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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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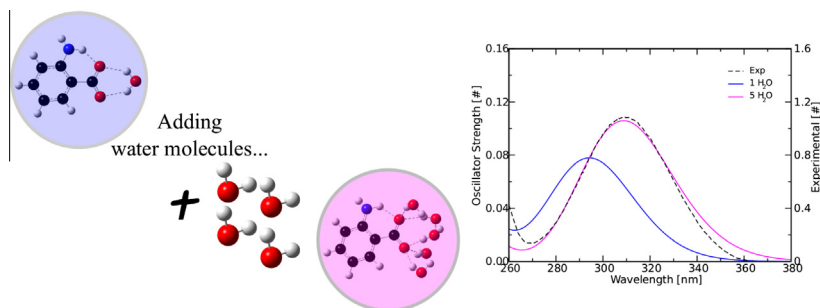
## Microhydration effects on geometric properties and electronic absorption spectra of *ortho*-aminobenzoic acid

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### HIGHLIGHTS

- Simulation of the theoretical electronic absorption spectra of *ortho*-aminobenzoic acid by TD-DFT.
- Use of microhydration and PCM models to obtain spectra in aqueous medium.
- Analysis of geometric properties as well as intermolecular and intramolecular hydrogen bonds.
- When more water molecules surround *ortho*-aminobenzoic acid, the spectrum resembles the experimental data more closely.
- Microhydration and PCM models are necessary to fit the spectrum correctly.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 26 November 2014

Received in revised form 20 March 2015

Accepted 27 March 2015

Available online 2 April 2015

#### Keywords:

*ortho*-Aminobenzoic acid

Microhydration

Implicit and explicit solvation

TD-DFT

Absorption spectra

### ABSTRACT

TD-DFT and a combination of polarized continuum model (PCM) and microhydration methods helped to simulate the optical electronic absorption spectrum of *ortho*-aminobenzoic acid (*o*-Abz). The microhydration method involved the use of different numbers, from 1 to 5, of first solvation layer water molecules. We examined how implicit and explicit water affected the energies of the HOMO–LUMO transition in the *o*-Abz/water systems. Adding until five water molecules, the theoretical spectrum becomes closer to the experimental data. Microhydration combined with the PCM method leads to agreement between the theoretical result for five water molecules and the experimentally measured absorption bands.

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### Introduction

The *ortho*-aminobenzoic acid (*o*-Abz) or anthranilic acid plays an important role in the pharmaceutical industry: some of its

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derivatives have been tested as a novel class of inhibitors of Hepatitis C NS5B Polymerase [1]. *o*-Abz also exhibits several biological and biochemical activities; for example, it is a constituent of lenticular pigmentation in humans and some diurnally active animals [2], it is a component of media used to grow some fungal species, and it induces changes in pigmentation [3] that will further aid microorganism identification. Besides these applications, *o*-Abz presents convenient spectral properties that allow for its widespread use as a fluorescent probe in peptides [4] and

substrates during protease assays, a result of energy transfer to an acceptor group labeling the same substrate [5]. Several reports have demonstrated that the *o*-Abz spectral features are sensitive to the polarity and donor properties of organic solvents [6]. Many authors have used *o*-Abz to monitor how it interacts with amphiphilic membrane aggregates [7,8]. Depending on pH, *o*-Abz displays three different absorption bands, a consequence of the protonation or not of its carboxyl and amino groups. This is relevant when one wishes to employ *o*-Abz bound to an alkyl chain to probe local membrane surface pH [9].

Theoretical studies based on implicit solvation models have also contributed, to the characterization of *o*-Abz in gas phase [10] and in aqueous solvent [11]. The use of the polarizable continuum model (PCM) generally improves the calculation of spectroscopic data like the absorption and emission spectra [11–13].

The amino and carboxy groups in *o*-Abz can establish an intramolecular hydrogen bond (H-bond) and this bond have been studied in the ground and excited states [14,15]. Intermolecular H-bonds can also stabilize the *o*-Abz/water system, which affects the electronic spectra [16,17]. Furthermore, researchers have conducted theoretical calculations using the B3LYP/TZVP level to investigate the electronic properties of *o*-Abz as it interacts with increasing number (1–3) of water molecules [18,19]. This model improved on the PCM model because it was not possible to fit the computational characterization of the *o*-Abz structural and spectroscopic properties with experimental data by using only the implicit representation of the solvent, especially in the case of protic solvents in which the H-bond interaction plays a relevant part [20–23].

The objective of this work is to understand how the first water solvation shell in the polar region of *o*-Abz affects the absorption spectra. To do so, we applied two methodologies to calculate the optical absorption spectra of *o*-Abz in neutral pH. The first method involved explicit solvation provided by the microhydration model; the second method relied on the addition of solvent effects to the *o*-Abz–water complexes using (PCM). We compared theoretical results with the experimental data to find out whether the combination of both methods would furnish good agreement and to evaluate their separate contributions to the absorption spectra.

## Methodology

*o*-Abz geometry was optimized in the anionic protonation ground state, which corresponded to neutral pH. The initial position of the water molecules was obtained by molecular dynamics (MD) simulation performed with an OPLS/AA force field, for 10 ns with steps of 1 ps. The water molecules were chosen according to its distance to the polar region of the *o*-Abz. To prepare the *o*-Abz molecule for the molecular dynamics simulation (MDS), the charges were calculated using the ChelpG model. The topology was generated by Mktop and all the parameter values were taken from the OPLS/AA FF based on its quantum-mechanical geometry. The NpT ensemble was applied using a temperature of 298 K and pressure of 1 bar. The molecular modeling package GROMACS (v. 4.5.x) was used to conduct MD simulation.

Different computational models were tested by combining functionals/basis set. Therefore, the B3LYP, WB97XD, CAM-B3LYP and PBE functionals were tested. The following basis set: 6–31G(d,p), 6–311++G(d,p), TZVP and aug-cc-pVDZ were applied to the systems. However the results that better fitted the experimental spectra were obtained with the B3LYP/TZVP model.

The B3LYP/TZVP [24,25] computational model was employed to optimize the geometry and vibrational frequencies in the gas phase. Calculations were made using one to five water molecules. All the systems were local minima, as verified by vibrational analysis.

The electronic transition calculations were performed using TD-B3LYP/TZVP. The Gaussian09 suite of software was used [26], and the results were analyzed with GaussView 5.0 [27] and Chemission [28].

The BSSE calculations were done for the systems containing one and two water molecules. For the other systems we estimated the BSSE error based on the error for the systems with one and two water molecules.

*o*-Abz was purchased from Sigma Aldrich (Steinheim, Germany). A concentrated *o*-Abz stock solution ( $10^{-3}$  mol L $^{-1}$ ) was prepared in phosphate buffer 15 mM and pH 7.35. The absorption spectra were acquired on a spectrophotometer *Ultrospec 2100 pro*. Diluted solutions (around  $4 \times 10^{-4}$  M) were employed in the experiments.

## Results

Geometry optimization in the gas phase revealed that *o*-Abz was planar (Fig. 1). The presence of water molecules altered the distances and angles between the atoms in the *o*-Abz molecule. The donor group (NH $_2$ ) and the acceptor group (COO $^-$ ) established an intramolecular H-bond (N–H15...O9). This H-bond distance increased with water addition from 1.747 Å without water to 1.853 Å in the presence of five water molecules (Fig. 2). Therefore, formation of H-bonds between water and *o*-Abz weakened the intramolecular H-bond.

Microhydration also modified the *o*-Abz geometry (Table 1). The (N7–H15) bond length increased from 1.018 to 1.026 Å upon solvation with one water molecule. Further microhydration shortened this bond to 1.016 Å when five water molecules surrounded the carboxy region. Comparison with the constant (N7–H16) bond length indicated that these changes originated from solvation. On the other hand, the (C8–O9) bond length did not have a monotonic behavior but oscillated between 1.260 and 1.264 Å.

Microhydration reduced the distances between the amino group and the benzyl ring and between the benzyl ring and the carboxylate group as seen from the changes in C2–N7 and C1–C8 bond lengths. This could stem from increased resonance-assisted hydrogen bond (RAHB) upon the rise in number of waters molecules. Compared with multiple solvation, hydration with one water molecule elicited a different behavior, indicating that the importance of RAHB diminished.

The carboxylate bond angle, O9–C8–O10, decreased from 126.25° to 123.69° in the presence of one and five water molecules, respectively. In the amino group, the H15–N7–H16 angle increased

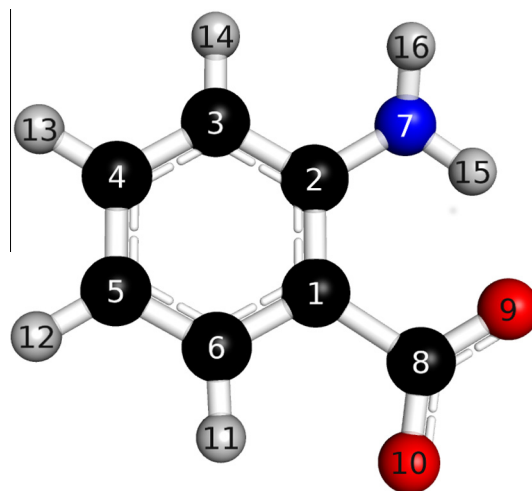


Fig. 1. *o*-Abz in anionic protonation optimized at the B3LYP/TZVP level.

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