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Microcomputer-aided apparatus for optical spectra and fluorescence lifetime analysis*

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A microcomputer assisted analyzer of optical signals is presented. The system is intended to perform three experimental tasks. Two of them, namely the measurement of either fluorescence spectra or excitation spectra after pulsed excitation, are of spectroscopic character. The third one involves the time domain of a process and consists in analysing the fluorescence decay curves. The investigated media were caesium dimers in caesium vapour, but a great variety of other gaseous, liquid or solid samples could be analysed in the same system. An excitation spectrum of Cs_2 is given as an example of the performance of the apparatus.

1. Introduction

The system reported is based, in some of its components, on a described in [1] microcomputer-aided spectrum analyzer with thermionic diode detector, it is, however, significantly modified to perform quite new experimental tasks. First of all, in the new system the optical signals of emitted light are detected while in the previous one the ionization current was measured.

The main identical elements of the two apparatuses are the pulsed tunable laser and the microcomputer C–64 with the same home-made interface described in [1]. The most general principles of the computer program routines, enabling the communication between the computer and the rest of the system, are the same as in [1], but a number of essential modifications necessary because of new experimental situations had to be developed and built into the program.

The concept of a simple interface, allowing flexible adaptations on software level without any changes in its hardware, proved to be very practical, and so did the overall idea (also stressed in [1]), namely building an apparatus in a modular form with the help of easily accessible measuring devices which, if necessary, could be replaced by some other ones. The system presented here meets the requirements of the continued by us investigations on Cs_2. It could be also regarded as an example of the adaptive powers of the system described in [1].

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Present studies are to contribute to the problem of Cs_2 states excited directly from the ground state by absorption of blue light [2]. The Cs_2 molecules, after being excited by blue light, emit green fluorescence with a strong distinct narrow band at 522 nm. The experiments performed with the help of the apparatus described here are aimed at clarifying the origin of this band.

The apparatus can measure two kinds of spectra [2]: *fluorescence spectra* for a given excitation wavelength, and *excitation spectra* when fluorescence is observed at a fixed wavelength and the exciting light wavelength is tuned. It can also register and analyse *fluorescence decay curves* after pulsed excitation.

2. Apparatus and the applied methods

2.1. Basic components of the system

The scheme of the apparatus is shown in Fig. 1. The medium under investigation, caesium dimers (in caesium vapour), is contained in a vacuum cell made of alkali-resistant 1720 Corning glass, placed in a double chamber oven. The temperature inside each chamber is stabilized by a separate heating unit at the values T_1 and T_2 for the lower and upper chamber, respectively. The bottom of the cell sticks in the lower chamber and the upper part of the cells is surrounded by the upper chamber outfitted with windows.

Excitation laser light is only slightly focused (the focal point of the lens L_1 – of 2 m focal length – is behind the oven) inside the upper part of caesium cell. The temperature T_2 is always kept higher than T_1. This prevents condensation of caesium on the cell walls in the light paths, provided the temperature difference is not less than a few degrees. A drop of metallic caesium condenses at the bottom of the cell.

In the present investigations the light exciting the caesium molecules is tuned in the range of 458–480 nm. The Coumarine 460 dye was used. The laser light bandwidth is set to 6 (2) cm^{-1}. The laser configuration is the same as in [1] except for the new dye cells. Each dye cell – that of the oscillator and that of the amplifier – is provided with its own (internal) dye circulator, hence the proper dye concentration can be estimated for each cell to the best performance of the laser.

Due to the linear polarizer P and the polarization plane rotator R inserted across the laser beam, an arbitrary polarization plane of the exciting light can be set.

Fluorescence light, observed at right angle to the laser beam, is directed onto a slit of a monochromator (SPM2, Zeiss, Jena). The edge filter F cuts off any residual scattered laser light. A flat spectral response photomultiplier (PM1), RCA 4832, is attached to the monochromator at its output slit. The signal from the photomultiplier, proportional to the fluorescence intensity, is sent to one channel of a box-car integrator (BCI 280, ZWG, GDR). A fraction of the laser light beam is reflected by a beam splitter onto a cathode of another flat spectral response photomultiplier (PM2), Hamamatsu 943–02, protected by a set of neutral density filters (NDF). The signal from this photomultiplier, proportional to the laser light intensity, is

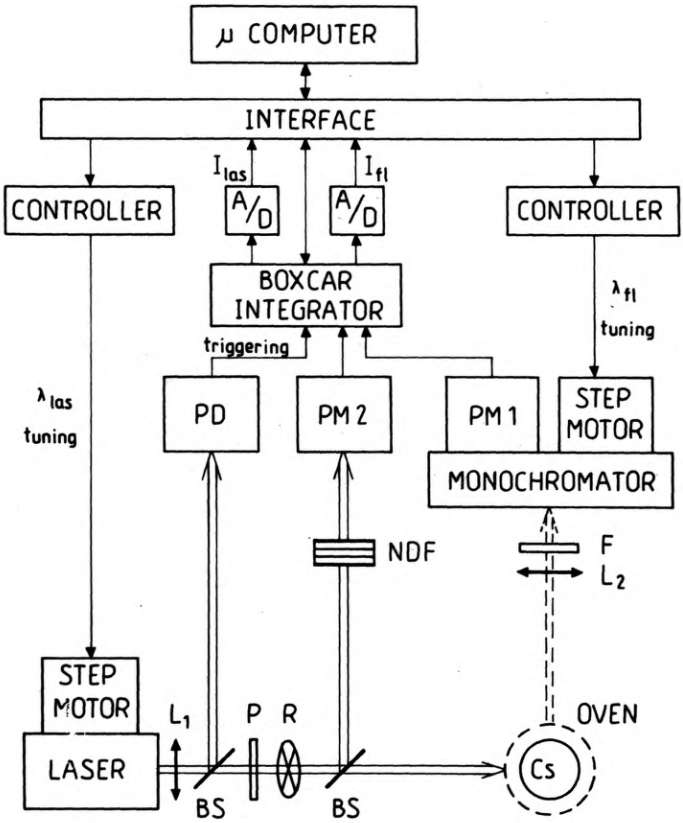

Fig. 1. Apparatus: A/D – analog to digital converters (digital voltmeters); PM1, PM2 – photomultipliers; PD – photodiode; F – edge filter; NDF – neutral density filter; L_1, L_2 – lenses; BS – beam splitter; P – polarizer; R – polarization plane rotator

detected in the other channel of the boxcar integrator. The triggering signal for boxcar is provided by a fast rise time (< 1 ns) photodiode (PD) monitoring laser light pulses. The values of the output voltages from two boxcar channels are measured by two dual slope digital voltmeters (V 543 MERATRONIK) and directed, via the interface, to the microcomputer Commodore 64 (C–64, CBM).

Tuning of the laser wavelength is accomplished by the microcomputer revolving the step motor of the laser tuning mechanism in the way described in [1]. In a similar way the observed fluorescence wavelength can be advanced with the help of a second step motor connected to the monochromator. In this experiment monochromator was tuned in the range of 506.3–532 nm.

2.2. Experimental

As already stated, two signals are measured: one is proportional to the fluorescence intensity I_{fl} and the other one to the laser light intensity I_{las}. In spectral investigations both signals are measured as integrals over the pulse duration,

whereas in the experiment aimed at studying fluorescence decay, a sequence of instantaneous values of fluorescence intensity, measured and plotted against time, reproduces the decay curve $I_{fl}(t)$. The fluorescence intensity (I_{fl} or $I_{fl}(t)$ for each t) is normalized to the parallely measured value of I_{las} to minimize the influence of pulse to pulse variations as well as of other kinds of variations in I_{las} on I_{fl} or I_{fl} (t).

2.2.1. "Prompt" spectra

Boxcar BCI 280 is a modular device with a set of exchangeable panels. In spectral investigations both boxcar channels accepting input signals operate in a stationary gate regime. The panels detecting the laser and fluorescence intensity are chosen to be the same, namely TOR. In these panels the gate width can be selected; the gates are open for 40 ns after the onset of the laser pulse. This time interval was chosen to cover completely the laser pulse and to be long enough to cover most of the fluorescence decay, as observed on the oscilloscope. On the other hand, detection of fluorescence lasts for a relatively short time following the excitation. Therefore, the contribution to the measured signals of any possible delayed processes [3] is much smaller that in cw experiments. In this sense, the spectra can be named "prompt" spectra. As mentioned earlier, the system measures two kinds of spectra:

– *Fluorescence spectrum* is obtained when the laser wavelength is set to a certain value and the monochromator is continuously tuned. Then the laser wavelength is advanced to a new value and another fluorescence spectrum is taken, etc.

– *Excitation spectrum* is obtained for a fixed selected setting of the monochromator, the laser wavelength being tuned.

The resolution of the spectral details is determined both by the laser light bandwidth (here ca 6 cm^{-1}) and by the width of the monochromator slit. In the case of our spectra, the slit was set to give spectral resolution of 20 cm^{-1} (FWHM). In principle, the apparatus allows a much higher resolution.

An example of an excitation spectrum of Cs_2, taken for the fluorescence wavelength $\lambda_{fl} = 522.3$ nm, is shown in Fig. 2. The detailed description and discussion of the spectra are given in [2].

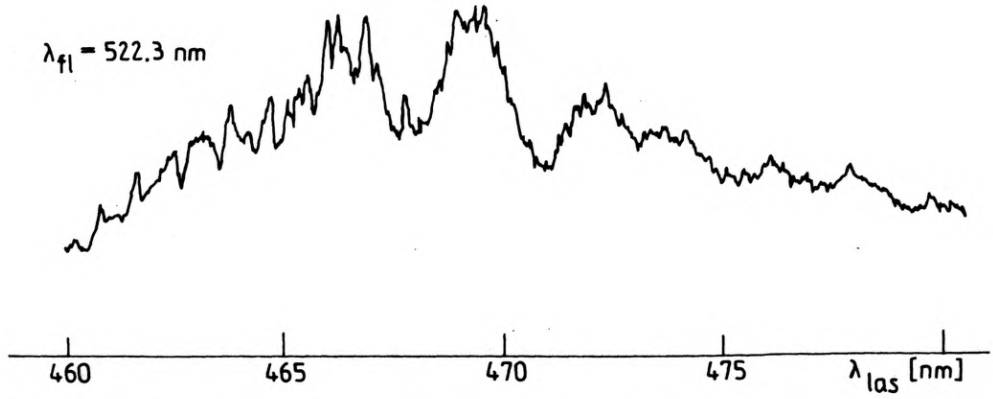

Fig. 2. Excitation spectrum of Cs_2 for the fluorescence wavelength $\lambda_{fl} = 522.3$ nm (λ_{las} – tuned laser wavelength)

2.2.2. Decay curve analysis

To investigate the time dependence of the florescence the TOR boxcar panel in fluorescence channel must be replaced by the one with most narrow gate, namely SAM. In this experiment this channel of the boxcar is set to a scanned mode (the gate delay increases step by step) and from the measurement the shape of a decay curve is obtained. As it has been stated above, the observed prompt fluorescence of Cs_2 decays in the nanoseconds time scale (up to a few tens of nanoseconds). Thus, as far as this time scale is concerned neither the excitation pulse duration (3 ns) nor the photomultiplier rise and fall time (extending the above duration to 6 ns, which is FWHM of the laser pulse observed by photomultiplier PM1) can be considered as being negligeably small. Further computer analyses of the decay curve are accomplished by fitting the experimental data to a formula which gives a convolution of exponential decay (one or more exponents) with the excitation laser pulse shape as viewed by the photomultiplier PM1. Therefore, an auxiliary measurement of this laser pulse shape should be also performed.

3. Course of the computer-aided experiment

The most general principles concerning the way of microcomputer Commodore–64 incorporation into the system, described in the first part of Sect. 2.3 of [1], were preserved. The new experimental procedures and new devices applied compelled us to develop a new version of a computer program which would enable the control over the measurements, data storage and processing. One program with three options is used for the three above mentioned tasks.

Prior to any measurements both the monochromator setting and the laser light wavelength were calibrated versus step numbers of the respective motors.

The boxcar integrator has to be preset to measure either the spectra or fluorescence decays (exchange of one of the panels in the boxcar and selection of its regime of operation (see Sect. 2.2.1 and 2.2.2)). Proper ranges of all devices have also to be established. The measured signals must be checked to make sure the saturation does not occur.

After these preliminary routines and some similar ones, the experiment is started. It consists of the following parts:

– *The measurement of the background.* It is the simplified procedure of the main measurement described below. We found it necessary to know the background because of long-term drifts in zero level of the boxcar and of some noise level observed.

– *The measurement of a spectrum or a decay* (see Fig. 3) which also includes (not shown in Fig. 3): *storing data* on a diskette, *printout* and *plotting* by a printer.

– *Further processing* of experimental data transferred to another computer IBM PC. (Some preliminary operations on the data are executed during the measurement procedure, see Fig. 3). In the case of decay curves, the decay parameters are obtained by fitting the data to formula as described in Sect. 2.2.2.

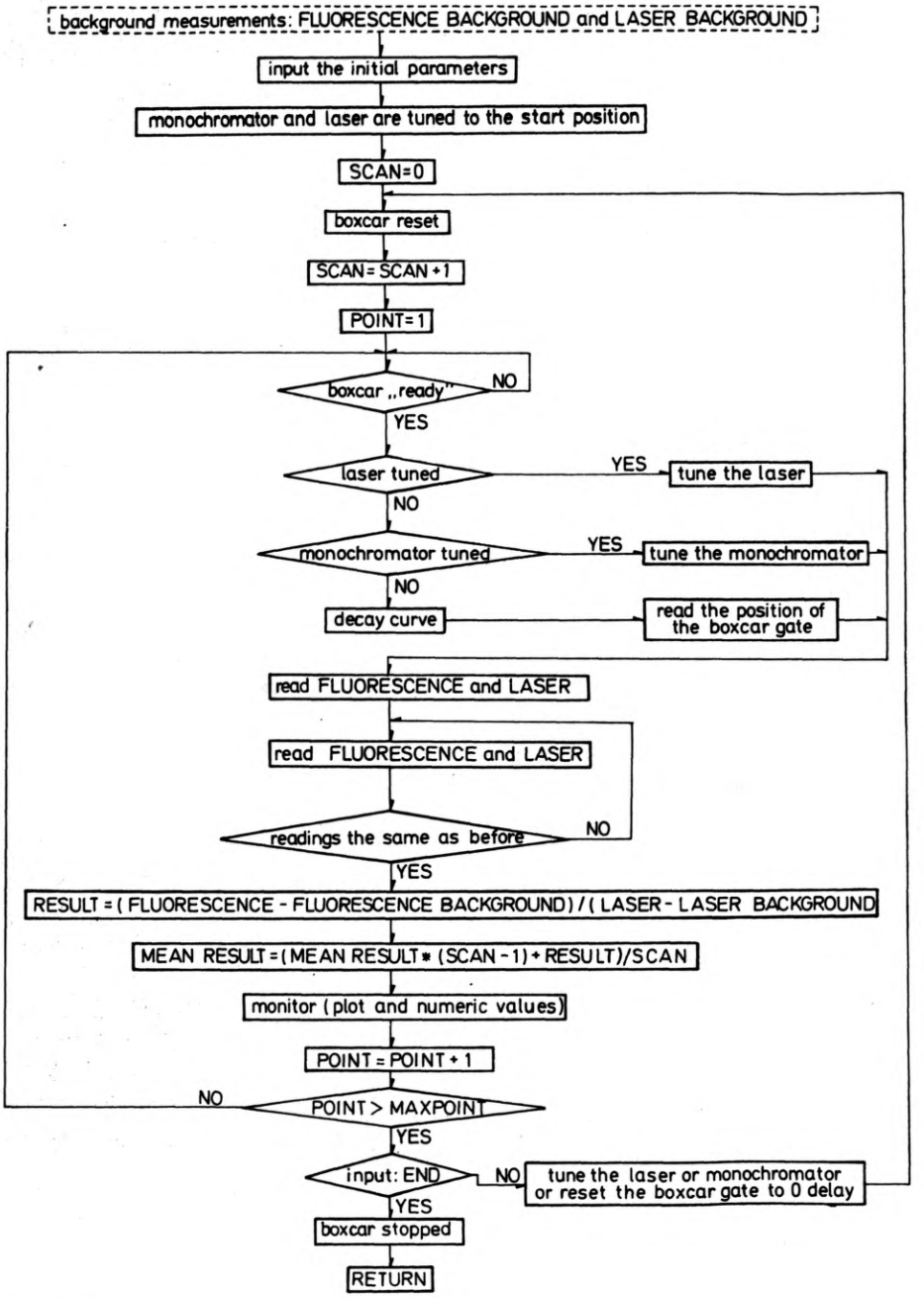

Fig. 3. Flow diagram for the program controlling the measurements

Successive stages of the measurement procedure are shown in Fig. 3 which is a flow diagram for the program controlling the experiment. Before the main measurement is started, the values of the variables FLUORESCENCE BACKGROUND and LASER BACKGROUND are known to the computer from the preceding background measurement. Other initial parameters, such as the choice of the option, the total number of experimental points, MAXPOINT, are introduced from the keyboard. For spectra, the spectral width (the number of step motor steps per point) should also be defined at this moment.

The monochromator and the dye laser are set at a selected wavelength value. If one of the devices is to be tuned during the experiment, this is its initial value of the tuning range.

As soon as the boxcar is initialized, it starts to measure the fluorescence intensity and the laser intensity, averaging over the number of laser pulses preset (at the boxcar) before the experiment, then it sends the signal "ready" to the computer. According to the selected option, the computer either performs a proper tuning to the next experimental point or reads the position of the boxcar gate (which then advances ahead). Then the boxcar begins to measure again (boxcar triggering is disabled by the computer before the necessary tuning is accomplished), but it preserves the previously measured values at its outputs for a sufficiently long time. These analog signals are converted by A/D converters (digital voltmeters) to a digital form and read by the computer. When the readings are stabilized, they are taken as the values of the variables FLUORESCENCE and LASER. Background values are subtracted and the results of normalization appears as the RESULT.

The MEAN RESULT, which for the first scan (SCAN = 1) is equal to the RESULT, is displayed on a computer monitor as a number and as a dot of a graphic plot.

The measurements of the second experimental point and of the subsequent ones proceed in a similar way until POINT > MAXPOINT; the value of the variable POINT is the current number of experimental points.

When the maximal number of points is reached first, the scan ends the system can return to the initial position to start the next scan. During each scan the MEAN RESULT for each point is modified, being calculated as an averaged value over all previous RESULTs for this POINT and the current RESULT (see formula in Fig. 1). The whole procedure terminates when one decides that a satisfactory value of the signal to noise ratio is reached and the computer obtains an information "END" from the keyboard.

The averaging over the results of several subsequent scans, as described above, lowers the effect of the irregular shorter-term drifts of the boxcar baseline.

4. Final remarks

The apparatus presented in this paper provides the opportunity to perform complex investigations, i.e., spectral measurements of prompt fluorescence and the studies of the dynamics of the decay processes following excitation.

The fluorescence can be investigated as a function of various parameters, controlled and measured by the computer. For example, we have also studied the dependence of excitation spectra on the caesium vapour temperature to determine the range of the initial levels for absorption. At present a system adapting analog multiplexer is in preparation. It will allow transmission of values of several different parameters in sequence through a single channel of the computer interface.

Since no essential limitation concerning the type of sample to be investigated could be observed, it seems that the system can also find applications in various laboratories of solid state and chemical physics.

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Компьютерно управляемая установка для измерения оптических спектров и времени жизни флуоресценции

Представлено анализатор оптических сигналов с компьютерным управлением. Система предназначена для проведения трех экспериментальных задач. Две уз них имеют спектроскопический характер, именно, измерение флуоресценционного спектра либо спектра возбуждения после импульсного возбуждения. Третья связана с временной зависимостью затухания флуоресценции. Исследовано димеры цезия в парах цезия. Однако множество других газовых, жидких или твердых веществ может быть анализировано этой системой. Показано спектр возбуждения Cs_2 в качестве примера возможностей установки.