

MEASUREMENT OF QUANTUM YIELDS: PROBLEMS CAUSED BY CHANGES IN THE ABSORPTION CHARACTERISTICS OF THE MEDIUM WITH PERCENTAGE CONVERSION

NIGEL J. BUNCE

*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario
N1G 2W1 (Canada)*

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Summary

Expressions have been obtained for the change in rate of a photochemical reaction in homogeneous media as the absorption characteristics of the medium alter with percentage conversion. In the general case, the differential equation relating the incident photon flux to the unreacted concentration of the reactant must be integrated numerically. Two special cases have analytical solutions; they are irradiation at an isosbestic point, and formation of a product that is transparent at the irradiation wavelength. The results are discussed in the context of obtaining quantum yields from actinometry experiments.

1. Introduction

The progress of a photochemical reaction in a homogeneous phase is influenced by the photon flux, the quantum yield of reaction and the absorption characteristics of the reaction mixture. As the reaction progresses, the composition of the reaction mixture changes and hence so do the absorption characteristics. Consequently the progress of the reaction will not be linearly related to the accumulated photon dose. This poses problems for the experimentalist who wishes to determine a quantum yield. If the quantum yield ϕ_p of product formation is desired, the usual strategy is to analyse for product at very low conversion so that the change in the absorption characteristics of the reaction mixture during the experiment will be negligible. This is not possible when the quantum yield ϕ_r of reactant disappearance is to be measured, since the extent of reaction in the test solution can only be determined with sufficient accuracy at moderate conversion of the reactant, e.g. 15% - 30%. Many investigators still use the simple formulation

$$\phi_r = \frac{\text{moles reactant consumed}}{\text{moles photons absorbed}} \approx \frac{c_0 - c_t}{I_0} \quad (1)$$

to determine ϕ_r even though substantial inaccuracies are known to result when reactant and product absorb competitively at the excitation wavelength [1, 2].

When a chemical actinometer is used to determine the accumulated photon dose I_0 , the problem is compounded because the absorption characteristics of both actinometer and test solution change with the conversion of the respective reactant. For this reason, all the commonly used actinometers are monitored by measuring product formation at low conversion rather than by following the consumption of the reactant in the actinometer.

Jackson and Lishan [3] have recently pointed out the potential complexities that arise when the progress of photoreaction is considered in the light of factors such as light filtering by products and by inert substances, secondary photoreactions, and inhomogeneity of the photolysis medium. In the present work, consideration was restricted to the effects of competitive light absorption by reactants and products, and the following restrictions were imposed on the types of photoreaction studied: (1) no secondary photolysis, *i.e.* the product distribution is stable with time; (2) the reaction vessel is well stirred.

Strictly, actinometry means determining the number of photons in a beam, as opposed to determining the number of photons absorbed by the solution. Most actinometric measurements are in fact made under one of two limiting conditions: (a) high absorbance (all the incident radiation is absorbed); (b) very low absorbance (the light absorption is directly proportional to concentration: $I_{\text{abs}} = I_0 - I_{\text{trans}} = I_0(1 - 10^{-\text{Abs}}) = I_0\{1 - \exp(-2.303\text{Abs})\} \approx 2.303I_0\text{Abs}$).

The results presented here are valid over the whole range of absorbance values.

2. Results and discussion

The explanation of the symbols is given in Appendix A.

We begin with definitions of ϕ_r , the absorbance Abs_t , the total light absorbed $dI_{\text{abs},t}$ and the fraction of light absorbed $dI_{\text{abs},r,t}$ between reactant and product:

$$\phi_r = - \frac{dc_{r,t}}{dI_{\text{abs},r,t}} \quad (2)$$

$$\text{Abs}_t = l(\epsilon_r c_{r,t} + \epsilon_p c_{p,t}) = l\{\epsilon_p c_0 + (\epsilon_r - \epsilon_p)c_{r,t}\} \quad (3)$$

$$dI_{\text{abs},t} = dI_0\{1 - \exp(-2.303\text{Abs}_t)\} \quad (4)$$

$$dI_{\text{abs},r,t} = \frac{dI_{\text{abs},t}\epsilon_r c_{r,t}}{\epsilon_r c_{r,t} + \epsilon_p c_{p,t}} \quad (5)$$

The quantity $dI_{\text{abs},r,t}$ is eliminated by combining eqns. (2) and (5), and $dI_{\text{abs},t}$ is eliminated by combining eqn. (4) with this result. This affords

$$-\frac{dc_{r,t}}{dI_0} = \frac{\phi_r \epsilon_r c_{r,t} \{1 - \exp(-2.303 \text{Abs}_t)\}}{\epsilon_r c_{r,t} + \epsilon_p c_{p,t}} \quad (6)$$

Further substitution of eqn. (3) into eqn. (6) eliminates Abs_t and changes the denominator of eqn. (6) to yield

$$-\frac{dc_{r,t}}{dI_0} = \frac{\phi_r \epsilon_r c_{r,t} (1 - \exp[-2.303I \{ \epsilon_p c_0 + (\epsilon_r - \epsilon_p) c_{r,t} \}])}{\epsilon_p c_0 + (\epsilon_r - \epsilon_p) c_{r,t}} \quad (7)$$

For the general case, eqn. (7) cannot be integrated analytically. Two special cases have analytical solutions, namely (i) irradiation at an isosbestic point ($\epsilon_p = \epsilon_r$) and (ii) photobleaching ($\epsilon_p = 0$). We shall consider the special cases first and then the general case of eqn. (7) which requires numerical integration.

2.1. Irradiation at an isosbestic point ($\epsilon_p = \epsilon_r$)

Equation (7) simplifies immediately to

$$-\frac{dc_{r,t}}{dI_0} = \frac{\phi_r c_{r,t} \{1 - \exp(-2.303 \text{Abs}_0)\}}{c_0} \quad (8)$$

This can be integrated to give

$$\ln\left(\frac{c_0}{c_t}\right) = \frac{\phi_r I_0 \{1 - \exp(-2.303 \text{Abs}_0)\}}{c_0} \quad (9)$$

At high absorbances the term $1 - \exp(-2.303 \text{Abs}_0)$ is approximately unity, and hence eqn. (9) corresponds to the form that has been obtained previously [1, 2] for the case of total light absorption by the photolyte. According to eqn. (9) the concentration of the photochemical substrate decays exponentially with accumulated photon dose, the steepness of the decay depending on the values of ϕ_r , c_0 and Abs_0 , all of which are constant in any experiment. Figure 1 illustrates this behaviour for different initial values of Abs_0 . (All calculations were carried out using the spreadsheet software Lotus 1-2-3.) Also shown on this and later figures is the linear relationship between photon dose and concentration as calculated using eqn. (1). Deviation from eqn. (1) occurs at lower percentage conversion the lower the initial absorbance (see also Table 1). Table 1 records the percentage conversion where the deviation between the two calculations reaches 2%; this would probably be a quite acceptable error for most actinometric work.

2.2. Photobleaching ($\epsilon_p = 0$)

Equation (7) now simplifies to

$$-\frac{dc_{r,t}}{dI_0} = \phi_r \{1 - \exp(-2.303 \epsilon_r c_{r,t} I)\} \quad (10)$$

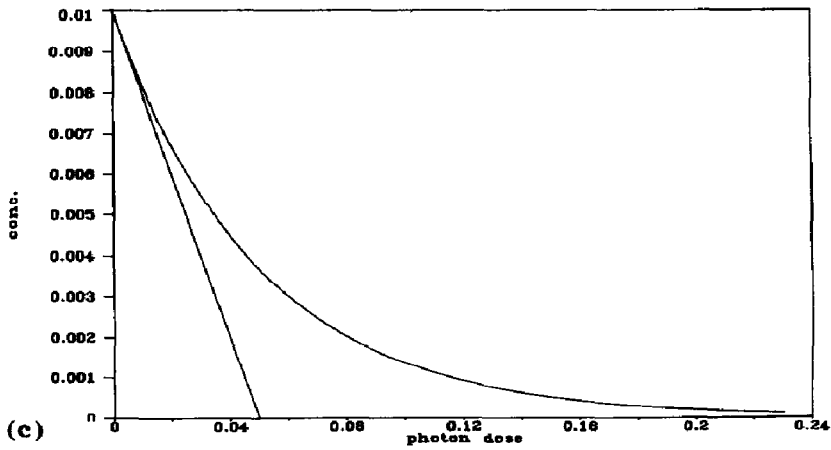
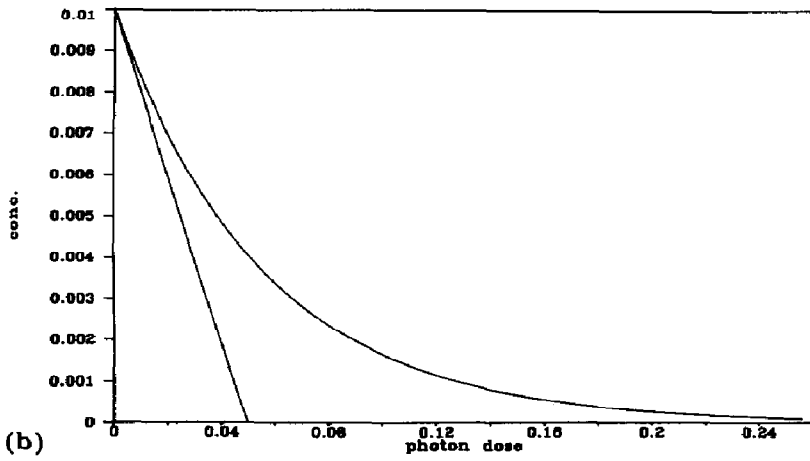
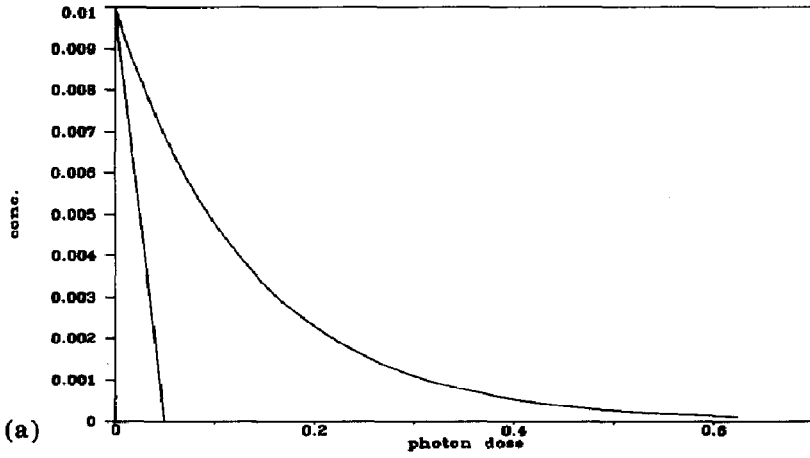


Fig. 1. Photon dose vs. concentration (isosbestic model) ($\phi_r = 0.2$; $c_0 = 0.01$): (a) $Abs_0 = 0.2$; (b) $Abs_0 = 1$; (c) $Abs_0 = 5$.

TABLE 1

Comparison between linear (eqn. (1)) and non-linear (eqns. (9), (12) and (15)) calculations of the dependence of absorbance on photon dose

	Abs ₀	Conversion (%)	
Isosbestic (eqn. (9))	> 5	17	Results independent of c ₀ , φ _r , etc.
	1	10	
	0.2	1	
Photobleaching (eqn. (12))	10	95	Results independent of c ₀ , φ _r , etc.
	5	84	
	3	64	
	2	26	
	1	< 5	
	0.2	< 1	
Numerical integration (eqn. (15))	5	17	ε _p = ε _r
	5	9	ε _p = 4ε _r
	5	6	ε _p = 10ε _r
	5	25	ε _p = 0.4ε _r
	5	87	ε _p ≈ 0
	2	17	ε _p = ε _r
	2	8	ε _p = 5ε _r
	2	22	ε _p = 0.5ε _r
	1	10	ε _p = ε _r
	1	2	ε _p = 10ε _r
	1	33	ε _p = 0.1ε _r
	0.5	4	ε _p = ε _r
	0.5	2	ε _p = 2ε _r
	0.5	21	ε _p = 0.1ε _r
	0.2	1	ε _p = ε _r
0.2	9	ε _p = 0.1ε _r	

It is convenient to write eqn. (10) in terms of absorbance. Rearrangement gives

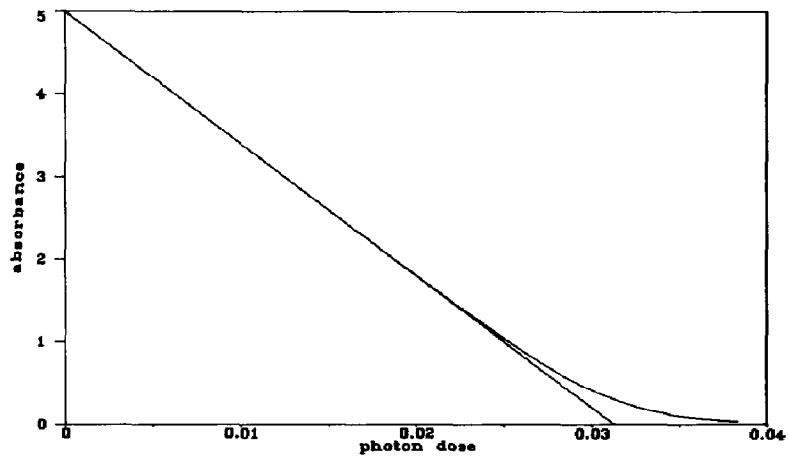
$$-\frac{d\text{Abs}_t}{1 - \exp(-2.303\text{Abs}_t)} = \epsilon_r l \phi_r dI_0 \quad (11)$$

Since the left-hand side of eqn. (11) is a standard form [4], it follows that

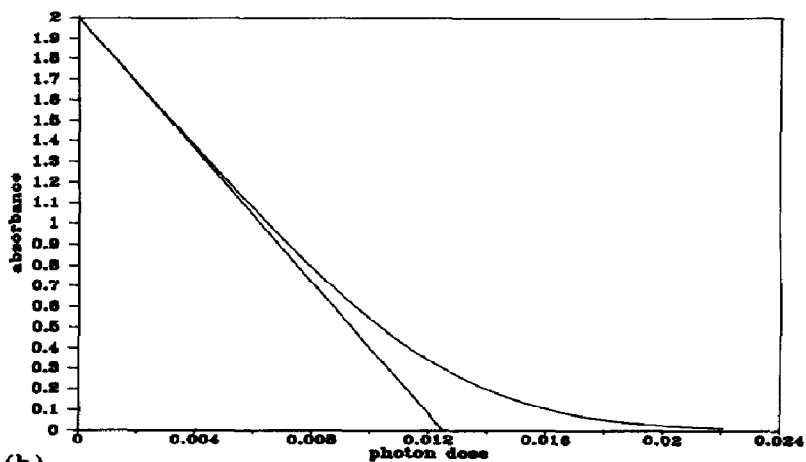
$$I_0 = \frac{1}{\phi \epsilon_r l} \left[(\text{Abs}_0 - \text{Abs}_t) + \frac{1}{2.303} \ln \left\{ \frac{1 - \exp(-2.303\text{Abs}_0)}{1 - \exp(-2.303\text{Abs}_t)} \right\} \right] \quad (12)$$

The form of eqn. (12) makes it convenient to write I_0 as a function of absorbance rather than the other way around. The term $\phi \epsilon_r l$ behaves as a single constant.

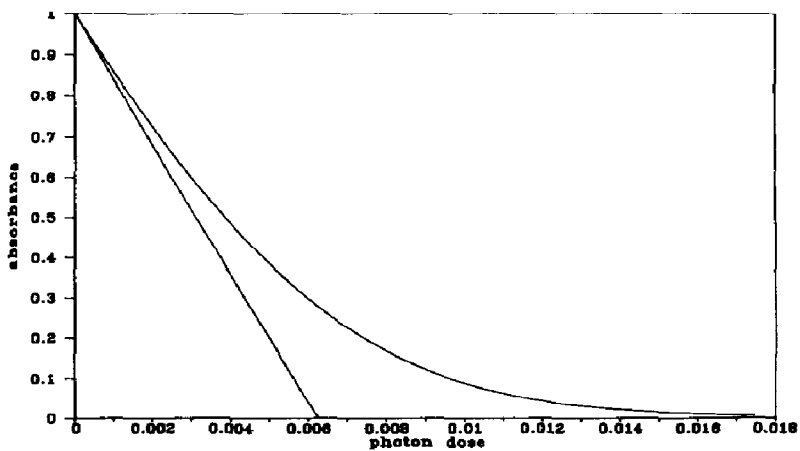
Figure 2 shows examples of the relationship between I_0 and Abs_t for different values of Abs_0 . At high initial absorbances, eqn. (1) is an excellent approximation to the actual photon dose *vs.* absorbance curve but, as the light absorption becomes incomplete, serious deviations occur. This



(a)



(b)



(c)

Fig. 2. Absorbance vs. photon dose (photobleaching) ($\phi_r = 0.2$; $\epsilon_r = 8000$; $l = 0.1$): (a) $Abs_0 = 5$; (b) $Abs_0 = 2$; (c) $Abs_0 = 1$.

is explicable in terms of eqn. (12) where, at large absorbances, the logarithmic term is negligible and the equation is then in fact identical with eqn. (1).

An interesting point about the photobleaching is that the result should be equally applicable to an inhomogeneous medium, for example, the case of a photochemically active solute immobilized in polymer solution. In that case I_0 would be expressed in moles per unit area, rather than the conventional moles per unit volume. The example of a photobleaching reaction would thus be more appropriate for the development of a solid state actinometer than the examples that we have reported recently [5], where product build-up at the exposed edge of the polymer and competitive (but wavelength-dependent) light absorption by product and reactant make the device difficult to calibrate.

2.3. Competitive but unequal light absorption by reactant and product

In this case, eqn. (7) must be integrated numerically. The modified Euler method was chosen, with the interval from c_0 to c_t divided into 100 equal steps. The incremental photon dose ΔI_0 is given by

$$\Delta I_0 = \frac{(c_0 - c_t)\{f(i) + f(i + 1)\}}{200\phi_r\epsilon_r} \quad (13)$$

where

$$f(i) = \frac{(\epsilon_r - \epsilon_p) + \epsilon_p c_0/c_i}{1 - \exp[-2.303\{\epsilon_p c_0 + (\epsilon_r - \epsilon_p)c_i\}]} \quad (14)$$

Then the accumulated photon dose is given by

$$I_0 = \sum_{i=1}^{100} \Delta I_0 \quad (15)$$

Figure 3 shows the results of such calculations for cases where the molar absorptivity of the product is larger than (Fig. 3(a)), equal to (Fig. 3(b)) and smaller than (Fig. 3(c)) that of the reactant. As might be expected from the discussion in Section 2.2, the deviation between the curve calculated by eqn. (15) and the line defined by eqn. (1) is greater the larger the molar absorptivity of the product relative to that of the reactant and also the larger the initial absorbance (see Table 1).

2.4. Determination of quantum yields

Equations (9), (12) and (15) all relate the quantities ϕ_r , c_t and I_0 in terms of quantities such as molar absorptivities and absorbances, which are both measurable experimentally and constant over the course of any reaction. Then if ϕ_r is to be determined for a reaction under study, the value of I_0 will be known from a separate actinometry experiment, and c_t will be the experimental parameter to be measured. The present results make the following options available to the experimentalist. The first

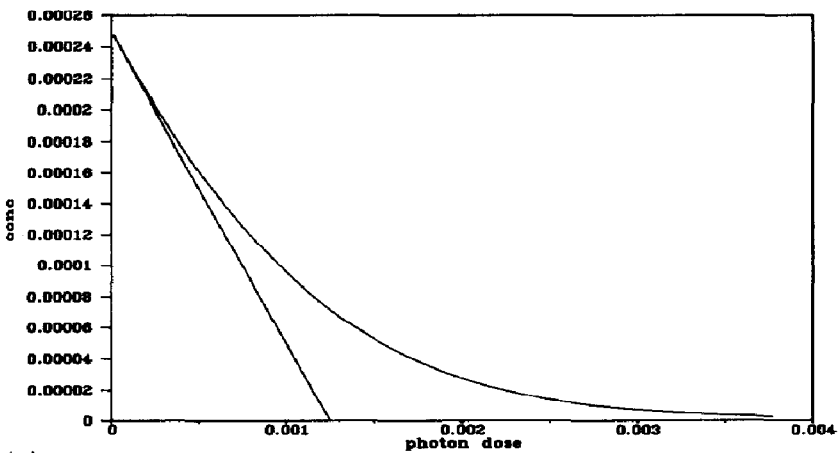
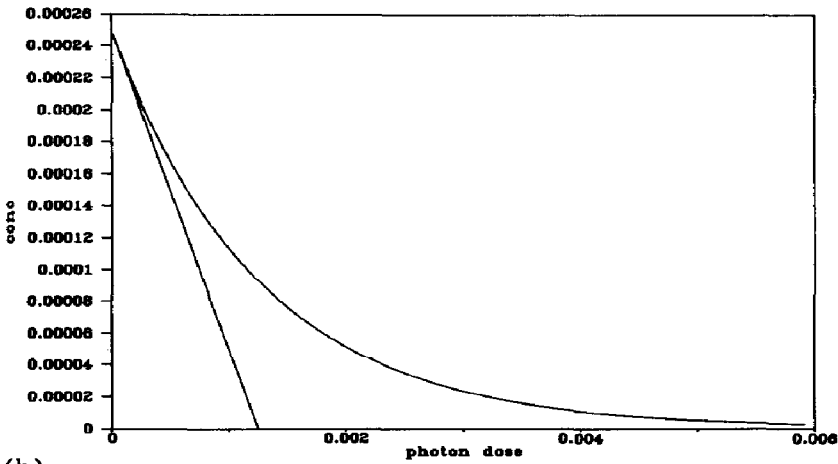
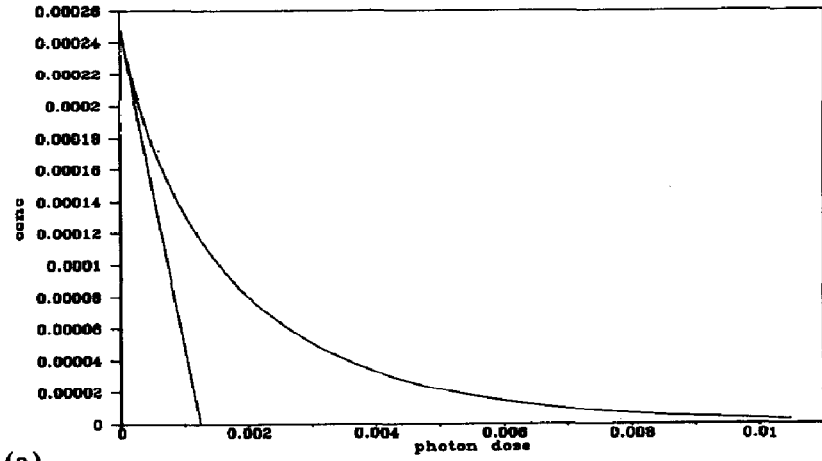


Fig. 3. Concentration vs. photon dose (Euler) ($c_0 = 0.00025$; $\epsilon_r = 8000$; $l = 1$; $\phi_r = 0.2$):
 (a) $\epsilon_p = 16000$; (b) $\epsilon_p = 8000$; (c) $\epsilon_p = 4000$.

option is to use eqn. (15) and to carry out the numerical integration for trial values of ϕ_r until concordance between the calculated and experimental values of c_f is obtained for different photon doses. The alternative approach would be to set up the experiment in such a way that eqn. (1) can be used over a useful range of experimental conditions. If it is realized that an accurate determination of the loss of starting material will require about 20% - 30% conversion of reactant, it can be seen from Table 1 that if $\epsilon_p \geq \epsilon_r$ it is never possible to use eqn. (1) to estimate ϕ_r within $\pm 2\%$. The larger the ratio ϵ_r/ϵ_p and the higher the initial absorbance, the more feasible becomes the determination of ϕ_r using eqn. (1). Inevitably, the spectral regions where $\epsilon_p \ll \epsilon_r$ are likely to be limited and may not be convenient in terms of suitable light sources. In that case, the full treatment of eqn. (15) will be necessary to determine ϕ_r .

The same considerations would apply to the potential development of an actinometer whose method of analysis depended on the loss of reactant. Here ϕ_r would be predetermined, and the value of I_0 would be calculated from the experimental measurement of c_f . The same conditions, namely $\epsilon_p \ll \epsilon_r$ and high Abs_0 , would be needed unless the full calculation of eqn. (15) were to be followed, and this would seriously limit the development of such an actinometer.

In the present context, the ideal method of analysing a solution, either to determine ϕ_r or to use it as an actinometer, would be spectrophotometric, since the changes in the absorption characteristics of the solution with percentage conversion are the cause of the problems addressed here. Given that the practical range of absorbances is 0 - 2, we see from Table 1 that it would be feasible to use eqn. (1) at $\pm 2\%$ precision only under the very restrictive condition that the photoproducts were all essentially transparent at the irradiation wavelength and conversion was limited to 26% or less.

The arguments presented here have all been directed to reactions where reactant disappearance is being monitored. As mentioned earlier, the usual strategy is to study product formation, if that is possible, and to restrict the percentage conversions to such low values that the absorption characteristics of the reaction mixture are essentially constant over the course of the reaction. However, Table 1 shows that there will be conditions sufficiently adverse, *i.e.* $\epsilon_p \geq \epsilon_r$, that even product analysis will give ϕ_r within $\pm 2\%$ only at high initial absorbances when eqn. (1) is used. The methods described here can be used to simulate the conditions where the use of eqn. (1) will be appropriate if this difficulty is anticipated.

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Appendix A: Nomenclature

Abs_t	absorbance at time t
Abs_0	initial absorbance
c_t	final concentration of reactant
$c_{p, t}$	concentration of product at time t
$c_{r, t}$	concentration of reactant at time t
c_0	initial concentration of reactant
I_0	accumulated incident photon dose
$dI_{abs, r, t}$	incremental photon dose absorbed by reactant at time t
$dI_{abs, t}$	incremental photon dose absorbed by the reaction mixture at time t
l	depth of solution
ϵ_p	molar absorptivity of product (or, where there are several products, their weighted average molar absorptivity)
ϵ_r	molar absorptivity of reactant
ϕ_r	quantum yield for reactant disappearance