A CRITIQUE OF EXCITATION MODELS FOR PARTIAL SATURATION OF TRANSIENT ABSORBANCE

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Summary

A method to measure excited state extinction coefficients and quantum yields of formation and to calibrate laser intensity, based on the partial saturation of, for example, transient absorbance, is analyzed. Previous discussion of this method has been based on a two-state model of the excitation process. For cases such as excited triplet–triplet absorption, the participation of a third state, the first excited singlet, can disrupt this simple picture. In the current work we develop a three-state model of the excitation–deactivation process which satisfactorily incorporates the effect of the intermediate level. Complications such as spatial inhomogeneity of the exciting pulse and hence of transient concentration are not dealt with and samples are assumed to be optically thin. From the more general model it can be seen that interpretation of the partial saturation method based on the two-state model will work properly only under restrictive conditions of relatively short singlet lifetime $\tau_S \ll k_{ex}^{-1}$ (the inverse of the excitation rate) and relatively long pulse lengths $\Gamma_p \gg k_{isc}^{-1}$ (the inverse of the intersystem crossing rate). Numerical simulations are performed on some typical systems to illustrate the limits of the methods. These simulations also indicate that even when it appears the method is working well, *i.e.* the saturation curve is well described, the derived parameters may not be related to the underlying photophysical properties of the system.

1. Introduction

Recently it has become popular to use a two-state model to describe the excitation process in photochemical and photophysical measurements involving saturation of transitions due to high intensity lasers [1 - 5]. More complicated kinetic mechanisms have been used in discussions [6 - 9] of the various multiphotonic processes that are often a complication in saturation regions. However, the two-state model of excitation seems to be the description of choice when these higher order processes are not likely to be a problem, such as in the lower intensity partial saturation regions.

The two-state model of excitation is easy to derive. The model can be expressed by the kinetic equations

$$\frac{d[^1M]}{dt} = -\Phi_T k_{ex}[^1M] \tag{1}$$

and

$$\frac{d[^3M^*]}{dt} = +\Phi_T k_{ex}[^1M] \tag{2}$$

where $[^1M]$ and $[^3M^*]$ are the ground state concentration and the transient concentration respectively and Φ_T is the transient yield. The excitation rate constant k_{ex} is defined by [10]

$$k_{ex} = 2303\epsilon_G I_p(x, t) \tag{3}$$

where ϵ_G (l mol^{-1} cm^{-1}) is the extinction coefficient of the ground state at the exciting laser frequency and $I_p(x, t)$ is the intensity of the exciting laser as a function of distance into the cell and as a function of time. The units of I_p are einsteins per square centimeter per second. In this communication we shall ignore the x dependence of I_p and treat optically thin samples. It should also be noted that spatial homogeneity of the exciting flash is assumed throughout. We defer consideration of such complications and focus instead on the deficiencies of the underlying experimental idealization.

For a square excitation pulse, eqns. (1) and (2) can be solved for $[^3M^*]$, with the initial conditions $[^1M] = c_G$ and $[^3M^*] = 0$ to give

$$[^3M^*] = c_G\{1 - \exp(-2303\epsilon_G I_p \Phi_T t)\} \tag{4}$$

for the concentration of transient at any time t up to the end of the constant pulse. Substitution of eqn. (4) into the expression for optical density change

$$\Delta OD = (\epsilon_T^* - \epsilon_G)[^3M^*]l \tag{5}$$

gives

$$\Delta OD = a\{1 - \exp(-bI_p)\} \tag{6}$$

with

$$a = (\epsilon_T^* - \epsilon_G)c_G l \tag{7}$$

and

$$b = 2303\epsilon_G t \Phi_T \tag{8}$$

In these equations ϵ_T^* is the extinction coefficient of the transient, which is monitored along a path length l.

These equations have been used to obtain the extinction coefficient and the transient yields [1, 3] from the a and b defined by eqns. (7) and (8). The values for a and b are obtained by fitting the curve of ΔOD versus I_p to the functional form given in eqn. (6). In order to obtain both a and b, the partial saturation curve must contain non-linear regions; otherwise only the product

of a and b can be obtained from eqn. (6). However, the non-linear regions can fall far short of the total saturation region. Herein lies the great advantage of the method in that it can be used with low laser powers relative to the total depletion method. (For a review of extinction coefficient methods and a compilation of ϵ_T^* values for triplet states see ref. 11.)

In a related measurement, the above equations have been suggested as a convenient way to measure intensities of lasers [2]. To do this the above method is worked in reverse. If both the quantum yield and the extinction coefficient, together with the fraction of ground state converted to transient, are known then eqn. (4) can be used to obtain the intensity delivered to the cell during a square pulse of width Γ_p by taking $t = \Gamma_p$ and solving eqn. (4) for $I_p\Gamma_p$.

It is obviously appropriate to base the partial saturation methods on a two-state model whenever the process can be described solely in terms of two states. Conceptually, however, the problem with these methods comes when they are applied to cases where the state being pumped is not the same as the state being observed. Such is the case when the transient is a triplet state formed by intersystem crossing from, for example, the first excited singlet state of an organic molecule in solution. The factor Φ_T superficially takes care of this, but the intermediate state does not appear in the kinetic equations. The question naturally arises as to when this intermediate state can be so ignored.

In this paper we address this question by first generalizing the excitation model to a three-state model, which can be solved exactly, and then analyzing the general conditions under which the equations of the two-state model can be obtained. Secondly we use a differential equation package to solve the three-state model numerically and then test these numerical solutions with the functional form of the two-state model. It will be seen that the conditions for the three-state model to collapse into the two-state model are somewhat restrictive and can lead to substantial errors in the parameters obtained from fitting data to eqns. (4) and (6).

2. An alternative model for photoexcitation

In order to see under what conditions the state being pumped can be ignored in a kinetic model of excitation, we introduce a more complete model for the excitation process than the two-state kinetic model in eqns. (1) and (2). Since we are questioning the application of the two-state model to methods involving triplet states, we adopt the appropriate notation and the following three-state kinetic model:

$$\frac{d[^1M]}{dt} = (k_f + k_{ic})[^1M^*] - k_{ex}[^1M] \tag{9}$$

$$\frac{d[^1M^*]}{dt} = k_{ex}[^1M] - k_S[^1M^*] \tag{10}$$

and

$$\frac{d[^3M^*]}{dt} = k_{isc}[^1M^*] \tag{11}$$

In these equations k_f, k_{ic} and k_{isc} are the rate constants for fluorescence, internal conversion and intersystem crossing respectively from $^1M^*$, the pumped state in this model. The other rate constant is defined as

$$k_S = k_f + k_{ic} + k_{isc} \tag{12}$$

In this photophysical model, the triplet is not allowed to decay on the time scale under consideration, in analogy with the two-state model in Section 1.

The equations can be solved exactly. We choose to focus on the solution for all times t less than or equal to the pulse length Γ_p of a square excitation pulse. For the initial conditions $[^1M] = c_G$ and $[^1M^*] = 0 = [^3M^*]$ the solutions for $t \leqslant \Gamma_p$ are [10]

$$[^1M] = \Xi\left\{\frac{(\lambda_2 - k_{isc})\exp(-\lambda_2 t)}{\lambda_2} + \frac{(k_{isc} - \lambda_3)\exp(-\lambda_3 t)}{\lambda_3}\right\} \tag{13}$$

$$[^1M^*] = \Xi\{-\exp(-\lambda_2 t) + \exp(-\lambda_3 t)\} \tag{14}$$

and

$$[^3M^*] = k_{isc}\Xi\left\{\frac{\exp(-\lambda_2 t)}{\lambda_2} - \frac{\exp(-\lambda_3 t)}{\lambda_3} + \frac{\lambda_2 - \lambda_3}{\lambda_2\lambda_3}\right\} \tag{15}$$

The definitions of the symbols used in eqns. (13) - (15) are

$$\Xi = \frac{k_{ex}c_G}{\lambda_2 - \lambda_3} \tag{16}$$

$$\lambda_2 = \frac{X + Y}{2} \tag{17}$$

$$\lambda_3 = \frac{X - Y}{2} \tag{18}$$

where

$$X = k_{ex} + k_f + k_{ic} + k_{isc}$$

$$= k_{ex} + k_S \tag{19}$$

and

$$Y = (X^2 - 4k_{isc}k_{ex})^{1/2} \tag{20}$$

At this point it can be observed that the approach to saturation does not depend on the optical density [1] or the concentration of the ground

state. The initial concentration c_G appears only in the factor Ξ which is a simple multiplicative factor in time-dependent concentrations of all three species (eqns. (13) - (15)).

To relate this solution of the three-state model to the two-state model, eqn. (15) can be rearranged as

$$[^3M^*] = c_G \left\{ 1 + \frac{\lambda_3 \exp(-\lambda_2 t)}{\lambda_2 - \lambda_3} - \frac{\lambda_2 \exp(-\lambda_3 t)}{\lambda_2 - \lambda_3} \right\} \tag{21}$$

It is then useful to rewrite Y as

$$Y = X \left(1 - \frac{4 k_{isc} k_{ex}}{X^2} \right)^{1/2} \tag{22}$$

showing, from eqns. (17) and (18), that λ_2 will be larger than λ_3 if the parameter

$$\gamma = \frac{k_{isc} k_{ex}}{X^2} \tag{23}$$

is small. Under these conditions the term $\exp(-\lambda_2 t)$ in eqn. (21) will be smaller in magnitude than the term $\exp(-\lambda_3 t)$ for two reasons. Firstly, since $\lambda_2 > \lambda_3$, the exponential itself will be smaller, and secondly the factor multiplying $\exp(-\lambda_2 t)$ will be smaller because of the relative magnitudes of the values of λ_2 and λ_3. Equation (21) then becomes

$$[^3M^*] \approx c_G \left\{ 1 - \frac{\lambda_2 \exp(-\lambda_3 t)}{\lambda_2 - \lambda_3} \right\} \tag{24}$$

Again if λ_3 is ignored relative to λ_2 in the factor multiplying $\exp(-\lambda_3 t)$

$$[^3M^*] \approx c_G \{ 1 - \exp(-\lambda_3 \Gamma_p) \} \tag{25}$$

where we have specialized to $t = \Gamma_p$, the end of the pulse. To simplify eqn. (25) further, the approximation that γ (from eqn. (23)) is small can be used on λ_3 itself giving

$$\lambda_3 \approx \frac{k_{ex} k_{isc}}{k_{ex} + k_S} \tag{26}$$

If the further approximation that

$$k_{ex} \ll k_S \tag{27}$$

holds, then

$$\lambda_3 \approx \frac{k_{ex} k_{isc}}{k_S}$$

$$= k_{ex} \Phi_T \tag{28}$$

and eqn. (25) finally reduces to

$$[^3M^*] = c_G\{1 - \exp(-k_{ex}\Phi_T\Gamma_p)\} \tag{29}$$

Since k_{ex} is proportional to I_p by eqn. (3), eqn. (29) is equivalent to eqn. (6), which is the working equation of the two-state model. It is precisely equal to eqn. (4) of the two-state model for $t = \Gamma_p$.

Thus in order for the three-state model to collapse into the two-state model, eqn. (27) must hold. Physically this condition means that the decay of $^1M^*$ is very fast compared with the rate of loss of population in the other two states, and thus the model can act as though the excited singlet state does not exist.

That the condition in eqn. (27) is truly a hindrance to using the partial saturation method can be seen by considering two cases from the literature where non-linear behavior was observed. In one experiment [2] non-linear behavior was seen with pulses of 1.2×10^{-8} einstein cm^{-2}, and in the second experiment [6] with power densities of 0.2 MW cm^{-2}. For the pulses used, these two values translate into $k_{ex} = 1.4 \times 10^7$ s^{-1} and $k_{ex} = 6.7 \times 10^7$ s^{-1} respectively using 5000 l mol^{-1} cm^{-1} for ϵ_G in eqn. (3). Since fluorescence lifetimes are of the order of 10 ns ($k_S \approx 10^8$ s^{-1}) condition (27) is not well satisfied.

It turns out that there is another condition other than $k_{ex} \ll k_S$ that must be satisfied in order for the standard partial saturation method (eqns. (6) - (8)) to give reliable extinction coefficients and yields of triplet states. The condition in question concerns the necessity of being in non-linear regions of the ΔOD *versus* I_p curve mentioned in Section 1. From eqn. (29) it can be seen that this condition can be expressed as

$$k_{ex}\Phi_T\Gamma_p \gtrsim 1 \tag{30}$$

For values smaller in magnitude, the exponential in eqn. (29) can be expanded in a power series with the result that the constant term cancels with the "1" already present in the expression, and the leading term in eqn. (29) is then proportional to k_{ex} (or I_p), frustrating attempts to determine a and b separately.

The restriction in eqn. (30) puts a severe limitation on the applicability of the partial saturation method when coupled with the condition in eqn. (27). The two conditions can be combined to give

$$k_{isc}\Gamma_p \gg 1 \tag{31}$$

Since usually $k_{isc} \leqslant 10^8$ s^{-1} for most systems, using pulsed lasers it will be impossible to find non-linear regions in the ΔOD *versus* I_p curve where the two-state model (eqns. (6) - (8)) will give correct extinction coefficients and quantum yields. Only by going to very long laser pulses or conventional flash photolysis equipment will the method have much chance of giving correct results. (See Appendix A for another derivation of the restrictions imposed on the two-state model in the partial saturation region.)

3. Numerical solution of the model

Section 2 shows that the standard equations (eqns. (6) - (8)) are likely to fail under many common conditions when used to measure triplet extinction coefficients and quantum yields. There is little information about what constitutes "much less than" in condition (27), and so it is not clear whether the model will work or not when the conditions are such as the actual experimental conditions mentioned earlier when k_{ex} was "less than" k_S, but not really "much less than". Rather than use the analytical solution of Section 2 to test the conditions further, we decided to study the solutions using a numerical solution to the three-state model. This was done for two reasons. First, the analytical solutions become somewhat cumbersome to work with, especially when they are extended beyond the excitation pulse. Second, the numerical solution can be done with a variety of pulse shapes.

The central numerical routine used was a standard software package for solving differential equations. It is called the Livermore Solver for Ordinary Differential Equations (LSODE) [12]. The version of LSODE used was that of August 13, 1981. Our main program calls LSODE as a subroutine and does all the input–output and other assorted bookkeeping. For example, there are options in the program to step over time or intensity, plots can be made on a Digital VT100 Retro-Graphics terminal or on a Versatec electrostatic plotter, options are available to use square, gaussian or triangular pulses and a call can be made to a routine which fits the output of LSODE to an exponential growth. The fitting subroutine [13] is a non-linear least-squares program with an iteration procedure described by Pitha and Jones [14] and a weighting scheme described by Wentworth [15, 16].

4. Results of the numerical solution

To illustrate some of the problems with the partial saturation method of measuring quantum yields and extinction coefficients, we solved the three-state model numerically for several typical situations. We did not need to introduce an $\epsilon_T{}^*$ to test the equations of the two-state model. In fact, eqn. (4) of the two-state model was much more convenient to compare with eqn. (15) of the three-state model than eqn. (6). Thus instead of using a in eqns. (6) and (7) we looked at eqn. (4) and computed an $\tilde{a}$ defined by

$$\tilde{a} = c_G \tag{32}$$

We also chose to compute a $\tilde{b}$ defined by

$$\tilde{b} = 2303\epsilon_G\Phi_T \tag{33}$$

instead of the b defined by eqn. (8). This $\tilde{b}$ is more analogous to the original parameter of Lachish *et al.* [3] than eqn. (8). Also in practice we actually calculated what the $\tilde{a}$ and $\tilde{b}$ parameters should be, according to eqns. (32) and (33), from the input parameters and compared them with those

obtained from fitting the functional form

$$[^3M^*] = \tilde{a}\{1 - \exp(-\tilde{b}I_p\Gamma_p)\} \tag{34}$$

to the numerical simulation. In case eqn. (32) is seen as a trivial check on the two-state model in actual experiments, it must be remembered that the triplet concentration cannot be known directly from optical experiments. We are able to use these simple relations because we are simulating experiments.

Figure 1 shows the simulated intensity dependence of anthracene in ethanol. The photophysical parameters of anthracene in ethanol that were used in the simulation are listed in the caption [17, 18]. In Fig. 1 instead of ΔOD *versus* I_p the ratio of the concentration of a given species to that of the original ground state concentration c_G is plotted against I_p. The fit of the triplet curve to eqn. (34) was also plotted, but it was so close to the triplet curve that it would not have been discernible in the figure. However, even with something that looked to be an excellent fit, the $\tilde{a}$ parameter was 18.2% too low and the $\tilde{b}$ parameter was 10.8% too high. The species were monitored for Fig. 1 at the end of the 20 ns square pulse so that a close correspondence with the two-state model could be made.

Another simulation was done on the same anthracene system where the triplet was monitored at 20 ns after the end of a 20 ns pulse. There was little singlet present at this delay. In this simulation additional triplets were formed from the singlets left after the pulse was turned off. Again a good fit was obtained, but the fitted parameters were still low by 9.8% for $\tilde{a}$ and high
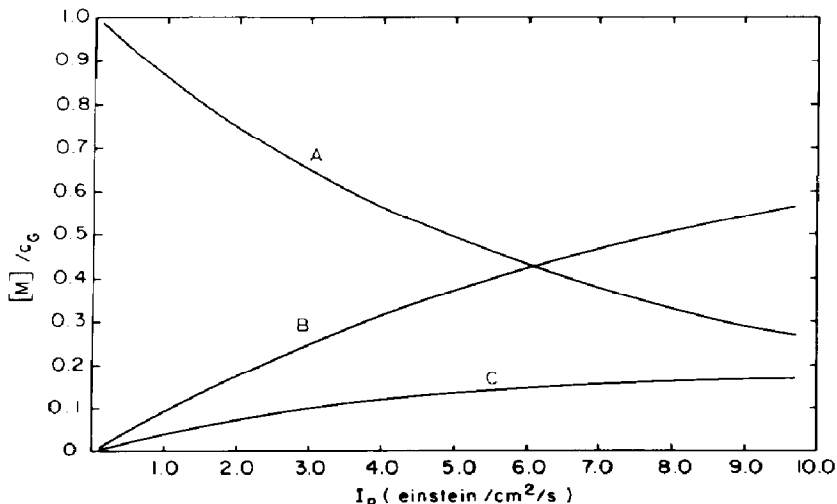

Fig. 1. Numerical simulation of anthracene in ethanol with a 20 ns excitation pulse: curve A, ^1M; curve B, $^3M^*$; curve C, $^1M^*$. The concentrations were sampled at the end of the pulse; $k_S = 1.92 \times 10^8$ s^{-1}; $k_{isc} = 1.40 \times 10^8$ s^{-1}; $k_T = 330$ s^{-1}; $\Phi_T = 0.73$; $c_G = 1.0 \times 10^{-5}$ mol l^{-1}; $\epsilon_G = 4000$ l mol^{-1} cm^{-1}; $k_{ex} = 9.2 \times 10^6$ I_p (s^{-1}). From these input parameters the two-state model should give $\tilde{a} = 10^{-5}$ mol l^{-1} and $b = 6.72 \times 10^6$ cm^2 mol^{-1}. The parameters obtained from the fit are $\tilde{a} = 8.18 \times 10^{-6}$ mol l^{-1} and $\tilde{b} = 6.06 \times 10^6$ cm^2 mol^{-1}.

by 9.2% for $\tilde{b}$. Since the two-state model has formally no singlets present, it is not clear whether the triplet should be measured at the end of the pulse or after the singlet has decayed in order to obtain the best agreement with the two-state model. This issue is discussed again below in the case of the acridinium ion.

In the case of anthracene in ethanol, condition (27) was satisfied roughly over most of the region from $I_p = 0$ to $I_p = 10$ einstein cm^{-2} s^{-1} because $k_{ex} = 9.2 \times 10^6 I_p$ and $k_S = 1.92 \times 10^8$ s^{-1}. Condition (31) was satisfied since $k_{isc}\Gamma_p = 2.8$. Also as seen from Fig. 1 some degree of non-linearity was present in the curves. From these considerations some agreement would be expected to be seen with the predictions of the two-state model, and indeed there is some agreement. However, it can be noted that the fit, which was almost perfect, gave no hint that the answers from the fit could be different by over 9% from the parameters of the two-state model.

To show that the two-state model can really work well when conditions (27) and (31) hold, a simulation was done on the same system but with a different pulse width. Γ_p was taken to be 2 μs so that $k_{isc}\Gamma_p = 280$. With this change a non-linear region in the ΔOD *versus* I_p curve could be found for $I_p < 0.15$ einstein cm^{-2} s^{-1}. The agreement between the fit to the numerical simulation and the predictions of the two-state model agreed to 0.08% for $\tilde{a}$ and 0.2% for $\tilde{b}$. With this intensity range eqn. (27) was really well satisfied over the whole range, and the two-state model realistically portrays the numerical three-state problem. (In the spirit of the analytical models discussed above, the triplets were not allowed to decay in this simulation.)

Figure 2 shows a case that exhibits a more extreme failure of the two-state model of excitation than the case of anthracene in ethanol. The simulation plotted is based on the photophysical parameters of the acridinium ion in sulfuric acid [17, 19]. Since the acridinium ion has a relatively long fluorescence lifetime (32 ns) it might be chosen to monitor the triplet state somewhat after the pulse but before much triplet decay has taken place. Figure 2 is the result of monitoring the various species at 101 ns after a 20 ns pulse. This type of procedure is equivalent to the experimental procedure of extrapolating the triplet decay back to the end of the pulse. Again the numerical solution to the three-state model can be fit very well with the $\tilde{a}$ and $\tilde{b}$ parameters using the functional form in eqn. (34). However, if the values obtained from the fit were used to estimate the values of $\tilde{a}$ and $\tilde{b}$ for the two-state model given by eqn. (32) and eqn. (33) respectively the errors would be −47.7% for $\tilde{a}$ and +84.1% for $\tilde{b}$.

Since so far we have only shown the equivalence of the two-state model to the three-state model at the end of the pulse, it might be thought that the large discrepancy between the model prediction and the fit was due to the procedure of extrapolating back to the end of the pulse. However, when the simulation was repeated with sampling carried out at the end of the pulse, the situation did not improve. In this simulation it turned out that the triplet concentration was much less than that of the singlet, and furthermore that the ΔOD *versus* I_p plot for the triplet was linear. It should be noted that for
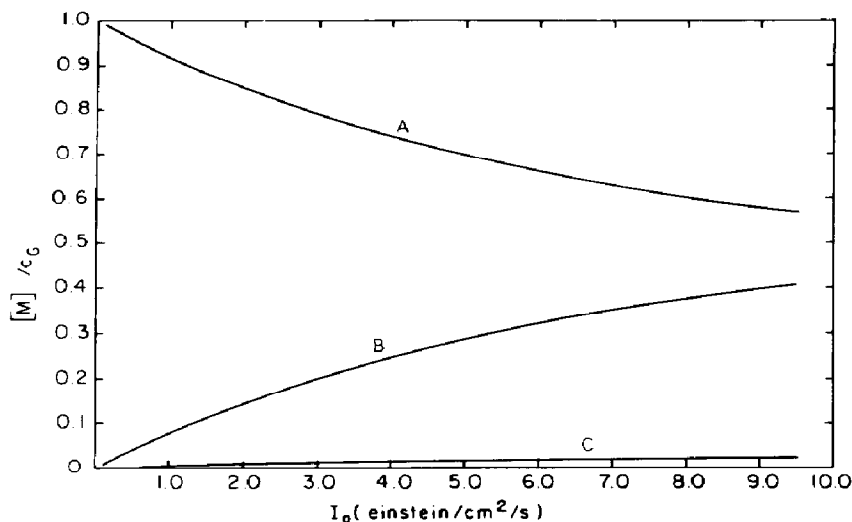
Fig. 2. Numerical simulation of the acridinium ion in sulfuric acid with a 20 ns excitation pulse: curve A, ^1M; curve B, $^3M^*$; curve C, $^1M^*$. The concentrations were sampled 101 ns after the end of the pulse; $k_S = 3.13 \times 10^7$ s^{-1}; $k_{isc} = 1.47 \times 10^7$ s^{-1}; $k_T = 1.49 \times 10^3$ s^{-1}; $\Phi_T = 0.47$; $c_G = 1.0 \times 10^{-5}$ mol l^{-1}; $\epsilon_G = 4000$ l mol^{-1} cm^{-1}; $k_{ex} = 9.2 \times 10^6$ I_p(s^{-1}). From these input parameters the two-state model should give $\tilde{a} = 10^{-5}$ mol l^{-1} and $b = 4.33 \times 10^6$ cm^2 mol^{-1}. The parameters obtained from the fit were $\tilde{a} = 5.23 \times 10^{-6}$ mol l^{-1} and $\tilde{b} = 7.96 \times 10^6$ cm^2 mol^{-1}.

both simulations on the acridinium ion $k_{isc}\Gamma_p = 0.32$ which does not satisfy the condition in eqn. (31).

The same issue arises here as with the case of anthracene as to whether the triplet concentration should be monitored at the end of the pulse or extrapolated back to the end of the pulse to obtain the closest correspondence with the two-state model. In order to answer this question, the solutions to the three-state model must be extended to times after the pulse. After the pulse k_{ex} in eqns. (9) - (11) becomes zero and the equations decouple. The solutions are now easy even if they are somewhat messy. The solution for the triplet concentration with $t > \Gamma_p$ is

$$[^3M^*] = [^3M^*](t = \Gamma_p) + \Phi_T[^1M^*](t = \Gamma_p)[1 - \exp\{-k_S(t - \Gamma_p)\}] \qquad (35)$$

The concentrations on the right-hand side of eqn. (35) are found by putting $t = \Gamma_p$ in eqns. (14) and (15). The value of the triplet concentration extrapolated back to the end of the pulse in the experimental sense is just the value at $t \to \infty$, since the analytical models considered have no triplet decay. This concentration is given by

$$[^3M^*](t \to \infty) = [^3M^*](t = \Gamma_p) + \Phi_T[^1M^*](t = \Gamma_p) \qquad (36)$$

To obtain the two-state model, again the analysis leading up to eqn. (29) is employed. It is found that the first term on the right-hand side of eqn. (36) is again given by eqn. (29) but that the second term on the right-hand side of eqn. (36) is zero. Thus in the limit of $k_{ex} \ll k_S$, the three-state model gives

the same result for the triplet concentration at the end of the pulse as for the value extrapolated back to the end of the pulse. (See Appendix A for a different limiting behavior.) Furthermore this value is the two-state value. That the values are the same is reasonable, since the two-state model has no singlet population anyway. However, the fact that particular simulations give different values for these two limits is just another symptom that the two-state model does not work for the particular parameters of the simulation.

With respect to the other method concerning the measurement of laser intensities [2], not much can be said at this point. This is mainly because, as can be seen from the above simulations, the curves are not saturating at 100% conversion. This general problem will be discussed elsewhere [20]. If the fraction η converted cannot be easily obtained, the two-state model cannot be used for lack of parameters. If this parameter can be obtained, the three-state formula for the intensity is

$$I_p \Gamma_p = -\frac{k_S \Gamma_p \ln(1-\eta)}{2303\epsilon_G \{\ln(1-\eta) + k_{isc}\Gamma_p\}} \tag{37}$$

instead of simply

$$I_p \Gamma_p = -\frac{\ln(1-\eta)}{2303\epsilon_G \Phi_T} \tag{38}$$

for the two-state model [2].

5. Conclusions

The simple two-state model for excitation can be derived from a more complete three-state model under very restrictive conditions. These are that the rate constant for decay of the singlet state is much faster than those for all other processes, in particular the excitation rate constant (see eqn. (27)). Under these conditions the singlet state can be ignored and treated implicitly by only using the quantum yield Φ_T of triplet formation in the two-state model. Furthermore, meaningful parameters for the two-state model will only be obtained for conditions in eqn. (30) or eqn. (31) which cause the relevant ΔOD *verus* I_p plots to be non-linear.

These conditions which were established by looking at the analytical solutions to the three-state model are supported by the numerical simulations. The numerical simulations also show what happens in intermediate regions where the inequalities in eqns. (27) and (31) are not well satisfied. The simulations show that if these two inequalities are only "less than" the results can still be quite poor. In fact, from the cases considered, it can be seen that most of the molecules with lifetimes longer than about 5 ns would be very unlikely to give good results when partial saturation is used with lasers having pulse widths in the nanosecond time range. We did see that anthracene could give excellent agreement with the two-state model when excited with a microsecond pulse. This suggests that the appropriate place

for the partial saturation method may be with the more intense flashes from conventional flash photolysis equipment. However, results from this method using nanosecond laser flash photolysis should be viewed with scepticism unless it can be shown that the conditions in eqns. (27) and (31) are truly well satisfied.

Finally it was seen that saturation phenomena can be quite deceptive. Figure 2 shows what appears to be an approach to saturation according to the two-state model. However, if the technique of extrapolating back to the end of the pulse is not used, then no approach to saturation can be seen at all. The most deceptive feature of the partial saturation technique is that so many of the ΔOD *versus* I_p simulations showed excellent fits to the functional form of eqn. (34). The only exceptions that we found were the linear plots, which can be easily excluded from consideration on other grounds. However, just because the functional form appears to be that of the two-state model, other checks, especially those in eqns. (27) and (31), must be made before the results can be certified.

Acknowledgments

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Appendix A

The expansions in the text are heuristic derivations of the two-state model from the three-state model. The reason these derivations were used is that mathematically it is not possible to carry out an expansion in a parameter such as k_{ex} and hope to see something similar to an exponential dependence on that expansion parameter unless the expansion in k_{ex} is taken to an infinite order.

However, an expansion of the triplet concentrations in terms of k_{ex} is useful to put the conclusions on a more rigorous basis. After much tedious calculus, the following expansions for the triplet concentration can be reached. At $t \rightarrow \infty$

$$\frac{[^3M^*](t \rightarrow \infty)}{c_G} \approx \Gamma_p \Phi_T k_{ex} - \frac{(\Gamma_p \Phi_T k_{ex})^2}{2} + k_{ex}{}^2 (\Phi_T{}^2 - \Phi_T) \times$$

$$\times \left\{ \frac{\Gamma_p}{k_S} + \frac{\exp(-k_S \Gamma_p)}{k_S{}^2} \right\} \tag{A1}$$

which comes from expanding eqn. (36). At the end of the pulse

$$\frac{[^3M^*](t = \Gamma_p)}{c_G} = \Gamma_p \Phi_T k_{ex} + \frac{k_{ex} \Phi_T \exp(-k_S \Gamma_p)}{k_S} + O(k_{ex}{}^2) \tag{A2}$$

which comes from expanding eqn. (21). A similar expansion of the two-state model to second order in k_{ex} gives

$$\frac{[^3M^*]}{c_G} \approx \Gamma_p \Phi_T k_{ex} - \frac{(\Gamma_p \Phi_T k_{ex})^2}{2} \tag{A3}$$

These rigorous expansions amplify two points in the text. First, although the heuristic derivations in the text gave the two-state model from both the three-state model at the end of the pulse and at $t \rightarrow \infty$, the expansions in eqns. (A1) and (A2) give different results even to first order in k_{ex}. However, under the condition

$$k_S \Gamma_p \gg 1 \tag{A4}$$

these two expansions give the same result to first order in k_{ex}.

Second, the expansions show the same type of requirements on the two-state model with regard to the pulse width and photophysical parameters as did the heuristic derivation. To lowest order in k_{ex}, the expansion at $t \rightarrow \infty$ in eqn. (A1) for the three-state model gives the same result as the lowest-order term in the expansion of the two-state model (see eqn. (A3)).

This means that the two-state model will be fine as long as the excitation rate constant is small, and this was expressed in the form of the condition in eqn. (27) in the text. However, it can be seen that the expressions in eqns. (A1) and (A3) do not agree to higher order in k_{ex}. In fact they disagree in the lowest-order term that is non-linear in k_{ex}, which will probably be the term determining the onset of partial saturation behavior. The k_{ex}^2 terms in eqns. (A1) and (A3) will agree if the condition in eqn. (A4) holds because then the term proportional to Γ_p^2 in eqn. (A1) will always dominate the Γ_p/k_S and $1/k_S^2$ terms in eqn. (A1). Condition (A4) is analogous to the condition in eqn. (31) in the text. Hence even with the rigorous expansions it can be seen that, in order for the two-state model to describe partial saturation behavior, the excitation rate constant must be small in some sense as in condition eqn. (27) and, in addition, there must be some restriction on the pulse width which is set by the photophysical parameters of the molecule being measured, such as the conditions in eqns. (31) or (A4).