

PHOTOIONIZATION MECHANISM OF ACRIDINE IN AQUEOUS SOLUTION STUDIED BY LASER EXCITATION

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The present work reports results on the photoionization mechanism of acridine (Ac) induced by pulses of different durations obtained from a Nd laser.

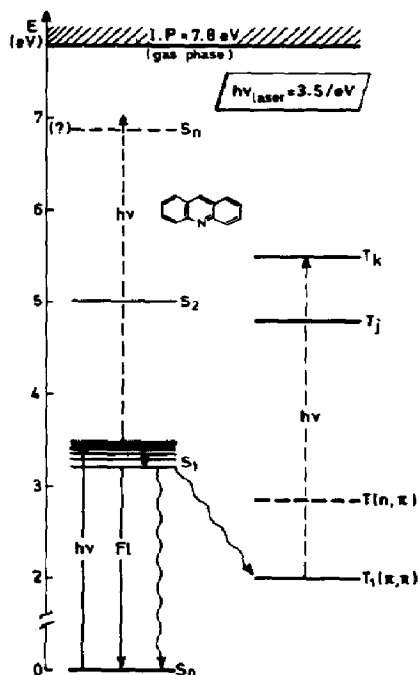


Fig. 1 - Energy level of the *S* and *T* states of Ac.

$\sim 7$ . ns and  $\sim 30$  ns fwhm. In table I values are given for the relative yields measured for the three pulses at constant and low energy (a few mJ).

The excited electronic states of acridine are shown in Fig. 1. The Nd laser third harmonic (353 nm, i.e. 3,5 eV) was used for excitation into the first excited singlet state of Ac.

Fig. 2 shows the relative hydrated electron ( $e_{aq}^-$ ) yield as a function of the laser energy. The non-linear dependence observed implies that under the present excitation conditions  $e_{aq}^-$  are formed mainly in a biphotonic process.

This observation raises the question of the nature of the intermediate states involved in the photoionization: The first excited singlet ( $S^*$ ), the lowest triplet (*T*) or both states.

In order to discriminate between the possible pathways, three different pulse durations were used:  $\sim 1.5$  ns,

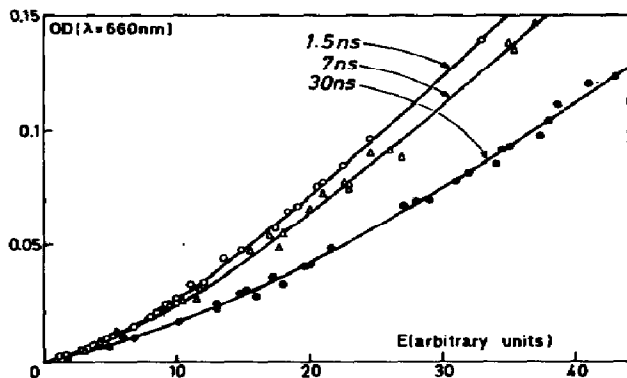


Fig. 2 - Dependence of the transient absorption of  $e_{aq}^-$  on the laser energy  $E$  for the 3 pulses : 1.5 ns, 7 ns, 30 ns.

30 ns. This trend indicates that  $S^*$  is more efficient than  $T$  as an intermediate in the biphotonic process.

To confirm the relative contribution of  $S^*$  and  $T$  to the photoionization mechanism, experiments using potassium iodide (IK) were carried out

Pulse $\tau$ (ns)	$e_{aq}^-$ yield
1.5	1
7	0.9
30	0.6

Table 1 - The relative  $e_{aq}^-$  yield as a function of the pulse duration.

increased by a factor  $\sim 1.7$  (about the same values are obtained with the three pulse durations). These experiments clearly indicate that both  $S^*$

Since the lifetime of  $Ac S^*$  in water is 10 ns <sup>(1)</sup> and the intersystem crossing rate constant only  $4 \times 10^7 s^{-1}$  <sup>(2)</sup>, it is clear that for the 1.5 ns pulse  $S^*$  is the predominant species absorbing a second photon. With the 30 ns pulse, population of the lowest triplet state is quite enhanced so that  $T$  may be partially involved in the absorption of a second photon. The results in table 1 show a significant decrease in  $e_{aq}^-$  yield when the pulse duration is changed from 1.5 to

with the three pulses at the same laser energy.  $I^-$  is a very efficient quencher of the  $Ac$  fluorescent state ( $S^*$ ) <sup>(3)</sup>: In a solution containing 0.11 M IK, about 95 % of the fluorescent state are quenched. The results are given in table 2. They show that the relative  $e_{aq}^-$  yield is lowered by a factor  $\sim 1.7$ , while the  $T$  population is

and T states are intermediates in the biphotonic process. Furthermore the decrease in the  $e_{aq}^-$  yield induced by the transfer of  $S^*$  to T implies that  $S^*$  is more efficient than T in the  $e_{aq}^-$  formation.

$[I^-]$	Fl	T	$e_{aq}^-$
0	1	1	1
0.11 M	0.05	$\sim 1.7$	$\sim 1.7$

Table 2 - *The effect of 0.11 M IK on the relative yields of fluorescence, T, and  $e_{aq}^-$  in Ac aqueous solution. The laser energy (a few mJ) is the same in all measurements.*

In conclusion, the experimental evidence given here indicates that acridine is photoionized in a consecutive two photon-mechanism, in which the intermediates are the lowest excited singlet and to a smaller extent the lowest triplet states. These experimental results are consistent with approximate calculations which have been performed for this study.

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