

REGULAR ARTICLE

Change in Energy of Intermolecular Hydrogen Bonds Upon Excitation of Coumarin 120 in Water: A Combined Time-dependent Density Functional Theory / Effective Fragment Potential Study

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Abstract: Hydrogen bonding (HB) sites of 7-amino-4-methylcoumarin (C120) in water are investigated theoretically using density functional theory (DFT) interfaced with the effective fragment potential (EFP) method of salvation. The original EFP model (EFP1) is used to form C120-(H₂O)₇ complex. Six HBs are formed by C120 with water molecules; one A-type (N··H-O), two B-type (C=O··H-O), two C-type (N-H··O) and one HB (O··H-O) similar to B-type. Excited state properties are computed using time dependent density functional theory (TDDFT) combined with the polarizable continuum model (PCM) and EFP1 method. In S1 state, A type HB energy is increased by 10.18 kJ mol⁻¹, whereas B and C type HB energies are decreased by 6.31 and 11.52 kJ mol⁻¹, respectively.

AMS subject classifications: 74E40, 78M50

Keywords: TDDFT, EFP, B3LYP, HB, C120-(H₂O)₇ complex.

1. Introduction

The hydrogen bond interaction in both the ground and excited-states, play a fundamental role in the photochemistry of organic and biological chromophores in solution [1-12].

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Several theoretical [13-21] and experimental [22-27] investigations were performed to determine the intermolecular hydrogen bonds, including their structure, energy in the ground state, and energy change upon electronic excitation of molecules. The excited-state HB weakening can heighten the excitation energy of a related excited state and induce an electronic spectral blueshift, whereas the excited-state HB strengthening can lower the excitation energy of a related excited state and induce an electronic spectral redshift [15, 28, 29]. Apart from the influence of the solvent polarity and polarizability, HBs formed between the probes and solvents also influence their structure and photophysical properties [30-34]. The formation of hydrogen bonds can often lead to the appearance of new individuals like S_0 -complexes and S_1 -exciplexes [35-40].

The EFP method [41-44] provides a polarizable QM-based force field to describe intermolecular interactions. The EFP method embedded with PCM, have been applied successfully to QM/MM studies of molecules in clusters and in solution. The interface of the EFP model with the TDDFT method has been developed for describing electronically excited states of solvated molecules [44-47]. The combined linear response TDDFT (LR-TDDFT) method with the original EFP model (EFP1) was applied successfully to calculate the change in HB energy of aminocoumarins in water [13, 14, 21].

The aminocoumarin molecules represent an important class of organic compounds with extensive and diverse applications [48-51]. They possess distinct biological activity [51] and have been indicated as agents with potential antibiotic, anticancer and anticoagulant activity. They exhibit strong fluorescence in the visible region (from 350 nm to 500 nm), which makes them suitable for use as laser dyes and nonlinear optical chromophores. Aminocoumarins can form one A type HB and two B type HBs due to hydrogen-bond donor properties of electronegative heteroatoms N and O, and two C type HBs via the participation of amino hydrogen atoms with oxygen atom of water molecules [11].

TDDFT/EFP1 calculations have been performed to study the spectral properties and HB dynamics of aminocoumarins [1, 2, 9, 10, 12-14, 21]. The excited-state hydrogen bonding dynamics of aminocoumarin molecules in water have been studied, [12,13,14,21] and demonstrated that A type HB is the strongest in the ground state and it is extremely weakened in an excited state, whereas B and C type HBs are strengthened in the excited state as compared to ground state. A TDDFT/EFP1 study of hydrogen bonding dynamics of C151 in water shows the formation of additional HB between the oxygen atom of pyrone ring and hydrogen of a water molecule [21].

In the case of C120, there are at least six sites for HB formation with protic solvent molecules as shown in Figure 1; one intermolecular HB $N\cdots H-O$ (type A) is formed by the amino group of C120 with one water molecule, two intermolecular HBs $C=O\cdots H-O$ (type B) are formed by the carbonyl group of C120 with two water molecules, and two HBs of N-