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HOW TO BUILD UP AN UP-TO-DATE DECAY TIME SPECTROMETER FOR THE NANOSECOND REGION

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Design problems of a nanosecond decay time spectrometer are discussed and suggestions are made as to the most appropriate components for building up a sensitive, single pulse and relatively inexpensive instrument.

Introduction

Research work in molecular physics, chemistry and biology requires, to a continuously increasing extent, excitation lifetime data for investigating the intra- and extramolecular mechanisms of energy transfer. With modern instruments excitation lifetimes can be measured in the wide time range from fs to 10 s. In the present work we deal with the determination of lifetimes longer than ns because the shorter lifetimes require highly sophisticated instrumentation.

The primary excited state of a single molecule can be populated by light absorption in about 10^{-18} s. The spontaneous emission time of single molecules is the same as the absorption time. The macroscopic excited state lifetime is a molecular statistical event and the experimental decay curve D(t) can be described as usual by the sum of exponentials

$$D(t) = \sum A_i \exp(-t/\tau_i), \tag{1}$$

where A_i-s are the emission intensities in t=0 and τ_i-s are the experimental average lifetimes. The physical meaning of eq. (1) is not completely clear. It is probably only a mathematical description of a non-exponential time evolution.

Eq.(1) will be more complicated when τ_i-s and the halfbandwidth of the exciting pulses are commensurable. In this case the experimental decay curve B(t) is a convolution integral of the exciting function k(t) and the sum of exponentials

$$B(t) = \int k(t) \cdot D(t-t')\, dt\,. \tag{2}$$

The experimental task is to measure B(t) (or D(t)) as precisely as possible. Evaluation of the measurement, i.e. the determination of the A_i and τ_i parameters, is computational work using any type of deconvolution procedure [1].

Functional block diagram of a decay time spectrometer

The technique of decay time measurements has improved considerably together with the general instrumentation level. However, here, we have no wish to analyse the route of this development, our aim is now to select the components for building up the most suitable instrument based on our evaluation. Basically, two types of decay time instruments are known:

a) Phase and/or amplitude modulation decay time meters are commercially available [2]. They are suitable for precise and relatively fast measurements because of the extreme frequency selectivity attainable by the state-of-the-art electronics. The disadvantages of these instruments are:

- A high intensity light source (450 W Xenon lamp) is required and this may cause significant photochemical damage;
- The parameters of only a single exponential can be determined.

b) Pulsed light instruments are also highly advanced and commercially available. They are suitable for determining the complete decay curves without any supposition. Because of the minimum illumination intensity any photochemical damage can be neglected.

These are the reasons that hereafter we shall deal only with pulsed light methods.

In Fig. 1 the functional block diagram of a pulsed light decay time spectrometer is outlined. Spectrometers in this category differ from each other only with regard to the light source and the measuring electronics.

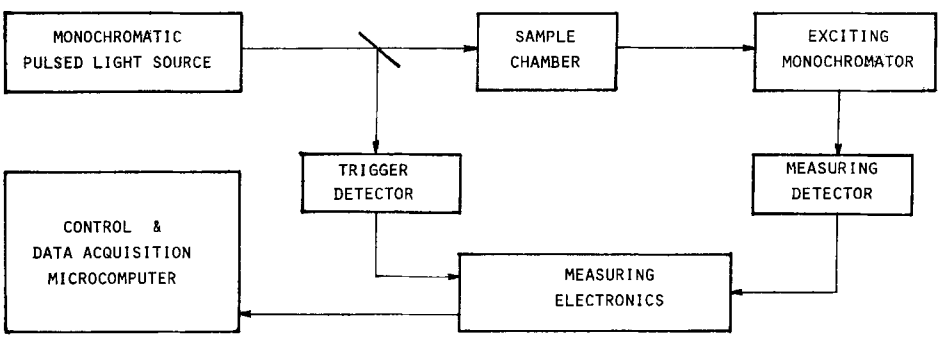

Fig. 1

Requirements for the modules

The specification of the spectrometer components can be defined as follows:

For the exciting light: (i) Continuously variable in the full range of the UV/VIS region (from 220 to 750 nm). (ii) The monochromaticity is better than the half-bandwidth of the vibronic transitions in the vapour state (~5 cm^{-1}). (iii) The light intensity is high enough to have emission light from samples with low quantum efficiency or low concentration.

For the sample chamber: (iv) Variable (wide temperature range cryostat, high precision thermostat, application of polarization adapters, etc.).

For the emission monochromator: (v) Interchangeable (high resolution measurements require 1 m or longer collimator focal length, for applied spectroscopic works 0.25 m of that is enough).

For trigger detectors: (vi) The rise time must be less than 200 ps to eliminate time jitter.

For the measuring detector (now in most cases PMT-s): [3] (vii) Low time spread to decrease the convolution effect of the instrument. (viii) Wide spectral sensitivity (from 180 to 750 nm). (ix) High quantum efficiency. (x) Low noise. (xi) Good magnetic and radio-

frequency shielding. (xii) Low dark current. (xiii) High gain (up to 10^{-8}). (xiv) High loadability.

For the electronic measuring system: (xv) The decay curve must be measured with higher precision than 1 per cent. (xvi) Wide time range (from ns to 10 s). (xvii) Utilization - if possible - of the full decay curve in each pulse.

Built-up systems and experience

The most important types of pulsed light decay time instruments have been built-up in our laboratory. All parts of the equipments except the detectors, electronic components and oscilloscopes were developed in our own laboratory or other departments of our institute.

A summarized description of the measuring set-ups and the experience gained is as follows:

a) A time correlated single photon counting system was built-up from two constant fraction discriminators, a time-to-amplitude converter, ICA-70 multichannel analyser, controller, gated nanosecond flashlamp with 50 kHz repetition rate, and two monochromators with 25 cm focal length [4].

b) The original high speed storage oscilloscope method [5] was reproduced by using a TEKTRONIX Mod. 7633 oscilloscope with 7A26 dual trace amplifier and 7A22 differential amplifier plug-ins. The fastest calibrated sweep rate is 5 ns/div, the highest sensitivity of the vertical deflection is 5 mV/div with plug-in 7A26. The same values for plug-in 7A22: 1 μs/div(hor) and 10 μV/div(vert).

A 400 kW N_2-laser was used as a light source (made by Institute for Experimental Physics, JATE Szeged) with a repetition rate of 25 pulses/s. The other components are the same as described for the time correlated single photon counting system.

For recording the analog results a photographic procedure was applied and for the computerized evaluation the digital data were prepared manually.

The required light intensity in this case must be high enough to produce a good measurable pulse shape at the detector output. This means that the required light intensity is 2 or 3 orders of magnitude higher than in the case of time correlated single photon counting.

c) For the sampling oscilloscope technique [6] a sampling unit was developed with 200 ps sampling time. (The most advanced version of this type of instruments is the Mod. 400 Signal processing System by EG&G PARC. The price of this instrument is very high, and we have not experience in its use.) The other version of the sampling instruments - the so called transient recorders - and the conventional multichannel analyser (e.g. ICA-70) were also used. The conversion times are in these cases 100 ns/point and 100 μs/point, respectively.

d) Digital oscilloscope forms the last step in this field. Information represented by the time evolution of the emitted light is stored in an analog manner which is converted automatically to digital form and stored in the built-in random access memory. Data processing takes place by an on-line microcomputer.

The optimum system and its evaluation

On the basis of our experience the most suitable measuring system consists of the following components: High pressure N_2-laser light source with 400 kW power combined with dye laser and frequency doubler the pulse-width in this case is less than 500 ps. Variable

sample chamber and interchangeable emission monochromators are as defined in (iv) and (v). Trigger detector: vacuum photodiode with ~120 ps risetime. Interchangeable measuring photomultipliers: Philips XP-2020, and 56-TVP, RCA 8850, 8852 and C31024. Measuring system: IWATSU TS-8123 digital oscilloscope and ICA-70 multichannel analyser. On-line microcomputer with Z-80 microprocessor was used to collect the measured data.

Evaluating the optimum system we can state: (i) The intensity of the light source is high enough to excite the samples in the spectrum range from 230 to 750 nm. (ii) High intensity signals can be achieved by selection of the measuring detectors. (iii) The computerized IWATSU oscilloscope together with the ICA-70 multichannel analyser provide for automated high precision and highly sensitive measurements in the full time range. (iv) The pulsed light source and the streaming sample minimize photochemical damage. (v) The time jitter (less than 0.2 ns), the noise (in general less than 5 per cent in the ns range as a slowly waving signal is superimposed on the measurements), and the reproducibility of the pulse shape (maximum deviation is 3 percent) can be reduced by averaging repeated measurements. In our experience the agreement between two consecutive (averaged) measurements is better than 1 per cent summing 25 repeated decay curves. (vi) The evaluation software based on the Meiron non-linear least squares procedure [7] gives a numerical precision in the decay time better than 0.1 per cent. The program is written for a Z-80 based and IBM XT microcomputers in compiler BASIC and the most time consuming procedures in machine language. The evaluation time in general is less than 5 to 10 minutes [8] depending on the type of computer employed.

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