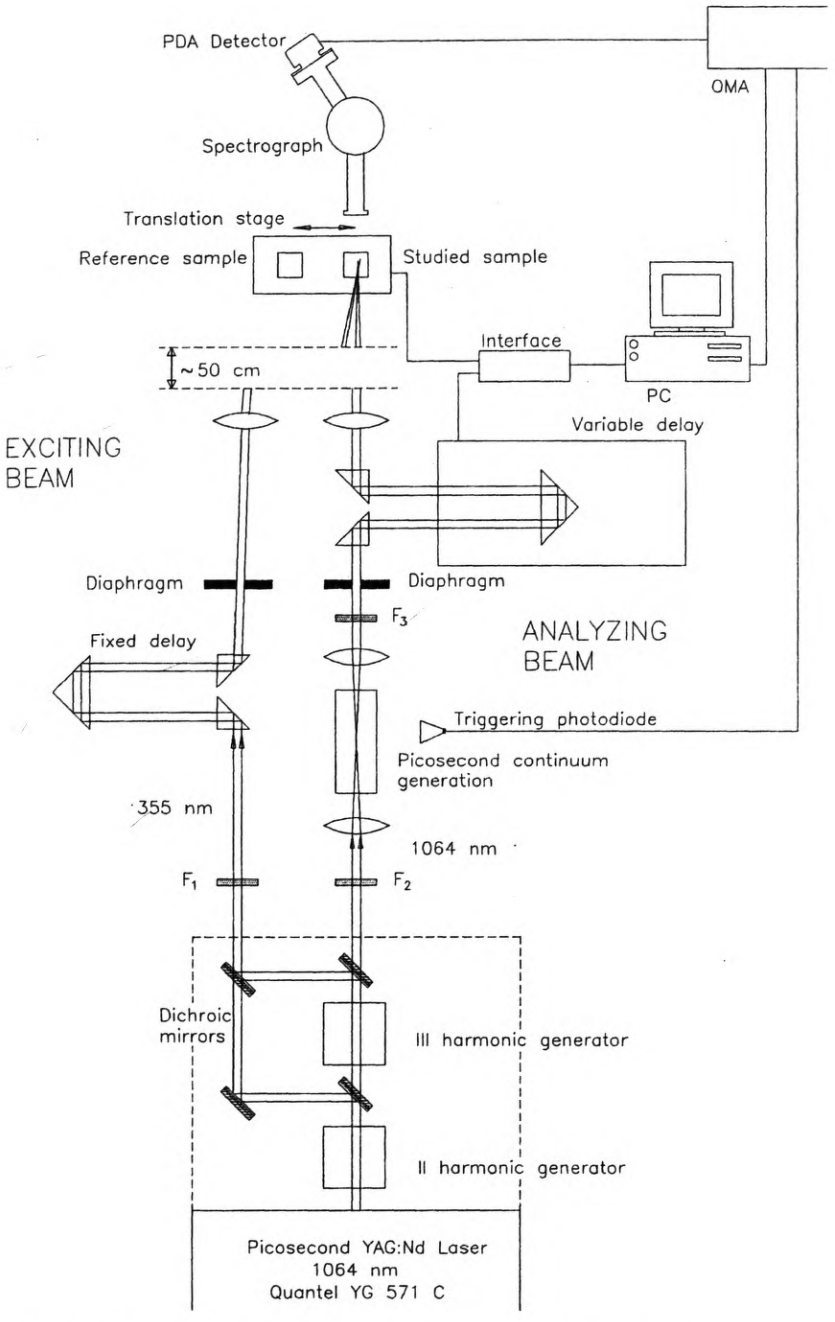

Fig. 2. Diagram of the picosecond transient absorption spectrometer

observed while in perfluoro-1,3-dimethylcyclohexane the intensity of the broadened radiation was very weak. We also checked the quality of continua obtained with 90% and 50% isopropanol solutions in water. Some results are shown in

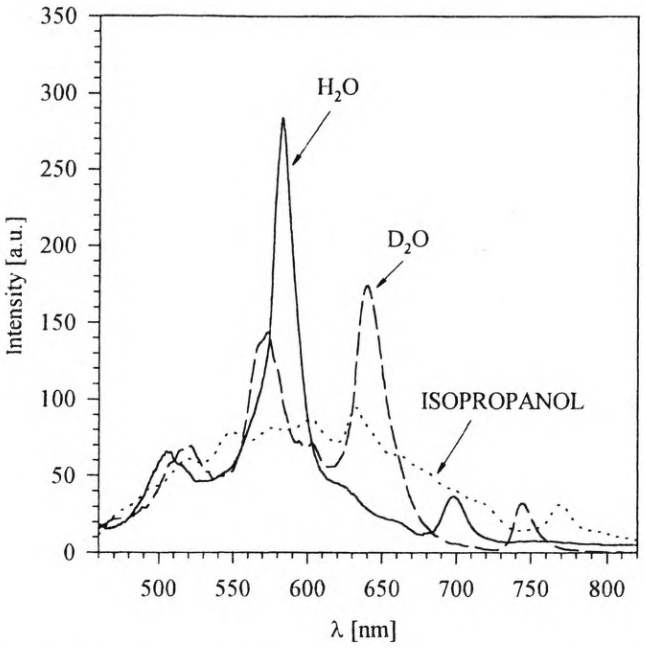

Fig. 3. Spectra of the picosecond continua generated in water, heavy water and isopropanol

Fig. 3. The best and most stable continuum was obtained with a pure isopropanol in a 10 cm long cell.

The white picosecond beam used for analysis of the sample is passed from the generating system to the sample through a variable delay line. The line consists of two fixed right angle prisms and a cube corner prism (retroreflector) mounted on M-525.22 type linear stage (Physik Instrumente) of 200 mm travel range driven by a backlash-free DC-motor/gear system. The positioning resolution of 0.16 μm and repeatability of 0.4 μm ensured the time resolution of the delay line of a few femtoseconds.

The exciting and the analysing beams intersect at an angle of ~20° in the sample which usually is a solution of a studied substance placed in a 1 cm optical cell. The focal point of the exciting beam falls in front of the measuring cell wall and the cross-section of this beam restricted by a special diaphragm makes in the cell a circular spot of 3 mm in diameter. The diameter of the "white" analysing beam, smaller than 1 mm, is chosen so that throughout the length of the cell the beam passes through almost uniformly excited volume of the sample, Fig. 4. To carry out the optical alignment of the two beams in the cell, the trace of the ultraviolet exciting beam was made visible by introducing a fluorescent solution into the measuring cell. Against this trace the optimum position of the white analysing beam was adjusted in two perpendicular planes. Thanks to the noncollinear geometry of the measurement the exciting beam could be directed to the side of the spectrometer slit and blocked, which drastically reduced the background level.

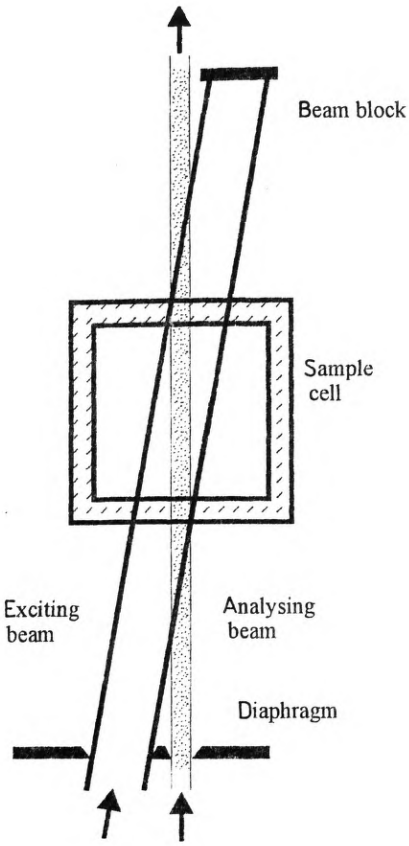

Fig. 4. Geometry of the measurement

The diagram of the experimental setup (Fig. 2) shows also the position of a reference sample. This sample is mounted beside the studied one on an additional translation stage and during a series of measurements each of the samples is alternatively introduced into the region of the intersection of the exciting and analysing beams. Usually a pure solvent has been used as the reference sample. Alternative performance of the full cycle of measurements (data collection and averaging) for the two samples permits accurate determination of the zero line of the transient absorption spectrum and the level of background due to all kinds of light scattering effects. Moreover, it enables elimination of the effects caused by long-term changes in the intensity of the exciting and analysing beams. The transient absorption spectrum was analysed with a low dispersion prism spectrometer. Its use ensures high efficiency of the recording system but entails nonlinearity of the dispersion curve and the need for careful calibration of the wavelength scale.

Spectra of the studied sample were recorded by an optical multichannel analyser (OMA), EG&G/Princeton Applied Research, model 1460, equipped with a 1453A silicone photodiode array (PDA) composed of 1024 elements over a length of 1″. The photodiode matrix works at a temperature of −5 °C. Apart from the 1024 photoelectric channels, the OMA has the 1025th channel for the input of the

reference signal, which permits correction of the effects of changes in the incident light intensity on the spectra of transient absorption and emission of the sample.

Assignment of a given wavelength of the recorded absorption spectrum to a channel of a particular number (PDA calibration) depends on the prearranged position of the prism spectrometer. A change in the spectrometer arrangement enabled a change in the recorded spectral range.

For some selected wavelengths, the calibration was achieved by inserting interference filters of exactly known transmission and half-intensity width in the path of the continuum beam in front of the prism spectrograph. Such an assignment was made for a few chosen channels at points covering the whole recorded spectral range. For the intermediate wavelength, the calibration was performed by analytical interpolation. The best fit was obtained for a single-exponential curve and for the curve obtained for polynomials with terms in even powers. For thus found parameters of the fit, wavelengths corresponding to each particular channel were calculated. The wavelength scale was calibrated after the data from the optical multichannel analyser had been fed to a computer.

The work of the entire setup was controlled by an AT 286 microcomputer which was also used for data acquisition. The use of a computer ensured full automatization of the measurement and accumulation of a great number of data, *i.e.*, a result of single measurement was derived from 20 to 50 spectra both for the studied and the reference sample, covering the range of 1024 points. The two translation stages and the optical multichannel analyser were connected with the computer through two serial ports of RS-232 type and controlled using the internal computer languages. The use of the computer to control the translation stages permitted determination of:

- the travel rate of the translation stage,
- the value of acceleration of the translation stage at the start and breaking,
- the value of the initial delay, as well as,
- programming of a change in the delay within a sequence of measurements,
- measurements with or without the reference sample.

The control of the optical multichannel analyser was limited to blocking the measurement during the adjustment of the delay or change of samples, and to transmission of data. The computer was fed with the data which were results of a preselected number of accumulations. A full cycle of measurements includes:

1. Initial positioning of the translation stage.
2. Performance of a prefixed number of accumulations.
3. Data transmission and storage.
4. Replacement of the studied sample by the reference sample.
5. Performance of a prefixed number of accumulations.
6. Data transmission and storage.
7. Replacement of the reference sample by the studied sample.
8. Next positioning of the translation stage.

Procedures 2–8 were executed in cycles for each particular point on the time scale. The applied software, entirely in the C language enabled continuous

monitoring of the current delay of the analysing pulse relative to the exciting one, ensured access to the result of the preceding measurement and access to the information on the current state of the system.

4. Tests, preliminary results

One of the most important parameters of a picosecond spectrometer is the instrument response function which was determined from autocorrelation measurements performed by the two-photon fluorescence method (TPF). The phenomenon of two-photon fluorescence was first applied for measurements of picosecond light pulses by Giordmaine in 1967 and later used by many authors [25]–[29]. Thorough analysis of the two-photon fluorescence signal indicates that interpretation of the obtained picture of interference of two series of pulses or two replicas of the pulse (obtained by division of the pulse into two equal parts), superimposed in a two-photon absorber, is ambiguous. The most important experimental factor derived from TPF autocorrelation measurements is the contrast ratio C, the ratio of the maximum fluorescence intensity to the background fluorescence. The prolem of contrast in interference pattern has been studied by KLAUDER [30], WEBER [31], FLECK [32], HARRACH [33], [34] and DREXHAGE [35].

The detection system measures the intensity of fluorescence integrated in time as a function of time delay between the two replicas of the pulse. This signal is a second order autocorrelation function of the intensity of the two pulse replicas (1) depending on the time delay of one of them relative to the other δ, and can be used to estimate the light pulse duration τ_1. The integrated intensity of TPF is

$$I_{\mathrm{TPF}}(\delta) \sim 1 + 2G^{(2)}(\delta) \tag{1}$$

where $G^{(2)}(\delta)$ is the autocorrelation function of the light intensity and can be expressed as

$$G^{(2)}(\delta) = \int I(t)I(t+\delta)dt / \int I^2(t)dt. \tag{2}$$

The value of this autocorrelation function depends on the characteristics of the exciting beam and for a laser with a full mode locking it is 1, whereas for free generation it is 1/2 [25]–[36].

In our experiments, as a two-photon absorber we used a solution of Rhodamine 6G at a concentration of 2×10^{-3} M in methanol, placed in a 10 mm long quartz cell. The fundamental beam was divided into two replicas by a dielectric beamsplitter (Fig. 5). The use of the M-525.22 micropositioner (Physik Instrumente-Polytec) secured the preselected delay between the two replicas which were combined in a cell containing the two-photon absorber.

A fragment of the two-photon fluorescence band (590 nm $\pm \Delta\lambda$) was filtered off by the M33 monochromator (COBRABiD), and measured by the M12 FQC 51 photomultiplier. The large time constant of the photomultiplier system was $RC =$ $= 2$s, which ensured integration of a signal appearing at a frequency of 10 Hz.

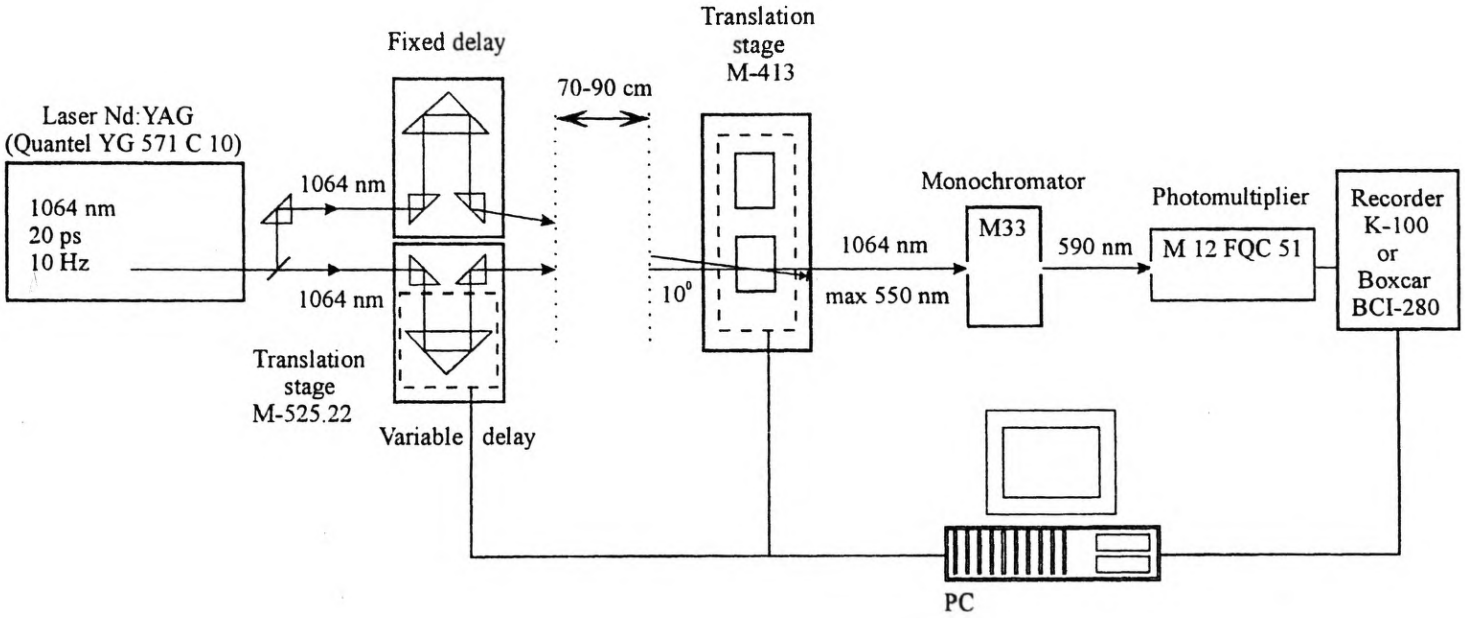

Fig. 5. Diagram of the system used for the instrument response function determination by the TPF autocorrelation measurements

The intensity of the photomultiplier current was measured by the K-100 recorder (Zeiss – Jena). This device was sometimes replaced by a BCI 280 boxcar type integrator. The achieved contrast ratio was $C = 1.98 \pm 0.04$ (Fig. 6) and the width of the autocorrelation trace (fwhm) was $\tau_A = (22.7 \pm 0.9)$ ps (Fig. 7).

In the majority of the autocorrelation models the pulses are assumed to run in the opposite directions and thus to form a standing wave in the measuring cell. In our system, a standing wave was not formed as the pathways of the pulses which meet in the TPF medium intersected at a small angle, see Fig. 5. The Harrach model [33], [34] proved inadequate for our experimental conditions. Therefore, another model of generation of the TPF signal was proposed and used to determine duration of the laser fundamental pulse τ_1, and its appropriate shape.

In our system the integrated intensity of two-photon fluorescence is

$$I_{TPF}(\delta) \sim 1 + G^{(2)}(\delta) \tag{3}$$

where $G^{(2)}(\delta)$ is the autocorrelation function of the intensities of the light pulses (2). A value of autocorrelation function (2) now falls in the (0, 1) range and for $\delta = 0$ it is 1, while for $\delta \gg \tau_1$ it is 0 and does not depend on the characteristics of the exciting beam. Therefore, the contrast measured for such a system cannot be a measure of the quality of the mode locking. The maximum value of contrast factor C in a system of such a geometry is 2, and it can be lower only in the case of unequal division of the pulse. The pulse duration is determined by dividing the experimental value τ_A by a selected value of the τ_A/τ_1 ratio depending on the assumed shape of the pulse. From among the considered types of the pulse intensity shape: rectangular, triangular, Gaussian, Lorentzian, sech^2, exponential on one side, the experimental pulse shape was best approximated by sech^2 $(1.759\ t/\tau_1)$. For such a shape $\tau_A/\tau_1 = 1.44$ and thus, the corresponding pulse duration was $\tau_1 = 15.8 \pm 0.6$ ps.

The zero-point of the delay line, *i.e.*, the position of the translation stage at which the exciting and the analysing beam coincide in the sample, was determined for benzophenone. Benzophenone is characterized by a large cross-section for the $T_1 - T_n$ transient absorption with the maximum at ~530 nm. The time constant of this transition was determined in a number of different solvents [37] – [39], and the transient absorption rise for this transition can be well described by a single-exponential dependence. The profile of the $T_1 \rightarrow T_n$ transition determined in our spectrometer (Fig. 8), can be well approximated by a convolution of the curve of the transient absorption rise with the time constant of 10 ps and the instrument response function of the half-width 15 ps.

A characteristic feature of our spectrometer is high energy of the exciting pulse which apart from some obvious advantages, may sometimes permit considerable overpumping of the sample, much above the experimental optimum. For an exciting beam of $\lambda_{exc} = 355$ nm and a typical single pulse energy $E \approx 4$ mJ, the absorbance of a studied sample usually amounts to $A_{355} \approx 0.6$, which corresponds to the absorbed energy

$$E_{abs} = E(1 - 10^{-A}) \tag{4}$$

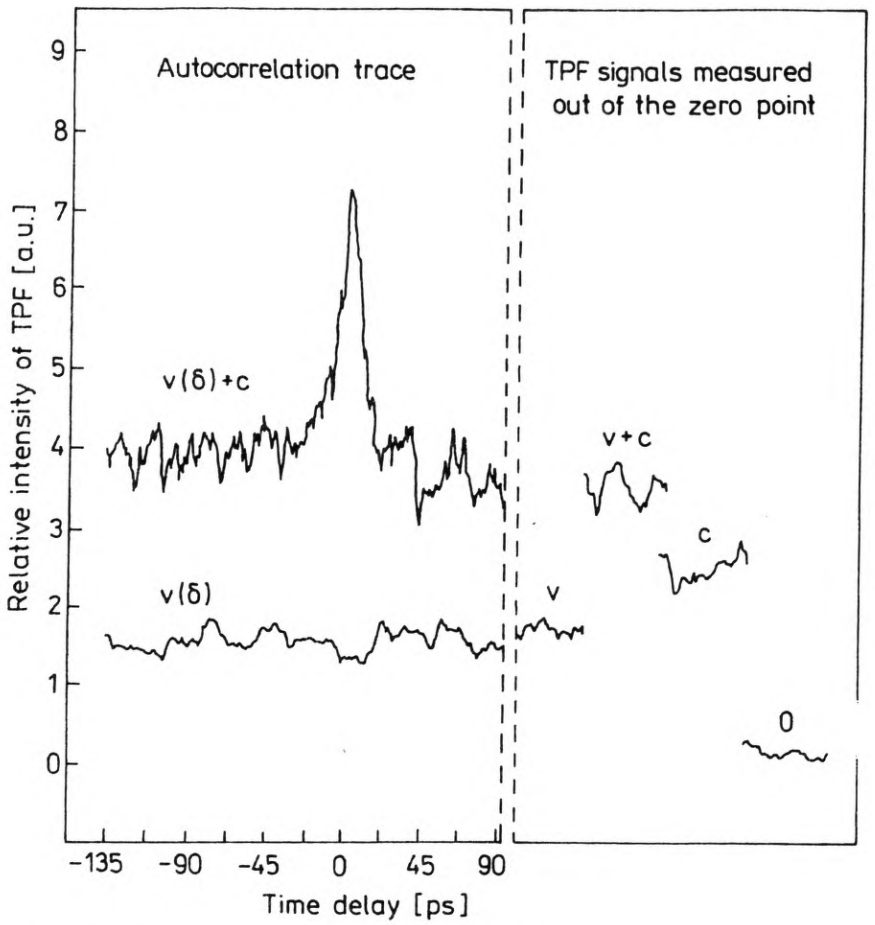

Fig. 6. Autocorrelation traces and levels of the TPF signal measured in the system: *v*, *c* indicate that the TPF signal was excited by the beams passed through the variable delay or constant delay channels, respectively; *v*(*δ*) denotes the TPF measurement as a function of the variable delay while *v* indicates the measurement recorded during a period of time with the translation stage stopped, 0 — both beams blocked

of about 3 mJ. For the exciting beam diameter of $2r = 0.3$ cm in the sample, the volume of the excited region, $V = \pi r^2 l$, is 0.07 cm^3. A typical sample of the solute concentration $c = 1 \times 10^{-4}$ M contains in this volume $N = cV = 4.2 \times 10^{15}$ molecules. The number of quanta absorbed in the volume V is $N_{h\nu} = E_{abs}/h\nu$. For the above specified experimental conditions $N_{h\nu} = 5.4 \times 10^{15}$, so a situation when $N_{h\nu} > N$, *i.e.*, the number of the absorbed quanta is greater than the number of molecules in a given volume V can be easily achieved. Of course, when the lifetime of the energy state to which a molecule is excited by $\lambda_{exc} = 355$ nm is longer than the duration (fwhm) of the exciting beam $\Delta\tau_{1/2}$, and the multiphoton transitions in the system can be neglected, it is impossible to achieve $N_{h\nu} > N$. To avoid the effects of interaction of the excited molecules, measurements should be performed at the

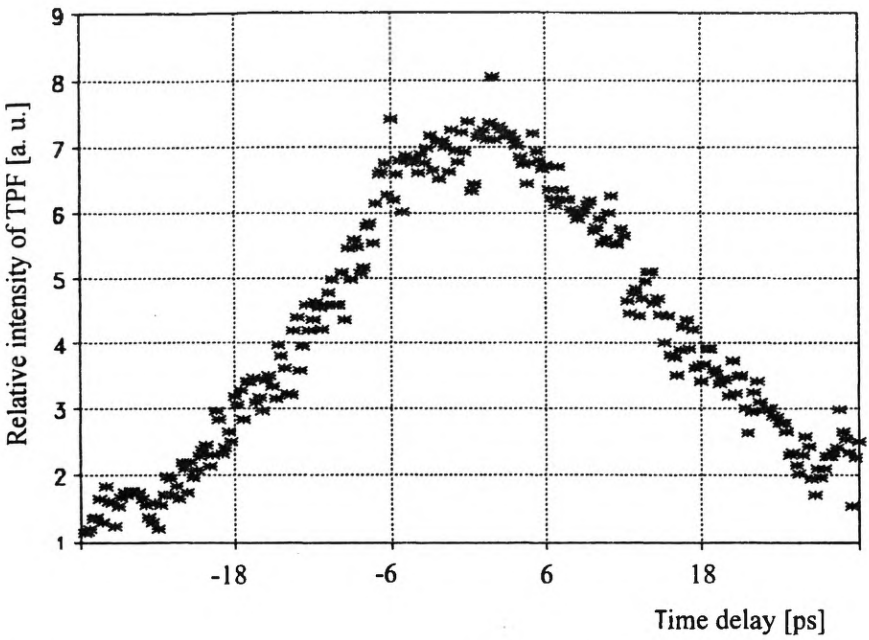

Fig. 7. Autocorrelation profile measured by the TPF method

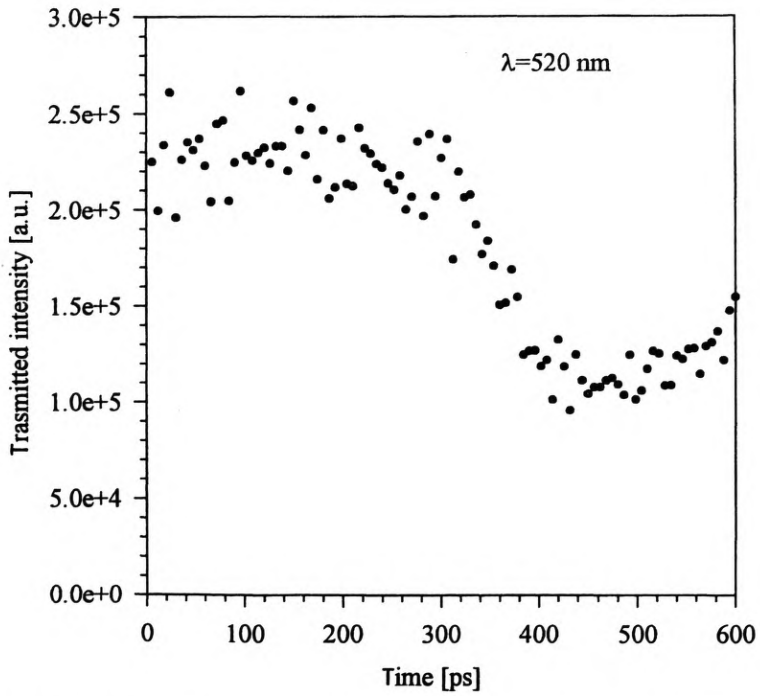

Fig. 8. $T_1 \rightarrow T_n$ transient absorption signal measured for benzophenone in n-heptane at 520 nm

lowest possible concentration of the excited molecules so that a well detectable and undistorted signal of transient absorption could be obtained. BEBELAAR recommended [40] a value of the ratio of the number of excited molecules to the number of all solute molecules in the excited volume $\alpha = \frac{N_{ex}}{N}$, to be 0.4. Taking into account that our spectrometer permits detection of transient absorption changes of $\Delta A = 0.02$, its sensitivity expressed in terms of the lowest detectable value of the molar extinction coefficient

$$\Delta\varepsilon = \frac{\Delta A}{c\alpha l}, \tag{5}$$

where c is the total concentration of molecules in the solution, is equal to 500 M^{-1} cm^{-1} at $\alpha = 0.4$.

5. Exemplary application of the system: measurement of transient absorption in xanthione

The transient absorption spectra obtained for xanthione in benzene are presented in Figs. 9 and 10. Figure 9 shows a three-dimensional representation of absorption

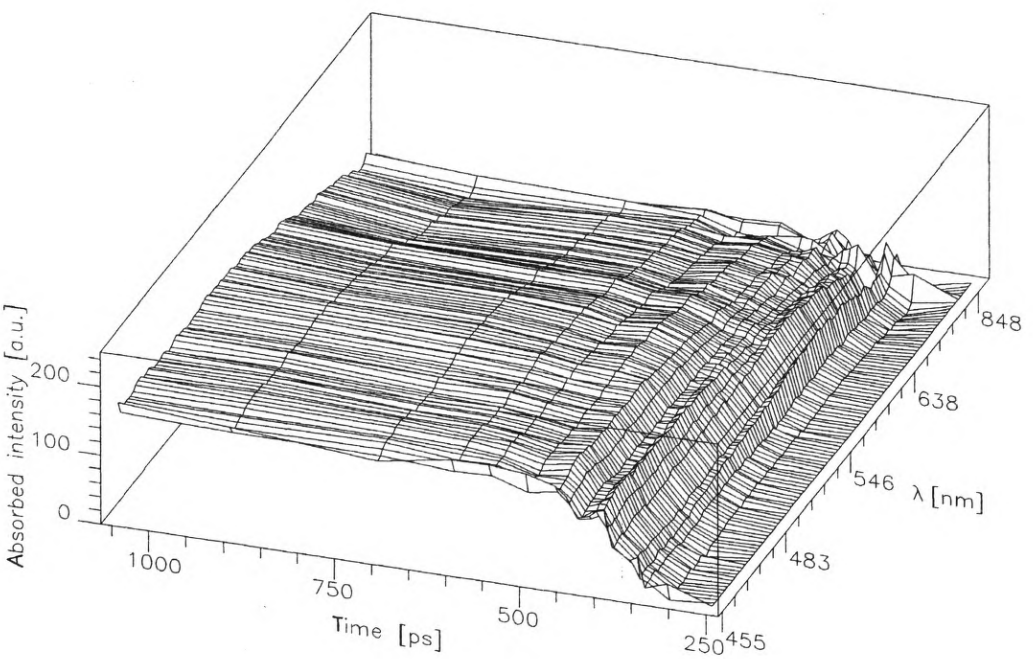

Fig. 9. Transient absorption spectrum of xanthione in benzene

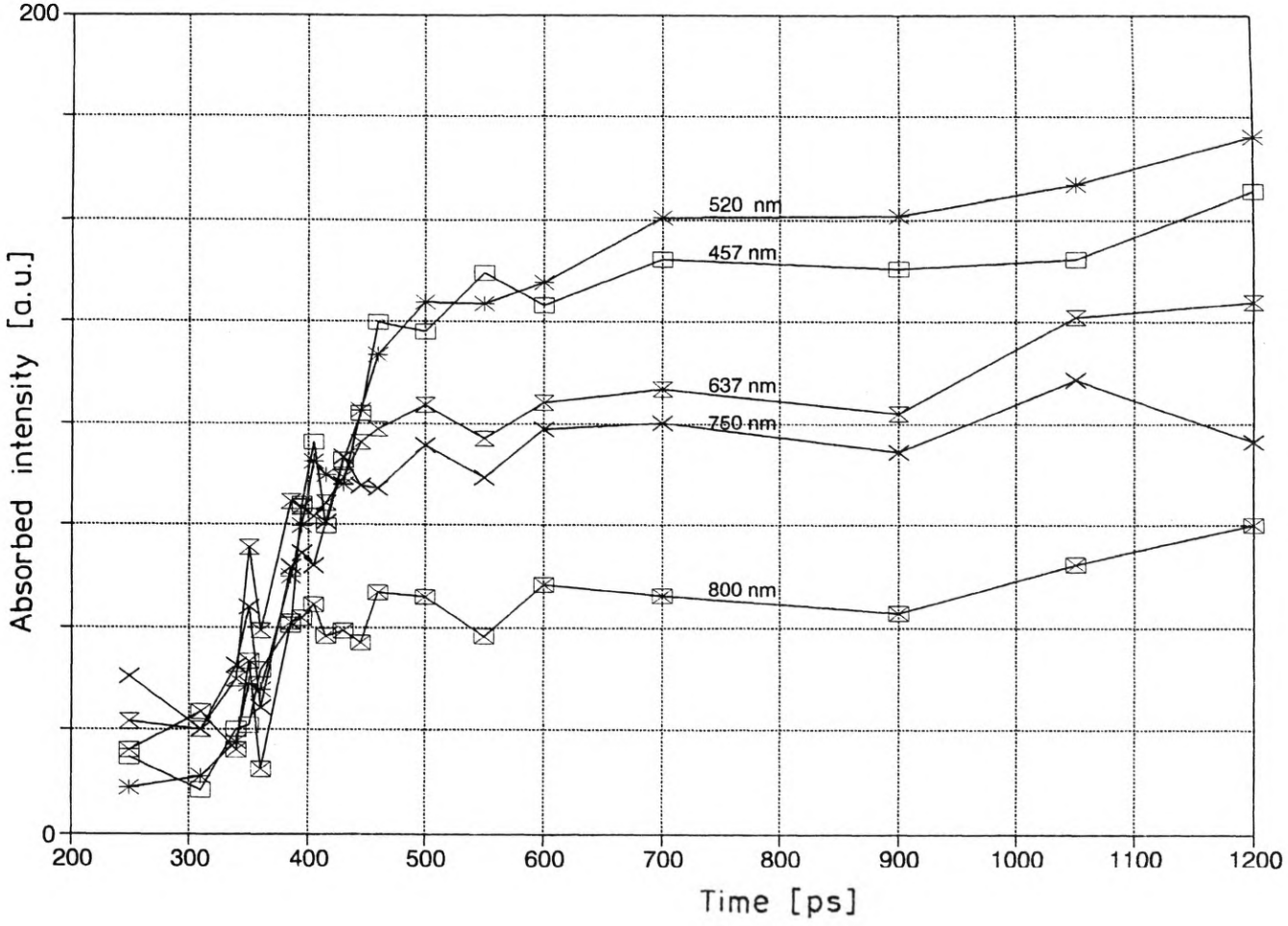

Fig. 10. Changes of transient absorption spectra of xanthione in benzene measured for a few selected wavelengths

changes in the coordinates: time and wavelength, whereas Fig. 10 presents the course of absorption changes as a function of time for a few chosen wavelengths. Both figures give the same course of evolution of absorption from the excited states of xanthione. In the beginning of the time scale, the spectrometer records the state before the incidence of the exciting pulse, when absorption transitions can take place only from the ground state. After the incidence of the pulse exciting the S_2 state, a short-time broadband $S_2 \rightarrow S_n$ absorption with the maximum at ~ 650 nm appears. Changes in the intensity of this absorption correspond to the changes in the S_2 state population due to the simultaneously running processes of population and depopulation. With decreasing signal of transient absorption from the S_2 state, a long-lived broadband absorption, with the maximum shifted towards shorter wavelengths, develops. At the end of our time scale this absorption can be identified as due to the $T_1 \rightarrow T_n$ transitions, in consistence with results of DAS [41]. However, analysis of the rising fragment of this long-lasting absorption curve permits drawing important conclusions about the nature of the interactions between the molecules of xanthione and hydrocarbons, that is, it indicates the formation of an exciplex deactivating to the T_1 and S_0 states as an efficient channel of decay of the excited molecules of thioketones. The results of these studies are thoroughly discussed elsewhere [42].

6. Conclusions

The spectrometer for transient absorption studies of the picosecond resolution described in this paper has proved to be a universal, experimentally tested instrumental solution, although it has been initially designed to study simple organic molecules like thioketones. It has been successfully applied to study xanthione and thiocoumarin in alkane and benzene solutions. The studies performed on this spectrometer have, on the one hand, brought about important decisive data on the mechanism of decay of the S_2 state of the thioketones [43] and, on the other hand, established the limits of the experimental capacity of the system.

At present, the spectrometer parameters ensure successful investigation of standard hydrocarbon solutions of the solute concentration of an order of 1×10^{-4} M. However, in photophysical studies it is frequently necessary to use solvent of particular properties, *e.g.*, perfluoroalkanes [44] which are extremely poorly soluble. The concentration limit of, *e.g.*, aromatic thioketones in these solvents varies from 10^{-4} M to 10^{-7} M depending on the system. Extension of the experimental possibilities of the spectrometer to study systems of very low solute concentration would require an increase of the spectrometer sensitivity by one or two orders of magnitude. This could be possible with a two-beam detection of the transient absorption system applied, in which the signal of transient absorption would be at each flash, referred to the reference signal of the picosecond continuum with the help of a double-diode matrix. Such a procedure will permit normalization of the spectral distribution and the intensity distribution of each subsequent transient absorption signal measured to the corresponding characteristics of the picosecond continuum.

Acknowledgments – The authors wish to thank M. Fidecka, M.Sc., for her skilful assistance in samples preparation. The financial support of the KBN (State Committee for Scientific Research) research grant 2 2337 92 03 is gratefully acknowledged.

References

[1] TURRO N. J., *Modern Molecular Photochemistry*, Benjamin Commings, Menlo Park 1978.
[2] BIRKS J. B., *Photophysics of Aromatic Molecules*, J. Wiley, Interscience, New York 1970.
[3] RABEK J. F., *Experimental Methods in Photochemistry and Photophysics*, J. Wiley, New York 1974.
[4] DEMTRÖDER W., *Laser Spectroscopy*, Springer-Verlag, Berlin 1988.
[5] KHUNDKAR L. R., ZEWAIL A. H., Annu. Rev. Phys. Chem. **41** (1990), 15.
[6] FELKER P. M., ZEWAIL A. H., Adv. Chem. Phys. **70** (1988), 265.
[7] KAISER W. [Ed.], *Ultrashort Laser Pulses and Application*, Topics in Applied Physics, Vol. 60, Springer-Verlag, Berlin 1988.
[8] FLEMING G. R., *Chemical Applications of Ultrafast Spectroscopy*, Oxford University Press, 1986.
[9] IPPEN E. P., SHANK C. V., BERGMAN A., Chem. Phys. Lett. **38** (1976), 611.
[10] RENTZEPIS P. M., Chem. Phys. Lett. **2** (1968), 117.
[11] LAUBEREAU A., SEILMEIER A., KAISER W., Chem. Phys. Lett. **36** (1975), 232.
[12] ANFINRUD P. A., CAUSGROVE T. P., STRUVE W. S., [In] *Ultrafast Phenomena V*, [Ed.] G. R. Fleming, A. E. Siegman, Springer-Verlag, Berlin 1986.
[13] MASUHARA H., MIYASAKA H., KAREN A., VENIYA T., MATAGA N., KOISHI M., TAKESHIMA A., TSUCHIYA Y., Opt. Commun. **44** (1983), 426.
[14] MIYASAKA H., MASUHARA H., MATAGA N., Laser Chem. **1** (1983), 357.
[15] CORNELIUS P. A., HOCHSTRASSER R. M., *Picosecond Phenomena III*, [Ed.] K. B. Eisenthal, Springer-Verlag, Berlin 1982.
[16] GREENE B. I., HOCHSTRASSER R. M., WEISMAN R. B., J. Chem. Phys. **70** (1979), 1247.
[17] EBBESEN T. W., Rev. Sci. Instrum. **59** (1988), 1307.
[18] GAUDUEL Y., MIGUS A., MARTIN J. L., LECARPENTIER Y., ANTONETTI A., Ber. Bunsenges. Phys. Chem. **89** (1985), 218.
[19] ERNSTING N. P., KASCHKE M., Rev. Sci. Instrum. **62** (1991), 600.
[20] NORRISH R. G. W., PORTER G., Nature **164** (1949), 658.
[21] PORTER G., Proc. R. Soc. A **200** (1950), 284.
[22] ALFANO R. R., SHAPIRO S. L., Phys. Rev. Lett. **24** (1970), 584.
[23] ALFANO R. R., SHAPIRO S. L., Chem. Phys. Lett. **8** (1971), 631.
[24] ALFANO R. R. [Ed.], *The Supercontinuum Laser Source*, Springer-Verlag, New York 1989.
[25] CLOBES A. R., BRIENZA M. J., Appl. Phys. Lett. **14** (1969), 287.
[26] SHAPIRO S. L., DUGUAY M. A., KREUZER L. B., Appl. Phys. Lett. **12** (1968), 36.
[27] BASS M., WOODWARD D., Appl. Phys. Lett. **12** (1968), 275.
[28] COMLY J., GARMIRE E., LAUSSADE J. P., YARIV A., Appl. Phys. Lett. **13** (1968), 176.
[29] RENTZEPIS P. M., DUGUAY M. A., Appl. Phys. Lett. **11** (1967), 218.
[30] KLAUDER J. R., DUGUAY M. A., GIORDMAINE J. A., SHAPIRO S. L., Appl. Phys. Lett. **13** (1968), 174.
[31] WEBER H. P., Phys. Lett. **27 A** (1968), 321.
[32] FLECK J. A., Phys. Rev. B **1** (1970), 84.
[33] HARRACH R. J., Phys. Lett. **28 A** (1968), 393.
[34] HARRACH R. J., Appl. Phys. Lett. **14** (1969), 148.
[35] DREXHAGE K. H., Appl. Phys. Lett. **14** (1969), 318.
[36] MOLLOW B. R., Phys. Rev. **175** (1968), 1555.
[37] HOCHSTRASSER R. M., NELSON A. C., [In] *Laser in Physical Chemistry and Biophysics*, [Ed.] J. Joussot-Dubien, Elsevier, Amsterdam 1975.

[38] HOCHSTRASSER R. M., LUTZ H., SCOTT G. W., Chem. Phys. Lett. **24** (1974), 162.
[39] ANDERSON R. W., HOCHSTRASSER R. M., LUTZ H., SCOTT G. W., Chem. Phys. Lett. **32** (1975), 204.
[40] BEBELAAR D., Chem. Phys. **3** (1974), 205.
[41] KUMAR C. V., QIN L., DAS P. K., J. Chem. Soc. Faraday Trans. 2, **80** (1984), 783.
[42] SZYMAŃSKI M., BALICKI M., KUBICKI J., MACIEJEWSKI A., WRÓŻOWA T., Acta Phys. Pol. (submitted).
[43] MACIEJEWSKI A., STEER R. P., Chem. Rev. **93** (1993), 67.
[44] MACIEJEWSKI A., J. Photochem. Photobiol. A **51** (1990), 87.

Received July 31, 1995