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Construction and Performance of a Time-Resolved Apparatus for Measuring Emission Lifetimes

By

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An instrument for measuring emission lifetimes was constructed. As examples of its application, the fluorescence lifetimes of quinine in aqueous sulfuric acid, and pyrene in water and cyclohexane were measured to be 20.3, 186 and 22.4 ns, respectively. It was shown that this apparatus is efficiently powerful for spectroscopic studies in the nanosecond range. The construction of the apparatus is also given in detail.

1. Intrdoduction

Recently, much of the information concerning mechanisms of photochemical reactions in aqueous, micellar and cyclodextrin solutions has been obtained by spectroscopic methods including absorption and fluorescence measurements.

For example, studies were performed on fluorescence quenching[1–3] and energy transfer[4,5] in homogeneous and (pre)micellar systems, and inclusion phenomena in cyclodextrin solutions.[6] Measurements of the spectroscopic properties in such systems are essential for investigating the photophysics and photochemistry of the excited states as well as ground states of the species. Especially, the chemical and physical properties of fluorescent molecules can be quantitatively studied by the detailed measurements of fluorescence lifetime and time-resolved spectrum. It is well established that time-resolved decay measurements serve as an important tool in photophysics and photochemistry.

In this paper, the experimental details for obtaining the emission lifetime of excited species are presented along with some applications.

2. Experimental Section

2.1. *Instrumentation*

The experimental apparatus consists of excitation light source, spectrometer and photo-detection system including microcomputers. The schematic diagram of the apparatus is shown in Fig. 1.

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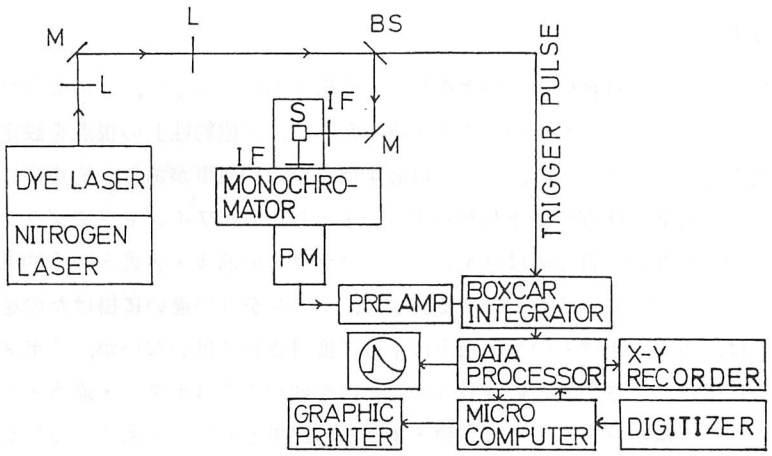

Fig. 1. Block diagram of the emission decay apparatus.
S: sample, IF: filter, M: mirror, L: lens, BS: beam splitter, PM: photomultiplier.

A Lambda Physik M100A Nitrogen laser and an Omnilite 60–30 Dye laser (Nippon Dynamic Distribution Co.) were used as the excitation source. This nitrogen laser consists of three parts; the laser head, the power supply and control unit, and the vacuum pump (Model VP15). This laser can be operated at high impressed voltage up to 20 kV and emitts intense radiation at 337.1 nm, the laser pulse being 4–5 ns in width (fwhm). This repetition frequency can be adjusted between 5 and 100 Hz. All measurements in the present study were carried out at a repetition rate of 70 Hz, and an averaged pulse energy of 1.5 mJ. The beam dimensions are 7 mm × 15 mm and its divergence (half angle) is 2.5 mrad × 7 mrad.

The dye laser has the following specifications: exchange efficiency (more than 10%), limited tunability (340–760 nm) and wavelength resolution (2–3 nm).

The laser light is directed to a quartz cell in a cell box, as is shown in Fig. 1. The emission is observed at an angle of 90° relative to the incident laser beam. The discrete spectral lifetime is measured with a filter (IF) and 0.5–5.8 nm bandpass set on the CT-25N monochromator (Japan Spectroscopic Co., Ltd.). The filter (IF) mounted at a monochromator entrance rejects the scattered light from the laser.

The photons are detected with an RCA 8850 photomultiplier tube (response time < 2.5 ns) equipped with a thermoelectric cooler. For a detection in the red and near infrared regions an RCA 8852 or a Hamamatsu R1333 photomultiplier is used.

The signal passes through a 50-Ω coaxial cable from the photomultiplier and is analyzed by a PAR Model 162 Boxcar integrator which is combined with a PAR Model 164 Processor Module. The boxcar averaging is a process of controlled sampling and averaging. The boxcar integrator is triggered by the trigger output of the pulsed laser and is used to determine the exact shape of repetitive waveform. Fig. 2 shows the basic timing relationships of this device. This system synchronously samples the input signal with an aperture that can be fixed at desired points.

The output signal of the boxcar averager was stored by using a Data Processor

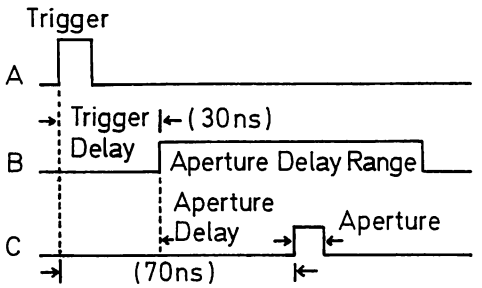

Fig. 2. The basic timing relationships of boxcar integrator.

Model R800DPF (Japan Spectroscopic Co., Ltd.) as a digital signal, and then fed to an X–Y recorder. The storing process is conveniently monitored with the use of a Trio 7904 Oscilloscope. This data processor serves as a gated photon counter by controlling the boxcar integrator. Furthermore, a time-resolved spectrum can also be measured by using this device. The block diagram of this data processor is shown in Fig. 3.

Data is analyzed with OKI if 800 Model 30 and 50 microcomputers.[7,8]

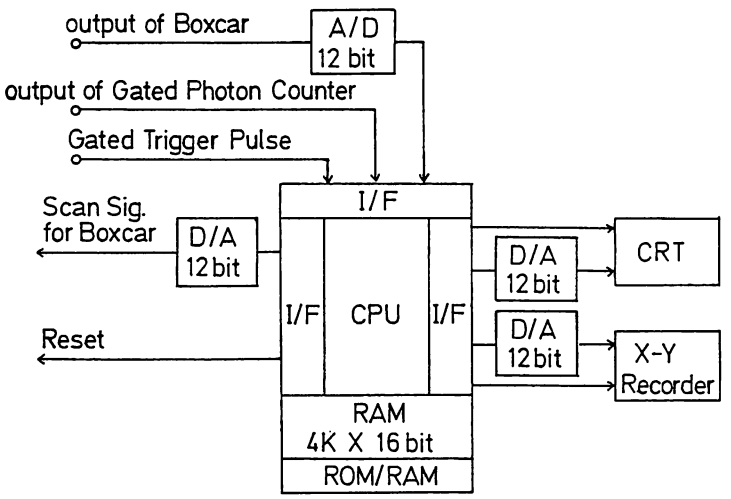

Fig. 3. Block diagram of data processor.

2.2. *Materials*

Quinine sulfate dihydrate was purchased from Wako Chemical Industries Ltd. and was recrystallized from water. The quinine was dissolved in 1.0 N aqueous H_2SO_4 in a concentration of 1×10^{-5} mol dm^{-3}. Pyrene (UP grade, zone refined) was obtained from Tokyo Kasei Kogyo Co., Ltd. and was used without further purification. Cyclohexane (Dotite Luminasol) and H_2SO_4 (reagent grade) were obtained from Wako Chemical Industries Ltd. Laboratory deionized water was twice distilled.

3. Results and Discussion

3.1. *Instrument Performance*

The measurements were made at 25°C using a 337.1-nm beam from the N_2 laser as

the excitation wavelength.

In order to test the performance of the apparatus, we measured the fluorescence lifetime of quinine in 1.0 N aqueous H_2SO_4, since quinine has been used as one of standard materials for fluorescence lifetime measurements.[9-13]

Figure 4 shows the observed decay curve of quinine in aerated aqueous H_2SO_4. Emission from quinine was observed at 460 nm with spectral resolution of 1.5 nm.

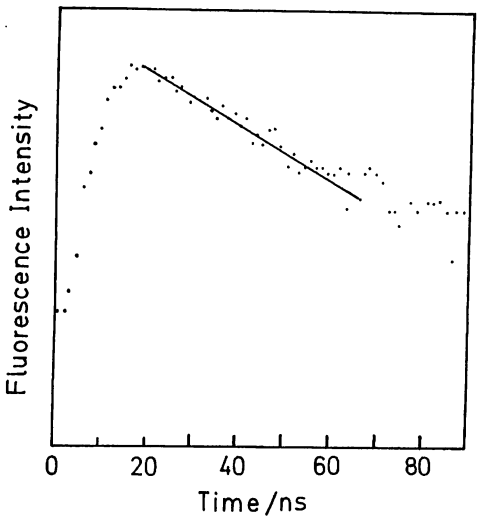

Fig. 4. Log-converted fluorescence decay curve of quinine in aerated aqueous H_2SO_4 (1.0 N). The points: the observed fluorescence intensity, solid line: a simulated fit to a single exponential decay.

O'Connor et al.[14] have found the wavelength dependence of the decay curves of quinine bisulfate and suggested that they are composed of the two components having the lifetimes of ≈ 20 ns and ≈ 2 ns, though the latter component (2 ns) has a small contribution (2%) to the total fluorescence. On the other hand, Barrow and Lentz[10] have pointed out that quinine exhibits a single-exponential decay.

Although we improved signal-to-noise ratios and fluorescence wavelength resolution by adjusting an optical system, the short-lifetime component could not be observed because of low time resolution. The decay curve obtained in the present work could be fitted to a single-exponential function. The lifetime was determined to be 20.3 ± 1.56 ns from the least-squares treatment of linear portion of the logarithmic intensity *vs.* time curve. This is in excellent agreement with those (18.9[9], 19.27[10], 19.4[11], 20.1[12] and 20.4[13] ns) obtained by previous investigators.

3.2. *Applications*

The present apparatus has been developed to study dynamic processes of photochemical reactions of fluorescent molecules such as pyrene and chlorophyll, in micellar and premicellar solutions. Pyrene has been used as a suitable fluorescent probe for investigating the mechanisms of electron and energy transfers between solute molecules because it has a long-lived fluorescence.

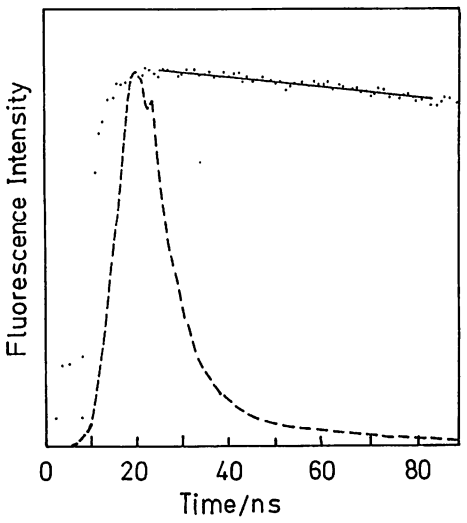

Fig. 5. Log-converted decay curve of pyrene (4×10^{-7} mol dm^{-3}) in aerated aqueous solution. The points: the observed fluorescence intensity, solid line: a simulated fit to a single-exponential decay. Lamp (N_2 laser) flash profile is given by the broken line in linear scale.

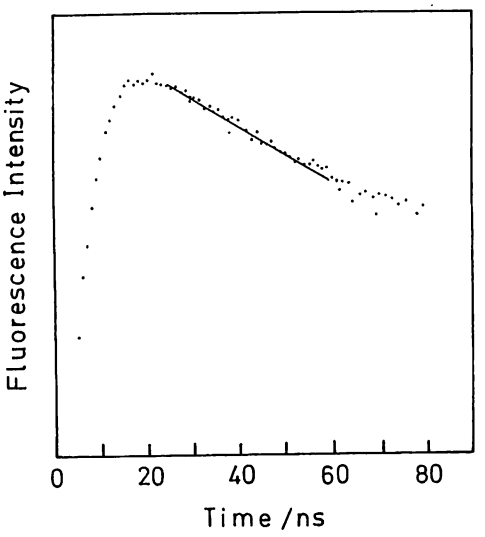

Fig. 6. Log-converted decay curve of pyrene (1×10^{-6} mol dm^{-3}) in undegassed cyclohexane solution. The points: the observed fluorescence intensity, solid line: a simulated fit to a single exponential decay.

Figure 5 shows the decay curve of pyrene fluorescence monitored at 373 nm, in aerated aqueous solution of 4×10^{-7} mol dm^{-3} (monitored by absorption spectrum). The result shows a single-exponential decay with a lifetime of 186 ± 20 ns, which is consistent with those (200[15] and 175[16] ns) by previous workers.

The lifetime of the fluorescent molecule is known to depend on the concentration, the solvent and the presence of quenchers. For example, the decay curve of pyrene in undegassed cyclohexane solution (Fig. 6) gives a lifetime of 22.4 ± 6 ns which agrees with that (20.5 ns) obtained by Craig et al.[17] It was found[17] that the lifetime depends on the solvent used.

4. Concluding Remarks

Emission lifetime measurements are a powerful technique for investigating dynamic processes of photoexcited species. The apparatus capable of measuring precise lifetime has been described. This system allows us to measure the lifetime as short as ≈1 ns and to analyze complex decay curves composed of multicomponents. An application of the instrument for studies of the molecular interactions in heterogeneous as well as homogeneous systems, such as aqueous, (pre)micellar or cyclodextrin solutions or polymer particles is in progress.

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References

1) S. Hashimoto and J. K. Thomas, *J. Am. Chem. Soc.*, **105**, 5230 (1983).
2) H. Sato, M. Kawasaki, M. Haga, K. Kasatani, T. Ban, H. Suenaga and N. Kitamura, *Nippon Kagaku Kaishi*, **1984**, 51, and references cited therein.
3) Y. Kusumoto, M. Shizuka and I. Satake, *Chem. Lett.*, **1986**, 529, and references cited therein.
4) K. F. Koglin, D. J. Miller, J. Steinwandel and M. Hauser, *J. Phys. Chem.*, **85**, 2363 (1981).
5) Y. Kusumoto and H. Sato, *Chem. Phys. Lett.*, **68**, 13 (1979); H. Sato, Y. Kusumoto, N. Nakashima and K. Yoshihara, *Chem. Phys. Lett.*, **77**, 326 (1980); Y. Kusumoto, H. Sato, M. Maeno, S. Yahiro and N. Nakashima, *Bull. Chem. Soc. Jpn.*, **54**, 60 (1981).
6) For example, see: Y. Kusumoto, M. Shizuka and I. Satake, *Chem. Phys. Lett.*, **125**, 64 (1986), and references cited therein.
7) Y. Kusumoto, G. R. Seely, M. Tokunaga, J. Kurawaki and S. Kamata, *JAPC*, in press (1986).
8) Y. Kusumoto, M. Tokunaga, J. Kurawaki and S. Kamata, *JAPC*, in press (1986).
9) R. F. Chen, *Anal. Biochem.*, **57**, 593 (1974).
10) D. A. Barrow and B. R. Lentz, *Chem. Phys. Lett.*, **104**, 163 (1984).
11) W. R. Ware and B. A. Baldwin, *J. Chem. Phys.*, **40**, 1703 (1964).
12) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc. Lond.*, **A275**, 135 (1963).
13) J. Alsins, S. Claesson and H. Elmgren, *Chemica Scripta.*, **20**, 183 (1982).
14) D. V. O'Connor, S. R. Meech and D. Phillips, *Chem. Phys. Lett.*, **88**, 22 (1982).
15) T. Yorozu, M. Hoshino and M. Imamura, *J. Phys. Chem.*, **86**, 4426 (1982).
16) K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.*, **99**, 2039 (1977).
17) B. B. Craig, J. Kirk and M. A. J. Rodgers, *Chem. Phys. Lett.*, **49**, 437 (1977).