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Figure 1 Experimental configuration consisting of a 0.64 m triple spectrograph (A) for Raman spectroscopy, a 0.25 m flat field spectrograph (B) for absorption and fluorescence spectroscopy, and a streak camera (C) for time-resolved spectroscopy. The delay prism used in the “pump-and-probe” experiments is shown by (D).

Time-resolved spectroscopy has become an established technique for the investigation of the dynamic properties of matter. At the heart of time-resolved spectroscopy lies the mode-locked laser that generates ultrashort pulses. The first ultrashort pulses were generated 20 years ago by mode locking a ruby and a Nd:YAG laser. In the late 1970s femtosecond (fsec) duration pulses were generated by mode locking of dye lasers. In fact, pulses as short as 8 fsec (8 × 10⁻¹⁵ sec) have been generated by mode locking and pulse compression. The advances in the technologies of time-resolved spectroscopy have opened up new areas of research in physics, chemistry, and biology.¹⁻³

The development of high repetition lasers has improved the chemist’s ability to study phenomena that were too weak to be observed with single-pulse lasers. It has, however, placed stringent requirements on the computer interface for real-time experiments. For example, a 10-Hz laser combined with a 1024-channel array would require the transferring and the processing of more than 10,000 words in a second. Although this is not a difficult task for a specialized computer, it is a demanding job for a minicomputer.

Figure 1 shows the basic experimental configuration. The experimental system consists of a 0.64 m triple spectrograph (A) for Raman spectroscopy, a 0.25 m flat field spectrograph (B) for absorption and fluorescence spectroscopy, and a streak camera (C) for time-resolved fluorescence spectroscopy. The advantage of this arrangement is that it is possible to study the emitted light simultaneously in the frequency and time domains. The two spectrographs and the streak camera are used with a one-dimensional, 1024-channel, intensified pho-

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ULTRAFast spectroscopy continued

Figure 2: Schematic diagram of the operation of the streak tube. Photoelectrons emitted by light striking the photocathode are deflected by an applied voltage ramp. Photoelectrons released at different times from the photocathode strike the phosphorescent streak at different positions, causing a track with a spatial intensity profile directly proportional to the incident temporal intensity profile of the fluorescence.

Photoconductive array (Princeton Applied Research [PAR] OMA IR). In addition, two other silicon intensified target vidicon systems (PAR OMA II and Hamamatsu camera systems) can be used.

In picosecond spectroscopy the timing mechanism of the apparatus is the speed of light itself. If the path length of the pump pulse is decreased by 1 mm, the exciting pulse will arrive at the sample site 3.3 psec before the probe pulse. This is accomplished by moving the delay prism by 0.5 mm (D in Figure 1). Therefore, the kinetics of any absorption changes can be followed point by point by moving the delay prism across the time domain of interest. The second harmonic at 530 nm from Nd:YAG or Nd:glass laser is commonly used as a pump pulse. A broadband source is required for the probe pulse so that a large region of the spectrum can be probed at one time. Such a spectrally white ultraviolet pulse (known as the super-continuum) is available. When a very strong laser pulse, the Nd:YAG 1064 nm in this case, is focused in CCl₄ (or any condensed material or gas for that matter), it generates a broad band pulse by self-phase modulation and four photon mixing covering the entire visible and IR regions. Generally, the duration of the continuum is approximately the same as the generating laser pulse. For absorption spectroscopy, the probe beam is divided into two pulses of approximately equal intensity $I'(\tau)$ and $I''(\tau)$, where $\tau$ is the delay time between pump and probe pulses. $I'(\tau)$ is transmitted through the area of the sample that is excited by the pump pulse. The intensity of the transmitted probe beam depends on the photochemical changes initiated by the exciting pulse. $I'(\tau)$ is the reference beam through the sample. The change in the optical density is obtained as:

$$\Delta OD(\tau) = -\log \left( \frac{I'(\tau)}{I''(\tau)} \left[ \frac{I'}{I''} \right] \right)$$

where the ratio $I'/I''$ is the normalization factor for the two laser pulses before the sample. The resolution of the picosecond absorption technique is limited only by the duration of laser pulse and the dispersion of the supercontinuum.

For luminescence time-resolved spectroscopy, the most commonly used technique employs a streak camera. At the streak camera, the time information of the luminous event is converted into spatial information. For a detailed description of the streak camera, see Ref. 5. Photons striking the photocathode of the streak tube produce an emission of electrons that is proportional to the intensity of the incident light. The photoelectrons are deflected by an applied voltage ramp and impinging across a phosphorescent screen (Figure 2). Photoelectrons released at different times from the photocathode strike the phosphorescent screen at different positions, causing a track with a spatial intensity profile directly proportional to the incident temporal intensity profile of the fluorescence. The phosphorescent track may be analyzed by various detection systems (for example, a video camera). A detailed discussion of picosecond techniques can be found in Refs. 6 and 7.

This paper describes a computer interface for spectroscopic studies in both the frequency and time domain.

The interface has the following features:

1) **Flexibility.** Without major modifications the system can both be used to perform standard measurements such as fluorescence, Raman, and time-resolved spectroscopy and also be easily tailored to meet requirements of a specific experiment.

2) **Central control of the entire experiment.** Data can be collected, processed, and analyzed to the laboratory's needs.

3) **Fast communication and data processing.** Rapid communication between devices and the capability to collect and process data in real time allow the direction of the experiment to be changed before completion.

4) **Simple command structure.** Different researchers are able to use the system.

5) **Specialized and flexible data collection modes.** (For example, collection of individual single pulse data while averaging them together at a high repetition rate.)

6) **Double precision data.** A large dynamic range (32 bits) is provided.

7) **Survivability.** An experiment can be performed even when some of the equipment does not work. This requires a certain degree of redundancy in the system.
Hardware

The PAR photocathode array is scanned and data are collected under control of a Motorola 68000 microprocessor-based board in a VME standard card cage. Ideally, it would have been desirable to have had direct control of the microprocessor. This would have allowed data to be collected and manipulated quickly and exactly according to the laboratory’s needs. However, this was not an option available to the authors. The PAR OMA III was interfaced to a Digital Equipment Corporation (DEC) PDP 11/23+. While working with the PAR OMA III detector interface, its command language was found to be somewhat limited for picosecond pulse spectroscopy where timing was critical, and external triggering systems were needed. Consequently we developed our own command superstructure to alleviate this problem. Although the PAR OMA II and the Hamamatsu camera system can also be used with the system, they do not allow for real-time data acquisition. This report will discuss only the interface.

Special consideration had to be given to variations in the energy of each pulse, because in the picosecond regime, where nonlinear processes occur, small fluctuations in incident energy can produce significant changes in the recorded spectra. Therefore, the energy of each pulse must be measured. The PAR OMA III has an analog to digital (A/D) converter that accepts a signal and stores it on the 1025th channel of the incoming data block. However, the 2-5 nsec-long signal emitted by the photodiode is too fast for the A/D converter. Therefore, to record the energy, the signal from a calibrated photodiode is sent to a gated box car integrator which would latch the signal so that it can be sent to an A/D converter of the computer and then stored in the same file with the data. The authors’ experimental setup requires a calibrated photodiode for the pump pulse and another for the probe pulse.

One must also realize that in picosecond laser experiments, the sample is more likely to be damaged as opposed to a continuous wave (cw) laser. Therefore, it is often necessary to translate to a new area on the sample after each probe. This is accomplished by using a stepping motor driven sample platform. The user types into the computer the number of data sets wanted and the spacing on the sample between the probes. The rest of the operation is handled automatically, with the data collected individually and/or cumulatively. This feature shows the power and flexibility of a centrally controlled experiment. Figure 3 shows the diagram of the hardware arrangement. A certain degree of redundancy was implemented by the development of both the serial and parallel interfaces, the capability to use different detectors, digital output or analog display modes, and different data storage modes. This would allow an experiment to be continued even with a partially operating system.

Software

The major segment of the software was written in MACRO-11 assembly language, which is the only language that can be used in time-critical applications. Subroutines called by the main program for data manipulation and graphics can be written in Fortran-IV, C, Pascal, or any other high level language. The software runs under the RT11XM operating system. The advantages of this operating system are that it is established and reliable, and that it allows the program to take

![Diagram](https://via.placeholder.com/150)
complete control of the computer. A minimum of 128K of memory is needed by the RT11 system.

The program can be used to send all PAR OMA III commands and receive responses including the transfer of data files from the memory of the OMA III. Faster data transfer rates have been achieved by implementing the device's live scan capabilities. In this case, data can be collected directly from the A/D converter of the detector. The live data can be viewed in real time. This gives the investigator the capability of modifying experimental conditions during the experiment.

The data can be displayed directly off the detector as an analog signal on an oscilloscope or digitized and sent to the computer. These digitized data can be seen on a cathode ray tube (CRT) connected to the digital to analog (D/A) converter of the computer. More elaborate graphics were implemented using ReGIS, a graphics language supported by the DEC VT240 video terminal. Some of the features include the ability to scale and display more than one data file at a time. The software also supports some data manipulations such as addition, subtraction, multiplication, and division of files by a constant, as well as file additions and subtractions and simple data fitting routines. The data can be analyzed and plotted with publication-quality graphs, or sent to the VAX 11/780 for more elaborate computations.

The operation of the system can be seen in the following example (see Figure 4). A command sequence has been written that enhances the capabilities of the PAR OMA III. It is desired to collect data from a specified number of pulses, where each pulse irradiates a new part of the sample. The data should be accumulated into one memory location and be collected in separate memory locations, so that the individual identity of each piece of data can be preserved. Furthermore, data should be collected only when the energy of the laser pulse falls within a narrow window of energy levels. It is also necessary to have the background noise subtracted from each shot. The system accomplishes this task by first requesting that the user enter the number of pulses to be collected. The program then asks the user if automatic vertical translation of the sample platform is desired. In this example, the answer is yes. The program now initializes the stepping motor controller and then requests from the user that he/she specify the spacing between consecutive target sites on the sample. This spacing is solely dependent on the user's needs.

The diameter of the laser beam is usually the determining factor. Subsequently, the program requests the energy windows. If the readings from the calibrated photodiodes are outside the set windows, the data will be discarded. Next the program asks the user questions regarding how the interface is to be set up, such as whether the user wants certain interface memory locations cleared, what memory locations the data should be stored in, and how many scans should take place before data collection is initiated. In this example, the
interface is instructed to take one scan and store it in a memory location, this being done with the laser shutter closed. These data will be used as a background subtraction file. The system is then instructed to send a pulse to the laser shutter controller and to wait for a transistor-transistor logic (TTL) trigger pulse to collect and save the scan. The pulse to the laser shutter controller causes one laser pulse to be emitted. Part of the laser pulse then irradiates the trigger photodiode. The photodiode in turn triggers a pulse generator, which supplies the interface with the TTL pulse that it was waiting for. At the same time, the calibrated photodiodes read the energy and transfer the readings to the computer through the A/D converter. If the voltages are within the set windows, the OMA III collects the scan. The OMA III is then instructed to subtract out the background, using the already collected background file, and then to store the result in two locations; one of which will be used to accumulate the data, the other to retain individual identity. The computer now instructs the platform to move to the next location. Upon completion of this translation the process is repeated until the desired amounts of data have been collected.

Summary

An interface for picosecond spectroscopy has been described. The fact that the system is centrally controlled allows the data collection process to be automated. This means that the investigator no longer has to perform tedious and repetitive data collection techniques. There are several advantages to this:

1) The experiment can be more precisely repeated and controlled;
2) Large amounts of data can be collected rapidly;
3) The time normally spent on manually collecting data can be spent on theoretical analysis of the data.

References