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REGULAR ARTICL

Excited-state proton transfer and charge transfer study in 6-amino-2-(2′-methoxyphenyl)benzoxazole

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Abstract : The proton transfer coupled charge transfer in the excited state of 6-amino-2-(2′-methoxyphenyl)benzoxazole (6A-MBO) were investigated, using the time-dependent density functional theory with IEFPCM model by choosing n-heptane and dichloromethane (DCM) as solvent. The primary bond length and angles, the frontier molecular orbitals, absorption and fluorescence spectrum and the potential energy curves in the ground and excited state were calculated. The simulated absorption spectra were found to accord with the experimental data, which suggested that the calculated method is valid. And the fluorescence spectra show a normal Stokes shift, which gradually became larger with increasing the solvent polarity. This indicated that the charge transfer process taking place in the 6A-MBO upon photo-excited. The calculated frontier molecular orbitals confirmed the fact that the intramolecular proton transfer was promoted by charge transfer and redistribution. From the construction of two abrupt veers on the excited-state potential energy curves of 6A-MBO in both n-heptane and dichloromethane (DCM) solvent, it can be concluded that the ESIPT of 6A-MBO cannot happen in the excited state, only charge transfer occurred by photo excitation.

AMS subject classifications: 65D18, 78M50; 74E40

Keywords: 6-amino-2-(2′-methoxyphenyl)benzoxazole (6A-MBO), Proton transfer, Charge transfer.

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1. Introduction

N.J.Turro has pointed out that the study of photochemical concentrates on chemical behavior and physical process of the electronic excited-state molecules [1]. It is easy for the excited-state molecules in the high energy and unstable state to release energy and then back to the relatively stable ground state in various ways. These behaviors of the excited state molecular were known as the deactivation process, in which the excited-state molecules release energy, and it could occur within a single molecule and also between the molecules [2]. It is worth to mention that hydrogen bonding play an important role in these processes. In the past decades, studies of hydrogen were mainly concentrated in the thermodynamic properties of hydrogen and the nature of the bonding issue [3-6]. With Han et al proposing the excited-state hydrogen bond dynamics [3,4,7-12,23,25,52-54], it attracted more and more attention in both theoretical and experimental ways. The studies mentioned above further explain the luminescence materials fluorescence or phosphorescence emission problems [12-16], intermolecular and intramolecular charge transfer [17-27], excited state proton transfer [28-30], intersystem crossing [14-16] and so on. The explore of these problems would facilitate physical chemists in understanding the essence of the hydrogen bonds by studying the interaction between light and hydrogen bonding, and help organic chemists design more kinds of stable and efficient luminescent material. Excited state proton transfer (ESPT) is an important reaction of photochemical and light physical process, and a hot topic in the field of dynamics. The target molecular could produce isomers after the proton transfer. This feature of the target molecular attracted researchers to design, and applied to light-emitting diodes (leds), laser fuel and ultraviolet filter [31-35], etc. Charge transfer is another important topic in biological, chemical and physical fields. Photo-excited charge transfer reaction is the basis of the solar energy conversion, widely applied in the field of solar cells [36-40]. As a result, the theoretical and experimental researches on proton and charge transfer are continuous.

6-amino-2-(2′-hydroxyphenyl)benzoxazole (6A-HBO) and its derivative which are typical intramolecular proton transfer dye show remarkable changes in the ESIPT process and correlated spectroscopy, due to it has both proton donor (-OH) in the phenol part and the proton acceptor (-N=) in the benzazole ring. It has been studied comprehensively by Cukier group and Gutierrez group from theory and experiment; they studied the problem of couple proton and electron transfer from different perspectives [41-44]. However, 6-amino-2-(2′-methoxyphenyl)benzoxazole (6A-MBO) as a kind methoxy derivative of 6A-HBO did not attract a lot of attention. Only Alarcos et al. researched the subtle associations between intramolecular proton transfer and charge transfer; it showed that 6A-MBO cannot undergo an ESIPT process [42]. To understand the behavior of 6A-MBO better, we study the excited-state charge and proton transfer mechanisms of 6A-MBO in