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The effect of hydration on the photo-deactivation pathways of 4-aminopyrimidine

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ABSTRACT

The influence of water on the photo-deactivation process of 4-aminopyrimidine has been investigated by means of microsolvation and continuum solvation models. Two- and four-water models were used for the former purpose. Vertical excitations, stationary points on the first excited singlet surface, conical intersections (minima on the crossing seam) and reaction paths have been investigated at the state-averaged complete active space self-consistent field (CASSCF) and multistate CAS perturbation theory to second order (MS-CASPT2) levels of theory. A destabilizing effect of 0.2–0.3 eV has been observed for $n\pi^*$ states while the $\pi\pi^*$ state is almost unaffected. The two-water model gives already a good representation of hydration effects, especially when combined with the continuum model. A small enhancement of energy barriers (~0.1 eV) is observed leading to the conclusion that the photodynamics of 4-aminopyrimidine should be affected only little by these solvent effects.

1. Introduction

The ultrafast photodecay and the related photostability of DNA and RNA bases is a remarkable property in view of their strong absorption in the ultraviolet region of the spectrum [1]. The protection mechanisms against mutagenic and carcinogenic effects are of greatest importance and have induced a large number of experimental and theoretical investigations. Recent high-resolution femtosecond measurements [1–6] accompanied by advanced theoretical calculations [7–16] provide detailed information about the ultrafast photo-deactivation leading to a better understanding of the mechanistic processes responsible for the afore-mentioned photostability.

Environmental effects are predicted to play an important role for the properties of nucleobases. Experimental investigations were performed on solvated nucleobases ranging from interactions with small water clusters [17–21] up to aqueous solution [1–3,5,22–26]. Interesting details of microsolvation effects could be deduced from resonant two-photon ionization studies in which for adenine/water clusters [17] it was observed that the ratio between hydrated adenine clusters and unhydrated ones was anomalously small because of a facile decomposition of the adenine–water complexes in the excited state. In investigation in aqueous solution a small solvent effect on the lifetime of adenine has been observed by Reuther et al. [26] in femtosecond photoionization experiments who reported a value of 1.1 ps (vs. 1.0 ps in the gas phase [3]). On the other hand, transient absorption experiments by Cohen et al. [25] or femtosecond fluorescence upconversion by Gustavsson et al. [24] revealed two time constants of approximately 0.2 and 8 ps that were assigned to the two tautomers of adenine present in water, with the smaller value attributed to the 9H form and the longer one to 7H, respectively.

The theoretical analysis of photophysical and photochemical processes comprises several tasks with respect to the computation of: (i) the character and excitation energy of the bright state from which the photodynamics is starting, (ii) dark states which may play an important role at later stages of the dynamics, and (iii) the shape of excited-state reaction pathways leading from the Franck–Condon (FC) region via eventual energy minima to conical intersections (minima on the crossing seam, MXSs) at which ultrafast radiationless transition to the lower state occurs. Extensive investigations along these lines have been performed for isolated nucleobases including explicit photo-dynamical simulations [7–16,27,28]. However, consideration of solvent effects performed at similar sophistication as for the gas phase is still rather scarce [29–32] with main emphasis restricted to explaining the nature of solvatochromic shifts of UV spectra [20,33–35].

The purpose of the present study is to perform a detailed survey of solvent effects on the photophysical processes in 4-aminopyrimidine (4-APy, see Fig. 1a). This compound was chosen because of its potential as convenient model for the nucleobase adenine (Ade) since it is computationally better accessible due to its smaller size. The characteristics of 4-APy in relation to Ade have been investigated in detail for the isolated compounds (see Refs. [36,37] on 4-APy and Ref. [10] on 9H-Ade). It was shown that 4-APy

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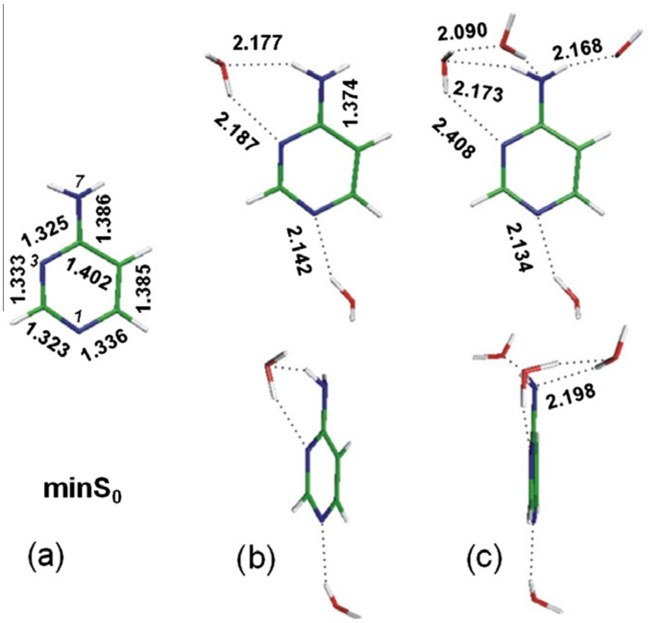

Fig. 1. Geometries of the ground-state minima of isolated 4-APy (a) and solvated by two (b) and four water molecules (c). Only bond distances that change more than 0.005 Å relative to the gas-phase structure (a) are indicated.

represents Ade in several interesting aspects (vertical excitations, MXS structures and reaction paths) very well. Moreover, 4-APy is also of interest in connection with investigations on the photophysics of diaminopyrimidine [38,39], which forms an unnatural base pair with xanthine [40]. Water was chosen as solvent because of its outstanding importance for biological systems. The main objective was to construct structural models appropriate for describing the specific interactions of 4-APy in the excited state and to investigate the effect of hydrogen bonding on the photodynamical reaction paths. In particular, the interaction of water with the amino group and with the pyrimidine nitrogen atoms will affect the properties of different excited states of 4-APy. For that purpose a microsolvation model including two and four explicit water molecules, respectively, has been chosen. Beyond these specific interactions bulk hydration effects have been taken into account as well using the conductor-like screening model (COSMO) [41] for excited states. Comparison of specific and global solvation is of particular interest since little experience is available in that respect for the description of the solvation along reaction paths.

2. Computational details

Geometries of all stationary points and MXSs considered in the present study were optimized at the complete active space self-consistent field level (CASSCF). The active space chosen for the calculations was a CAS(10,8) consisting of 10 electrons in eight orbitals (six orbitals of π character and two lone-pair (n) orbitals centered on the ring nitrogen atoms). The water orbitals were located in the doubly occupied space. In the CASSCF calculations, state-averaging (SA) was performed with equal weights for the lowest three singlet states (SA-3). Optimizations of the ground and excited state minima and MXSs were performed at the SA3-CASSCF level using analytical gradients [42–44] and nonadiabatic coupling vectors [45,46]. Multireference second order perturbation theory calculations in its multistate version (MS-CASPT2) [47,48] were used to account for dynamic electron correlation effects. COSMO [41] was employed for the description of bulk water. Non-equilibrium and equilibrium versions were used for the excited state as described in Refs. [49,50] (see also Ref. [51,52] for further discussion on excited-state solvation using continuum models). In the first case only the fast electronic re-orientational response of the solvent to the electronic excitation state is considered keeping the orientation of the solvent in the ground state equilibrium. In the second case full equilibrium conditions are assumed for the excited state. Vertical excitations were treated at the non-equilibrium level whereas for optimized geometries and reaction paths the equilibrium approach was used. Only single-point calculations were performed with the COSMO approach. Geometries were taken from respective calculations on isolated systems or those from 4-APy/water cluster calculations. An average of S_0 and S_1 energies was taken for the COSMO MXS energy. Energetic splittings between the two states in the range of 0.1–0.3 eV were observed. Reaction paths between the Franck–Condon region represented by the ground-state minimum structure and the MXS structures were generated by linear interpolation of internal coordinates (LIIC). All geometry optimizations, SA-CASSCF, MRCI and COSMO calculations have been carried out with the program system COLUMBUS [53–55]. For the CASPT2 investigations MOLCAS [56] was used. All calculations were performed at the 6-31G* basis set level [57].

3. Results and discussion

3.1. Vertical excitation energies and stationary points

The effect of microsolvation on the vertical excitation energy has been computed first by studying the interaction of two water molecules with 4-APy. Geometries of 4-APy minima and the solvation complexes computed in the electronic ground (SA3-CASSCF level) state are presented in Fig. 1a and b. The two water molecules in Fig. 1b are arranged such that they interact with the lone pairs of the two nitrogen atoms of the pyrimidine ring. The vicinity of N_3 and the amino group provides a natural situation for a water molecule to form two hydrogen bonds at the same time. In fact, one water molecule connects simultaneously to the nitrogen atom N_3 and the hydrogen atom of the amino group. Both hydrogen bonds are, however, rather weak, with hydrogen bond distances somewhat larger than 2.1 Å (see Fig. 1a and b). The second water molecule forms a hydrogen bond with the ring nitrogen N_1 and a hydrogen atom H_w of the water molecule with a similar $N_1 \cdots H_wO$ bond length as for the other hydrogen bridge.

This picture of 4-APy microsolvation by water is consistent with the work of Slanina et al. [58], where three closely lying ground-state minima (within around 0.15 eV) for 4-APy interacting with one water molecule were reported. The positions of the water molecule found there for the two lowest minima are similar to the two-water structure obtained here. In the third minimum reported in Ref. [58] the water molecule forms a hydrogen bond with the amino group on the side opposite to N_3. Its energy is located only 0.04 eV above the one with water connected to N_1. Since the NH_2 group forms hydrogen bonds as well, two more water molecules were added interacting with the N_7 lone pair and the other hydrogen atom of the amino group, respectively. Resulting structures are shown in Fig. 1c. The main purpose of these additional water molecules was the validation of the two-water model as a minimal system to study the influence of microsolvation on photodecay paths. The geometry of 4-APy itself within the complex with two and four waters is not significantly distorted from the gas-phase structure. The largest change amounts to 0.012 Å for the C_4–N_7 bond for the cluster with two waters; otherwise differences in the bond distances are smaller than 0.005 Å. The only notable change between two and four water cluster was the elongation of the $N_3 \cdots H_wO$