Excited-State Dynamics and Coupled Proton–Electron Transfer of Guanine**

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Dedicated to Professor Michele Parrinello on the occasion of his 60th birthday.

Introduction

Photophysical and photochemical properties of nucleic acids are of fundamental interest for understanding the mechanisms of radiation-induced damage to DNA, as well as the UV-protection mechanisms.[1] Time-resolved spectroscopy has placed the excited-state lifetimes of isolated DNA bases on the (sub-)picosecond timescale.[1] There have been numerous theoretical attempts at unravelling the pathways of radiationless decay in bioorganic molecules.[2–6] A very successful model has been proposed by Sobolewski and Domcke,[2–4] whereby a transition takes place from the initially populated, optically bright, \( \pi \pi^* \) state to a dark \( \pi \sigma^* \) state characterised by a diffuse, Rydberg-like \( \sigma^* \) orbital promoting proton–electron or hydrogen detachment. Along this dissociative coordinate, the system can access a conical intersection with the ground state, providing an efficient route for radiationless decay, which leads either to recombination of the (temporary) radical and the hydrogen atom or to detachment of the latter. Most of these theoretical investigations have been based on static single-point gas-phase calculations along a preselected hypothetical reaction coordinate. Recently, however, it has become possible to study the full-dimensional coupled electronic–nuclear nonadiabatic dynamics[7,8] in condensed-phase systems, such as solvated molecules, by extending Car–Parrinello molecular dynamics[9,10]

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[**] From the Gas Phase via Microsolvation to Aqueous Solution.
beyond the Born–Oppenheimer approximation. An efficient implementation is obtained by exploiting the restricted open-shell Kohn–Sham (ROKS) representation of the first excited singlet state\[11,12\] as previously used for adiabatic dynamics,[11–17] in conjunction with Tully’s powerful nonadiabatic surface-hopping technique.[18] Generally speaking, our nonadiabatic extension\[7,8\] permits the simulation of systems of comparable chemical complexity to those known from conventional Car–Parinello simulations.[9,10] Such “on the fly” nonadiabatic simulations, taking into account the nonadiabatic coupling between the first excited singlet state, $S_1$, and the ground state, $S_0$, have already been carried out for two photoexcited guanine (G) tautomers in the gas phase,[19] as well as for other (bio)organic molecules.[20,21] These studies have shown that the $\pi\pi^*$ state, and thus the dissociative decay channel, is not readily accessed at moderate excess energies. Instead, internal conversion takes place from the $\pi\pi^*$ state mainly through out-of-plane vibrations. In this Communication, we present the first simulation of coupled proton–electron transfer in a photoexcited, fully solvated molecule—guanine in ambient water—explicitly treating the $S_1/S_0$ nonadiabatic coupling.

Simulations and Discussions

Solvating an acidic molecule by water can open up additional reaction channels, such as dissociation, as well as subsequent secondary reactions. These reaction pathways, however, typically only become accessible beyond a minimum number of solvent molecules.[22,23] Stimulated by this observation, we raise the question whether phenomena, such as de- and reprotonation of the solute mediated by proton migration through the solvent, could be triggered in a photoacid, for example, by increasing the number of solvating molecules. A first step in this direction was made recently in an ingenious experiment in which a hydrogen-bonded linear wire consisting of three ammonia molecules was suspended between two anchoring sites of a photoexcited chromophore.[24]

Since our nonadiabatic simulation technique\[7,8\] allows us to treat isolated, microsolvated, and also fully solvated molecules on an equal footing, we have studied photoexcited G, G-H$_2$O, and G(aq) in order to address such issues. The calculations were performed microcanonically at 300 K using the CPMD package\[10,25\] the BLYP functional and 60 H$_2$O molecules in a periodic orthorhombic cell in the case of G(aq). To overcome the reaction barrier within current restrictions of computer time, the hydrogen coordination number of the hydroxylic oxygen was forced to decrease from unity to zero by applying a suitable constraint.[26] By thermodynamic integration it is possible to determine the free-energy barrier height for this process including solvent effects.

The top panels of Figure 1 illustrate that an isolated G molecule (in its enol form) undergoes a $\pi\pi^*$ (a) to $\pi\pi^*$ (b) transition when adiabatically evolving in its $S_1$ state upon enforced elongation of the hydroxylic OH bond, which ultimately leads to hydrogen detachment (c). Along this OH dissociation coordinate, we also find a conical intersection between the $\pi\pi^*$ state, $S_1$, and the ground state, $S_0$. In the microsolvated case, G-H$_2$O, depicted in the middle panels of Figure 1, a similar scenario was observed. The $S_1$ wavefunction changes character from $\pi\pi^*$ (d) to $\pi\pi^*$ around 1.3 Å (e), accompanied by the formation of a G and H$_3$O radical pair (f) without, however, featuring an $S_1/S_0$ conical intersection along this particular dissociation process.

Figure 1. Representative trajectory snapshots showing the nuclear skeleton and the two canonical SOMOs ($\pi^*/\sigma^*$: green and yellow, $\pi$: blue and red) at different stages of OH-bond dissociation. Top panel: isolated G at an OH distance of 1.11 Å (a), 1.36 Å (b), and 1.62 Å (c). Middle panel: G-H$_2$O at an OH distance of 1.26 Å (d), 1.44 Å (e), and 1.62 Å (f). Bottom panel: G(aq) at an OH distance of 1.21 Å (g), 1.59 Å (h), and 1.59 Å (i); note that the identity of the proton that recombines with N to form 7H-keto guanine in (i) is different from that detached from the 7H-enol tautomer in (g), and that an H$_3$O$^+$ charge defect migrated through water between (h) and (i).
tion coordinate. Here, the oxygen–oxygen distance across the G–H₂O hydrogen bond was kept fixed at 2.92 Å, and the temperature was reduced to 50 K to avoid trivial dissociation of the hydrogen bond. In both cases, the Sobolewski–Domcke scenario[2–4] is born out in view of the diffuse, Rydberg-like σ* orbital attached to the transferred proton, thus leading to hydrogen transfer in the adiabatic first excited state. It is worth emphasising that both the present BLYP and previous CASSCF hydrogen transfer in the adiabatic first excited state. It is worth emphasising that both the present BLYP and previous CASSCF calculations[2–4] favour hydrogen transfer over proton transfer, that is, the formation of a radical pair over an ion pair, for a small number of solvent molecules. Sobolewski and Domcke[2,3] have shown, however, that the H₂O radical decomposes into a hydronium cation and a solvated electron as the cluster size increases.

To further investigate this issue beyond the cluster model, we have performed a series of constrained adiabatic simulations of fully solvated cis-7H-enol guanine, G(aq), in the S₁ state, ππ*, following vertical excitation from an equilibrated ground-state run (see bottom panels of Figure 1). During a previous unconstrained 4 ps excited-state run no spontaneous reaction was observed. Moreover, the system was found to remain in the initially populated ππ* state (see Figure 1g) throughout this simulation, that is, a potential barrier crossing to the dissociative ππ* excited state did not take place. To explore hypothetical solvent-assisted decay pathways, we break the enol OH bond by performing constraint simulations at incrementally decreasing, but for each run fixed, values of the hydroxyl oxygen coordination number. For rather small OH bond lengths the S₁, singly occupied molecular orbitals (SOMOs) retain their localised ππ* character, see Figure 1g, very similar to the gas phase. However, at an OH distance of approximately 1.27 Å, the highest SOMO is observed to change its character from ππ* localised on G to σ* delocalised over the solvent, see Figure 1h. The subsequent processes identified are the detachment of the formed hydronium, H₃O⁺, followed by Grothuss diffusion,[27] that is, charge-defect migration through bulk water, which is also captured by Figure 1h. At the same constraint value, the migrating proton is found to recombine with G after about 2.5 ps forming the so-called 7H-keto tautomer and shortly after this recombination, the character of the S₁ state switches back to ππ* as depicted in Figure 1i.

A more detailed analysis of the recombination process, that is, the step leading to Figure 1i and thus to isomerisation, is given in Figure 2a which illustrates the time evolution of the NH distance as well as the spatial extension of the two SOMOs in their localised Wannier representation.[28,29] Roughly 50 fs after the NH bond has been formed, the highest SOMO undergoes a transition from an extremely broad delocalised σ* to a localised ππ* orbital, as indicat-

![Figure 2](image-url)
O–O distance was not allowed to contract during the simulation. However, the transition state for proton transfer along hydrogen bonds is known to be stabilised by shortening of this distance,[27] which implies that relaxation of this coordinate would probably lower the barrier for G·H₂O as well.

Summary and Outlook

We have studied coupled proton–electron transfer in the first electronically excited state of guanine using nonadiabatic “on the fly” excited-state dynamics in the spirit of Car–Parrinello molecular dynamics. Our *dynamic* treatment confirms the static Sobolewski–Domcke scenario for both isolated and microsolvated G in the gas phase, that is, a change of character of the S₁ state from ππ* to πσ* including an S₃/S₅ conical intersection along the OH dissociation coordinate for naked G, if deprotonation of the hydroxyl oxygen is enforced to overcome the rather high reaction barriers.

However, when fully solvated in bulk water, an additional channel is opened up; photoexcited G undergoes solvent-assisted isomerisation, interconverting the 7H-enol and 7H-keto tautomers. Upon breaking the enol OH bond by means of a coordination constraint, a proton is detached, and the first excited state changes its character from a solute-localised ππ* state to πσ*, the σ* orbital being delocalised over the solvent. What remains to be clarified is the character of the detached electron, that is, delocalised versus trapped (polaronic or molecular radical),[30] since semilocal functionals, such as BLYP, are known to favour delocalised spin densities, whereas for hybrid functionals, such as BHLYP or B3LYP, this deficiency is partially remedied by the inclusion of Hartree–Fock exchange.[31,32]

However, these details are still controversially debated even for the “solvated electron” as such. Furthermore, we recall that BLYP is known to underestimate the HOMO/LUMO gap of pure liquid water, which might lead to an occupation of the water LUMO, which is indistinguishable from the delocalised σ* orbital observed here.

Following Grotthuss diffusion through the solvent via an H₂O⁺ species, the detached proton recombines with G to form an NH bond and thus the 7H-keto tautomer accompanied by a change from a πσ* back to a ππ*–like S₃ state. Simulations including the nonadiabatic coupling of S₁ and S₃ have revealed that radiationless decay is much more likely to occur in the ππ* state compared to the πσ* state. More generally speaking, the present study opens up an avenue for studying the crucial role that solvent water might also play in photoinduced chemical reactions, beyond that of just being an inert spectator.

Acknowledgements

Funding by DFG (DO 768/1-1) and FCI is gratefully acknowledged, and we thank NIC (Jüllich), Rechnerverbund-NRW (Aachen), and BOVL@BARUB (Bochum) for CPU time.

Keywords: nonadiabatic dynamics • nucleobases • photochemistry • proton transport • solvent effects

Received: November 30, 2004
Published online on August 5, 2005