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Assembly of a fast multi resolution spectrophotometer system for simultaneous measurement of absorption and luminescence spectra

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In this work, the design and assembly of a dual spectrophotometer system capable of measuring the absorption as well as time resolved luminescence spectra of liquid, gaseous, or solid samples are reported. The system incorporates a 1024×376 elements coupled charge detector (CCD) capable of monitoring changes in optical spectra with time delays as short as few microseconds time scale. Such a design reduced significantly the costs of purchasing two separate systems containing similar optical and electronic components. In addition, the design enabled further investigations on the photodegradation mechanism for a benzimidazole based pesticide.

Keywords: dual spectrophotometer, multiresolution spectrophotometer, low temperature fluorescence, benomyl, carbendazime.

1. Introduction

Absorption and luminescence spectrophotometers contain basically the same electronic and optical components. The only difference is the arrangement of the optical components, *i.e.*, the arrangement of the optical components determines whether the system will be used for photo-absorption, photo-luminescence or Raman measurements [1]. While in absorption measurements, the excitation source is located in line with the sample and detector. In luminescence, Raman, as well as other measurements, the excitation source is located at an angle normally 90° with respect to the sample and detector. Therefore, the requirement for obtaining absorption or luminescence spectra requires same optical components in addition to electronic controllers, amplifiers and data processors [2]. This work is considered as an extension of the work [3], in which, the design and assembly of a compact and multifunction spectrometer are presented. The same optical and electronic components are used for recording the absorption, luminance, and time resolved spectra of solid, liquid, and gaseous samples. This design is expected to reduce significantly the cost of spectrophotometric instruments. Moreover, the design enables tracing any changes in

the sample using absorption and luminescence spectra simultaneously, which is not possible with the classical spectrophotometers. This can be achieved by recording the absorption spectra which takes several microseconds followed by recording the luminescence spectra which can also be recorded in time scales as short as several microseconds. The sequence can be repeated, and therefore in one-minute time scale thousands of absorption and luminescence spectra can be obtained without the need of removing the sample from its place.

The new system is designed in such a way as to enable easy replacement of the sample cell holder mentioned in reference [3] by a home-made, open cycle, liquid cryostat. To demonstrate the capabilities of the new system, the luminescence spectra for a number of organic compounds at different temperatures and resolutions are presented.

2. Experimental

A block diagram of the experimental arrangement is shown in Fig. 1. It consists of four major units: light source unit, spectrograph (3), optical 2D diode array detector (4), control electronics and data station (5, 6, 7).

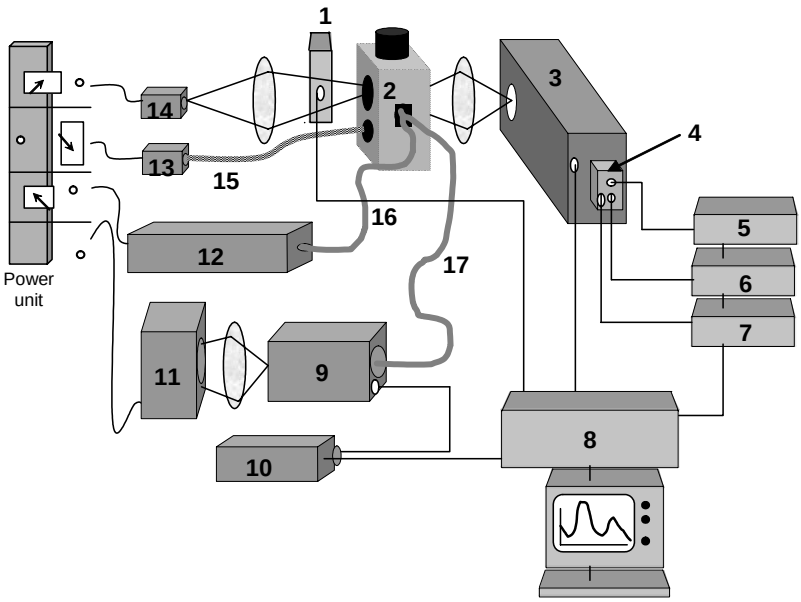


Fig 1. Block diagram of the experimental set-up: 1 – electromechanical shutter, 2 – sample cell holder, 3 – spectrograph, 4 – CCD unit, 5 – fast high voltage pulser, 6 – detector controller, 7 – delay generator, 8 – computer, 9 – excitation monochromator, 10 – excitation monochromator drive unit, 11 – xenon lamp, 12 – nitrogen laser, 13 – tungsten lamp, 14 – deuterium lamp, and 15, 16, 17 – 1 mm UV passive optical fiber.

The light source consists of four main blocks: deuterium lamp (14) for the wavelength range (190–350 nm), tungsten lamp (13) for the wavelength range (350–900 nm), xenon lamp (11) for the wavelength range (190–900 nm), and nitrogen laser (12) emitting at the wavelength of 337.1 nm.

The deuterium light beam is focused into the middle part of the sample cell (2) using a quartz lens. The power supply that ignites and supplies the deuterium lamp with constant current was designed and built in our laboratory.

A 100 W tungsten lamp operated by a DC stabilized power supply (Ealing, model 021/026) is used as the visible radiation source. An optical fiber cable (15) is used to transfer the visible light beam to the lower part of the sample cell. Electromechanical shutter (1), driven by UniBitz shutter controller Model SD-1000, is used to control the exposure of the sample to light.

A 250W air-cooled xenon lamp operated by a power supply consisting of lamp igniter and DC source, (model: Muller SVX1530), is used as the excitation source for the emission part of the system. The beam output is focused into the input slit of a 0.3 m monochromator (9). The excitation monchromator drive unit (10) is interfaced to the computer enabling software selection of the excitation wavelength [4]. The output of the monochromator is focused into a wide bore (1.0 mm UV passive) optical fiber cable (17). The other end of the optical fiber cable is fitted into the sample cell holder at 90° to the deuterium and visible lamp. This configuration enables 90° excitation with respect to the detection surface.

A nitrogen laser, PRA Model LN 1000, with 337.1 nm wavelength and 1 mJ pulse energy is used as an optional excitation light source where its output is transferred to the sample via a wide bore 1 mm optical fiber (16). The nitrogen laser wavelength is suitable for exciting some of the samples used in our study, other lasers such as dye lasers can be used in place.

The sample holder block (2) was fabricated in the machine shop of the faculty [3]. It is designed to accept standard (10×10×50 mm) sample cells. Two 5 mm holes were drilled into the side perpendicular to the detection path as a modification on the cell holder used in reference [3]. The optical fiber cables, from the excitation light sources, are designed so as to fit into these holes, thus facilitative right angle sample excitation as well as facilitating other future applications for the system such as pulse probe techniques.

The spectrograph used in this setup is Chromex model 5001 [3]. It contains three gratings (75, 150, 300 grooves/mm) enabling the selection between three different resolutions. All spectrograph operations such as the selection of grating, slit width as well as wavelength calibration are fully controlled by Windows software.

The CCD detector, Princeton Instruments model LNCCD, consists of 1024×376 elements. It has a broad spectral response (200–900 nm). It is different from the detector used in reference [3] in that the spectral window is wider since the number of elements in the wavelength axis is double that in the ICCD unit. Moreover, the detector is cooled using liquid nitrogen to maintain the temperature at –90°C, hence

lower dark current and better sensitivity. A detector controller (model ST-38) driven by Windows 95 software is used to control and transfer the data to the computer.

A programmable delay generator model (DG-535) Stanford Research systems INC is used to synchronize the trigger of the diode array detector with the electromechanical shutters (7). Upon the reception of an input pulse it outputs as many as 4 pulses with a programmable time delay between each of them. This is extremely important for synchronization due to the large difference in response times between the electro-mechanical shutters and the electronic detectors.

The computer (8), DELL (P75t), includes a fast interface card driven by Windows software. To start data acquisition, the computer triggers the detector controller via the fast interface card installed on the computer motherboard. The detector controller outputs a trigger pulse that is fed into the programmable delay generator unit. The latter outputs two pulses with different time delays, the undelayed pulse is fed into the electromechanical controller unit to activate the mechanical shutters while the delayed pulse is used to trigger the detector. The software fully controls all the functions of this generator, *i.e.*, the gate pulse width, pulse delay, as well as the external or internal pulse trigger. The type of grating selected determines the spectral window, *i.e.*, the width of the spectrum. The spectral window that can be achieved here is double that mentioned in our earlier work [3]. For example, the 75 grooves/mm grating offered a spectral window of 150 nm while the spectral window for the same grating is 300 nm. The same idea applies to the other gratings. The wavelength selected by the monochromator is always the middle part of the spectrum. The whole spectrum is collected during the selected exposure time of the detector. Exposure times as short as few microseconds are possible, therefore a complete 300 nm spectrum can be obtained in this time scale. The main benefits of this setup are:

1. The short time during which the sample is exposed to probe light, this time can be as short as the detector exposure time. Since we use electromechanical shutters, we are limited to the shutter response time, which is of the order of milliseconds.

2. Two types of measurements can be obtained while the sample in its place and in a very short period, the only requirement is to control the electromechanical shutters in front of the light sources.

3. The new system offered a spectral window that is double the width of that in reference [3].

A variable temperature sample holder with open cycle liquid nitrogen cryostat was designed and fabricated in collaboration with the mechanical workshop to be used for low temperature measurements. The system was designed for easy replacement of the sample holder block described above. A block diagram of the system is shown in Fig. 2. It consists of a hollow aluminum cube 10×10×10 cm with 2-inch widow on each of the 4 sides (1). The windows are designed to accept 2-inch quartz windows for optical excitation and detection. The top side of the cube is machined in such a way as to accept Varian vacuum line adapters with 50 mm diameter (2). A steel vacuum cylinder, from Varian Vacuum Systems, is fitted to the top of the cube (5). A side tube is attached to the topside of the steel cylinder to evacuate the space around the sample

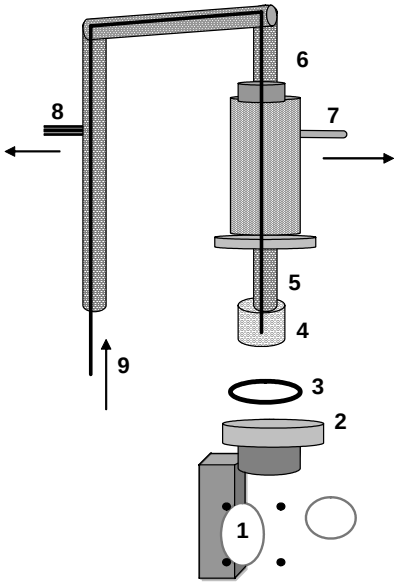


Fig. 2. Open cycle liquid nitrogen cryostat: 1 – aluminum block with quartz windows, 2 – Varian type adapter, 3 – Rubber O-ring, 4 – metal block with drilled volume to receive liquid nitrogen and to act as a heat exchanger, 5 – liquid nitrogen transfer line, 6, 7 – stainless steel cylinder with vacuum outlet, 8 – vacuum outlet to evacuate the transfer line, 9 – capillary tube for liquid nitrogen inlet.

cell holder. A liquid nitrogen transfer line consists of two copper tubes fitted into each other (4). The tube with smaller diameter (2 mm) is used for transferring liquid nitrogen from the liquid nitrogen dewar to the sample, while the tube with the wider diameter (1-inch) is used to shield the small diameter tube from the room temperature by evacuating the space between the tubes. One end of the transfer line is immersed into the liquid nitrogen dewar. The other end is designed to fit into the middle of the steel cylinder and continues to the aluminum cube (3). A specially designed sample cell holder is fitted to the other end of the transfer line.

The thin tube in the transfer line continues to the outside of the system where an oiless vacuum pump is used to suck the liquid nitrogen from the dewar as is shown in Fig. 3. The sample cell holder (1) is fabricated from a stainless steel metal block with

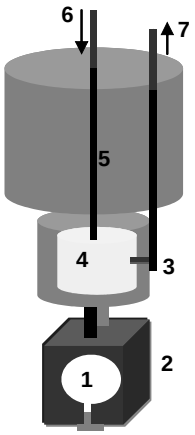


Fig. 3. Liquid nitrogen transfer line and sample cell block: 1 – sample volume drilled into the metal block with quartz window in the front, 2 – metal block from stainless steel, 3 – metal block with drilled volume 4 to receive liquid nitrogen to act as a heat exchanger, 4 – metal tube through which liquid nitrogen is removed, 5 – copper cylinder evacuated all over the transfer line, 6, 7 – liquid N_2 inlet and outlet.

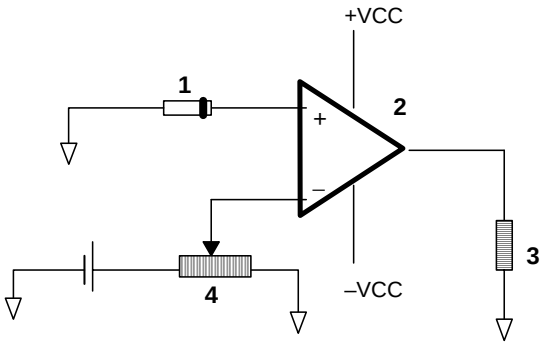


Fig. 4. Temperature controller circuit diagram: 1 – semiconductor diode, 2 – operational amplifier, 3 – power resistor, 4 – potentiometer.

a 10 mm diameter half sphere drilled in its middle. A 5 mm hole is drilled in the bottom side of the block for filling the cell with the liquid sample. The front side of the block is designed to accept a 1-inch quartz window for front surface optical excitation. Teflon gaskets are used between the quartz window and the stainless steel block to prevent the leak of the liquid sample due to outside vacuum. A semiconductor silicon *p-n* junction is used to measure the temperature of the sample. The voltage across the *p-n* junction is measured using a digital millivolt meter and calibrated to temperature. The sensitivity of the *p-n* junction was found to be as good as gold-copper thermocouple and easier to handle [5, 6]. A power resistor (10 Ω, 5 W) is attached to the side of the sample cell holder for heating the sample by passing electrical current through the resistor. An electronic circuit based on operational amplifier is used to compare the actual temperature determined by the voltage across the diode and the voltage set by a potentiometer which represents the required temperature. The operational amplifier outputs a voltage proportional to that difference to the power resistor. A block diagram of the circuit is shown in Fig. 4.

3. Results and discussion

For testing the wavelength calibration and resolution, the spectral lines from a low pressure standard mercury lamp (Ealing cat-no. 26-4812) at different resolutions were recorded. Figure 5 shows the optimum resolution of the system where the intense mercury line at 546 nm and the closely spaced 576 nm and 579 nm lines are well separated. The resolution capabilities of the instrument can be changed easily by selecting a grating from a set of three gratings using the computer software. The easy change of instrument resolution is important for low temperature luminescence studies where the fluorescence spectral lines get narrower with a decrease in temperature [7, 8].

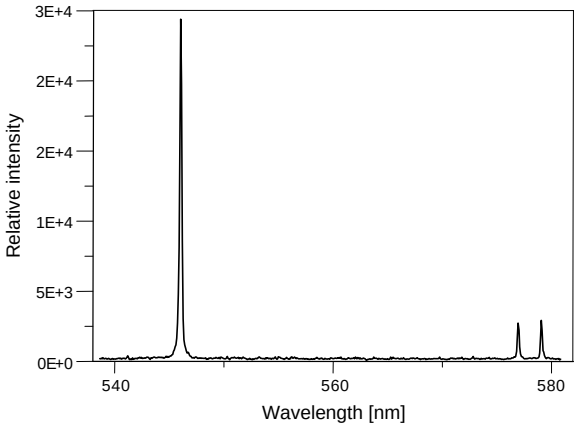


Fig. 5. Mercury spectral lines acquired using the high resolution grating (300 grooves/mm).

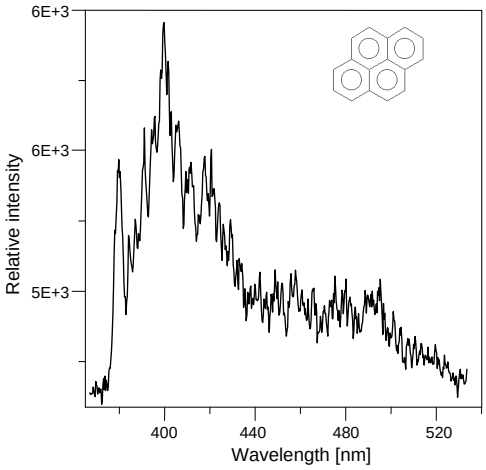


Fig. 6. Fluorescence spectrum of 1.0×10^{-6} g/l pyrene in cyclohexane at room temperature obtained with a single 15 nsec duration laser pulse at 337.1 nm using N_2 laser excitation source.

The speed and sensitivity of the system is demonstrated in Fig. 6 where the low resolution, fluorescence spectrum of 1 μg/l pyrene/cyclohexane solution at room temperature was acquired using a single 15 nsec, 1 mJ nitrogen laser pulse. The spectrum contains identical spectral characteristics of pyrene published in [9].

Figure 7**a** shows the low resolution fluorescence spectrum of benzo(a)pyrene in n-heptane at room temperature. The spectrum was acquired using 20 nitrogen laser pulses each of 15 nsec duration. The spectrum was compared with the data published in reference [7] and found to contain similar spectral characteristics. The low temperature high resolution fluorescnece spectrum of the same sample is shown in

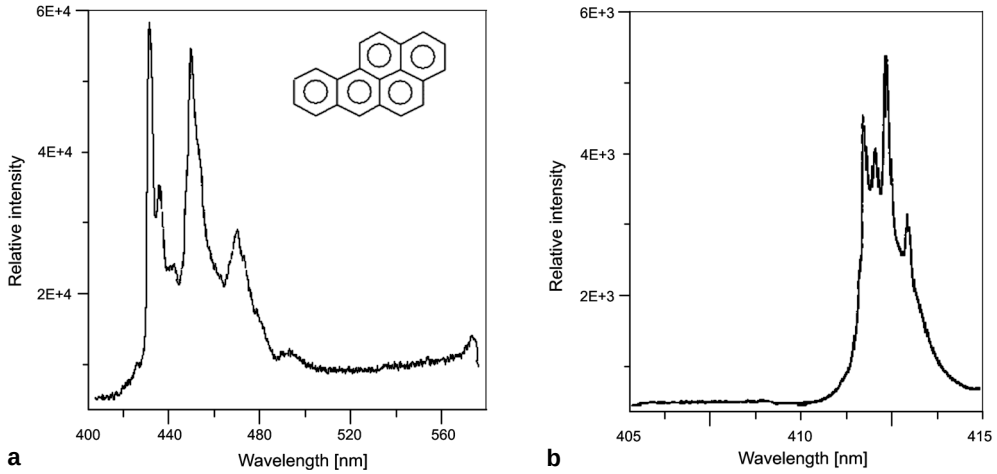


Fig. 7. Room temperature low resolution fluorescence spectrum (**a**) and low temperature (–150°C) high resolution fluorescence spectrum (**b**) of 2.0×10^{-5} g/l benzo(a)pyrene in n-heptane (λ_{exc} = 337 nm).

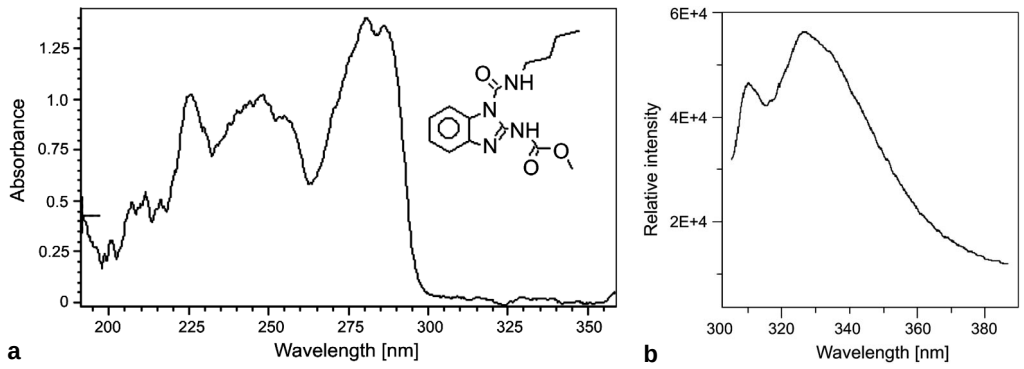
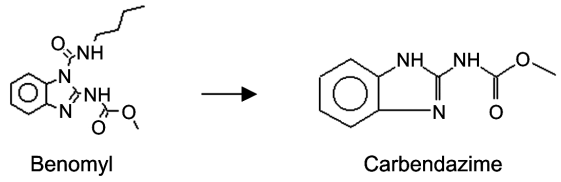


Fig. 8. Absorption spectrum (**a**) and fluorescence spectrum (**b**) of 1×10^{-3} M benomyl in CH_3CN, (λ_{exc} = 290 nm).

Fig. 7**b**. The results indicate the spectral capabilities of the system including variable temperature measurements, selection of excitation light sources and variation of resolution according to the experiment requeirments.

Figure 8**a** shows the absorption spectrum of a benzimidazole based derivative (benomyl) in CH_3CN solution while Fig. 8**b** shows the fluorescence spectrum for the same compound in CH_3CN solution excited at 290 nm. Knowing that some molecules, such as benomyl are very unstable in solution [10], the possibility of simultaneuous measurement of absorption and fluorecsence can be considered of high practical importance for monitoring the degradation process. The degradation process was



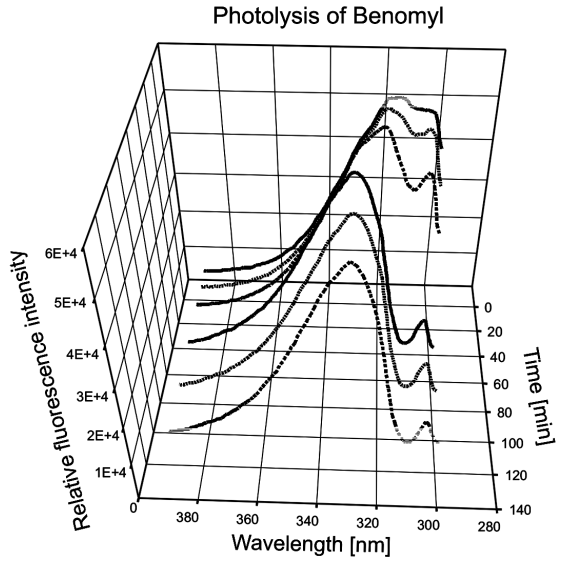


Fig. 9. Fluorescence spectrum of benomyl CH_3CN solution at different times of photolysis (λ_{exc} = 290 nm).

monitored using the fast monitoring absorption technique and published in a previous work [3]. In this work, the fluorescence technique is used to monitor the degradation process and shown in Fig. 9. The spectrum provides a conclusive evidence about the instability of benomyl in solution.

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