UV Photodynamics of Thymine-Thymine Stacked Nucleobases in Peptide Nucleic Acids



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ABSTRACT

Biological nucleobases exhibit sub picosecond excited state lifetimes, preventing potential damage from UV radiation and suggesting photochemical selection of the building blocks of life on a prebiotic earth. This intrinsic property shifts when as nucleobases are complexed with a sugar moiety or paired with another base, as changes to their electronic energies provide alternative decay pathways. For example, stacked bases are known in solution to exhibit an ultrafast exciplex formation channel, which safely decays to the ground state via charge recombination in the order of 100 picoseconds. We explore stacking effects in the gas phase by probing the excited state dynamics of two stacked homodimers: guanine-guanine (G-G) and thymine-thymine (T-T) bound to peptide nucleic acid (PNA), an analog of the negatively charged backbone of DNA. Laser desorption jet cooling coupled with resonance enhanced multiphoton ionization (REMPI) allows us to survey detailed stacking interactions in the gas phase in conjunction with theoretical calculations. We measured excited state lifetimes from picosecond pump-probe measurements, finding a lifetime in the order of 100 nanoseconds for T-T PNA. IR-UV double resonance spectroscopy revealed the diketo tautomeric form of T-T PNA. We conclude that in the absence of solvent an excimer decay channel is unavailable in isolated T-T PNA suggesting that solvation may be necessary for stabilization of base stacking.

BACKGROUND

DNA and RNA nucleobases absorbs UV radiation yet achieves photostability by dissipating their electronic electronic by ultrafast relaxation by various mechanisms. Structural motifs such as base pairing and stacking introduce unique photophysical pathways. For example, stacked bases in solution exhibit excimer formation in the orders of 150 picoseconds



To study the effects of base stacking independent of solvent, we use **peptide nucleic acid** as a pseudo backbone and attached homodimers thymine thymine or guanine guanine





TECHNIQUE

- 1. **Desorption**: Desorb intact solid molecule into gas phase using 1064nm Yd:YAG
- 2. **Jet cooling:** Entrain molecule into an argon molecular beam using pulse valve, which provides cooling to ~10K
- 3. Laser excitation and ionization
 - a. Resonance enhanced multiphoton ionization (REMPI): Bring molecule to excited state using picosecond scanning optical parametric generator and ionize using ps/ns 213 nm laser
 - b. IR-REMPI: Obtain structural information with IR spectra of excited molecule
 - c. Pump-probe: Measure excited state lifetime in orders of picosecond and nanoseconds
- 4. **Mass Detection**: Ion is detected with reflectron time of flight mass spectrometer



RESULTS

Resonance 2 Photon Ionization

- GG PNA and TT PNA in the excited states
- GG PNA = low signal to noise
- TT PNA comparable to isolated thymine

IR-UV Double Resonance

• TT PNA exhibits stacking and diketo tautomeric form in the excited state

Excited State Lifetime Measurements

• Biexponential fit shows a fast 30ps decay similar to isolated thymine and a long 100ns decay which may attribute to a triplet state



Conclusion: Excimer formation was *not* observed in isolated TT PNA **Future studies**: Examine adenine (AA) PNA homodimer



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