



Photocatalytic water splitting with acridine dyes: Guidelines from computational chemistry



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ABSTRACT

The photocatalytic splitting of water into H[•] and OH[•] radicals in hydrogen-bonded chromophore-water complexes has been explored with computational methods for the chromophores acridine orange (AO) and benzacridine (BA). These dyes are strong absorbers within the range of the solar spectrum. It is shown that low-lying charge-transfer excited states exist in the hydrogen-bonded AO–H₂O and BA–H₂O complexes which drive the transfer of a proton from water to the chromophore, which results in AOH[•]–OH[•] or BAH[•]–OH[•] biradicals. The AOH[•] and BAH[•] radicals possess bright ππ* excited states with vertical excitation energies near 3.0 eV which are predissociated by a low-lying repulsive πσ* state. The conical intersections of the πσ* state with the ππ* excited states and the ground state provide a mechanism for the photodetachment of the H-atom by a second photon. Our results indicate that AO and BA are promising chromophores for water splitting with visible light.

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1. Introduction

Splitting of water into H[•] and OH[•] radicals via photosensitization with a redox-active chromophore which absorbs within the range of the solar spectrum could be a particularly straightforward and cost-efficient way of generating clean and sustainable energy directly from sunlight. The ideal catalyst for this reaction should absorb strongly in the visible and be able to abstract a hydrogen atom from a water molecule in its excited state. Denoting the photocatalyzer by X, the first step of the water-splitting reaction is:



where X–H₂O denotes a hydrogen-bonded complex of the chromophore X with a water molecule. By photodetachment of the surplus H-atom from the XH[•] radical with a second photon



the photocatalyzer X is recovered and a water molecule has been split into H[•] and OH[•] radicals. Exothermic radical–radical recombination reactions may yield H₂ and H₂O₂ as closed-shell products. H₂O₂ can finally be catalytically decomposed into H₂O and O₂.

In recent work, we explored the mechanisms of the photoreactivity of pyridine (Py) and acridine (Ac) in hydrogen-bonded complexes of Py and Ac with a single water molecule using state-of-the-art computational methods [1–3]. We constructed minimum-energy reaction paths, their energy profiles and two-dimensional relaxed potential-energy (PE) surfaces for H-atom transfer from water to Py and Ac, respectively, in low-lying ππ* and nπ* excited states in the singlet and triplet manifolds. The results reveal the mechanisms by which photoexcited Py or Ac can abstract an H-atom from water via an electron-driven proton-transfer process. A key finding were hitherto unknown excited states of charge-transfer character (involving electron promotion from the p-orbital of water to the π* orbital of the chromophore) which are separated by low energy barriers from the spectroscopic states of the chromophore-water complexes. The charge-separated electronic states are strongly lowered in energy by the transfer of a proton from water to the chromophore, which results in XH[•]–OH[•] (X = Py, Ac) biradicals. The excess energy of the H-atom transfer reaction is sufficient to dissociate the biradicals into X[•] and OH[•] free radicals. Due to the existence of a low-lying repulsive ²πσ* state in the XH[•] radicals, the radicals can be photodissociated with a second photon. This regenerates the Py or Ac chromophores, which thus become photocatalyzers [1–3].

While Py absorbs in the far UV, Ac absorbs at 450 nm in aqueous solution [4] and thus at the upper edge of the solar spectrum at the surface of earth. Therefore, both chromophores are not suitable

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catalyzers for efficient water splitting with sunlight. Herein, we explore the photochemistry of two chromophores derived from acridine which absorb well within the solar spectrum, acridine orange (tetramethylacridine-3,6-diamine) (AO) and benzacridine (BA). The aim of this work is to provide evidence that these easily accessible chromophores are potential photocatalyzers for the splitting of water with sunlight. Ab initio multi-configuration multi-reference perturbation methods as well as propagator methods were employed for the calculation of electronic excitation energies, excited-state reaction paths and conical intersections among the relevant electronic states of the AO–H₂O and BA–H₂O complexes as well as of the AOH[•] and BAH[•] radicals.

In earlier investigations of the Py–H₂O and Ac–H₂O complexes, we explored the reaction mechanisms in both singlet and triplet manifolds [1–3]. While the bright ¹ππ* electronic states are populated by the absorption of light, the triplet states may come into play by intersystem crossing (ISC), which may compete with direct photoreactions in the singlet manifold. It was found that the topographies of the PE surfaces of the triplet states are quite similar to those of the singlet states in Py–H₂O and Ac–H₂O (see Refs. [1–3] for details). Since the excited-state electronic-structure calculations are considerably more tedious and expensive for the larger chromophores considered herein, we have confined the calculations to the singlet manifold.

2. Computational methods

The second-order Møller–Plesset (MP2) method was employed for the determination of the ground-state equilibrium geometries of the AO–H₂O and BA–H₂O complexes. Vertical excitation energies were calculated with the complete-active-space self-consistent-field (CASSCF) method, the CASPT2 method (second-order perturbation theory with respect to the CASSCF reference) as well as with the ADC(2) method. ADC(2) is a single-reference many-body Green's function method [5,6]. Vertical excitation energies, geometries of minimum-energy reaction paths and saddle points on the excited-state PE surfaces were determined with the ADC(2) method. Although ADC(2) is a single-reference method, it has been found to be reliable for the prediction of vertical excitation energies of singly-excited states of closed-shell systems [7]. In particular, ADC(2) PE surfaces are well behaved near conical intersections of excited electronic states, although the method may possibly fail near conical intersections of excited states with the electronic ground state. In recent investigations of the pyridine-water complex, we evaluated the accuracy of the ADC(2) method in comparison with CASSCF/CASPT2 results [1,2]. It was shown that the ADC(2) method is a qualitatively reliable and computationally efficient alternative to multi-reference perturbation methods and coupled-cluster-type methods for the calculation of excitation energies and the characterization of local regions of excited-state PE surfaces for such systems. Therefore, most of the calculations in the present work, in particular all excited-state geometry optimizations, were performed with the ADC(2) method. Being derived by diagrammatic perturbation theory for systems with a closed-shell ground state, ADC(2) is not readily applicable to the open-shell AOH[•] and BAH[•] radicals. The calculations for the AOH[•] and BAH[•] radicals were therefore performed with the CASSCF and CASPT2 methods.

The reaction paths were constructed as so-called relaxed scans. For the calculation of the reaction path for the H-atom-transfer process from water to the N-atom of the chromophore, the bond length of the OH bond of the water molecule involved in hydrogen bonding was chosen as the driving coordinate, while all other internal nuclear coordinates of the complex were relaxed in the electronic state under consideration. The distance between the O-atom of H₂O and the N-atom of the chromophore was taken as the second driving coordinate in the calculation of

two-dimensional PE surfaces in the vicinity of the saddle point of the H-transfer reaction. The latter calculations were performed as rigid scans on a two-dimensional grid in the R_{OH} and R_{ON} coordinates, since two-dimensional relaxed scans turned out to be prohibitively time-consuming. The reaction path for the photodetachment of the hydrogen atom from the AOH[•] and BAH[•] radicals was constructed as a rigid scan of the NH bond length, because the relaxation of the internal coordinates of the system is of little importance in this case [8]. The saddle points for the H-atom transfer reactions were estimated from the two-dimensional relaxed PE surfaces. The minimum-energy geometries of conical intersections were optimized using the CIOpt program of Martinez and coworkers [9].

In the CASSCF calculations for the chromophore–H₂O complex, 14 electrons were distributed in 13 orbitals, including the five highest π and five lowest π* orbitals of the chromophore, the n orbital of the N-atom, one p orbital of the O-atom and the lowest σ* orbital of water. The energies of the S₀ state and the lowest ¹ππ* and ¹nπ* states were averaged with equal weights in the calculations of the singlet states. The active space of the CASSCF calculations for the XH[•] radicals (X = AO, BA) consisted of 13 electrons in 12 orbitals: the five highest π orbitals and five lowest π* orbitals of the chromophore as well as one σ orbital and one σ* orbital of the NH bond. The CASPT2 calculations for the vertical excitation energies were carried out as single-state, single-reference calculations and a level shift of 0.3 au was employed. For the calculation of the PE functions for hydrogen detachment, a smaller active space had to be employed due to the computational cost of these calculations and due to convergence problems with the larger active space. This smaller active space consisted of 10 electrons in 9 orbitals: the four highest π orbitals and three lowest π* orbitals of the chromophore as well as one σ orbital and one σ* orbital of the NH bond. The state-averaging included the three lowest A' and the three lowest A'' states.

The MP2 and ADC(2) calculations were carried out with the TURBOMOLE program package [10], making use of the resolution-of-the-identity (RI) approximation [11]. The CASSCF and CASPT2 calculations were performed with the MOLPRO program package [12]. C_s symmetry (that is, co-planarity of the water molecule with the chromophore) was enforced throughout the calculations. The correlation-consistent split-valence double-ζ basis set with polarization functions on all atoms (cc-pVDZ) [13] was employed in the calculations for the AO–H₂O and BA–H₂O complexes. The Rydberg character of the ²πσ* state of the AOH[•] and BAH[•] radicals requires the augmentation of the cc-pVDZ basis with diffuse basis functions. The aug-cc-pVDZ basis was therefore employed for the calculation of the PE functions of the D₀, ²ππ* and ²πσ* states of the radicals.

3. Results

3.1. Equilibrium geometries and vertical excitation energies of the AO–H₂O and BA–H₂O complexes

The equilibrium structures of the AO–H₂O and BA–H₂O complexes, optimized at the MP2 level with C_s symmetry constraint, are shown in Fig. 1. The H₂O molecule acts as a hydrogen bond donor to the N-atom acceptor of the chromophore. The vertical excitation energies of the three lowest singlet states (two ¹ππ* states and one ¹nπ* state) calculated with the CASSCF, CASPT2 and ADC(2) methods are given in Table 1. The vertical excitation energies of the Ac–H₂O complex are shown for comparison (slight deviations of the CASPT2 excitation energies of Ac–H₂O from those reported in Ref. [3] are due to differences in the state averaging of the CASSCF reference wave function).

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