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## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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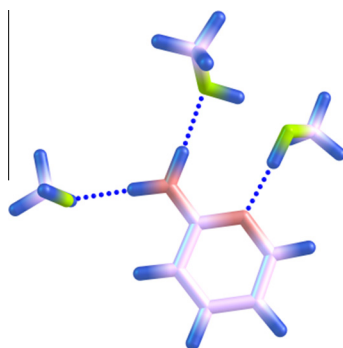
## Effects of hydrogen bond on 2-aminopyridine and its derivatives complexes in methanol solvent

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## HIGHLIGHTS

- Intermolecular hydrogen bond is strengthened in excited state.
- Multiple hydrogen bond enhances the hydrogen bond binding energy.
- Three kinds of binding sites and seven kinds of binding modes are reported.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 2 March 2014

Received in revised form 14 April 2014

Accepted 22 April 2014

Available online 30 April 2014

## Keywords:

Frontier molecular orbitals

Electronically excited state

Infrared spectra

Fluorescence spectrum

Intermolecular hydrogen bond

## ABSTRACT

In the present work, the time-dependent density functional theory (TD-DFT) method was adopted to investigate the excited state hydrogen-bond dynamics of 2-aminopyridine monomer (2AP) and its derivatives in hydrogen donating methanol solvent. The calculated steady-state absorption and fluorescence spectra agree well with the experimental results. Theoretical results state that the bond lengths of both O–H and N–H bands are lengthened, while the intermolecular hydrogen bond lengths are shortened in the excited state. Further, the intermolecular hydrogen bonds are proved to be strengthened according to the calculated binding energy. As a reasonable explanation, the hydrogen bonds binding energy increases with multiple hydrogen-bonding interactions in the electronically excited state. In addition, the hydrogen bonding dynamics in the excited state were visualized by the spectral shifts of vibrational modes. The calculated infrared spectra of both O–H and N–H stretching vibrational regions revealed that the O–H and N–H stretching bands red-shift.

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## Introduction

The excited state relaxation has not only been recognized for its importance in physics, chemistry, and biology, but also it is of paramount importance in the photochemical process [1–7]. Relatively important part of it can be induced through intermolecular

hydrogen bond. The excited-state dynamics of hydrogen-bonded complexes occurs on ultrafast time scales mainly set by vibrational motions of the hydrogen donor and acceptor groups. A number of studies have been studied about the vibrational motions of hydrogen-bonded excited-state dynamics by Han and co-workers [8–10]. Indeed, the solute–solvent interactions play a significant role for molecular nonequilibrium processes in liquids, and many experimental researches of it have been tested. Subsequently,

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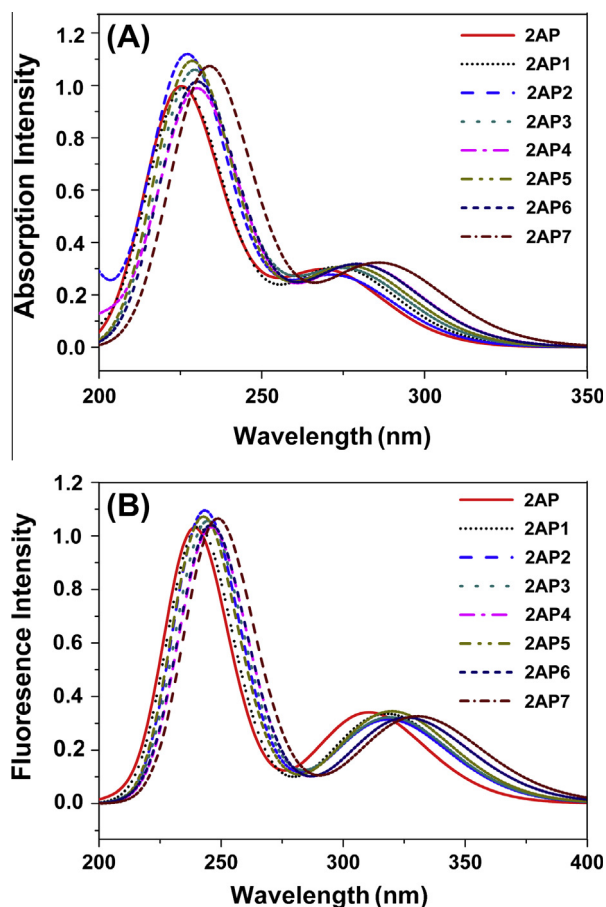


Fig. 1. The calculated absorption and fluorescence spectrum of the 2AP and its derivatives in methanol.

many a theoretical methods have been adopted to explain the phenomenon obtained from experiments [11–17].

2-Aminopyridine (2AP) is a heterocyclic molecule containing two nitrogen atoms, and it can be used as a model molecule for studying the photo-physics of biomolecules. Further, its dimer has been deliberated from the viewpoint of a nucleobase pair [18]. Several studies on clusters of 2AP with methanol, H<sub>2</sub>O, ethanol, and threshold photoionization spectroscopy have been reported by Hager and Wallace [19,20]. The resonant two-photon ionization spectrum of the 2AP dimer near by the electronic origin of the S<sub>0</sub> to S<sub>1</sub> transition and the red shift rationalized by a strengthening of the dimer bonds in electronic excited state have been reported by them. However, multiple hydrogen-bonding interactions and the influence bringing from multiple intermolecular hydrogen bonds in methanol are known fewer. In this study, we have investigated the 2AP and its derivatives complexes adopting the density functional theory (DFT) method for optimizing ground state and TD-DFT method for the calculations of the excited state minimum geometries, IR spectrum, and steady-state absorption and fluorescence spectra in methanol. Three kinds of binding sites and seven kinds of binding modes have been considered from the optimized geometries, and further we focused our attention on the changes of intermolecular hydrogen bonds among these 2AP derivatives complexes.

### Computational details

In the present work, the ground state and electronically excited state geometric optimizations were performed using the density

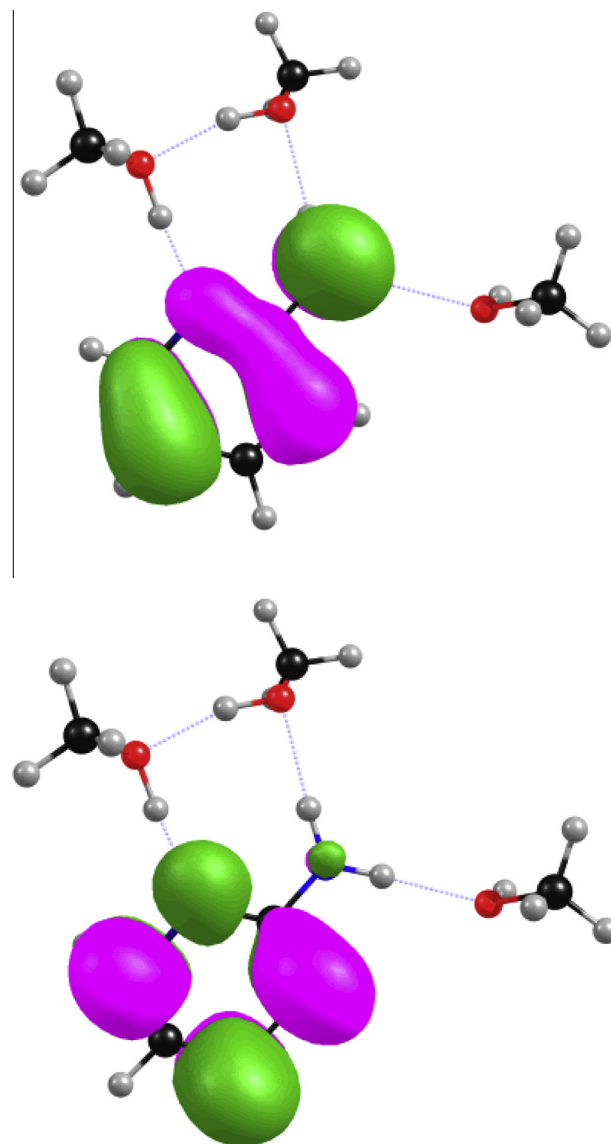


Fig. 2. Frontier molecular orbitals (MOs) of the hydrogen-bonded 2AP7 complex.

functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, respectively [21–24]. Becke's three-parameter hybrid exchange function with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) and 6-311+G (d) basis set were used throughout. There were no constraints to all the atoms, bonds, angles or dihedral angles during the geometric optimization. To evaluate the solvent effect, methanol was used as solvent in the calculations depended on the model of Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM). All the local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations. Fine quadrature grids of size 4 were also employed.

Harmonic vibrational frequencies in ground state and the excited state were determined by diagonalization of the Hessian. The excited-state Hessian was obtained by numerical differentiation of analytical gradients using central differences and default displacements of 0.02 Bohr. The infrared intensities were determined from the gradients of the dipole moment. All the electronic calculations were carried out depending on the Gaussian 09 program suite [25].

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