

ESIPT from the S₂ Singlet State in the 3-Hydroxyflavone

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The proton transfer in the excited state of organic molecules and their complexes belongs to the most frequently occurred primary photoreactions. The study and understanding of such processes is of a fundamental importance for chemistry and Life Sciences as they play a key role in the main photosynthesis reactions of plants and for functioning of various biological organisms.

Spectra of the dual fluorescence of 3-hydroxyflavone, the archetype molecule appearing in ESIPT state, in ethyl acetate with picosecond time resolution were obtained at excitation within S₁ and S₂ singlet bands of absorption by 44 ps pulses of the optical parametric generator. The detection part consists of the spectrograph 2501S (Bruker Optics, USA) and the streak camera C4334-01 (Hamamatsu, Japan). The spectrograph insures spatial resolution of the analyzed light (wavelength axes), whereas the streak camera allows for temporal resolution of the light beam coming out of the spectrograph.

Spectra dynamics reveals time development of the internal proton transfer in the excited state (ESIPT) of molecule from the hydroxyl to the carbonyl group, stable ratio intensities of the normal and the tautomer bands of fluorescence is accomplished for 210 ps at excitation in the first singlet band (wavelength 340 nm). At the same time excitation in the S₂ band gives stable value of the same ratio faster, for time 170 ps, besides, the relative contribution of the tautomer form to the integral emission remains higher during all interval of emission observation. For the first time the obtained data directly evidence an additional channel of ESIPT from the S₂ singlet state of 3-hydroxyflavone, the estimates show that the probability of this process k_{n2} is very high and amounts $0.84 \cdot 10^{12} \text{ s}^{-1}$ if the value of nonradiative transitions S₂→S₁ probability in the 3HF molecule p_{n2} is equal 10^{12} s^{-1} . For estimates of k_{n2} we used the expression

$$\frac{(I_N / I_P)_{S_2}}{(I_N / I_P)_{S_1}} = \frac{p_{n2}}{p_{n2} + k_{n2}},$$

where $(I_N / I_P)_{S_2}$ and $(I_N / I_P)_{S_1}$ are the relative intensities of fluorescence emission in maxima of the normal form and the tautomer at excitation in the S₂ and S₁ bands, respectively. The relative intensities should be taken after establishing the equilibrium between both forms of the luminophor in the excited states.

The obtained results may be applied for other chemical compound appearing in the ESIPT states, some of them are specially synthesised and tested as multiparametric sensors and possess by unique properties in determination of polarity of environment, local electric fields, detection of single molecules of water in membranes and vesicles, various properties of H-bonds [1, 2]. We think that registered process of creation of photoreaction products through the S_n^N states may be concerned and other primary photoreactions, such as redistribution of the electronic density (charge transfer) in the excited state, the protolytic reactions, the intramolecular proton transfer (phototautomerization), the creation of H-bonds, excimer and exciplexes.

[1] D. Altschul, S. Oncul, A.P. Demchenko, J. Mol. Recognit. 19 (2006) 459-477.

[2] A.P. Demchenko, Analytical Biochemistry 343 (2005) 1-22.