The Excited-State Dynamics of Kynurenine – UV Filter of the Human Eye

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Kynurenine (KN) and its derivatives act as UV-filters in the human lens. They absorb UV light in 300-400 nm spectral region and protect the eye tissues from the harmful sun irradiation. Kynurenines are weak photosensitizers and redirect the absorbed light energy into benign channels. They are characterized by a low fluorescence quantum yield and a short fluorescence lifetime, a low triplet yield and a high photochemical stability. These observations indicate the existence of a fast process deactivating the excited states of KN; the nature of this process is still unknown.

Here we report on the detailed study of the primary photoprocesses occurring in KN molecule after UV excitation. The main goals of this work are: (i) to understand the photophysical properties of the lowest excited state of KN, (ii) to establish the origin of the effective deactivation of this state and (iii) to determine the precursor of KN photoionization. The measurements were performed with the use of femtosecond and nanosecond resolved optical spectroscopy.

In aqueous solutions KN demonstrates a short fluorescence lifetime of about 30 ps which increases by more than one order of magnitude in alcohols and exceed 1 ns in aprotic solvents like DMF and DMSO. Internal conversion is shown to be the main channel of the lowest excited state of KN. The rate constant of IC is pH independent but it depends on temperature with a weakly solvent-dependent activation energy about 7 kJ/mol. The observation of a deuterium effect indicates that the hydrogen bonds are involved in the rapid decay of fluorescence in protic solvents. The nature of ultrafast deactivation is discussed in terms of a tight hydrogen-bonded complex and proton transfer from KN molecule to solvent. The obtained results show the crucial role of intramolecular charge transfer interactions in the fast IC.

The high density of UV irradiation results in the formation of KN cation radical and solvated electron. The measurements of the ionization quantum yield at different laser energies and at different excitation wavelengths show that the photoionization of KN proceeds by a biphotonic mechanism. Our experimental data speak in favor of triplet state as a precursor for KN biphotonic ionization.

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