Time-dependent density functional investigation on electronic spectra of 4′-N-dimethylamino-3-hydroxyflavone

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Abstract

The lower singlet excited states for 4′-N-dimethylamino-3-hydroxyflavone (DMA3HF) have been investigated. Theoretical calculations have been performed by using time-dependent density functional theory. The B3LYP and MPW1PW91 functionals with 6-31G(d,p) basis set have been used to compute transition energies. Ground-state geometries are optimized by using density functional theory with both B3LYP and MPW1PW91 functionals combined with 6-31G(d,p) basis set. The first excited state geometries are optimized by using configuration interaction all single-excitations methods with 6-31G(d,p). Vertical absorption energy and excited state electronic dipole moments calculations show that the singlet excited states S_1 of the normal of DMA3HF has the character of a large charge separation and effective charge transfer. Calculated emission energies for both the normal and tautomer show a large Stokes shift between the absorption and fluorescence maxima. The present calculations suggest that DMA3HF appears dual fluorescence in gas phase. Our results obtained explain the strong 'dual-fluorescence' feature that involves the excited-state intramolecular proton transfer and charge transfer of DMA3HF.
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1. Introduction

Proton tautomerism plays an important role in many fields of chemistry and biochemistry. The interest is explained by possible applications as electro-optical switches, chemical sensors, and fluorescence probes [1–7]. 4′-N-Dimethylamino-3-hydroxyflavone (DMA3HF) is one of the most intensively studied model compounds that undergo excited state intramolecular proton transfer (ESIPT) [8–17]. The important feature is the presence of two well-resolved bands in fluorescence emission spectra in both polar and weakly polar solvents like dimetylsulfoxide (DMSO) and decalin [13]. This behavior has been interpreted as normal emission (CT fluorescence) and the tautomer species emission (PT fluorescence). The relative contribution of two emission bands depends on the nature of

the solute's environment [16]. However, the nature of the ground and excited state is still unclear at molecular level.

The time-dependent density functional theory (TDDFT) is now well known as a rigorous formalism for the treatment of transition energies within the DFT framework [18–22]. However, the performance of TDDFT should be assessed by numerical application, due to the approximate nature of exchange-correlation functionals used [23]. It has been estimated that TDDFT often has difficulty with CT states. The assessment of the TDDFT method in calculating absorption energies for CT excited states has been discussed [24–26]. The data reported recently indicate that the computed energy gaps seem reasonable with respect to the experimental results even in cases where the excited state has CT character [27–29].

In the present work, electronic spectra of DMA3HF have been investigated using TDDFT method. For DMA3HF, experimental absorption and emission energies are known in non-polar solvents such as cyclohexane and n-hetane. Generally, nonpolar solvent has less influence on the nature of spectra of DMA3HF, allowing thus a direct comparison between computed and experimental results. The structure

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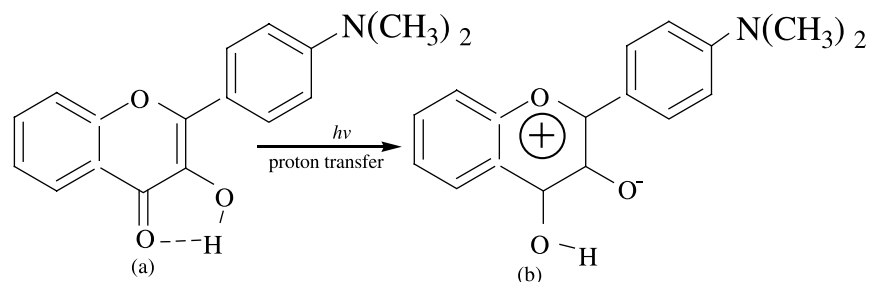*E-mail address:* sibitannin@163.com (B. Shi).

Fig. 1. Structures of the normal species (a) and tautomer (b) of DMA3HF.

of normal and tautomer forms and the corresponding relation are shown in Fig. 1.

2. Computational details

All calculations have been performed by using the Gaussian 98 package [30]. Ground state geometries of normal (N) and tautomer (T) forms of DMA3HF have been obtained by using DFT with both B3LYP and MPW1PW91 functionals combined with 6-31G(d,p) basis set. In the mean time, excited state geometries of DMA3HF have been optimized by employing the configuration interaction method including only single excitations (more often indicated as CI-singles, CIS) with 6-31G(d,p) basis sets. The functional and basis set used to calculate absorption spectrum in gas phase are the same as those used in the geometry optimization. The dipole moments for excited states are computed by using the one-particle density matrix. The fluorescence spectra of DMA3HF are calculated by using the same method as absorption spectra based on the excited state structure optimized by CIS.

3. Result and discussion

3.1. Optimization of geometries

Experimentally, the dynamic process of excited state proton transfer in DMA3HF has been investigated by nano- and picosecond laser spectrocopies [17,31]. The non-negligible normal emission in alkane solvents at room temperature has been interpreted by an exited-state equilibrium between the normal and tautomer associated with a rapid proton tunneling mechanism [10]. After optical excitation, the normal form undergoes ultrafast transfer of a proton from the hydroxyl group to the carbonyl oxygen (see Fig. 1), resulting in the appearance of a phototautomer emission band [31]. The structure of the normal form in the ground state has been confirmed by quantitative element analysis, proton magnetic resonance (PMR), UV–visible and infrared (IR) spectrometry [13,14], and the ground state tautomer has been detected by the transient absorption [31].

Theoretically, we obtained the stable ground structures by DFT method with both B3LYP and MPW1PW91 functionals combined with 6-31G(d,p) basis set, and the corresponding first excited state structures by CIS.

Optimized ground state and excited state geometries of both normal form and tautomer of DMA3HF were depicted in Fig. 2. A part of the structure parameters was filled in Fig. 2 (the C–H bond lengths are omitted). It can be noted that the optimized geometry is nearly planar, and the dihedral angle between the plane of the dimethylamino moiety and the phenyl of the DMA3HF molecule is about 4° for both the normal form and tautomer. From the calculated result of DMA3HF(N), bond lengths of phenyl ring C–N and all the three C–O in excited state are much longer than those in ground state, about 0.017–0.033 Å. Whereas, for the tautomer, the bond-lengths of the proton accepting C–O bond and phenyl ring C–N in the excited state are 0.032 and 0.035 Å longer than those in ground state. The ground-state dipole moments of the normal form and tautomer of DMA3HF are calculated to be 5.30 and 5.16 D at B3LYP/6-31G(d,p) level, 5.34 and 5.17 D at MPW1PW91/6-31G(d,p) level, respectively, which indicate the unsymmetrical charge distribution at the ground state.

3.2. The calculated absorption spectra

Experimental absorption spectra and calculated absorption energies as well as dipole moments and oscillator strengths were presented in Table 1. Molecular orbitals of the electronic ground state structure and of the excited state geometries were displayed in Fig. 3.

First, we discuss the gas-phase absorption of DMA3HF(N). An analysis of the TDDFT wave function shows that the first excited state (S_1) is described by the HOMO→LUMO transition (see Fig. 3 (a)), referred in the literature as charge transfer (CT) state [10]. HOMO is a π-type orbital included a strong mixing with the lone-pair orbital of the amine nitrogen, while LUMO is a π^*-type orbital (see Fig. 3). Thus, the S_1 state, corresponding to $\pi \rightarrow \pi^*$ transition, is a partial CT one characterized by electron transfer mainly from the $4'$-dimethylaminophenyl part to the chromone one. It could be demonstrated further by the fact that in the optimized S_1 state (see Fig. 2) the bond length of