

**Ultrafast Decay Dynamics of the Excited DNA Base Pairs :
Adenine-Thymine, Adenine-Adenine and Thymine-Thymine**

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Decay dynamics of the excited DNA base pairs of adenine-thymine (A-T), adenine-adenine (A-A) and thymine-thymine (T-T) were investigated in gas phase using femtosecond, time-resolved photoionization spectroscopy. All transients exhibited bi-exponential decay with two distinct time constants. The fast components of A-T and A-A ($\tau_f = 530$ and 390 fs respectively) were attributed to relaxation of locally excited adenine moiety in the base pairs from initially prepared $\pi\pi^*$ state to the electronic ground state through internal conversions, while the slow components ($\tau_s = 3.9$ and 3.1 ps respectively) were associated with formation of hydrogen-atom-transferred complex and its decay to the ground state. The transient of T-T showed the temporal behavior very similar to that of thymine monomer (T1), indicating that relaxation occurred through the same pathway of T1. However, we also found evidence in the transient of protonated thymine monomer that there would be another relaxation pathway of hydrogen-atom transfer in T-T. We suggest that hydrogen bonding in DNA base pairs plays an important role in decay dynamics, not only by facilitating fast relaxation of the locally excited adenine or thymine moiety in A-T, A-A and T-T, but also by opening a new relaxation pathway of hydrogen-atom transfer.