

The spectral and kinetic properties of molecular systems with ESIPT in studies of charge transfer reversibility, complex formation and polymerization processes

Abstract

Excited state intramolecular proton transfer (ESIPT) is a process of proton transfer occurs via an intramolecular hydrogen bonding bridge between the proximate proton donor and acceptor groups in the photoexcited molecule. It causes the occurrence of two molecular forms: the normal and the tautomeric species. This reaction is among the fundamental intramolecular processes taking place in various molecules. Therefore, a study of compounds with ESIPT is of significant scientific interest. This work focuses on photophysical properties of molecular systems with ESIPT and their applications in investigations related to complexation processes and monitoring photoinitiated polymerization reactions.

In this thesis, the theoretical description of ESIPT mainly from the photophysical point of view has been provided. The approach to investigate some characteristics of a molecular energy structure has been proposed for compounds with ESIPT. It is based on steady-state fluorescence spectroscopy. The difference between the energy levels of excited states of the normal and tautomeric forms has been defined for 3-hydroxyflavone (3-HF) and 4'-N,N-dimethylamino-3-hydroxyflavone (DMA3HF). Also, the difference between the energy levels of ground states has been estimated for both forms of these molecules.

The methodology to determine the degree of reversibility of ESIPT has been established and applied in the cases of 3-HF and DMA3HF. The proposed method involves time-resolved spectroscopy to determine fluorescence lifetimes and emission kinetics for the normal and tautomeric molecular forms. It has been demonstrated that the analysis of this data allows concluding whether the proton transfer is reversible or irreversible. For this purpose, the ratiometric parameter

has been introduced as a ratio between intensities of emissions of the normal and tautomeric forms. It has been found that the ESIPT process is irreversible in the case of 3-HF (dissolved in methanol) and it is reversible in the case of DMA3HF (in ethyl acetate).

Also, the approach to characterization of complexation reactions between ESIPT molecules and ions has been provided theoretically. Its application has been shown in the case of complexation between 3-HF molecules and lithium cations. For this case, the stability constant has been estimated and the obtained results show good agreement with the data reported in other works.

Moreover, the other discussed issue concerns a monitoring of photoinitiated polymerization reactions using ESIPT-based fluorescent probes. It has been shown how compounds with ESIPT can be applied for this purpose, and the practical example of 3-HF application for photopolymerization control in real-time mode has been demonstrated.

In this way, this work provides a theoretical framework and practical examples of application of molecular systems with ESIPT, and in particular flavonols, in investigations of complexation processes and in monitoring photoinitiated polymerization reactions.