



Dynamics of laser-excited stacked adenines: Semiclassical simulations

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ABSTRACT

The nonradiative decay of a π -stacked pair of adenine molecules, following laser excitation, was studied by semiclassical dynamics simulations. Two deactivation pathways were characterized. One pathway involves an ultrafast internal conversion within ~ 600 fs induced by an out-of-plane vibration of the H atom and deformation of the pyrimidine ring at the C₂ site. A slower process (~ 2400 fs) involves covalent bond formation between the stacked molecules, which lowers the excimer state energy and inhibits the deformation of the pyrimidine ring; the decay is also induced by an out-of-plane vibration of the H atom at the C₂ site of the pyrimidine ring.

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1. Introduction

Exposure of DNA to UV radiation in 200–300 nm range results in strong electronic excitations, which could lead to the photochemical reactions causing DNA damage [1–3]. Therefore, a rapid and efficient release of the excess electronic energy by excited DNA is essential to life. This characteristic of DNA molecules has attracted research interest for least a couple of decades [4–12]. In recent years, femtosecond laser spectroscopy combined with high level quantum mechanical calculations has provided many insights into the mechanisms responsible for the quick dissipation of the excess electronic energy. It is firmly established that highly efficient non-radiative decay pathways exist in DNA molecules, assuring that most excited molecules quickly relax to the electronic ground state without leading to harmful reactions.

The mechanisms for the fast nonradiative decay of monomer DNA bases are fairly well established. The vast majority of electronically excited nucleobases decay to the ground state on a subpicosecond timescale through conical intersections (CI) between the lowest electronic excited-state and the ground state. The conical intersections are accessed, in most cases, via out-of-plane deformations of the pyrimidine ring [2]. The excited-state

dynamics of DNA and nucleobase multimers show different nonradiative decay pathways because of interbase interactions, including base stacking and base pairing, and base-solvent interactions [13–16]. Single-stranded polyadenine oligomers [(dA)_n], in which base pairing is absent, show an ultrafast and a slower nonradiative decay channels [14,17–19]. It has been proposed that the fast decay channel, or monomer-like decay pathway, comes from poorly stacked bases while the slow decay channel is due to inter-base stacking interaction.

To understand the nature of electronic excitations, different hypotheses have been proposed. One sophisticated model proposed by Kohler and co-workers [14,20] is that stacked bases are initially excited to an exciton state, which is formed by dipolar coupling of excited states of base monomers. The exciton state decays in less than 1 ps to an excimer/excimer state that involves just two bases. The decay from the excimer/excimer state to the ground state usually occurs at a longer time scale. This model is now generally accepted.

The formation of a delocalized excimer state slows down ultrafast nonradiative decay [21,22]. The ab initio calculations at CASPT2 level [23] for two stacked adenines of different arrangements favor a mechanism involving two possible decay pathways. In this mechanism, unstacked or poorly stacked pairs of bases relax to the ground state by an ultrafast internal conversion through the conical intersection between the lowest excited state and ground state of the monomer. On the other hand, an excimer state formed between intrastrand stacked bases exhibits a slower decay time to the ground state because of an energy barrier along the path

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toward the conical intersection of the monomer [23]. It has been suggested [24] that the excimer state has a charge-transfer character and the state lifetime is correlated with the energy required to transfer an electron from one base to its stacked neighbor. An alternative explanation for the slow decay channel is that the base stacking hinders the out-of-plane deformations of the pyrimidine ring [25].

The aforementioned calculations are useful for understanding the main features of the mechanisms behind the ultrafast nonradiative decay dynamics of excited-state of stacked adenines. However, these calculations are incapable of describing the time-dependent properties of the deactivation process. QM/MM calculations are performed along one or two reaction coordinates with other coordinates fixed and, consequently, are inadequate for characterizing a real deactivation process where all reaction coordinates are significantly involved.

In this work, we study the dynamics of nonradiative decay of two stacked adenines following excitation by an ultrafast laser pulse using a semiclassical dynamics simulation technique. In our simulations, all the degrees of freedom of the system are included in the calculations and the laser pulse is explicitly coupled to electrons. By monitoring the nuclear motions triggered by a specific laser pulse, we are able to describe a realistic nonradiative decay pathway. Examining the interplay of the electronic and nuclear motions allows us to study the influence of different vibrational modes on the nonradiative decay process of stacked adenines. The results provide complementary information for understanding the nonradiative decay process of stacked adenines.

2. Methodology

Our technique for this study is semiclassical electron-radiation-dynamics (SERID). A detailed description of this method has been published elsewhere [26,27] and only a brief description is presented here. In this method, the valence electrons are treated with a quantum mechanical approach while both the radiation field and the motion of the nuclei are treated classically. The one-electron states are updated by solving the time-dependent Schrödinger equation at each time step (usually 0.05 femtosecond in duration) in a nonorthogonal basis,

$$i\hbar \frac{\partial \Psi_j}{\partial t} = S^{-1} \cdot \mathbf{H} \cdot \Psi_j \quad (1)$$

where \mathbf{S} represents the overlap matrix of the molecular orbitals. The vector potential \mathbf{A} of the radiation field is included in the electronic Hamiltonian via the time-dependent Peierls substitution [28]

$$H_{ab}(\mathbf{X} - \mathbf{X}') = H_{ab}^0(\mathbf{X} - \mathbf{X}') \exp(\mathbf{A} \cdot (\mathbf{X} - \mathbf{X}')) \quad (2)$$

where $H_{ab}(\mathbf{X} - \mathbf{X}')$ is the Hamiltonian matrix element for basis functions a and b on atoms at position of \mathbf{X} and \mathbf{X}' respectively, and $q = -e$ is the charge of the electron.

The forces acting on nucleus or ions are computed by the Ehrenfest equation using an “on the fly” model:

$$M_l \frac{d^2 X_{l\alpha}}{dt^2} = -\frac{1}{2} \sum_j \Psi_j^+ \cdot \left(\frac{\partial \mathbf{H}}{\partial X_{l\alpha}} - i\hbar \frac{1}{2} \frac{\partial \mathbf{S}}{\partial X_{l\alpha}} \cdot \frac{\partial}{\partial t} \right) \cdot \Psi_j - \partial U_{\text{rep}} / \partial X_{l\alpha} \quad (3)$$

where U_{rep} is the effective nuclear–nuclear repulsive potential and $X_{l\alpha} = \langle \hat{X}_{l\alpha} \rangle$ is the expectation value of the time-dependent Heisenberg operator for the α coordinate of the nucleus labeled by l (with $\alpha = x, y, z$).

The Hamiltonian matrix \mathbf{H} , overlap matrix \mathbf{S} , and effective nuclear–nuclear repulsive potential U_{rep} are calculated in the density-functional tight-binding approximation (DFTB) [29,30]. These quantities are functions only of the nuclear distance and

the results from the calculations for a dimer can be tabulated and employed in the time-dependent calculations. The basis functions used in the present simulations are the 1s atomic orbital of H and the valence s and p orbitals of C and N. No distinctions are made for spin-up and spin-down states. In this approach, the electronic energy of a molecule can be written as

$$E_{\text{elec}} = \sum_{i=\text{occ}} n_i \varepsilon_i + \sum_{\alpha > \beta} U_{\text{rep}}(|X_\alpha - X_\beta|) \quad (4)$$

where ε_i and n_i are the eigenvalue and occupation number of Kohn–Sham orbital i . The first summation goes over all occupied orbitals. Potential energy $U_{\text{rep}}(|X_\alpha - X_\beta|)$ is a function of the inter-atom distance.

The DFTB method has been successfully applied to study the ground state properties of various systems, including solid state physics and biochemical problems [31,32]. More recently, DFTB has been used for a simplified calculation for the DFDFDFT response equation [33]. The calculation was found to be reliable in reproducing excited state energies and geometries of ab initio TDDFT with remarkable quality. Applied to an amino acid model system, DFTB was found to be a promising method to describe polarization and charge-transfer effects in large systems [34], like the system that we investigate in this paper. We have previously applied the SERID technique to study the photoisomerization mechanism of azobenzene by $n\pi^*$ excitation [35] and isomerization quantum yields [36] for $n\pi^*$ and $\pi\pi^*$ excitations. The method has also been used in biologically-relevant studies (nonadiabatic decay for adenine [5], photodissociation of cyclobutane thymine dimer [37], and photoinduced dimerization of thymine [38]) and the results were found to be consistent with experimental observations. A limitation of this method is that the simulation trajectory moves along a path produced by averaging over all the terms in the Born–Oppenheimer expansion [39–43],

$$\Psi^{\text{total}}(X_n, x_e, t) = \sum_i \Psi_i^n(X_n, t) \Psi_i^e(x_e, X_n) \quad (5)$$

rather than following the time evolution of a single potential energy surface – which is approximately decoupled from all the others [44–46]. (Here, X_n and X_n represent the sets of nuclear and electronic coordinates respectively, and the Ψ_i^e are eigenstates of the electronic Hamiltonian at fixed X_n .) The strengths of the present approach include (1) the inclusion of all $3N$ nuclear degrees of freedom, and (2) the incorporation of both the excitation due to a laser pulse and the subsequent de-excitation at an avoided crossing near a conical intersection.

Fig. 1 shows the structure and atomic numbering scheme for an adenine molecule. To produce a ground state equilibrium geometry for these simulations, a “B configuration” consisting of two adjacent adenines is taken at random from a B-type duplex DNA strand, $(dA)_{20}$; the ribose and phosphate groups are ignored. The equilibrated geometry, obtained after the running the simulation through 1000 fs, is shown in Fig. 2. We will refer to the adenine molecule that ends up being excited as A and its atoms are labeled as N_1, C_2 , etc.; corresponding atoms in the other molecule, referred to as A' , are labeled as N'_1, C'_2 , etc. The two molecules are stacked such that the interatomic distances ($C_4-C'_4$) and ($C_5-C'_5$) are 4.01 and 3.81 Å, respectively, and the dihedral angle ($C_4-C_5-C'_5-C'_4$) is 36.2°. An alternate view (“from the top”) of the stacked adenines is shown on the right side of Fig. 2. Starting with the equilibrated geometry in Fig. 2, the simulation was run for an additional 100 fs; the geometries obtained at 1-fs intervals were used as initial geometries subjected to laser excitation. A laser pulse with a Gaussian profile (25 fs fwhm and 3.90 eV photon energy) was applied. This energy was selected to match the energy gap between the HOMO and LUMO. This energy is lower than the vertical excitation energy

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