

THERMAL-LENSING MEASUREMENTS OF SINGLET MOLECULAR OXYGEN ($^1\Delta_g$): QUANTUM YIELDS OF FORMATION AND LIFETIMES[†]

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Summary

Absolute quantum yields ϕ_{Δ} for singlet molecular oxygen ($^1O_2(^1\Delta_g)$) production were determined by time-resolved thermal-lensing (TL) using several sensitizers. The ϕ_{Δ} value is smaller than the quantum yield ϕ_{isc} for intersystem crossing for tetraphenylporphyrin, zinc tetraphenylporphyrin and anthracene in air-saturated benzene solutions. For anthracene, the values $\phi_{isc} = 0.78 \pm 0.08$ and $\phi_{\Delta}/\phi_{isc} = 0.78 \pm 0.16$ were measured using this method. The lifetimes of 1O_2 , determined by time-resolved TL in several solvents at concentrations similar to those detected by emission, are in good agreement with literature data for values up to about 100 μ s. For longer lifetimes the values are smaller than those in the literature. Various possible reasons for the discrepancies are discussed.

1. Introduction

A laser pulse traversing a weakly absorbing sample either in the gas or the condensed phase produces a local change in temperature, density and refractive index, if at least part of the absorbed energy is released as heat. The sample then acts as a diverging lens near the beam axis, provided the refractive index change is negative (which is normally the case) and provided the beam profile approximates a gaussian distribution. In a time range short enough (about 10^{-4} s) for thermal recovery (typically $10^{-1} - 10^{-2}$ s [1, 2]), the time dependence of the "thermal lens" is determined by the rate constants of the non-radiative transitions following excitation. The lifetimes to be measured should be longer than the acoustic transit time τ_a ($\tau_a = R/v_a$; R is the radius of the laser beam and v_a is the velocity of sound). For liquid samples and focused laser beams τ_a is about 10^{-7} s. A continuous laser beam which overlaps the pulsed exciting beam through the sample will be

[†]Dedicated to Professor D. F. Schulte-Frohlinde on the occasion of his 60th birthday.

defocused, leading to an irradiance change which is normally referred to as a thermal-lensing (TL) signal. The shape of the signal provides information about the relative magnitudes of the heat contributions from fast and slow (relative to τ_a) non-radiative processes and about the lifetimes of the latter.

Fuke *et al.* used this method to study the kinetics of decay of singlet molecular oxygen ($^1\text{O}_2(^1\Delta_g)$) in solution produced by energy transfer from several sensitizers [3, 4]. However, the accuracy of lifetime determinations by single-pulse experiments is limited, mainly by two effects. Firstly, increasing the excitation energy does not improve the signal-to-noise (S/N) ratio of the signal fraction produced by the slow non-radiative processes, since the population of the metastable transient states reaches saturation. Secondly, the shape of the slowly varying signal can be affected by thermal relaxation. Both problems can be solved by the use of electronic data acquisition and handling. The S/N ratio can be improved by signal averaging techniques and the thermally induced perturbation can be compensated before the lifetimes are determined by exponential analysis.

Through the evaluation of the fast and the slow heat dissipation subsequent to the laser pulse the absolute quantum yields ϕ_Δ of $^1\text{O}_2$ formation were determined using three sensitizers: anthracene, zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP) and the parent tetraphenylporphyrin (TPP). Furthermore, the intersystem crossing quantum yield ϕ_{isc} for anthracene, the lifetime of $^1\text{O}_2$ in several solvents and the rate constant for its quenching by triethylamine (TEA) were also evaluated.

2. Experimental details

2.1. Equipment and chemicals

The TL experimental set-up is shown in Fig. 1. A Nd-YAG DLPY2 laser of output energy about 100 mJ in its second harmonic (532.5 nm) and 20 mJ in its third harmonic (355 nm) was used to pump a System 2000 dye laser (J.K. Lasers, Rugby, Gt. Britain). Rhodamine 6G and Rhodamine B

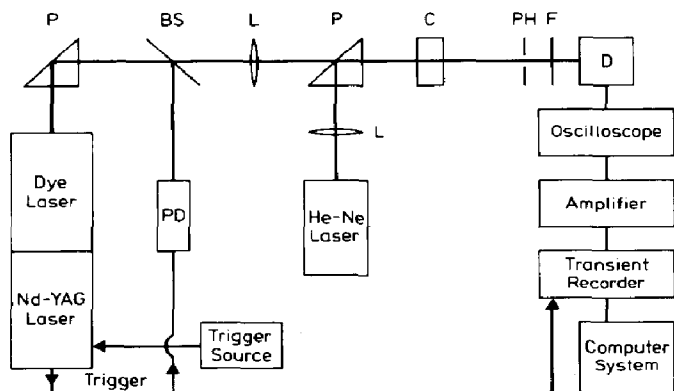


Fig. 1. TL spectrometer: C, sample cuvette; PH, pinhole; F, filter; BS, beam splitter; PD, pyroelectric detector; D, diode; P, 90° prism; L, lens.

dyes (Lambda Physik) in methanol were used to excite ZnTPP (560 nm) and TPP (590 nm) respectively. Anthracene was excited at 355 nm. The beam was focused inside the sample cuvette in order to improve the time resolution of the measurement by reducing the acoustic transit time (see Section 1).

The laser energy was monitored using a pyroelectric detector (Laser Precision R_j 7100 with an R_j P-735 detector head) which received part of the energy from a glass-plate beam splitter. Neutral density filters (Schott, Mainz) were used to decrease the laser energies.

The sample was placed in a UV absorption cuvette of path length 5 mm or 10 mm. An He-Ne laser beam (NEC GLG 5211; output power, 1 mW), which was focused just in front of the sample and made a small angle (less than 1°) with the exciting beam was used to probe the thermal lens. The irradiance in the centre of the probe beam was measured using a photodiode (Centronic BPX 65) placed behind a pinhole (P) 0.3 mm in diameter, which also cut off the exciting beam. Scattered light produced by the exciting beam was eliminated by an interference filter (Schott, Mainz; 633 nm, bandwidth, 3 nm). The signal from the photodiode was fed into the 1 MΩ input of a Tektronix 7603 oscilloscope equipped with a 7A12 amplifier. After further amplification with a Keithley 104 wideband amplifier the signal was stored by a transient recorder (Biomation 8100) with a lowest sampling time of 10 ns.

Data acquisition and signal averaging were performed by a computer system (PDP 11-04/VAX 11-780). In most cases 100 signal traces were averaged. The repetition rate of the exciting laser was 1 Hz, which was considered an appropriate value since typical thermal-recovery time constants are shorter than 0.1 s [1].

Ethanol (Merck, zur Analyse) was treated with KOH before distillation over a glass filled column. Tetrahydrofuran (Merck, zur Analyse) was treated with LiAlH₄ and distilled over a glass filled column. Benzene (Merck, zur Analyse) was washed with concentrated H₂SO₄ and with H₂O, and dried over Na₂SO₄ prior to fractionation over a column 1 m long. Acetone (Merck, zur Analyse) was dried with CaCl₂ and then with P₂O₅ and distilled over a column 1 m long. Acetonitrile (Merck, zur Spektroskopie) was boiled in the presence of P₂O₅ prior to distillation in the presence of K₂CO₃ and further fractionation over a column 1 m long. All distillations were performed in argon. Acetone-*d*₆, acetonitrile-*d*₃ and benzene-*d*₆ (Merck, Uvasol, for nuclear magnetic resonance spectroscopy) were used as provided. TEA (Merck-Schuchardt, Munich) was distilled over LiAlH₄.

Anthracene (Aldrich) was recrystallized three times from ethanol. For the lifetime measurements the anthracene was zone refined. ZnTPP was prepared from TPP (Aldrich). Both porphyrins were purified according to Barnett *et al.* [5].

For the determination of ¹O₂ yields and lifetimes air-saturated solutions were used. Deoxygenated solutions were prepared by bubbling through argon (99.996% pure) or by six thaw-freeze-pump cycles to a pressure of 5 × 10⁻⁴ mbar.

Absorbances were measured using a Perkin-Elmer 356 spectrophotometer. Fluorescence measurements were performed with a Perkin-Elmer LS-5 spectrofluorometer.

2.2. Signal handling

The TL signal at time t is defined as

$$U(t) = \frac{|V_0 - V(t)|}{V_0}$$

where $V(t)$ is the time-dependent voltage generated by the detector. $V(t)$ is proportional to the irradiance of the probe beam passing through the pinhole. V_0 is the value of $V(t)$ prior to excitation (Fig. 2). The laser energies used were in the range $10^{-5} - 10^{-6}$ J. $U(t)$ was linearly proportional to the heat released by radiationless processes in the range $0 \leq U(t) \leq 0.4$. This was controlled using copper chloride in methanol ($A_{700} = 0.13$), since this substance releases all the absorbed energy as heat in $t < \tau_a$ [6]. All the measurements were carried out within this linear region, in general with $U(t) \leq 0.04$.

The total magnitude U_{tot} of $U(t)$ at sufficiently long times (see below) and the height U_1 of the fast step at $t = 0$ are proportional to the total amount of heat emitted after the absorption and the fraction produced by fast non-radiative transitions respectively (Fig. 2). Therefore, $\Delta U = U_{tot} - U_1$ is a measure of the heat contribution from the deactivation of long-lived states. For the evaluation of the lifetimes of these states, only the slow part of the signal was measured and this was analysed by a fit program for exponential decay (Fig. 3). (The program was adapted from that developed for the analysis of fluorescence decays [7]. It has already been applied to the analysis of decays of transient absorbances [8].)

The time dependence of the thermal relaxation in TL experiments has been treated extensively [1, 2, 4, 9, 10]. The deviation from an ideal step

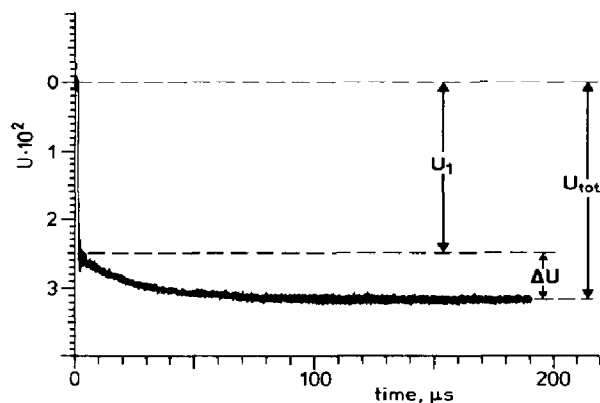


Fig. 2. Relative signal U of a TL experiment, corresponding to the total heat U_{tot} emitted after absorption of light, the heat U_1 dissipated promptly in a period $t < \tau_a = R/\nu_a$, and the heat ΔU dissipated slowly at $t > \tau_a$.

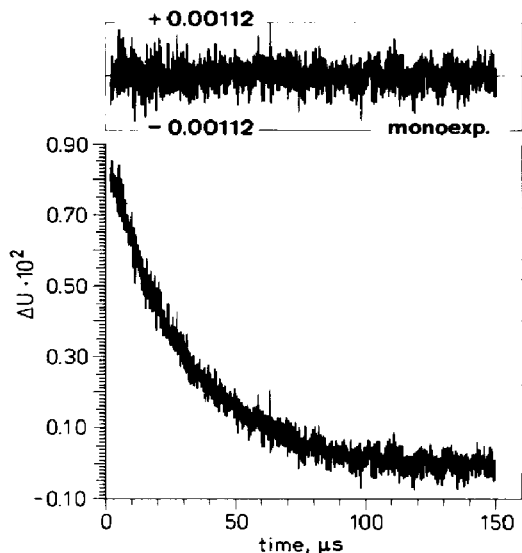


Fig. 3. Slow-decay TL signal due to $^1\text{O}_2$ decay (air-saturated solution of 10^{-4} M anthracene in benzene at room temperature). The experimental points were fitted to a monoexponential decay. Above the trace a residuals plot indicates the deviations of the computer-fitted decay from the measured points.

function of a signal trace generated by only fast heating processes ($U_{\text{tot}} = U_1$) is described, to a first approximation, by the relationship

$$U(t) = U_1(1 - \chi t) \quad (\text{I})$$

where the constant χ is calculated [1] to be $4/t_c$ (the time constant t_c is defined as $t_c = R^2/4k$, k being the thermal diffusivity of the sample). This approximation holds for $U_1 \ll 1$ and $t \ll t_c$, and it is applicable in our measurements. Typical values are $U_{\text{tot}} \leq 0.04$ and $t_c = 0.01$ s. In most cases $U(t)$ was monitored for up to $200 \mu\text{s}$, where the relative deviations of the traces from the ideal shape (neglecting thermal conductivity) were about 1%.

In the determination of the lifetimes, a satisfactory correction for this effect was obtained by measuring the TL signal of a substance with $U_{\text{tot}} = U_1$ and subtracting this signal from that to be analysed. For this purpose, solutions of the sensitizer plus TEA (about 0.1 M) in the same solvent and with identical geometries were used. (The solutions of ZnTPP showed a slight colour change upon addition of TEA. This effect, however, should not perturb the results, since the thermal diffusivity of the solutions should not be affected owing to the high dilution, and since all the heat was emitted promptly (a step-like signal was obtained).) Small reproducible instrumental perturbations are also compensated by this procedure which is essentially a baseline correction.

The yields and lifetimes were measured several times and the errors quoted in Tables 1 and 2 are the statistical standard deviations of the data.

TABLE 1

Quantum yield ϕ_{Δ} for $^1\text{O}_2(^1\Delta_g)$ production and quantum yield ϕ_{isc} for intersystem crossing of anthracene, TPP and ZnTPP

Sensitizer	λ_{exc} (nm)	ϕ_f^A ^a	$h\nu_f$ (kJ mol ⁻¹)	ϕ_{Δ}	ϕ_{isc}
Anthracene ^b	355	0.23 ^c	299.2	0.61 ± 0.06	0.78 ± 0.08
TPP ^b	590	0.075 ^d	174.2 ^e	0.58 ± 0.06	0.82 ^f
ZnTPP ^b	560	0.031 ^d	188.1 ^e	0.73 ± 0.07	0.88 ^g

^aFluorescence quantum yields in air-saturated solutions.

^bThe concentration of the solutions was in the range 10^{-4} - 10^{-5} M in benzene.

^c $\phi_f^A = 0.85\phi_f$. The quantum yield of fluorescence in the absence of molecular oxygen is $\phi_f = 0.26$ [12].

^dSee ref. 13.

^eSee ref. 14.

^fIn toluene [15]. Values in other solvents differ by no more than 5%.

^gIn toluene [16].

TABLE 2

Lifetimes τ_{Δ} for $^1\text{O}_2$ at room temperature

Solvent	τ_{Δ} (μs)		
	Anthracene sensitizer ^a	ZnTPP sensitizer ^a	Literature values
Benzene	30 ± 2	29 ± 2	23 ^{b,c} , 32 ^{c,d} , (26.7 ± 1.3) ^e
Acetone	40 ± 2	47 ± 5	25 ^{b,f} , 30 ^{b,c} , 51 ^{c,d} , 40 ^{d,g} , 39 ^{d,h} , (46.5 ± 2) ^e
Acetonitrile	48 ± 5		36 ^{b,f} , 61 ^{d,g} , 68 ^{d,h} , (54.4 ± 1.3) ^e
Tetrahydrofuran	18.5 ± 2		20 ^{c,d}
Ethanol	12 ± 2		11 ^{b,f} , (15.3 ± 0.7) ⁱ

^aThe concentrations were in the range 10^{-3} - 10^{-5} M and the laser energy was in the range 0.1 - $2 \mu\text{J}$ (pulse)⁻¹.

^bSee ref. 4.

^cSensitizer, TPP.

^dSee ref. 17 (τ_{Δ} , ±10%).

^eSee ref. 18, sensitizer not specified.

^fSensitizer, erythrosine.

^gSensitizer, rose bengal.

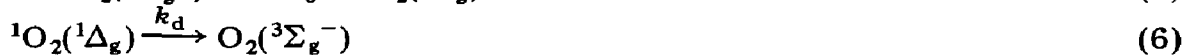
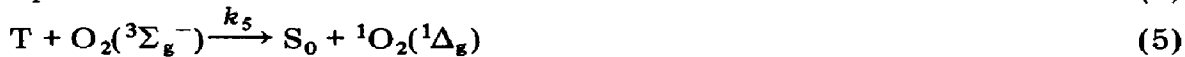
^hSensitizer, methylene blue.

ⁱSee ref. 19. Sensitizer, hematoporphyrin dimethylester.

3. Results and discussion

3.1. Quantum yield of formation of $^1\text{O}_2$ and of intersystem crossing

In order to interpret the TL signals obtained by the excitation of suitable sensitizers in the presence of O_2 , the following simplified mechanism should be considered.



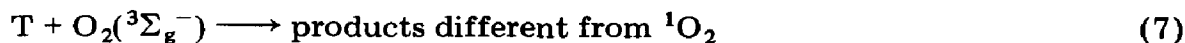
This involves the ground (S_0), first excited singlet (S_1) and first triplet (T) states of the sensitizer, and the ground state oxygen ($O_2(^3\Sigma_g^-)$) and 1O_2 .

The mechanism does not include chemical reactions of S_0 , S_1 or T with $O_2(^3\Sigma_g^-)$. It should be extended when additional photophysical processes become important, *e.g.* oxygen-assisted intersystem crossing, fluorescence quenching by oxygen [11], and triplet consumption by oxygen not leading to 1O_2 (see below). The total energy given by $N_A h(\nu_\ell - \phi_f^A \nu_f)$ per absorbed einstein, where ν_ℓ is the frequency of the exciting pulse, and ϕ_f^A and ν_f are the quantum yield and integrated average frequency respectively of the sensitizer fluorescence in air, N_A is Avogadro's number and h is Planck's constant. The "prompt heat" giving rise to the fast step U_1 in the TL signals (Fig. 2) results from processes (3), (4) and (5), provided the internal conversion (subscript *ic*, reaction (3)) and intersystem crossing (subscript *isc*, reaction (4)) processes are faster than τ_a and that all triplet states are quenched within this time.

The slow heat dissipation due to the relaxation of 1O_2 (k_d , reaction (6)) is $\phi_\Delta E_\Delta$ per absorbed einstein, with $E_\Delta = 94.1 \text{ kJ mol}^{-1}$ [20] for the energy content of $^1\Delta_g$. The slow TL signal ΔU (Fig. 2) is proportional to this slowly evolved heat. The quantum yield of 1O_2 production is

$$\phi_\Delta = \frac{\phi_{isc} k_5}{\sum_i k_i^{T, O_2}}$$

with $\sum_i k_i^{T, O_2}$ representing the sum of the rate constants of all the reactions of $T + O_2$ including those *not* leading to the production of 1O_2 :



The proportionality factor between the total, fast and slow heat dissipation and the respective TL signals (U_{tot} , U_1 and ΔU) includes geometrical, instrumental and thermal properties of the system. Since these conditions remain constant during any single measurement, from the above considerations eqn. (II) can be derived for the fraction of heat dissipated slowly.

$$\frac{\Delta U}{U_{tot}} = \frac{\phi_\Delta E_\Delta}{N_A h(\nu_\ell - \phi_f^A \nu_f)} \quad (II)$$

The results for ϕ_Δ are listed in Table 1 together with the values used for ϕ_f^A and ν_f .

The values of $\Delta U/U_{\text{tot}}$ considered for the evaluation of ϕ_{Δ} were a constant function of the laser energy E_{L} for $U(t) \leq 0.04$. Typical examples are shown in Fig. 4, in which ΔU versus U_{tot} (which is in turn proportional to E_{L}) has been plotted. At higher pulse energies a deviation was observed similar to that reported by Fuke *et al.* [4]. Since we always worked within the linear part of ΔU versus U_{tot} , the possibility of a pressure jump within the laser beam influencing the chemical reactions can be excluded.

Table 1 also contains values for ϕ_{isc} . For anthracene, this could be determined by the TL method, since in oxygen-free solutions the slow heat contribution is due to the relaxation of the anthracene triplet. Equation (II) is then replaced by

$$\frac{\Delta U}{U_{\text{tot}}} = \frac{\phi_{\text{isc}} E_{\text{T}}}{N_{\text{A}} h(\nu_{\text{r}} - \phi_{\text{t}} \nu_{\text{f}})} \quad (\text{III})$$

where $E_{\text{T}} = 178.5 \text{ kJ mol}^{-1}$ is the triplet energy [21]. The value of $\phi_{\text{isc}} = 0.78 \pm 0.08$ in benzene is in agreement with the literature value of 0.72 in toluene [22]. In this case the values of $\Delta U/U_{\text{tot}}$ considered were also a constant function of the laser energy, which rules out triplet-triplet annihilation. The slow-decay signal from anthracene in degassed benzene was fitted by a sum of two single-exponential terms. The time constant of one of these was $30 \mu\text{s}$, which is the lifetime of $^1\text{O}_2$ in benzene (*cf.* Table 2), and this means that even under the evacuation conditions employed some O_2 still remained. The coefficient of this slow component depended on the extent of evacuation. The time constant of the longer component was $220 \mu\text{s}$, and again was dependent on the evacuation conditions. This indicates that this is the rate of energy transfer between the anthracene triplet (lifetime, 20 ms ($5.4 \times 10^{-5} \text{ M}$) [23, 24]) and the quencher (O_2). Since both the energy transfer process and the lifetime of the energy storing species ($^1\text{O}_2$) occur in times longer than τ_{a} , the evaluation of ϕ_{isc} is not affected by them.

ϕ_{isc} for TPP and ZnTPP could not be evaluated by the same procedure, since these porphyrins exhibit a considerable triplet-triplet absorption at the probe wavelength. Instead, Table 1 includes literature values for ϕ_{isc} for

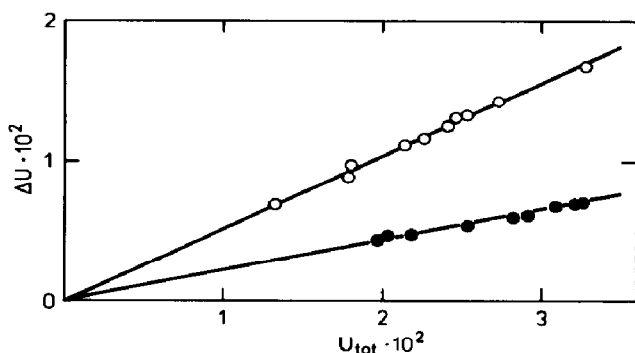


Fig. 4. Heat ΔU dissipated slowly as a function of U_{tot} for anthracene in benzene: \circ —, argon-saturated solution ($A_{355} = 0.62$); \bullet —, air-saturated solution. The slopes do not depend on the sensitizer concentration.

the purpose of comparison. In all cases $\phi_{\Delta} < \phi_{isc}$. Considering that ϕ_{isc} in the presence of oxygen is approximately equal to the value in the absence of oxygen [25], a ratio of $\phi_{\Delta}/\phi_{isc} = S_{\Delta} = 0.78 \pm 0.16$ results for anthracene, which is consistent with the value $S_{\Delta} = 0.7$ measured by Gorman *et al.* [25] by pulse radiolysis in the same air-saturated solvent and with the same sensitizer. More recently Gorman *et al.* [26] obtained a value $S_{\Delta} = 0.80$ by flash photolysis ($\lambda_{exc} = 355$ nm) relative to acridine. The values $S_{\Delta} < 1$ are in contrast to the value $S_{\Delta} > 1$ determined for anthracene in toluene [27]. In fact, our value $S_{\Delta} = 0.8$ might be taken, in principle, as an upper limit since oxygen-induced intersystem crossing has not been considered. There has been much speculation about the nature of the processes leading to $S_{\Delta} < 1$ [25]. The fact that different methods result in a similar value calls for a comprehensive investigation of the nature of the processes competing with reaction (5). The possibility of quenching of 1O_2 by the sensitizer can be ruled out on the basis of the observed lifetime (Table 2) which is the same as that obtained in the same solvent by other methods and with other sensitizers.

In the case of TPP our value $\phi_{\Delta} = 0.58 \pm 0.06 < \phi_{isc} = 0.82$ differs from that of $\phi_{\Delta} = 0.89$ (relative to ϕ_{Δ} of methylene blue) resulting in $S_{\Delta} > 1$ which was attributed to an oxygen-assisted intersystem crossing in the porphyrin [11]. Sensitizer singlet-singlet annihilation that competes with triplet production can be disregarded since for TPP and ZnTPP, as well as for anthracene (Fig. 4), ΔU is independent of the laser energy.

3.2. Lifetime of 1O_2

The lifetime τ_{Δ} of 1O_2 was evaluated in several solvents by fitting the slow-decay signal to a single-exponential decay. Anthracene and in some cases ZnTPP were used as sensitizers. The results are in good agreement with literature data (Table 2). We have selected for comparison only the data derived from the direct observation of the decay of 1O_2 . For data obtained through indirect methods see ref. 18 and references cited therein.

τ_{Δ} was also measured in deuterated solvents. With anthracene in benzene- d_6 , acetonitrile- d_3 and acetone- d_6 , the values $\tau_{\Delta} = 380 \pm 30$, $\tau_{\Delta} = 107 \pm 10$ and $\tau_{\Delta} = 122 \pm 10$ were obtained respectively. The values are in all cases smaller than those reported previously [17 - 19, 28]. The following may explain the differences for longer lifetimes.

(i) Difficulties arising from the correction for thermal recovery become more important at longer times (see Section 2.2).

(ii) The already observed variation of τ_{Δ} with the laser energy [17, 18, 29] might be of importance in time-resolved TL since the exciting beam is focused in the sample cuvette. We have made preliminary studies of this effect and observed an E_{λ} dependence, especially in polar solvents. This effect cannot, however, be the result of singlet-singlet annihilation as proposed in ref. 29, since the decay of 1O_2 did not deviate from simple first-order kinetics in any instance; this was also observed for the emission decay [18]. The lifetimes quoted in Table 2 were determined using sensitizer

concentrations in the range 10^{-3} - 10^{-5} M and laser energies compatible with a reliable decay signal, *i.e.* in the range 0.1 - 2 μJ (pulse) $^{-1}$.

(iii) The use of different sensitizers with a different $^1\text{O}_2$ quenching rate constant will also play a more important role at higher values of τ .

It is not yet possible to assess the importance of each of these factors. Time-resolved TL is, therefore, a simple and reliable method for determining lifetimes from 1 to about 100 μs . In order to evaluate its reliability for longer lifetimes more data must be accumulated.

With anthracene in benzene at room temperature a quenching rate constant of $^1\text{O}_2$ was determined as $k_q = 3.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ from a Stern-Volmer plot for TEA concentrations in the range $(0.7 - 3) \times 10^{-2}$ M. This value falls within the very spread range of literature data for this reaction (2.1×10^6 - $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ depending on the conditions and on the solvent; no results for aromatic solvents were reported) [30].

Time-resolved TL represents an alternative to the acoustic detection of the pressure wave generated after the absorption of a laser pulse [6, 31 - 36]. It overcomes the difficulties encountered for the time resolution of the optoacoustic signals delivered by ceramic [6, 31 - 34] and poly(vinylidene fluoride) film [36] piezo-elements, and it permits the evaluation of absolute quantum yields (*e.g.* ϕ_{isc} and ϕ_{Δ}) of slow heat dissipation processes without the use of a reference sample. However, in contrast to acoustic detection, TL is restricted to systems in which ground states and excited states are transparent to the wavelength of the analysing beam.

4. Conclusions

Time-resolved TL has been used for the determination of absolute quantum yields of production, and of lifetimes of the order 1 - 100 μs , *i.e.* of species living longer than the transit time τ_a of the acoustic wave through the cross section of a focused exciting laser beam. Furthermore, the method in its present form allows these properties to be measured in dilute solutions, down to molar absorbances of about 10^{-2} , which is difficult with flash photolysis for example.

The sensitivity of the method is comparable with that of emission detection [17 - 19, 29, 37] for the lowest sensitizer concentrations used in this work (down to 10^{-6} M).

It can be foreseen that the simplicity of the method will enable its rapid utilization, in laboratories already equipped with standard laser flash photolysis apparatus, for the determination of the absolute values of photo-physical parameters.

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