Short Communication

Expanding the time resolution of nanosecond laser flash photolysis experiments

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The time resolution of laser flash photolysis techniques is usually limited by the duration of the laser pulse used for excitation; in most cases the shortest lifetime that can be practically determined is slightly longer than the halfwidth of the pulse, even if the rise time of typical instruments is approximately 1 - 2 ns.

Our laser facility uses the pulses (337.1 nm, approximately 10 mJ) from a nitrogen laser for excitation [1]; the pulse duration is about 8 ns and the shortest meaningful lifetime that can be determined from the time evolution of the signal is about 12 - 15 ns. Gupta *et al.* [2] and Atik and Thomas [3] have estimated shorter lifetimes by comparing the effective "shift" in the time profile for a formally "instantaneous" process with that for the system of interest.

Another approach that can be used, and which we describe in this communication, is to measure the integral under the absorption curve. For a signal decaying with simple first-order kinetics and where the decay is considerably slower than signal formation, the integral (Fig. 1) is given by

$$S = A_0 \int_0^\infty \exp(-kt) \, \mathrm{d}t \tag{1}$$

$$S = A_0/k \equiv A_0\tau \tag{2}$$

where A_0 is the optical density immediately after completion of the rapid formation step. In terms of the dose I absorbed per unit volume, the quantum yield Φ of transient generation, the extinction coefficient ϵ for the transient and the optical path l of the reaction cell, the value of S can be expressed as

$$S = I\Phi\epsilon l\tau \tag{3}$$

For a series of pulses the total area S will be given by the sum of areas S_i, each for a pulse of energy I_i per unit volume:
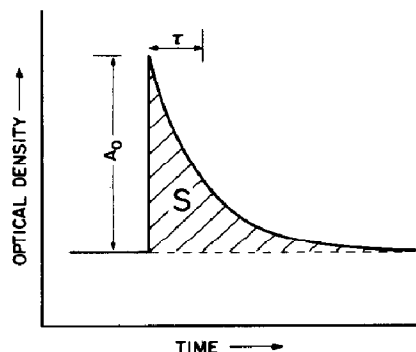
Fig. 1. Absorption curve integral corresponding to eqns. (1) and (2).

$$S \equiv \sum_i S_i = \sum_i I_i(\Phi \epsilon l \tau) \tag{4}$$

For a first-order process where significant depletion of the ground state does not take place, all the parameters in parentheses in eqn. (4) are independent of the number of "micropulses" and of the energy per pulse; then

$$S = \Phi \epsilon l \tau \sum_i I_i \tag{5}$$

No restriction has been introduced as to the energy, frequency or number of pulses of energy I_i. Thus we can view the actual laser pulse as a series of "micropulses"; from this we conclude that S is a function of the total energy of the pulse and not of its shape, regardless of whether τ is, or is not, comparable with the halfwidth of the laser pulse. In other words, when the lifetime of the transient of interest is shorter than the laser pulse, the signal approaches or follows the shape of the laser pulse; however, the integral under the absorption profile is still given by eqn. (3) as long as the time response of the system is such that it can easily respond to the time evolution of the laser pulse itself. If all other parameters are known or can be estimated, and if the transient decay can be taken to follow first-order kinetics, then the transient lifetime τ can be obtained from eqn. (3). The restrictions on the applicability of eqn. (3) are in fact less stringent than it may initially seem, and in the rest of this report we discuss two examples which make use of this approach.

The two examples involve reactions of xanthone triplets, which are produced with a quantum yield of intersystem crossing close to 1.0 [1] and which absorb strongly in the region 600 - 650 nm [1, 4]. To test the technique we quench the triplet state in carbon tetrachloride with *trans*-1,3-pentadiene, so that its lifetime is eventually reduced to below the time resolution of the instrument. Since the optical path is a constant, eqn. (6) will hold:

$$\frac{S}{I\Phi\epsilon\tau} = \frac{S}{I^0\Phi^0\epsilon^0\tau^0} \tag{6}$$

Here the superscript 0 refers to a reference sample for which the lifetime τ^0 is not beyond the resolution of the instrument. In this example the superscript 0 refers to the same sample before addition of quencher; therefore, we can take $I \equiv I^0$, $\Phi \equiv \Phi^0$ and $\epsilon \equiv \epsilon^0$. Then, replacement of eqn. (2) in eqn. (6) leads to

$$\tau = S/A_0 \tag{7}$$

Figure 2 shows quenching plots based on this approach for triplet lifetimes as short as 0.13 ns as well as plots based on the conventional technique following the triplet decay for the low concentration region.

Our second example is that which actually led us to examine the possibilities of this technique. The lifetime of xanthone triplets in diphenyl ether is quite short as a result of quenching processes similar to those described for benzophenone [5]; Fig. 3 shows a typical trace monitored at 645 nm. A transient spectrum showed that the maximum for the triplet–triplet absorption in diphenyl ether is located at 645 nm, virtually the same position as that found when carbon tetrachloride was used [1]. Since the spectra look virtually identical in these two solvents, we assume that we can eliminate the term $\Phi\epsilon$ in eqn. (6) (*i.e.* $\Phi\epsilon \approx \Phi^0\epsilon^0$). In addition, given two samples of somewhat different optical densities at 337.1 nm, the ratio I/I^0 will be given by
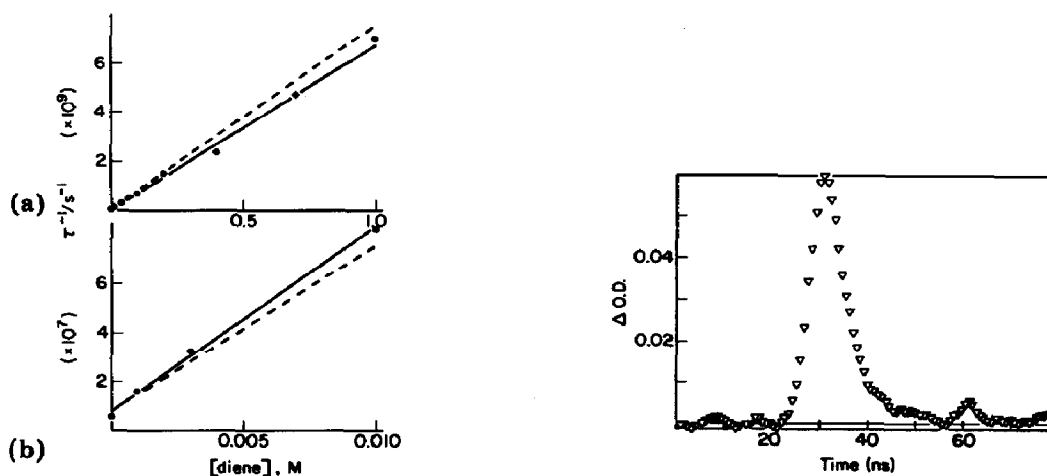

Fig. 2. Quenching of xanthone triplets by *trans*-1,3-pentadiene in carbon tetrachloride ([xanthone] = 0.00048 M; temperature, 25 °C): (a) data according to eqn. (7); (b) lifetimes obtained from a plot of log A *vs. t*. In each case the broken line shows the slope obtained in the other half of the figure.

Fig. 3. Time profile obtained for 0.0012 M xanthone in diphenyl ether at room temperature (average of ten traces).

$$\frac{I}{I^0} = \frac{1-T}{1-T^0} \tag{8}$$

where T is the transmittance at 337.1 nm. Replacement of eqns. (2) and (8) in eqn. (6) leads to

$$\tau = \frac{S}{A_0} \frac{1-T^0}{1-T} \tag{9}$$

Measurements for 0.00128 M xanthone in diphenyl ether (Fig. 3) and using a 0.00048 M solution in carbon tetrachloride as a reference led to a lifetime of 4.6 ns. Measurements at 645 and 625 nm led to the same lifetime.

The approach described here is obviously not a panacea for all examples of short transient lifetime. However, it would appear to be quite useful for those systems where strong signals and first-order decay processes predominate.

The experimental set-up used in these experiments has been described elsewhere [1].

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