



Spectroscopic methods for the study of energetic characteristics of the normal and photoproduct forms of 3-hydroxyflavones

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ABSTRACT

We report spectroscopic properties of 3-hydroxyflavone (3-HF) and 4'-N,N-dimethylamino-3-hydroxyflavone (DMA3HF) in acetonitrile and ethyl acetate at different temperatures in the range from 10 °C to about 67 °C. These compounds are characterized by excited-state intramolecular proton transfer (ESIPT) which leads to occurrence of two forms of these molecules. For this reason their fluorescence spectra have two bands which correspond to emission of normal and photoproduct (tautomer) forms. The correlation between ratio of integrated intensity of these two bands and inverse absolute temperature (the Arrhenius plot) have been applied to estimate energetic properties, such as difference between energy levels of excited states as well ground states for normal and tautomer forms for each molecule.

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1. Introduction

Flavonols are a class of organic compounds which play significant role in a wide spectrum of biological and chemical processes [1–4]. The last researches show that they play important role even in microevolution of plants [5]. It explains a high scientific interest for study various derivatives of flavonols [6–10] including study of their optical and spectroscopic properties [11–13]. Moreover, they are actively applied in medical, chemical and biological researches as non-toxic spectroscopic probes and indicators of different biochemical parameters, such as pH, concentration of salts, etc. [14–22]. 3-Hydroxyflavone (3-HF) is a basic structural element of flavonols family. This one and some other its derivatives are characterized by dual band emission spectrum due to the excited-state intramolecular proton transfer (ESIPT), which occurs in such molecular systems [16, 20, 21, 23–27]. Ones of the first works, which had described ESIPT in 3-HF, were carried out by P.K. Sengupta and M. Kasha [26, 27]. Moreover, a wide spectrum of organic compounds is characterized by ESIPT [28–30], including new synthesized classes of proton-transfer molecules [31], what allows to use such components in various applications.

ESIPT leads to appearance of photoproduct, which is also called tautomer. This process is described by widely known four-level energy scheme (see, e.g., [15, 23]), which is depicted in Fig. 1. Two levels correspond to ground (N) and excited (N*) states of molecule normal form

and another two levels correspond to ground (T) and excited (T*) states of photoproduct (tautomer form of molecule). Activation energy of proton transfer process and difference between energy levels of excited states of normal and tautomer forms can be estimated using the Arrhenius equation. It gives temperature dependence of the reaction rate constant. The Arrhenius equation is widely used to make the energetic characterization of isomerization and charge transfer processes in various compounds through spectroscopic measurements [32]. For instance, this method had been applied in studies of photoisomerization [33], twisted intramolecular charge transfer [34], trap-mediated charge transfer [35], ESIPT [36–38] and others [39, 40].

In this paper it was studied temperature dependence of emission spectra of 3-HF and 4'-N,N-dimethylamino-3-hydroxyflavone (DMA3HF), the chemical structure of which is shown in Fig. 2. Emission of DMA3HF is also characterized by two bands in the spectrum due to ESIPT. However, the presence of two methyl groups in DMA3HF leads to changing in difference between excited states energy levels of normal and tautomer forms in comparison with 3-HF. The measurements of steady-state emission spectra of 3-HF and DMA3HF at different temperatures allow one to estimate impact of the methyl groups on the above-mentioned parameter. Using the Arrhenius plot it was found the value of this energy difference for the both compounds. The obtained results may be used to make a suggestion about the degree of reversibility of the proton transfer reaction in each molecule.

Difference between excited states energy levels of the normal and tautomer forms can be used to predict whether the ESIPT reaction will be probably reversible or irreversible. The increase in this difference

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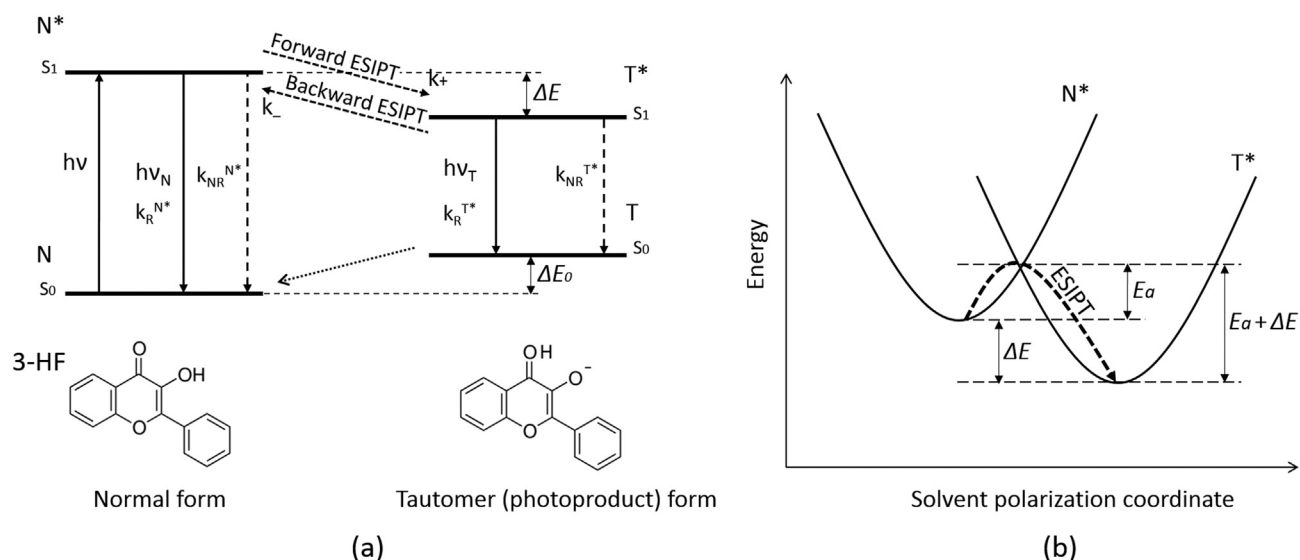


Fig. 1. (a) The four-level energy scheme with rates constants k of ES IPT process and the chemical structures of normal and tautomer forms of 3-HF. R and NR indexes at rates constants indicate radiative and non-radiative transfers. (b) Excited states energy levels for normal (N^*) and tautomer (T^*) forms. E_a is activation energy of the forward ES IPT which could be considered also as a solvent-induced energy barrier. $E_a + \Delta E$ is activation energy of the backward ES IPT.

prevents the backward proton transfer. For this reason, the study of the energetic characteristics is of interest in researches of charge transfer reactions reversibility [36, 41].

The obtained results show that the activation energy of backward ES IPT reaction in 3-HF is significantly greater than analogical parameter in DMA3HF. It allows to conclude that degree of proton transfer reversibility in 3-HF is less than in DMA3HF which is in agreement with results obtained in other works [36, 42].

2. Materials and Measurements

3-HF (purity $\geq 98\%$) was purchased from INDOFINE Chemical Co., Inc. (Hillsborough, NJ, USA). DMA3HF was synthesized by the research group of Prof. V.G. Pivovarenko at T. Shevchenko National University in Kyiv. It was obtained by means of the Algar–Flynn–Oyamada reaction [43–45] from 2-hydroxyacetophenone and the corresponding benzaldehyde. Absorption spectra were measured on the Hitachi U-2810 UV–Vis spectrophotometer at room temperature (about 21 °C); emission spectra were obtained on the Hitachi F-2500 fluorescence spectrophotometer at range of temperature from 10 °C to ≈ 67 °C.

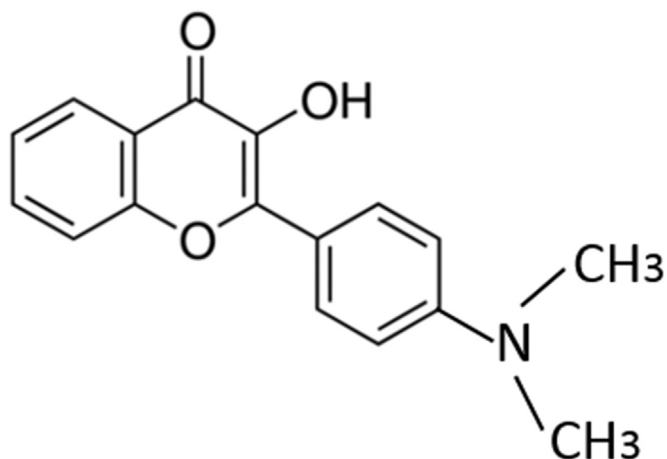


Fig. 2. The chemical structure of 4'-N,N-dimethylamino-3-hydroxyflavone (DMA3HF).

All emission spectra, which are presented in this paper, have been corrected for the wavelength dependence of the sensitivity of the instrument. Temperature of the studied samples was controlled by the Temperature sensor 016i (range: -18 °C to 110 °C; resolution: 0.07 °C; produced by CMA, the Netherlands) which was connected to the ULAB datalogger.

Acetonitrile and ethyl acetate were used as solvents. They were of the highest grade commercially available for spectroscopy (from Sigma-Aldrich). Additionally all solvents were checked for lack of fluorescent impurities in the wavelength ranges of interest. The dye concentration in the prepared samples was controlled by absorption measurements. Absorption at the maximum for all studied samples is not exceed 0.2 absorbance in 1 cm cuvette. The molar extinction coefficient of 3-HF is about $1.6 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ at the absorption maximum (about 350 nm) [46]. It means that concentration of 3-HF in the sample is $< 1.3 \times 10^{-5} \text{ M}$. The concentration of DMA3HF in the studied samples is in the range of $10^{-6} - 10^{-4} \text{ M}$.

3. Theoretical Section

Consider a typical case when the ES IPT molecule is excited at wavelength, which corresponds to the absorption band of normal form N, and describe this reaction based on theoretical explanation, which is given in [36]. Neglecting effect of the collisional quenching of the fluorescence, the balance equations [36] for the steady-state regime can be written as

$$(k_R^{N^*} + k_{NR}^{N^*} + k_+) [N^*] = k_- [T^*] + B_a u_{ex} [N_0], \quad (1)$$

$$k_+ [N^*] = (k_R^{T^*} + k_{NR}^{T^*} + k_+) [T^*], \quad (2)$$

where $[N_0]$, $[N^*]$, $[T^*]$ are the concentrations of the ground state of normal form N_0 and the excited states of normal N^* and tautomer T^* forms of the molecule, respectively; k_+ and k_- are the forward and backward ES IPT constant rates, respectively; these and other constant rates are shown in the Fig. 1, R and NR indexes at rates constants indicate radiative and non-radiative transfers; u_{ex} is a density of excitation radiation; B_a is the Einstein coefficient for the absorption process.

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