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Analysis of ultrafast relaxation in photoexcited DNA base pairs of adenine and thymine

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Abstract

The photoinduced dynamics in base pairs of adenine and thymine were analyzed by femtosecond pump-probe spectroscopy. On the short-time scale up to a few picoseconds, the characteristic time constants for the dimers are quite similar to the corresponding values of the monomers. This leads to the conclusion that ultrafast intramolecular relaxation proceeds via $\pi\pi^*$ and $n\pi^*$ states of one component within the dimer. On the long-time scale, we obtained a novel time constant of roughly 40 ps for the thymine dimer and the adenine–thymine base pair. This time constant was never observed in the monomers and is tentatively assigned to an intermolecular relaxation process, possibly via a hydrogen transfer state.

Keywords: Adenine; Thymine; Excited state relaxation; Internal conversion; Time-resolved spectroscopy; Multiphoton ionization; DNA photochemistry

1. Introduction

To elucidate the photostability of DNA structures, the study of fundamental processes in photoexcited, isolated base pairs can reveal essential information. The inherent properties of the molecular building blocks are studied in absence of a surrounding medium allowing direct comparison to ab initio theory. In this context, the theoretical work of Wolfgang Domcke, the honorary of this special edition, proved to be of outstanding value for the conception and interpretation of experimental studies as the one presented here.

The photophysics of the monomer bases provides a basis for the understanding of the base pairs. The photodynamics for the adenine monomer have been well characterized, experimentally and theoretically [1–3]. After excitation of the lowest $\pi\pi^*$ state, e.g. at a wavelength of 267 nm, a fast internal conversion ($\lesssim$100 fs) leads to the lower-lying $n\pi^*$ state or – with a certain branching ratio [4] – to a $\pi\sigma^*$ state. Whereas the lifetime of the $n\pi^*$ state is about 1 ps, the $\pi\sigma^*$ state decays much faster by internal conversion to the electronic ground state or by H atom dissociation [5–7]. Similar dynamics have been proposed for the thymine monomer: a $\pi\pi^*$ state is excited in the same wavelength region and decays within 100 fs to an $n\pi^*$ state with a lifetime of about 7 ps [1,8]. However, further decay channels leading to longer living electronic states up to the ns time scale [9,10] are discussed for thymine. A different assignment of the $\pi\pi^*$ and $n\pi^*$ dynamics was very recently proposed by theory [11].

With respect to the dimers, interesting results have been obtained for adenine by nanosecond laser spectroscopy [12]. The spectroscopic detection of AH radicals after $\pi\pi^*$ state excitation of the dimer A_2 is interpreted as the result of an H atom transfer in the excited state followed by dissociation [5]. The H-transfer reaction is initiated by a charge-transfer in a $\pi\pi^*$ state (i.e. intermolecular excitation from the HOMO of one monomer to the LUMO of the other monomer), followed by the transfer of a proton along the hydrogen binding coordinate. Such an H-transfer reaction has also been identified for a model system of base pairs, the aminopyridine dimer [13,14]. Theoretical studies

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suggested that this reaction should also dominate the photochemistry in the Watson–Crick (WC) base pairs of GC [15] and AT [16]. The latter study stated that the H-transfer predicted for the WC structure of AT is unlikely to occur in the AT structures formed in a molecular beam. This statement seems to be confirmed by corresponding nanosecond spectroscopic experiments where on one hand the WC structure of AT was not detected [17] and on the other hand no products of an H-transfer were observed [5]. No comparable results exist for the thymine dimer. In all cases, a nearly planar hydrogen bound structure is assumed for the dimers, which is in agreement with theoretical studies of planar and stacked structures of base clusters [18].

Our first pump-probe experiments on the dimers of adenine and thymine established that mainly intramolecular processes occur on the short-time scale (up to 3 ps): the dynamic behavior of the dimers A_2 and T_2 can be characterized in good approximation by the decay times measured for the corresponding monomers A and T [8]. Subsequent studies of dimer photoelectron spectra by femtosecond electron–ion coincidence (FEICO) detection have shown that the signals from secondarily populated states are scarcely observable in the dimer mass channels. This is due to nearly complete fragmentation of the corresponding ions after probe photon absorption. The dynamics of these states could instead be analyzed in the mass channels of the corresponding fragments AH^+ and TH^+ [19].

By including the fragment channels in our analysis of time-resolved mass spectroscopy, we now present a more comprehensive interpretation of the dynamics in the dimers of adenine and thymine. Measurements at larger delay times (up to 150 ps) between pump and probe pulses reveal novel decay dynamics on the extended picosecond time scale, which seem to reflect relaxation channels due to intermolecular interaction in the dimers.

2. Experimental setup

Samples of adenine and thymine (Sigma–Aldrich, 99% purity) were evaporated in a metal oven at 220 °C and then expanded into vacuum with 1–1.5 bar He as carrier gas. The expansion occurred through a heated pulsed valve (General Valve, series 9), modified for high temperatures with a repetition rate of ~100 Hz. Clustering was aided by attaching a small angle cone to the pulsed valve to increase the number of molecular collisions. The cluster distribution was controlled by changing the backing pressure of He and the time delay between the pulsed valve opening and the laser pulses. For all data shown here, we restricted the width of the cluster distribution to a minimum to avoid signals from trimers or larger clusters. Comparison with spectra for broader cluster distributions helped to assign signals from the fragmentation of larger clusters, but will not be discussed further. The ions were detected in a linear time-of-flight mass spectrometer. This experimental method allows no isomer selective excitation and we study the sum of ion signals from all dimer structures formed in the molecular beam.

A commercial femtosecond Ti:Sa laser (Clark MXR) was used for the pump-probe experiments. The clusters were excited by the pump pulses formed by the third harmonic of the fundamental wavelength ($\lambda_{pu} = 267$ nm). Both, the fundamental wavelength ($\lambda_{pr} = 800$ nm) and the second harmonic ($\lambda_{pr} = 400$ nm) were used for the probe beam. The pump and the probe pulses were focused into a spot of about 100 μm diameter while interacting with the molecules. The laser pulses had a pulse duration of ≈100 fs and a repetition rate of 1 kHz. The energy of pump beam (0.3 μJ) and probe beam (6–25 μJ) was further attenuated with neutral density filters until we observed <0.2 ions per laser shot from the pump beam or probe beam alone. The pump-probe signals at the temporal overlap of pump and probe pulses (delay time zero) were typically 10 times larger than the one-color signals; the latter were measured and subtracted to obtain the true pump-probe signal. With our multiphoton probe step, we must worry about the possible effect of intermediate (higher) resonances in the neutral. We observed no such effect in the monomers, where data for one-photon ionization are available [2,20]. Signals with higher pump or probe intensity were investigated to identify effects due to higher-order processes, such as above-threshold ionization or the absorption of additional photons in the ion.

The data acquisition routine collected mass spectra at different pump-probe delays. The time-resolved ion signals are proportional to the excited state populations and reflect the excited state lifetimes of the clusters. Each measurement point was obtained by accumulating $3–16 \times 10^3$ laser shots with alternating up- and down-scans of the delay unit. The signal-to-noise ratio was significantly worse for the experiments with 400 nm ionization.

3. Experimental results

Pump-probe cluster mass spectra with 267 nm excitation and 800 or 400 nm ionization showed base monomers and dimers, as well as protonated monomer signals (Fig. 1). Corresponding time-resolved measurements on a time scale up to delay times of 140 ps are shown in Figs. 2 and 3. The signals were fitted with a superposition of mono-exponential signal contributions with the time constants $\tau_1, \ldots, \tau_4$. The large τ_4 and τ_3 decay times determined here were used subsequently for a fitting of the time-dependent ion signals on the intermediate time scale (Fig. 4) and on the short-time scale up to 4 ps (Figs. 5 and 6). The signal strength for the different masses given in the ordinate are in scale within one figure but not between the figures. The ratio between the signal maximum near delay zero and the points at positive delays may be suppressed due to the large tuning steps of the delay time (here 3 ps) which may not properly sample the ultrashort peak near delay zero. In Figs. 2 and 3, we compare the time-dependent signals of the monomers A and T with those of the protonated