On the Intensity and Time Dependence of Product Yields in Biphotonic Processes

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It is often stated that the yields of photoproducts in biphotonic processes are proportional to the square of the light intensity, and deviations from the square intensity dependence are taken as evidence that monophotonic processes also contribute. As mentioned by various authors [1-3] this is not generally correct. We want to discuss this point more thoroughly and propose a method to find out if monophotonic processes contribute.

It has previously been shown [4,5] that in the case of a biphotonic process induced by monochromatic light of intensity I the number of degraded molecules at an exposure time t will be:

$$N_s = \frac{N_0 C_S \varepsilon_M C_M \varepsilon_0 I^2}{k + aI} \times \left[t - \frac{1}{k + aI} (1 - e^{-(k+aI)t}) \right] \quad (1)$$

N_0 is the initial number of molecules in the ground state, $1/k$ is the lifetime of the intermediate state which absorbs the second photon and a is given by eqn. (2):

$$a = C_S \varepsilon_M + C_M \varepsilon_0 \quad (2)$$

ε_0 and ε_M are the extinction coefficients of the ground state and the intermediate state, respectively. C_M is the probability that the absorption of the first photon will give rise to the intermediate and C_S is the probability that absorption of the second photon by the intermediate will give the photoproduct. Eqn. 1 is correct only if $N_s \ll N_0$. If N_s approaches N_0 the intensity dependence will be very complex, but since this case is rarely met with experimentally, we will not discuss it here.

We will consider two cases:

$$\text{Case I: } t \ll t_0' = \frac{1}{k + aI}$$

Eqn. (1) then becomes:

$$N_s \approx \tfrac{1}{2} N_0 C_S \varepsilon_M C_M \varepsilon_0 (It)^2 \quad (3)$$

Thus the quadratic intensity dependence is correct in this case.

$$\text{Case II: } t \gg t_0' = \frac{1}{k + aI}$$

Eqn. (1) becomes:

$$N_s \approx \frac{N_0 C_S \varepsilon_M C_M \varepsilon_0 I^2 t}{k + aI} \quad (4)$$

In this case the quadratic intensity dependence is correct only if $aI \ll k$. $N_s \ll N_0$ and $C_M \varepsilon_0 \approx C_S \varepsilon_M \approx \tfrac{1}{2} a$ in many experimental cases. Then we have:

$$\frac{N_s}{N_0} \gg \frac{a^2 I^2}{4(k + aI)^2} = \frac{1}{4(k/aI + 1)^2}$$

Hence, $N_s \ll N_0$ implies $aI \ll k$ in such cases, and we get quadratic intensity dependence. However, if either $C_M \varepsilon_0 \gg C_S \varepsilon_M$ or $C_M \varepsilon_0 \ll C_S \varepsilon_M$ one can attain $N_s \ll N_0$ and $k \approx aI$ or even $k < aI$ simultaneously. This will be the case in wavelength regions where the absorption of the ground state is either much higher or much smaller than that of the intermediate or in the case of equal absorption if the quantum efficiencies C_M and C_S are different by more than one order of magnitude.

If $aI \gg k$ the yields will be proportional to I. Therefore it is not generally correct to exclude biphotonic processes even if the yields are linearly dependent on the light intensity.

In the intermediate case when $aI \approx k$ the intensity dependence of the yields will be intermediate between linear and quadratic. When such an intensity dependence is found it may therefore be incorrect to conclude that both single- and biphotonic processes are involved. Such a conclusion was recently drawn by Pailthorpe and Nicholls [6] who studied UV-induced ionization of keratin and its component amino acids and found that the rate of radical production was:

$$dN_S/dt = \text{const.} \times I^n \quad (5)$$

where n was in the range 1.3 to 1.6.

The equation

$$dN_S/dt = k_m I + k_b I^2 \quad (6)$$

could be fitted to their data and they concluded that biphotonic and monophotonic processes proceed independently at 77 K. According to eqn. (4) the rate of

radical production by a pure biphotonic process (if $t \gg t_0'$) should be

$$\frac{dN_S}{dt} = \text{const.} \frac{I^2}{k + aI} \qquad (7)$$

It turns out that this equation may also be very nicely fitted to Pailthorpe and Nicholl's data. We also found that eqn. (7) fitted our data for photoionization by 250 nm light of L-tryptophan in ethylene glycol/water glass (volume ratio 1/1) at 77 K.

However, very accurate experimental data are needed to distinguish between eqn. (6) and eqn. (7). We here propose another way of seeing if monophotonic processes are present in cases where the intermediate state is a triplet state emitting phosphorescence. During irradiation the phosphorescence intensity I_p will increase according to:

$$I_p = \text{const.} \, (1 - e^{-t/\tau R}) \qquad (8)$$

It turns out [5] that $\tau_R = 1/(k + aI)$. If both mono- and bi-photonic processes contribute the concentration of products should follow the equation

$$N_s = K_1[t - \tau_R(1 - e^{-t/\tau R})] + K_2 t \qquad (9)$$

where K_1 and K_2 are constants depending on the light intensity. When t increases the curve described by eqn. (9) approaches a straight line which intercepts the t-axis in $t_0 = \tau_R K_1/(K_1 + K_2)$. Thus t_0 may be determined, as earlier described.[4,5] If monophotonic processes are of any significance it is obvious that $\tau_R > t_0$, but, if of no significance, $\tau_R = t_0$. Measuring the concentration of photoproducts by registering the luminescence emitted when trapped electrons and tryptophan ions recombine we found [5] that t_0 and τ_R were comparable. However, the thermoluminescence measurements showed large scatter and we have repeated the experiment, this time by simultaneously registering the optical absorption from the photoproduced trapped electrons and the phosphorescence of tryptophan. (For description of apparatus and procedure, see Ref. 7.) Fig. 1 shows that τ_R is significantly larger than t_0. Bleaching of the trapped electrons by scattered light may contribute to the difference, but it seems likely that either monophotonic processes are present or in-
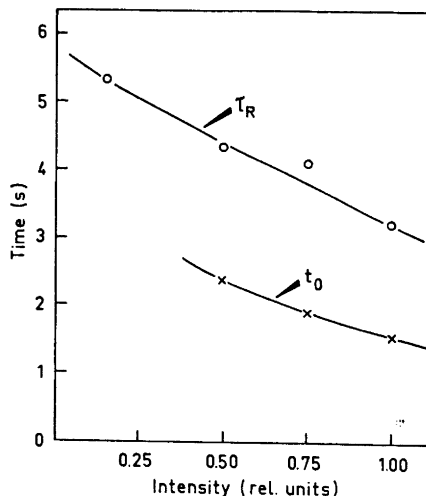

Fig. 1. Variation of the rise time τ_R (see eqn. (8)) of phosphorescence emitted from 5×10^{-4} M tryptophan in ethylene glycol/water (1:1) glass at 77 K and t_0 (defined in the text) with light intensity when irradiated with monochromatic light of wavelength 250 nm.

termediates other than molecules in the triplet state are involved.

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