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Ground and excited state hydrogen bonding effects of 6-aminocoumarin in water: An *ab initio* study

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ABSTRACT

The hydrogen bonded complexes of 6-aminocoumarin (6AC) with several water molecules in their ground and lowest excited singlet electronic state have been investigated using the *ab initio* methods. It was shown that the complex containing five water molecules in the surrounding of the amino group of the 6AC molecule has the lowest stabilization energy in the ground electronic state. This complex can serve as a model of the first solvation shell of the 6AC molecule in bulk water. The energies of hydrogen bonds formed by the carbonyl group with up to two water molecules were also determined. The calculated change in the total hydrogen bond energy due to $S_0 \rightarrow S_1$ excitation is in good agreement with the experimental data [E. Krystkowiak, A. Maciejewski, Phys. Chem. Chem. Phys. 2011;13:11317–11324]. The maxima of absorption spectra of the hydrogen-bonded complexes, calculated taking into account nonspecific solute–solvent interactions, are in reasonable agreement with the experimental data.

1. Introduction

A number of molecules of donor–acceptor character, often used as probes, can form the hydrogen bonds with protic solvent molecules in their ground and excited electronic states. Hydrogen bonds formed between the probes and solvent molecules influence the absorption and/or emission spectra of the probes as well as their structure and photophysical properties [1–6]. The formation of hydrogen bonds can often lead to the appearance of new individuals like S_0-complexes and S_1-exciplexes [7–12]. Important properties of intermolecular hydrogen bonds, including their equilibrium structures, energy in the S_0 state, and the energy change upon electronic excitation were discussed in a number of theoretical, *e.g.* Refs. [13–16] and experimental works, *e.g.* Refs. [17–20].

Aminocoumarin derivatives belong to the group of hydrogen donor–acceptor compounds, as they contain a donor amino group and an acceptor carbonyl group. These dyes are usually considered to be very good probes to investigate the hydrogen bonding dynamics, because they are sensitive to the solvent polarity and can form hydrogen bonds with the solvents of both hydrogen donor and acceptor properties [2,5,21–31].

As a working example, we have chosen to study 6-aminocoumarin (6AC) in water solution. The 6AC molecule shows a simple structure of the 1,2-benzopyrone moiety substituted only by the donor amino (NH_2) and acceptor carbonyl (C=O) groups, and it was the object of our studies for several years [32–35]. In this molecule, the amino group is at the position 6, so that the donor and acceptor central bonds, C–N and C=O, are arranged along the same molecular axis, in contrast to their positions in often investigated derivatives of 7-aminocoumarin. There are at least three reactive sites where the hydrogen bond between 6AC and protic solvent molecules can be formed: the hydrogen bond between the electron lone pair of the amino group and the hydrogen atom of a protic solvent molecule (an A type hydrogen bond), between the electron lone pairs of the carbonyl oxygen atom and the hydrogen atom of a protic solvent molecule (a B type hydrogen bond), and between the hydrogen atom of the amino group and the electron lone pairs of the basic center of a solvent molecule (a C type hydrogen bond) [34]. As shown in Ref. [36], the carbonyl oxygen atom, which has two lone electron pairs, can be involved simultaneously in two hydrogen bonds. Thus 6AC, like other aminocoumarin derivatives, for example similar in structure 7-aminocoumarin C120 [29], can form with water molecules one hydrogen bond of the A type, two hydrogen bonds of the B type, and two hydrogen bonds of the C type [32].

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The absorption and emission spectra, as well as the photophysical and photochemical properties of 6AC, were thoroughly studied experimentally in solvents of different properties, especially in hydrogen-bond forming ones [32–35]. On the other hand, theoretical studies on properties the intermolecular 6AC–solvent hydrogen bonds in the ground and electronic excited states are rather scarce. Theoretical calculations of the ground state structure and absorption spectra of the isolated 6AC molecule and the hydrogen bonded complexes, 6AC–(H_2O) and 6AC–$(H_2O)_3$, were reported by Zhang et al. [37]. These authors used the density functional theory (DFT) and the time-dependent density functional theory (TDDFT) to study the formation of the three 6AC–water hydrogen bonds: one of the A type, one of the B type, and one of the C type; the latter two hydrogen bonds are denoted in our work to as B1 and C2, respectively. Ramegowda [38] calculated recently the structure, electronic excitation energies, oscillation strengths, and transition dipole moments for the isolated 6AC molecule and the 6AC–$(H_2O)_5$ and 6AC–(H_2O) complexes involving the hydrogen bonds of the A, B1, B2, C1, and C2 type using the DFT/TDDFT method combined with the effective fragment potential (EFP) method [38]. Very recently Yang et al. [39,40] studied, also using the DFT/TDDFT method, the structural and spectral properties of hydrogen-bonded clusters formed by 6AC with solvents of different hydrogen-bonding abilities, including water.

In the present work, we discuss the hydrogen bond energies for the complexes of the 6A molecule with several water molecules in their ground S_0 and lowest electronic excited S_1 state. The molecular parameters are determined here by the *ab initio* approach using extensively correlated wavefunctions calculated with the correlation-consistent basis sets of *spdf* quality. The bulk solvent effect – the nonspecific solute–solvent interactions – is also taken into account. A comparison of the experimental and theoretical results obtained for 6AC in water, including a comparison of the position of absorption maxima corresponding to the $S_0 \rightarrow S_1$-LE transition, is presented.

2. Computational and experimental methods

The energy of the hydrogen bond, E_{HB}, is defined as a difference between the sum of the total energies of the isolated 6AC and water molecules and the total energy of the 6AC–H_2O complex. The hydrogen bond energies in the ground S_0 and electronic excited S_1 state were thus calculated in this work according to:

$$E_{HB}(S_0) = \{E_{S_0}(6AC) + E_{S_0}(H_2O)\} - E_{S_0}(\text{complex})$$

$$E_{HB}(S_1) = \{[E_{S_0} + E_{S_0 \rightarrow S_1}](6AC) + E_{S_0}(H_2O)\} - [E_{S_0} + E_{S_0 \rightarrow S_1}] \times (\text{complex}),$$

where E_{S_0} is the ground state energy determined using the MP2 [41], CC2 [42], and CCSD [43] methods, and $E_{S_0 \rightarrow S_1}$ is the $S_0 \rightarrow S_1$ transition energy determined using the CIS(D) [44], EOM-CC2, and EOM-CCSD [45] methods, respectively, all in conjunction with the augmented correlation-consistent basis sets of double-zeta (aug-cc-pVDZ) or triple-zeta quality (aug-cc-pVTZ) [46]. The calculations were performed applying the Molpro [47], CFOUR [48], and Turbomole [49] packages of *ab initio* programs.

The experimental details have been described in detail previously [32,34].

3. Results and discussion

3.1. Hydrogen bonds in the 6AC–(H_2O) complexes

The hydrogen-bonded complexes formed by the 6AC molecule with a single water molecule are shown in Fig. 1. The hydrogen bond formed by the nitrogen atom is referred to as **A**, two hydrogen bonds formed by the carbonyl oxygen atom are referred to as **B1** and **B2**, whereas those formed by the hydrogen atoms of the amino group are referred to as **C1** and **C2**.

Table 1 gives the predicted hydrogen bond energies in the ground state S_0 of five 6AC–(H_2O) complexes, each with a single hydrogen bond. It can be noted that the hydrogen bond energies determined with the MP2, CC2 and CCSD methods with the correlation-consistent basis sets of double-zeta or triple-zeta quality do not differ significantly from each other. Irrespective the calculation method used, the energies of the hydrogen bonds **A** and **B1** were determined to be similar, being lower than the energy of the hydrogen bond **B2**. The energies of the hydrogen bonds **C1** and **C2** did not differ significantly from each other and they were always the lowest. Results obtained in this work are generally consistent with those obtained by Ramegowda [38] for the 6AC–(H_2O) complexes, but the hydrogen bonds **C1** and **C2** were predicted in the latter study to be different in energy. Zhang et al. [37] in their study on the 6AC–(H_2O) complexes containing a single water molecule calculated that the length of the **B1** hydrogen bond was shorter than those of **C2** and **A** ones. For the 6AC–$(H_2O)_3$ complex, with three hydrogen bonds **A**, **B1** and **C2**, these authors obtained the similar lengths of the **A** and **B1** hydrogen bonds, which were significantly shorter than that of the **C2** one. Unfortunately, Zhang et al. [37] did not consider in their study any 6AC–(H_2O) complexes with the **B2** hydrogen bond. The results presented by Zhou et al. [29] for the Coumarin C120–$(\text{methanol})_5$ complexes clearly show that the relationships between the equilibrium hydrogen bond lengths do not necessarily parallel those between the hydrogen bond energies. The same conclusion follows from the results presented by Ramegowda [38] for the 6AC–(H_2O) complexes. Therefore, it is not possible to compare directly results of this work with those presented in Ref. [37]. As shown in Table 1, the **B2** hydrogen bond energy of the 6AC–(H_2O) complex was predicted to be significantly higher than the **B1** hydrogen bond energy. This indicates that two lone electron pairs of the carbonyl oxygen atom of the 6AC molecule can form two not necessarily similar hydrogen

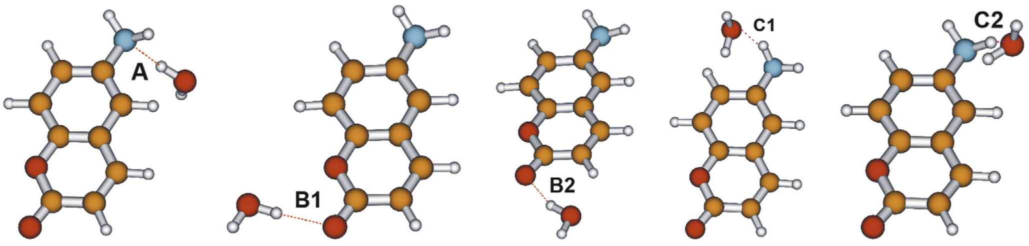

Fig. 1. Predicted equilibrium structures of the 6AC–(H_2O) hydrogen-bonded complexes in the ground state S_0.