

## PULSED PHOTOACOUSTIC DETERMINATION OF THE QUANTUM YIELD OF TRIPLET STATE FORMATION

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### Summary

A method of determining the quantum yield  $\Phi_T$  of triplet state formation based on pulsed photoacoustic measurements is presented. The values of  $\Phi_T$  obtained for anthracene, acridine, phthalazine and quinoxaline are 0.66, 0.80, 0.69 and 0.90 respectively in excellent agreement with literature data. The error in the measurement is less than 10%. The method is limited to compounds with a triplet lifetime much longer than 1  $\mu$ s.

### 1. Introduction

Understanding of the photophysical processes following photoexcitation has long been limited by the difficulty of direct observation of radiationless deactivation. The origin of the problem can be seen with reference to the Jabłoński energy diagram (Fig. 1) which shows the principal pathways by which an organic molecule relaxes after absorption of a photon of energy  $h\nu_{exc}$ . In order to specify completely the deactivation pathways of the molecule the five rate constants shown on the diagram must be determined ( $k_f$  and  $k_t$  are the radiative deactivation rates of phosphorescence and fluorescence respectively, and  $k_{IC}$ ,  $k_{ISC}$  and  $k_{TG}$  are the radiationless deactivation rates of internal conversion, intersystem crossing (ISC) from the singlet to the triplet state and ISC from the triplet to the singlet ground

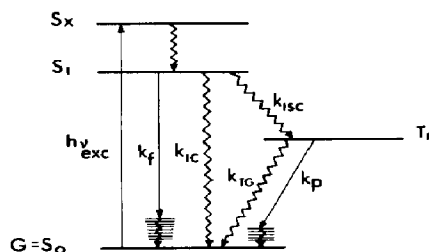


Fig. 1. Jabłoński energy diagram showing the principal deactivation pathways of a photoexcited molecule.

state respectively). Usually, luminescence measurements can yield only four values dependent on these rates: the fluorescence lifetime  $\tau_f = (k_f + k_{IC} + k_{ISC})^{-1}$ , the phosphorescence lifetime  $\tau_p = (k_p + k_{TG})^{-1}$ , the quantum yield of fluorescence  $\Phi_f = k_f \tau_f$  and the quantum yield of phosphorescence  $\Phi_p = k_p \tau_p \Phi_T$ . The quantum yield of triplet state formation  $\Phi_T = k_{ISC} \tau_f$  remains unknown. Therefore we need an independent measurement of  $\Phi_T$  to determine all the deactivation rates.

Photoacoustic (PA) spectroscopy is already well established as a tool for monitoring de-excitation processes in organic compounds in the condensed phase [1]. Continuous-wave modulation PA measurements are usually used to determine the fluorescence quantum yield [2 - 5] or the triplet lifetime [6 - 8]. From PA spectroscopy measurements we also obtain an absorption-like spectrum which, by comparison with a conventional absorption spectrum, can supply some extra information about radiationless processes.

In 1969 Callis *et al.* [9], in one of the first PA studies in the condensed phase, used their "flash calorimeter" with pulsed broad band excitation to determine the quantum yields of formation of the triplet states of anthracene in ethanol solution and acridine orange in glycerol solution. In recent years, mainly owing to the development of high power pulsed lasers, there has been increasing interest in the use of pulsed photoacoustics for measuring very small absorptions by the ground state [10] and the excited states [11 - 13] of molecules in solution.

The purpose of our work is to use laser pulsed PA measurements to determine the triplet yields of some aromatic compounds in solution at room temperature.

## 2. Method

The theory of the pulsed PA effect is well established [10, 14 - 16]. Its detection can be described briefly as follows. A fraction of the energy absorbed by the sample from an incident light beam is transformed into heat during non-radiative relaxation processes. Local thermal expansion then generates an acoustic pressure wave which, owing to the elastic properties of the medium, propagates through the sample. This pressure wave can be detected and converted to a voltage using a piezoelectric transducer. The height  $S$  of the peak of the PA signal, *i.e.* the amplitude of the voltage produced by the transducer, is proportional to the energy dissipated in the sample. The dependence of the PA signal on the properties of the medium and the geometry of the laser beam, the PA cell and the transducer arrangement can be described for picosecond and nanosecond laser pulses and for weakly absorbing media by the following expression [16]:

$$S = KE_L \alpha \frac{\beta c^2}{\pi C_p R^{3/2} r^{1/2}} \quad (1)$$

where  $K$  (in volts per pascal) is the proportionality constant and is a measure of the sensitivity of the transducer-cell system,  $E_L$  (in joules) is the energy of the laser pulse,  $\alpha$  (in reciprocal metres) is the absorption coefficient of the solution,  $\beta$  (in reciprocal kelvins) is the solvent thermal expansion coefficient,  $c$  (in metres per second) is the velocity of sound in the solvent,  $C_p$  (in joules per kilogram per kelvin) is the heat capacity of the solvent,  $R$  (in metres) is the radius of the illuminated cylindrical volume of the solution and  $r$  (in metres) is the distance from the laser beam to the transducer.

Equation (1) is based on the assumption that all absorbed energy is totally and immediately converted to heat. This is the case when the quantum yield of luminescence is negligible and all radiationless deactivation processes are fast enough to create the heat in a time shorter than that required to generate the acoustic pressure wave, which is less than a microsecond (Section 3). In the case when the radiative processes are important in the deactivation of the excited molecules and/or some of the excited states have long lifetimes (much longer than  $1 \mu\text{s}$ ) we have to remember that the PA signal is proportional only to the specified part of the absorbed energy. Therefore eqn. (1) must be modified to the following form [14]:

$$S_{\text{PA}} = S\eta_{\text{FNR}} = K'E_L\alpha\eta_{\text{FNR}} \quad (2)$$

where

$$K' = K \frac{\beta c^2}{\pi C_p R^{3/2} r^{1/2}}$$

is a proportionality constant for a given solvent and laser beam-transducer geometry and  $E_L\alpha\eta_{\text{FNR}}$  is the total heat created per unit length of optical path by radiationless deactivation from short-lived (less than  $1 \mu\text{s}$ ) excited states. We define the energetic efficiency  $\eta_{\text{FNR}}$  of the fast non-radiative processes as follows:

$$\eta_{\text{FNR}} = 1 - \Phi_f \frac{\overline{h\nu_f}}{h\nu_{\text{exc}}} - \Phi_T \frac{E_T}{h\nu_{\text{exc}}} \quad (3)$$

The term  $\Phi_f \overline{h\nu_f}/h\nu_{\text{exc}}$  represents the fraction of absorbed energy which is emitted in the form of fluorescence ( $\overline{h\nu_f}$  is the average fluorescence photon energy) and the term  $\Phi_T E_T/h\nu_{\text{exc}}$  represents the fraction of absorbed energy stored in the long-lived triplet state ( $E_T$  is the energy of the triplet state whose lifetime is usually much longer than  $1 \mu\text{s}$ ) if there are no other long-lived products, *e.g.* of a photochemical reaction.

If we substitute eqn. (3) into eqn. (2) we can determine the direct dependence of the measured PA signal  $S_{\text{PA}}$  on the quantum yield  $\Phi_T$  of triplet state formation as follows:

$$S_{\text{PA}} = K'E_L\alpha \left( 1 - \Phi_f \frac{\overline{h\nu_f}}{h\nu_{\text{exc}}} - \Phi_T \frac{E_T}{h\nu_{\text{exc}}} \right) \quad (4)$$

Therefore our method of determining  $\Phi_T$  from PA measurements requires a precise value of  $K'$  and the values of  $\Phi_f$ ,  $\overline{h\nu_f}$ ,  $E_T$  and  $\alpha$  which can be obtained from spectroscopic experiments.

### 3. Apparatus

The pulsed PA calorimeter shown in Fig. 2 was constructed in this laboratory.

A nitrogen laser ( $N_2$  IGL/300/2, ZWG AWDDR, G.D.R.) (pulse length, 2.5 ns; wavelength, 337.1 nm) was used as the source for exciting the sample solution. The laser beam, which had an energy of about 1 mJ, was slightly focused and was then passed through a circular aperture (diameter, 2 mm) followed by UV filters in some experiments and finally through the centre of a 1 cm Suprasil sample cell. The sample cell was closed at the top using a vacuum-tight stopcock and could be connected to a vacuum line to enable the sample solution to be deoxygenated by repeated freeze-pump-thaw cycles until the equilibrium pressure of air over the solution was of the order of  $10^{-6}$  Torr. The sample cell was also employed to measure the quantum yields of fluorescence in luminescence experiments using Jasny's spectrofluorometer [17].

The PA detector was based on the piezoelectric transducer devised by Patel and Tam [10], but we used a much thinner piezoelectric ceramic (Unitra, Poland). It was an axially poled circular plate with silver electrodes of radius 5 mm and thickness 1 mm (thickness resonance frequency, about 1 MHz) mounted inside a metal casing. The transducer was directly attached to the wall of the sample cell from the outside with a thin vacuum grease layer between these components to prevent acoustic reflections.

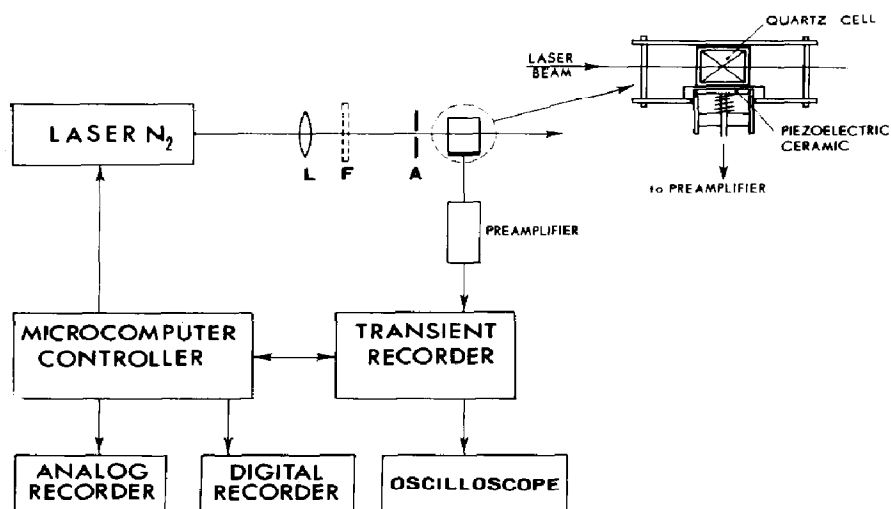


Fig. 2. Block diagram of the experimental arrangement of the pulsed PA calorimeter and the PA cell (L, lens; F, filter; A, aperture).

The transducer was connected using a home-made broad bandpass preamplifier with a voltage gain of 100. The signal from the preamplifier was fed into a transient recorder (Data Lab DL 905) and recorded in digital form using a microcomputer controller (Neptun, Poland) which also served as a simultaneous trigger for the laser and the transient recorder. A typical PA signal trace is shown in Fig. 3. On this signal pattern the slight distortion  $L$  of the zero line corresponds to the firing of the laser and the first peak of the PA signal appears after about  $5 \mu\text{s}$  (this is the time that the acoustic wave needs to cover the distance in the solution from the illuminated region to the transducer at the speed of sound). For weakly absorbing samples the PA signals can be averaged over 255 pulses using a microcomputer, thus increasing the signal-to-noise ratio by at least a factor of 10.

The difference between the first minimum and the first maximum in the PA signal is an arbitrary measure of the amplitude of the signal. We chose that difference instead of the height of the first peak [18] because then we did not need to define the position of the zero line. The amplitude of the PA signal depends strongly on the geometry of the laser beam-PA cell-transducer system, but for a fixed geometry the scatter of its value from shot to shot of the laser is within 10%. This is probably mainly due to variations in the laser pulse energy, and the scatter of the averaged amplitude of the PA signals for 100 laser pulses is less than 1%.

Finally, we want to emphasize that the halfwidth of the first peak is about  $1 \mu\text{s}$  and therefore our assumption that the PA signal is proportional to the heat deposited in the sample in a time shorter than  $1 \mu\text{s}$  is valid.

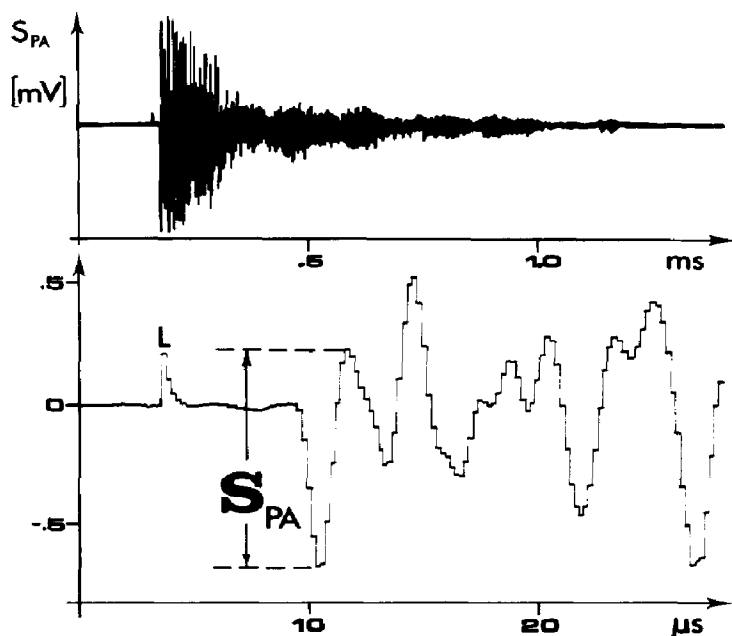


Fig. 3. Single pulse trace of the PA signal in microsecond and millisecond time scales.

#### 4. Results and discussion

In order to perform PA measurements of the quantum yield  $\Phi_T$  of triplet state formation, we first verified the linear dependence of the PA signal on the laser energy  $E_L$  and on the solution absorption  $A = \alpha l$ . In both experiments we obtained results in good agreement with theoretical prediction (see eqn. (2)). The dependence of the PA signal on  $E_L$  is shown in Fig. 4.

The linear dependence of the PA signal on the absorption  $A = \alpha l$  for anthracene and triphenylene solutions is shown in Fig. 5. Two different slopes of straight lines fitted to the experimental points reflect two different yields of non-radiative processes for these compounds (the  $\Phi_f$  values are about 0.27 for anthracene and only 0.09 for triphenylene).

The dependence of the PA signal on  $\eta_{FNR}$  described by eqn. (4) was verified. To achieve this, substances were chosen for which complete spectroscopic data ( $\Phi_f$ ,  $\overline{h\nu_f}$ ,  $\Phi_T$  and  $E_T$ ) were known, *i.e.* acridine, anthracene, benzanthracene and triphenylene. The PA signals (divided by the absorption  $A$  in the 1 cm cell) for the deaerated ethanol solutions of these compounds are plotted in Fig. 6 against  $\eta_{FNR}$  ( $\eta_{FNR}$  was calculated using eqn. (3)). The

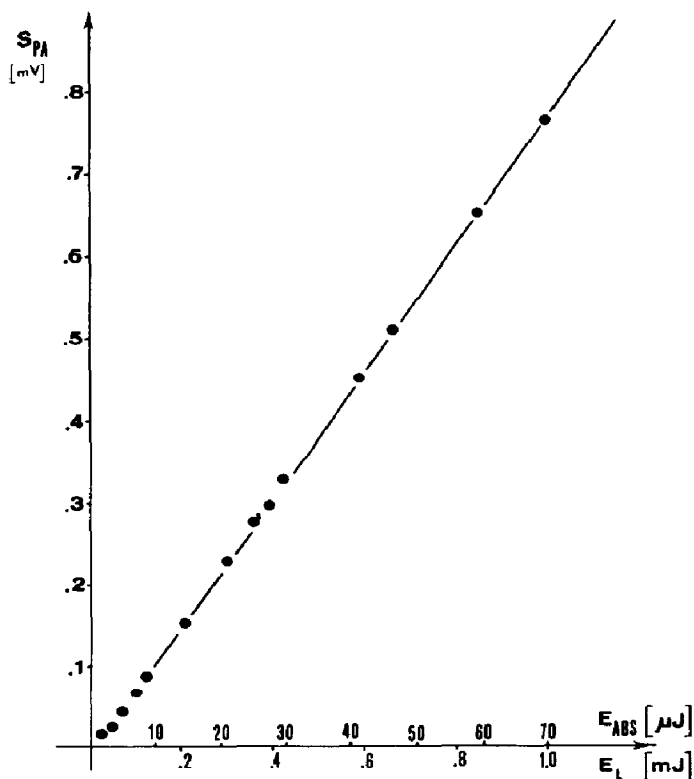


Fig. 4. Linear dependence of the PA signal  $S_{PA}$  in millivolts on the laser energy  $E_L$  changed by means of a set of UV filters from 1 mJ to  $10^{-2}$  mJ. The measurements were made for a solution of  $3 \times 10^{-5}$  M anthracene in ethanol ( $E_{abs} \approx E_L \alpha l$ ).

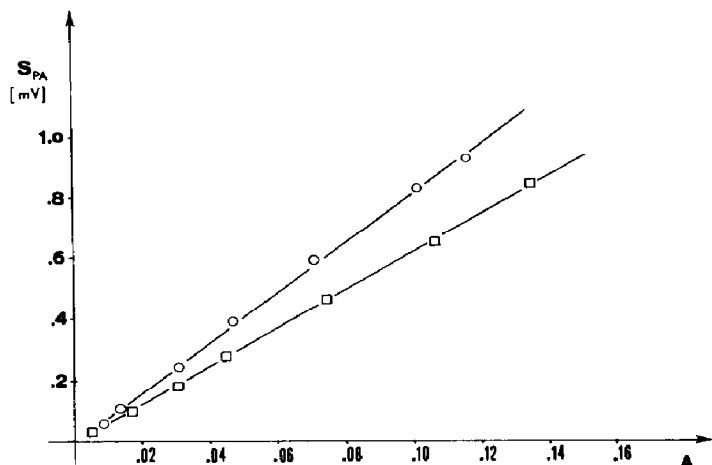


Fig. 5. Linear dependence of the PA signal on the absorption  $A = \alpha l$  for the optical path length  $l = 10^{-2}$  m for anthracene ( $\square$ ) and triphenylene ( $\circ$ ) solutions in ethanol.

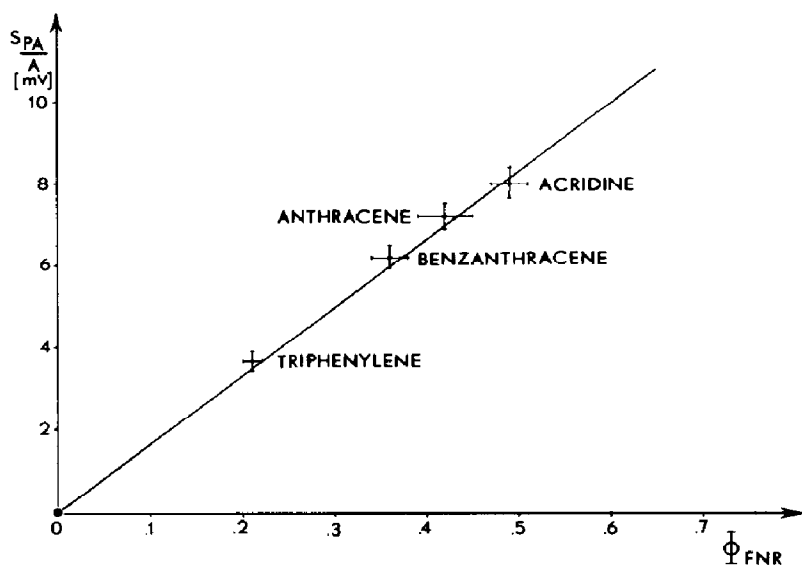


Fig. 6. Linear dependence of the PA signal divided by the absorption  $A$  (in ethanol) on the energetic efficiency  $\eta_{FNR}$  of fast non-radiative deactivation processes in which heat is released in times shorter than  $1 \mu s$  after the laser pulse.

triplet ground state of oxygen in solution is an excellent quencher of most triplet states and shortens the lifetimes of the triplet states of the compounds investigated to less than a microsecond [19]. Equation (3) is then no longer a good approximation for the quantum yields of fast non-radiative processes. However, a direct comparison of PA signals for various compounds requires the geometry of the laser beam-sample cell-transducer system as well as the contact between the transducer and the sample cell to be kept constant. Both these conditions are almost impossible to satisfy for solutions deaerated using repeated freeze-pump-thaw cycles. Compari-

son of the PA signals for various compounds in deaerated solutions was therefore carried out in two steps. First we compared the PA signals  $(S_{PA}^{O_2}/A)_i$  measured for the compounds  $i$  of comparable absorption  $A$  in air-saturated ethanol solutions. The measurements were performed for a fixed position of the sample cell. The cell was very carefully washed and dried before measurement using another compound without changing any of the parameters on which the value of  $K'$  depends. Next we compared the PA signal generated in a deaerated solution of each compound  $i$  separately with that of the solution containing dissolved oxygen after carefully opening the sample cell and obtained the value  $(S_{PA}/S_{PA}^{O_2})_i$ . By combining the comparisons we obtained indirectly PA signals for deoxygenated solutions of the compound under investigation:

$$\left(\frac{S_{PA}}{A}\right)_i = \left(\frac{S_{PA}^{O_2}}{A}\right)_i \left(\frac{S_{PA}}{S_{PA}^{O_2}}\right)_i$$

We emphasize that the efficiency and mechanism of triplet quenching by oxygen may differ from compound to compound, but this is not important in our measurements. The results are collected in Fig. 6. All experimental points are on a straight line passing almost exactly through the origin of the coordinate system, which is also an experimental point as we observe no signal for the pure solvent.

The results shown in Figs. 4 - 6 provide proof of eqn. (4) and confirm the validity of the assumption that only heat released in a time shorter than  $1 \mu s$  takes part in generation of the PA signal.

#### 4.1. Determination of $\Phi_T$

In order to determine the quantum yield  $\Phi_T$  of triplet state formation we need a value of  $K'$  to substitute in eqn. (4). We obtain this by finding the relation between the PA signal and  $\eta_{FNR}$  for triphenylene and benzanthracene in ethanol solutions, which we use as the standards with a high value of  $\Phi_T$  (0.89 and 0.82 respectively [20]). We obtained  $K' = 0.17 \pm 0.01 \text{ V m J}^{-1}$  which means that the  $10 \mu J$  of heat released in our 1 cm cell in a time shorter than  $1 \mu s$  causes the generation of a PA signal of  $170 \mu V$  at the output of our piezoelectric transducer.

The results of our measurements of  $\eta_{FNR}$  and  $\Phi_T$  are summarized in Table 1 in which we also show the values of the PA signals in air-saturated solution (divided by absorption), the ratios of the signals for the solutions with oxygen to those for the solutions without oxygen and the spectroscopic data which we need to calculate  $\Phi_T$  from  $\eta_{FNR}$ . The error in the  $\Phi_T$  value is less than 10% and is mainly due to the uncertainty in the spectroscopic data for  $\Phi_t$ ,  $h\nu_t$  and  $E_T$  and also to the scatter in the results of PA measurements which is about 5%.

Our results are compared with the literature data for  $\Phi_T$  obtained using other methods and very good agreement is evident.



TABLE 1

Energetic efficiency  $\eta_{\text{FNR}}$  of fast non-radiative deactivation processes and the quantum yields  $\Phi_{\text{T}}$  of triplet state formation determined by photoacoustic measurement in ethanol solution (calibrated using triphenylene and benzanthracene data)

Compound	Measured PA values		$\eta_{\text{FNR}}$	Spectroscopic data			$\Phi_{\text{T}}$ (PA)	$\Phi_{\text{T}}$ (literature)
	$\text{SPA}_{\text{O}_2}/A$ (mV)	$\text{SPA}/\text{SPA}_{\text{O}_2}$		$\Phi_{\text{f}}$	$\overline{h\nu_{\text{f}}}$ ( $\text{cm}^{-1}$ )	$E_{\text{T}}$ ( $\text{cm}^{-1}$ )		
Triphenylene	11.2	0.33	0.22 <sup>a</sup>	0.09	27200	23300	0.89 [20]	0.82 [20]
Benzanthracene	9.1	0.68	0.36 <sup>a</sup>	0.22	24500	16500	0.72 [20]	0.70 [20]
Anthracene	10.6	0.71	0.44	0.27	24900	14900	0.66 $\pm$ 0.05	0.66 [9]
Acridine	10.1	0.79	0.47	0.03 <sup>b</sup>	23250	15850	0.82 $\pm$ 0.06 <sup>c</sup>	0.76 [21]
Phthalazine	10.7	0.79	0.50	—	—	21400	0.69 $\pm$ 0.04	0.70 <sup>d</sup> [22] 0.99 <sup>d</sup> [23]
Quinoxaline	8.3	0.71	0.35	—	—	21300	0.90 $\pm$ 0.02	0.99 [24]

<sup>a</sup> $\eta_{\text{FNR}}$  value calculated from the literature data for  $\Phi_{\text{f}}$ ,  $\overline{h\nu_{\text{f}}}$ ,  $\Phi_{\text{T}}$  and  $E_{\text{T}}$  using eqn. (3).

<sup>b</sup>There is additionally a photoreduction process of the excited singlet contributing to the  $\eta_{\text{FNR}}$  value; its quantum yield is 0.13 [21] and the energy stored in the products is lower than that of the  $\text{S}_1$  state. If it is arbitrarily assumed to be  $\frac{1}{2}h\nu_{\text{exc}}$  we obtain the  $\Phi_{\text{T}}$  value indicated.

<sup>c</sup>The error does not include the arbitrary nature of assumption b.

<sup>d</sup>Ether-isopentane-ethanol at 77 K.

## 5. Conclusion

A new method of determining the quantum yields of triplet state formation in solutions at room temperature is described. The measurements are performed using a simple and inexpensive pulsed PA calorimeter. This calorimeter allows the measurement of heat dissipated in the solution during the fast non-radiative deactivation of electronically excited states which have a lifetime shorter than 1  $\mu$ s.

The measurement of the quantum yield of triplet state formation is possible for all photostable compounds which fulfil only a single condition, *i.e.* their triplet lifetimes must be much longer than 1  $\mu$ s in deoxygenated pure solution at room temperature. Any chemical deactivation path not included in the Jabłoński energy diagram interferes only if it contributes significantly to the  $\eta_{\text{FNR}}$  value. Additional data are then needed to evaluate  $\Phi_{\text{T}}$ . The results for  $\Phi_{\text{T}}$  obtained using the pulsed PA method are in very good agreement with existing literature data.

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