

ON THE IONIZATION ENERGY THRESHOLD OF AQUEOUS TRYPTOPHAN

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It has long been recognized that in photoexcited aqueous indole derivatives, the main primary photoprocess consists in electron ejection. However, the relative contribution of mono and biphotonic processes is still debated, as well as the existence of a threshold for the one photon ionization process.

The latter point has been considered and continuous irradiations with monochromatic light of variable frequency of aqueous or alcoholic tryptophan (TH) solutions, containing N_2O as an electron scavenger, have led to the following conclusions :

- i) Present findings and some literature data converge to show that the one-photon ionization of indole or TH is a threshold process .
- ii) For TH at room temperature and neutral pH, the ionization threshold energy is $I_{aq} = 4.5 \pm 0.1$ eV in aqueous solutions and 4.85 ± 0.1 eV in alcoholic solutions which corresponds to a lowering with respect to gas phase ionization potential of 3.4 and 3.0 eV respectively ; photoionization would thus take place not from the fluorescent state but from the vibrationally excited singlet state .
- iii) Above the threshold I_{aq} , the solvated electron yield is about four times higher at 250 nm than at 265 nm where $\phi_{e_{aq}^-}$ is found equal to 0.08 ± 0.025 ; from a comparison with literature data pertaining to TH degradation, it turns out that at most one photoelectron out of 4-5 which have escaped geminate recombination would be efficient in inducing TH degradation in aerated solutions. For deaerated solutions, at most one photoelectron out of ≈ 20 would promote TH decomposition.

iii) Below I_{aq} , the rupture of the indole-N-H bond has been previously observed which means that for $\lambda_{exc} \geq 275$ nm the neutral radical would derive neither from TH^+ deprotonation nor from the ion pair recombination; in aerobic conditions, the opening of the indole ring with formylkynurenine formation would not imply the superoxide ion, as previously suggested, but reactions such as $T^{\cdot} + {}^3O_2$ (or HO_2) or $TH^{\cdot} + {}^3O_2$ (or HO_2).