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ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 190 (2007) 283–289
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Water effect on the excited-state decay paths of singlet excited cytosine

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Abstract

Two low-energy deactivation paths for singlet excited cytosine, one through a S_1/S_0 conical intersection of the ethylene type, and one through a conical intersection that involves the (n_N, π^*) state, are calculated in the presence of water. Water is included explicitly for several cytosine monohydrates, and as a bulk solvent, and the calculations are carried out at the complete active space self-consistent field (CASSCF) and complete active space second order perturbation (CASPT2) levels of theory. The effect of water on the lowest-energy path through the ethylenic conical intersection is a lowering of the energy barrier. This is explained by stabilization of the excited state, which has zwitterionic character in the vicinity of the conical intersection due to its similarity with the conical intersection of ethylene. In contrast to this, the path that involves the (n_N, π^*) state is destabilized by hydrogen bonding, although the bulk solvent effect reduces the destabilization. Overall, this path should remain energetically accessible.

Keywords: Cytosine; Photophysics; Computations; Solvation; Conical intersections

1. Introduction

The photophysics of the DNA nucleobases has been intensively studied in the last decade [1–9]. One of the most characteristic traits is a very short excited-state lifetime for all bases, and calculations have provided information about the mechanisms behind the fast radiationless decay of the bases [10–28]. However, while most computational studies have modeled the gas-phase photophysics, experiments on the nucleobase monomers have been carried out under different conditions. In addition to the gas-phase experiments on isolated bases [3,7,8], measurements have been carried out on gas-phase clusters of a base with one or more water molecules, or clusters of two bases [29–33], and in nucleosides and nucleotides in solution [1,2,4,5,9]. The purpose of this paper is to approach some of these experiments by modeling the effect of water on the excited-state decay of singlet excited cytosine. Water is considered here explicitly in calculations of clusters of cytosine with a single water molecule, and as a bulk solvent using the polarizable continuum model (PCM), where the molecule is embedded in a cavity that models the solvent [34,35]. The approach is similar to the one used recently for a study of solvent effects on the photophysics of uracil, thymine and some of their derivatives [22,25], although here the complete active space self-consistent field (CASSCF) and complete active space second order perturbation (CASPT2) methodologies are used for the excited-state calculations, instead of time-dependent (TD) density functional theory (DFT).

Most measurements of the excited-state lifetime of cytosine lie below 10 ps, although the exact value depends on the experimental conditions. Thus, the lifetime in the gas phase was first determined to be 3.2 ps [3]. However, more than one decay component has been detected in more recent experiments with higher resolution. Thus, the decay has been described with three components (one of less than 50 fs, one of 820 fs, and one of 3.2 ps) [7], while other authors describe a decay with two components of 0.16 and 1.9 ps [8]. In addition to that, a long living dark state of approximately 300 ns has been detected in the gas phase with a photoionization technique [36]. In water, transient absorption [1,5] and fluorescence up-conversion [2] experiments for cytosine, its nucleoside and its nucleotide gave a lifetime between 700 fs and 1.0 ps, while later on values of 400–530 fs were reported [4]. A biexponential fitting with one component of approximately 200 fs and another one of approximately 1 ps was also discussed for fluorescence experiments [4]. More recent transient absorption experiments have been described as a biexponential decay with a short component of up to 3 ps, approximately, and a longer one of 10–30 ps [9]. Turning to the computational results, calculations have established that the most favorable decay path for cytosine and cytidine,

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doi:10.1016/j.jphotochem.2007.04.015

in the gas phase, involves passage through a conical intersection of the ethylenic type, which is separated by a small barrier from the minimum of the spectroscopically active (π, π^*) state [18,20,28]. In a recent paper by one of us, the barrier was estimated as approximately 0.1 eV [37]. Other authors have suggested the existence of a barrierless channel from the Franck-Condon structure to the conical intersection, but this could not be confirmed [23]. Moreover, in the gas phase there is an additional, energetically accessible path that involves the (n_N, π^*) state (excitation from the nitrogen lone pair) [37]. The path leads from the (π, π^*) minimum to a minimum of the (n_N, π^*) state, and from there to a near-lying conical intersection with the ground state. The estimated barrier for this path was 0.2 eV, and the minima of the (π, π^*) and (n_N, π^*) states are isoenergetic. A third path involving the (n_O, π^*) state goes through a minimum of that state that is slightly higher in energy than the (π, π^*) minimum (approximately 0.1 eV), and leads to a higher-lying conical intersection (>1.0 eV) [37].

The effect of water on the two energetically favored paths, the one to the ethylenic type conical intersection and the one through the (n_N, π^*) state, has been studied here using the CASPT2//CASSCF methodology. The (n_O, π^*) path has not been considered as it lies substantially higher in energy in the gas phase, and it can be expected that the overall solvent effect will destabilize the (n_O, π^*) state. Critical points (excited-state minima and conical intersections) and minimum energy paths (intrinsic reaction coordinates) are calculated at the CASSCF level, and the gas-phase energetics are recalculated with single-point CASPT2 calculations on the CASSCF structures. For the ethylenic path, a valence-bond based characterization of the degenerate states at the conical intersection indicates that one of the states has zwitterionic character [37]. Thus, it can be expected that this path will be stabilized in water, and the present calculations confirm this hypothesis. In contrast to this, simple qualitative arguments indicate that the (n_N, π^*) state will be less accessible in water because of its destabilization by hydrogen bonding. The question then is if the (n_N, π^*) path is blocked in water or not, and the calculations suggest that it is destabilized but remains energetically accessible.

2. Computational details

The calculations were carried out at the CASSCF and CASPT2 levels of theory, using the 6-31+G* basis set for consistency with the previous gas-phase study [37]. Excited-state optimizations and minimum energy path calculations in the gas phase and in solvent are carried out at the CASSCF level using Gaussian03 [38], while the CASPT2 gas-phase energies are calculated with Molcas5.4 [39] (real level shift [40] parameter of 0.2 a.u.). The bulk solvent effect is taken into account in the CASSCF calculations using the self-consistent reaction field (SCRF) methodology and the conductor version of the polarizable continuous model (CPCM) implemented in Gaussian03 [41]. These calculations are referred to as CPCM–CASSCF. The density matrix used for the SCRF part in the CPCM–CASSCF optimizations and IRC calculations is the CASSCF state-averaged one. This is not the standard procedure, as ideally the density matrix of the root of interest (the second root here) should be used; however, the use of a state-specific root leads to convergence problems in the vicinity of conical intersections, presumably because of root flipping. To avoid these problems, the state-averaged density was used. A state-specific density matrix should also be used in CPCM–CASPT2 calculations, and therefore the solvent effect has not been calculated at the CASPT2 level. Conical intersections are not optimized at the CPCM–CASSCF level.

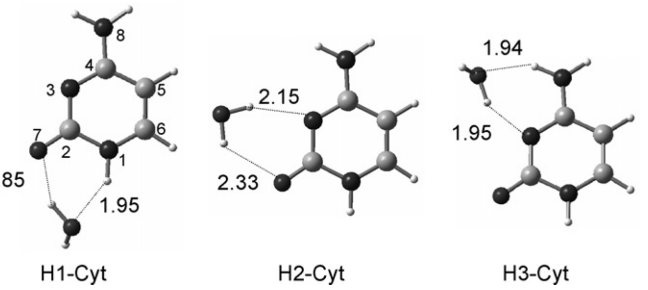

Fig. 1. B3LYP/6-311G** optimized structures of cytosine monohydrates (distances in Å).

2.1. Vertical excitations

The vertical excitations for isolated cytosine and the three monohydrates shown in Fig. 1 are calculated on geometries obtained at the B3LYP/6-311G** level of theory (see Table 1). The excitations are calculated in the gas phase at the CASSCF and CASPT2 levels, and in solution at the CPCM–CASSCF level (non-equilibrium [41] version). The CASPT2 energies in solution are approximated by adding the difference between the CASSCF gas phase and CPCM values to the CASPT2 gas phase value. Besides, the energies are obtained in two series of calculations, one with a (12,11) active space that yields the energy of the lowest-lying (π, π^*) and (n_N, π^*) states, and one with a (12,12) active space that yields the energy of the lowest-lying (π, π^*) and (n_O, π^*) states (see reference [37] for a description of the active space orbitals). For this reason, two values are reported in Table 1 for the energy of the (π, π^*) state for gas phase cytosine (Cyt) and H2-Cyt (see Fig. 1 for the labeling). The averages of the values in Table 1 for the three monohydrates are the estimated vertical excitations in water listed in Table 2.

2.2. CASSCF optimizations and minimum energy paths

The optimizations and minimum energy path calculations (intrinsic reaction coordinate, IRC [42]) were carried out with (10,9) and (12,11) active spaces for the path to the ethylenic type intersection and for the (n_N, π^*) path, respectively. The minimum-energy paths between the minima of the spectroscopic sate, $(\pi, \pi^*)_{Min}$, and the ethylenic type intersection $(Eth)_X$ or the minimum of the (n_N, π^*) state, $(n_N, \pi^*)_{Min}$, are the IRC from the corresponding optimized transition structures. The details of these calculations can be found in reference [37]. The CASSCF transition structures correspond to displacement 0.0 a.u. along