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An UV-Visible Spectrophotometer Provided with a Photon Counting System for the Studies of Very Weak Absorption Spectra

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An ultrasensitive UV-visible spectrophotometer, of a single-beam type provided with a photon counting system having a time resolution of 10 ns has been constructed. It has been shown that absorption spectra can be measured to within an error of 10^{-5} in optical density with this instrument. Noise levels, measured as a function of the photon count numbers, are found to agree with the theoretically expected statistical fluctuation of the photons. Absorption spectra of thin naphthacene films, 32 nm or below in thicknesses, deposited on a quartz plate, were obtained with this instrument, and found to change with the film thickness.

Most of the commercial UV-visible spectrophotometers employ a double-beam optical system. They can be used to measure absorption spectra of very weak absolute intensities or small changes in absorption, with the aid of a digital memory background corrector, for example. An absorption spectrum of a material in a cell or on a transparent substrate is obtained as a difference in optical densities of a sample containing the material and a proper reference. The optical density, *d*, is expressed as

$$d = \log (I_R/I_S), \quad (1)$$

where I_S and I_R indicate light intensities through the sample and the reference, respectively.

It is interesting to pursue how weak absorption is measurable spectroscopically throughout the near UV and the visible region. In the case of the double-beam spectrophotometers, the limit of exact measurement is set by the difficulty of providing highly equivalent double beams throughout the UV-visible region and from the instability of the analog amplifiers equipped. As the sample absorption becomes less and less, the requirements for a proper reference and a good alignment of the sample-reference system along the monitoring optical path in addition to the instrumental accuracy get more and more severe. Kuhn *et al.* reported on an instrument employing a single beam system and a lock-in-amplifier to measure the absorption spectra of monomolecular layers of organic dyes, and *suggested* the possibility that absorbing species of 10^{-5} in optical density was detected.[1] However, they did not give any result showing the limit of detection they reached.

We have constructed an ultrasensitive UV-visible spectrophotometer of a single-beam type having a photon counting system, in which the optical density can be represented by the following relation,

$$d = \log (N_R/N_S) = \log (T_S/T_R), \quad (2)$$

where N_S and N_R are the photon numbers passing through the sample and the reference, respectively, and T_S and T_R stand for the times required to count a given photon number for the sample and the reference. In this paper, the details of the instrument and a few experimental results obtained with it are described.

Experimental

The block diagram of the spectrophotometer is shown in Fig. 1. The light from a 25 W deuterium arc lamp or a 20 W tungsten-halogen lamp is focused with a spherical mirror onto the entrance slit of a 25 cm monochromator. The monochromatic light from it is approximately focused through a quartz lens on to the sample. The light is introduced alternately onto the sample and the reference by moving the sample-reference holder, and the intensity of the light passing through the sample or the reference is monitored with a Hamamatsu R818 photo-multiplier, a Princeton Applied Research (PAR) 1120-02 discriminator, and a PAR 1109 photon counter. The overall photon monitoring system has an 100 MHz count rate. The entrance and exit slit widths of the monochromator are manually controlled so as to set the count rate below 10^7 pps. The operation of the photon counter, the wavelength driving and the moving of the sample-reference holder are controlled by a 24 K microcomputer. The optical density was calculated using the digital data sent out from the photon counter into the computer, and then displayed on an X-Y recorder versus wavelength.

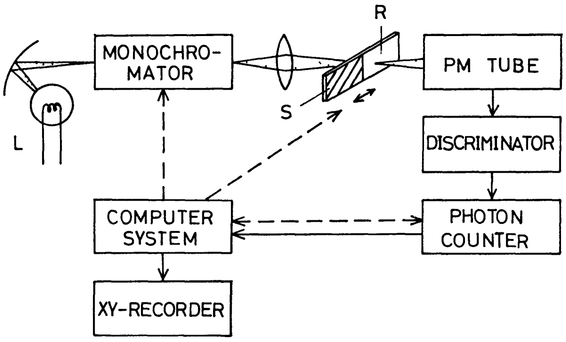

Fig. 1. Diagram of the spectrophotometer.
L: Light source, S: sample, and R: reference.

The monochromator and the sample-reference system are precisely driven with two step-motors sequentially as described below: The wavelength is set to λ_1. The sample is set into the position of light beam. Photon counting is started, and stopped when the number reaches a fixed value, say 10^7. The time required, T_S, is measured. The reference is moved into the beam position. Time, T_R required for a counting of the same number, is measured. Optical density at λ_1 is calculated from T_S and T_R and the value displayed. The wavelength is set to λ_2, different from λ_1 by a given interval, and the optical density for λ_2 is obtained by the same operation sequence as above. The spectrum can be measured in the range from 195 to 900 nm by a repetition of such procedures. The precision in the positioning of sample and reference is 1 μm or less.

Naphthacene from Wako Chemicals Co. was purified by vacuum sublimation. Naphthacene film was deposited on one half of the surface of an optically flat 26 mm×76 mm Suprasil quartz plate by vacuum evaporation, leaving the other half as the reference.

Results and Discussion

In order to show the limit of absorbances measurable with the instrument, an absorbance measurement was run using a clean Suprasil quartz plate, half of which is regarded as a sample and the other half as a reference. The measurements were performed by sampling from 195 to 900 nm at an interval of 1.0 nm. The result gave actually the magnitude of noise, or fluctuation. It was confirmed that the noise levels, in the whole wavelength region were essentially the same as in the small region in Fig. 2, as an example. The base line was flat throughout the whole wavelength range.

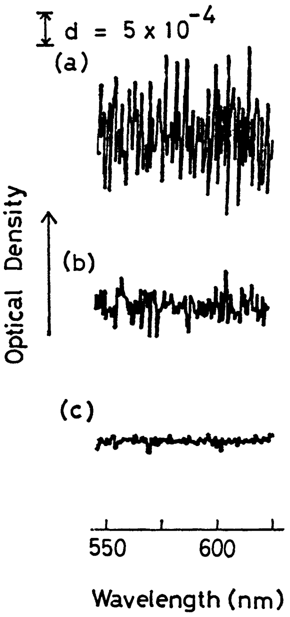

Fig. 2. Noise levels shown in an OD scale for operation between 550 and 625 nm at the photon count numbers of 10^6 for (a), 10^7 for (b) and 4×10^8 for (c), respectively.

The statistical fluctuation of the photons, ΔN, at the count number, N, is theoretically given by the following equation,

$$\Delta N/N = N^{-1/2}. \tag{3}$$

The magnitude of fluctuation in optical density, Δd, due to the statistical error can be given from Eqs. 2 and 3 as $\Delta d = (1/2.303)(\Delta N_S/N_S + \Delta N_R/N_R)$. The theoretical Δd values for the count numbers at which the noise curves (a), (b), and (c) in Fig. 2 were taken are 8.6×10^{-4}, 2.7×10^{-4}, and 4.3×10^{-5}, respectively. Comparison of these theoretical Δd values with the experimental noise levels shows that the fluctuations shown in Fig. 2 agree with the statistical fluctuations of the light intensity itself. It is, therefore, realized that all possible sources of error in our instrument, for instance, the fluctuation in the light source, the distortion and vibration of optical alignment, the sample-reference positioning imprecision, and the fluctuation of light monitoring system are not significant for the measurement of optical density of 10^{-5}.

The present instrument takes a count time of about 10 s or more for obtaining the optical density with an accuracy of the order of 10^{-5} at each of the wavelength, so that 2 h is at least necessary to get a spectrum over the region 200 to 900 nm with an interval of 1.0 nm. It is, of course, not difficult to detect absorption spectra less intense than the noise level by adopting an appropriate smoothing technique. In addition, the improvement of the time resolution of the counting system makes our absorption spectra measurements more accurate or speedy.

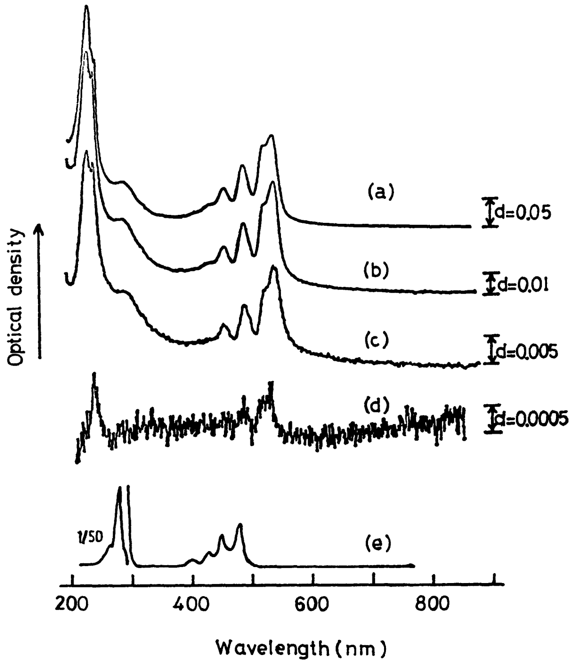

Fig. 3. Absorption spectra of naphthacene deposited on quartz plates measured at the photon count numbers of 10^7 for (a), (b) and (c), and 4×10^7 for (d), in the order of decreasing thickness. (e) is the absorption spectrum of naphthacene in an ethanol solution in an arbitrary unit.

Figure 3 shows the absorption spectra obtained for naphthacene films with various thicknesses, together with that taken in an ethanol solution with a Cary 15 spectrophotometer. The absorption in the visible region, ascribable to the ^1L_a band, of the films is largely red-shifted compared with that obtained in the solution. The spectra of the films, in the UV region, in (a), (b), and (c) have several absorption bands, presumably formed as a result of Davydov splitting of the ^1B_b band at 274 nm in the solution. The spectra of (a), (b), and (c) are essentially the same as those obtained for a naphthacene single crystal by Bree and Lyons[2] and for naphthacene films, 0.05—1 μm thick, by Maruyama and Iwasaki[3] and by us[4] at room temperature. However, there are some differences between the present spectra and others. For example, the peaks at 527 and 504 nm by Maruyama and Iwasaki are located at around 522 and 504 nm in (a), (b), and (c) in Fig. 3.

Though there is no marked shift in peak positions, the intensity ratio of the 504 peak to the 522 peak becomes small with the decreasing film thickness, (a) to (c). Similar change of the absorption intensity ratio on thickness is also found between the bands at 220 and 232 nm. These results suggest that the films are too thin to have the usual bulk properties.

The film thicknesses are roughly estimated from the peak absorption values at aroung 522 nm, assuming that the films produced are uniform in thickness. Taking the molar extinction coefficient at the peaks to be 1.0×10^4 and the density of the film to be 1.29,[2] the thicknesses are derived to be 32 nm for (a), 8.9 nm for (b), 3.3 nm for (c), and 0.13 nm for (d). The absorption spectrum of the thinnest film (d), though similar to (a), (b), and (c) in the visible region, is considerably different from them in the near UV region. It seems to lack the bands found for the thicker films at around 220 and 280 nm, and its absorption intensity in the near UV region is considerably smaller as compared to the visible band intensity. These suggest that, in the thinnest film, naphthacene molecules are separately deposited on the substrate surface: that is to say, a sub-monomolecular layer is formed. Though the reason for the decrease of the UV band intensity is not clear at present, such data for the very thin layers on solid surfaces will contribute to the elucidation of electronic structures of materials on solid surfaces.

We are also studying the absorption spectra of Langmuir films of fatty acids mixed with some organic dyes using this spectrophotometer.

In addition to the spectroscopy of thin films, this instrument will serve extensively for the accurate spectroscopy of very small quantities of materials in gaseous and liquid phases, or the spectroscopy of very weak bands arising from forbidden transitions.

The present results have shown that the optical density measurements can be performed in an accuracy of the order of 10^{-5} or better with our instrument. The limit of accuracy depends only on the performance of the photomultiplier, and the time resolution of the photon counter.

References

1) H. Kuhn, D. Möbius, and H. Bücher, "Techniques of Chemistry," ed by A. Weissberger and B. W. Rossiter, Wiley, New York (1972), Vol. 1, Part 3B, p. 577; G. R. Bird, G. Debuch, and D. Möbius, *J. Phys. Chem.*, **81**, 2657 (1977).

2) A. Bree and L. E. Lyons, *J. Chem. Soc.*, **1960**, 5206.

3) Y. Maruyama and N. Iwasaki, *Chem. Phys. Lett.*, **24**, 26 (1974).

4) M. Matsumura, H. Uohashi, M. Furusawa, N. Yamamoto, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **48**, 1965 (1975).