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Preliminary Note

Photodegradation and fluorescence of aqueous tryptophan

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Recent studies [1, 2] on the luminescence of aqueous tryptophan provide evidence that two components of fluorescence are observable. However, the results for the decay times from these two reports are in serious disagreement. Since one study employed a powerful mode-locked solid state laser for excitation at 264 nm and the other a conventional weak discharge lamp, we felt it worthwhile to investigate the possibility that high energy excitation produces a fluorescent photoproduct which could account for the discrepancy.

Aqueous solutions of dl-tryptophan (10^{-4} M) were excited at 293 nm using frequency-doubled cavity-dumped pulses from a Coherent Radiation 590 dye laser pumped by a 4W Spectra-Physics 166 argon ion laser. Second harmonic generation was achieved using a temperature and angle tuned ammonium dihydrogen arsenate (ADA) crystal. Fluorescence decay curves were recorded on an apparatus which has been described in detail elsewhere [3]. Excitation pulse widths were 7 ns full width at half maximum. Data analysis was performed using an iterative weighted least squares convolution procedure [4]. The "goodness of fit" was determined by visual inspection of residual plots and the magnitude of the reduced chi-square value (Figs. 1 and 2).

Table 1 shows the values obtained for freshly prepared samples. The magnitude of chi-square indicates a less satisfactory fit to single exponential decay kinetics than is normally obtained. This may be due to the presence of a weak short-lived sub-nanosecond component as suggested by Szabo and Rayner [1]. With the pulse width used in this study it was not possible to resolve this component. However, the fact still remains that our results are inconsistent with those from the high energy laser excitation [2]. Our results from the irradiation of tryptophan with the full output of a 450 W xenon arc lamp, using the procedure described above, are collected in Table 2. It is apparent that irradiation produces a further emitting species with a

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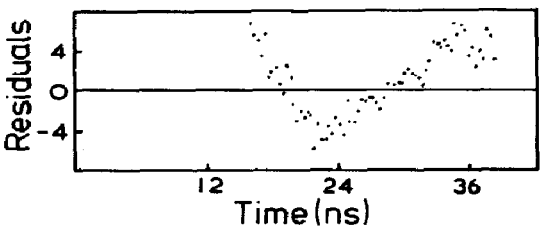

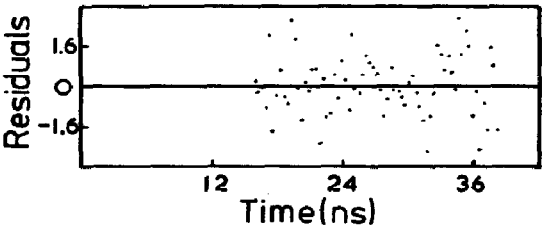

Fig. 1. Residual plot for a single exponential fit to a decay curve with two components.

Fig. 2. Residual plot for a "good fit" to double exponential decay kinetics.

TABLE 1

Fluorescence lifetimes of freshly prepared tryptophan

λ [a] (nm)	A	τ (ns)	chisqr[c]
320	0.068	3.00 (0.01)[b]	3.43
350	0.064	3.01 (0.01)	2.97
390	0.064	3.12 (0.01)	2.28

[a]Emission wavelength monitored.
[b]Numbers in parentheses refer to the standard deviation.
[c]Reduced chi-square [4].

TABLE 2

Fluorescence lifetimes of irradiated tryptophan

λ [a] (nm)	A_1/A_2	τ_1 (ns)	τ_2 (ns)	chisqr[c]
Samples irradiated for 3 h				
320	4.08	2.47 (0.14)[b]	6.57 (0.33)	1.71
350	4.05	2.69 (0.15)	7.23 (0.39)	2.10
390	3.8	2.97 (0.18)	7.81 (0.51)	1.6
Samples irradiated for 5 h				
320	2.61	2.64 (0.19)	6.55 (0.3)	1.19
350	2.91	3.02 (0.19)	7.43 (0.4)	1.17
390	2.74	3.23 (0.2)	8.02 (0.46)	1.19

lifetime of 7 ns, which can be identified as the component observed in the solid state laser study. An increase in the second component with irradiation time is consistent with the observed trend in the A_1/A_2 values.

It seems likely therefore that freshly prepared tryptophan should not exhibit this component which is most likely a photoproduct, although the spectral distribution of fluorescence from this species must closely resemble that of tryptophan.

References

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