Short Communication

A simple and convenient method of measuring the number of photons absorbed by a solution irradiated with polychromatic light

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We describe a simple and sensitive method of measuring the number of photons absorbed when a solution containing a stable chromophore is irradiated with a polychromatic parallel beam. This technique takes into account the geometry and the radiance properties of the experimental arrangement. It utilizes the emission monochromator and photomultiplier of a spectrofluorometer, the spectral characteristics of which are calibrated in photon units.

1. Introduction

In order to calculate the quantum yield of a photochemical process the number of absorbed photons must be measured with precision. When the irradiation is carried out with a parallel beam of monochromatic light the number of incident photons is usually measured by chemical actinometry in the same geometry as that used in the experiment [1, 2]. The absolute number of photons actually absorbed is then calculated taking into account the absorbance of the chromophore solution at the wavelength used in the experiment. Another less sensitive method utilizes differential measurement of the energy emitted from a cell containing either the solvent alone or the dye solution. The energy is measured using a calibrated thermal detector, *e.g.* a thermopile, and the calculated value is subsequently converted into photon units.

When the irradiation is performed with a parallel beam of polychromatic light these methods cannot be used. In this case the number of photons absorbed by the chromophore must be calculated at each wavelength. Information regarding the emission spectrum of the source and the absorption spectrum of each component of the optical bench (filter, cell and solution) is required to perform this calculation. This is a very long and tedious method when the behaviour of different dyes or of the same dye in different conditions (pH, solvent, concentration etc.) is being investigated. In this paper we report a simple, accurate and rapid method of obtaining the information required. The method is based on the use of the monochromator and photo-

multiplier of a commercial spectrofluorometer, the spectral response of which has previously been calibrated in photon units.

2. Materials and methods

A schematic diagram of the experimental arrangement is shown in Fig. 1. The light emitted by the source L is filtered by the filter F (Schott Jenaer GG475), is collimated by the slits S_1 and S_2 and impinges on the diffuse quartz plate. The dispersed light is then detected by the emission monochromator and the photomultiplier. A Perkin–Elmer MPF 44 spectrofluorometer equipped with an emission-corrected spectral unit was used. The width of the slits can be varied to control the intensity of incident light in order not to saturate the detector. Neutral filters can be placed in the beam when very intense light sources are being investigated.

The number of photons absorbed in aqueous solutions (pH 9) of fluorescein (F) and rose bengal (RB) was measured using standard 1 cm quartz cells. The samples were irradiated using a substandard 40 W tungsten lamp, the emission spectrum of which is well known. The absorption spectra were recorded with a Perkin–Elmer 559 spectrophotometer.

3. Results and discussion

Two methods of determining the number of photons absorbed when an aqueous dye solution was illuminated by a polychromatic parallel beam of visible light were compared. The number of absorbed photons is given by the relation

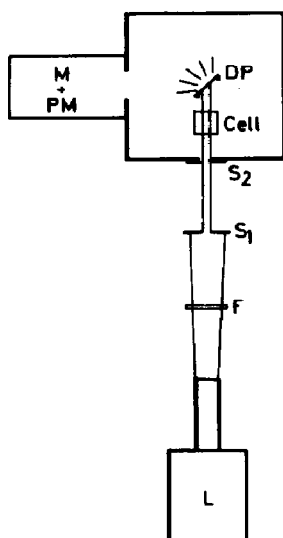$$I_{abs}(\lambda) = I_0(\lambda)T_r^F(\lambda)T_r^{solvent}(\lambda)(1 - 10^{-DO(\lambda)}) \tag{1}$$

Fig. 1. Schematic diagram of the experimental arrangement: L, lamp; F, filter; S_1, S_2, slits; DP, diffuse quartz plate; M + PM, monochromator and photomultiplier.
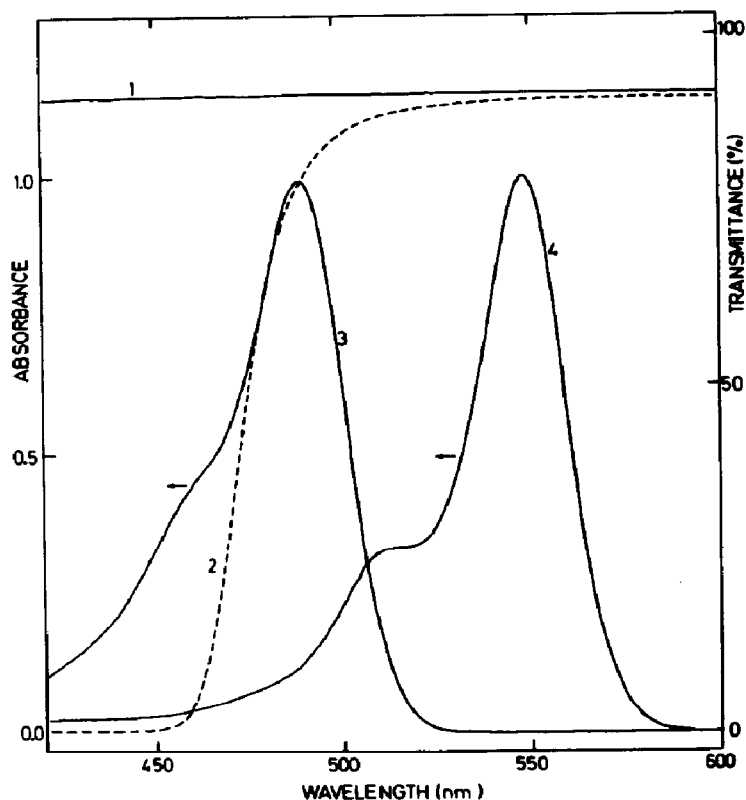
Fig. 2. Absorption spectra: curve 1, cell containing water; curve 2, filter; curve 3, aqueous solution of F; curve 4, aqueous solution of RB.

in which $I_0(\lambda)$ is the intensity of emission from the light source at wavelength λ and is expressed in photon units, $T_r^F(\lambda)$ is the transmission of the filter used in a specific experiment at wavelength λ, $T_r^{solvent}(\lambda)$ is the transmission of the cell containing the solvent and $DO(\lambda)$ is the absorbance of the dye at wavelength λ. If the solution contains substances other than the dye $T_r^{solvent}(\lambda)$ is replaced by $1 - 10^{DO_S(\lambda)}$ where DO_S represents the absorbance of that substance at wavelength λ. All these parameters are known and hence a curve showing the number of photons absorbed at each wavelength can be calculated. The area under this curve is proportional to the total number of photons absorbed by the solution. Since the photon energy is known, the absorbed energy can be calculated from the curve. A relative scale of absorption is established by applying this method to different dyes.

The absorption spectra of the different elements (filter, cell and dyes) used in the experiments are shown in Fig. 2. The number of photons absorbed at each wavelength can be calculated from these spectra and the emission spectrum. The results of the calculation are shown in Fig. 3. The areas S_F and S_{RB} under the curves for F and RB are 2.47 and 7.42 respectively. The calculated ratio is therefore $S_{RB}/S_F = 3.0$.
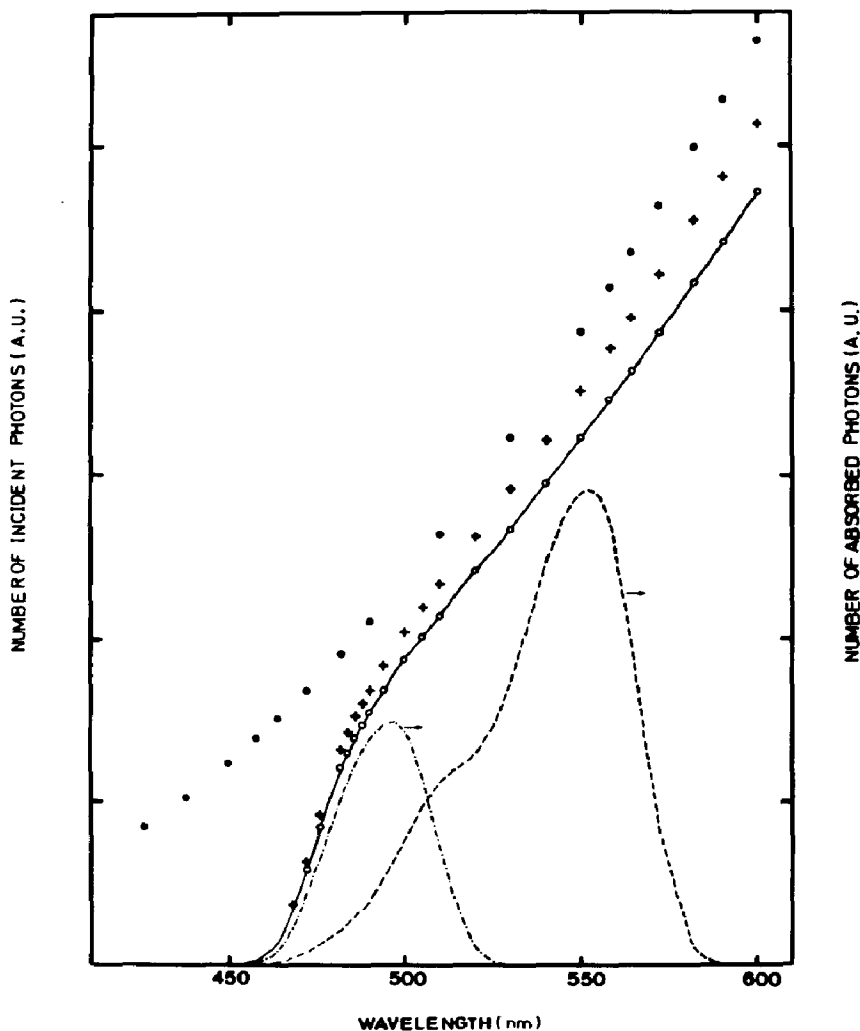
Fig. 3. Data and curves calculated using these data: ●, number of photons emitted by the source; +, number of photons transmitted by the filter; ○, number of photons transmitted by the filter and the cell; — · —, number of photons absorbed in the aqueous solution of F calculated from relation (1); — — —, number of photons absorbed in the aqueous solution of RB calculated from relation (1).

The alternative method we propose uses the arrangement illustrated in Fig. 1. The spectrofluorometer is equipped with accessories which allow the true emission spectrum to be measured by compensating for the spectral characteristics of the detection system (monochromator and detector). The signal detected is therefore directly proportional to the number of photons transmitted by the cell. The photon spectrum is recorded with the cell filled first with the solvent and then with the dye. The difference between the two spectra at each wavelength is therefore proportional to the number of photons absorbed by the dye and the area intercepted between the two curves is proportional to the total number of photons absorbed. Figure 3
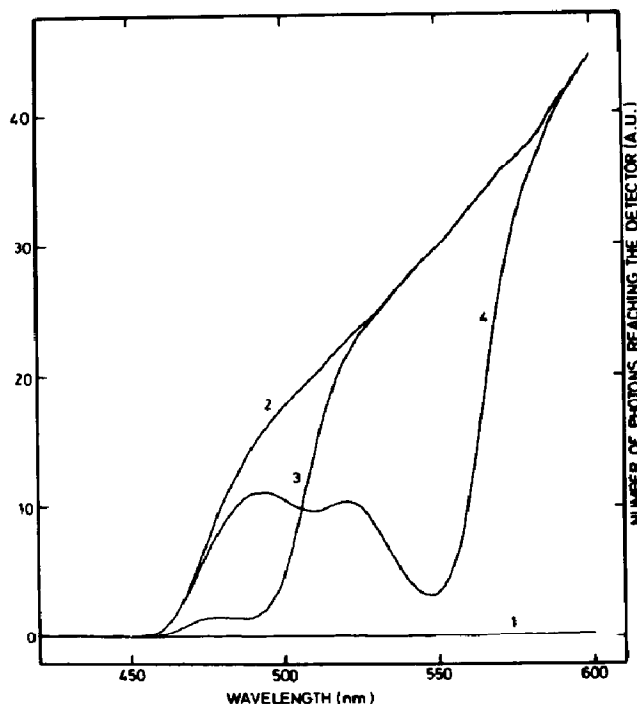
Fig. 4. Photon absorption curves determined by the method described in the text: curve 1, baseline; curve 2, cell containing water; curve 3, aqueous solution of F; curve 4, aqueous solution of RB.

shows the curves for F and RB. The ratio S_{RB}/S_F of the intercepted areas is $6.17/2.07 = 2.98$ which is within 1% of the calculated value. The curves shown in Fig. 4 were recorded under the same experimental conditions. However, if the experimental conditions such as the amplifier gain and the photomultiplier voltage vary, the area measured for each dye can be normalized by dividing the corresponding area by the blank area defined by the curve for the cell containing water (Fig. 4, curve 2) in the same wavelength range. The two methods gave the same results for the relative absorption in photon units.

The advantages of the proposed method are the sensitivity and the rapidity with which the curves can be recorded and measured. Moreover, if actinometry is carried out at one wavelength, the absolute total photon absorption can be calculated by comparing the ratio of the area related to the absorption of the dye with the area recorded under the monochromatic conditions corresponding to the number of photons measured by actinometry.

This method is currently being used in our laboratory to measure the number of photons absorbed in aqueous solutions of dyes in a comparative investigation of their ability to produce singlet oxygen when irradiated with polychromatic light.

1 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, *235* (1956) 518.
2 E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, *88* (1966) 394.