Potential Energy Surface for the Photophysics of Adenine-Uracil Monophosphate Dimer (ApU)

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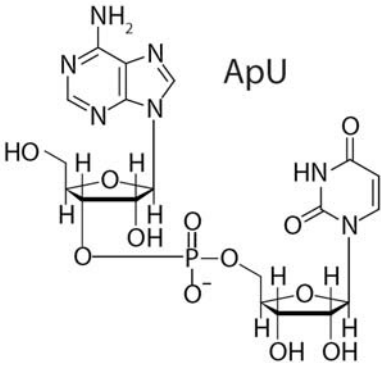
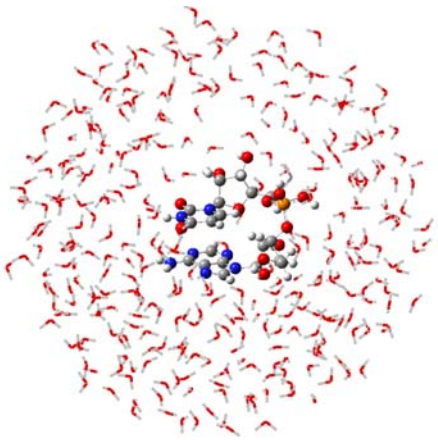
UV light is strongly absorbed by DNA, producing excited states that sometimes initiate damaging photochemical reactions. Highly efficient nonradiative decay pathways guarantee that most excited states do not lead to deleterious reactions but instead relax back to the ground state. The photophysics of the DNA bases, which are the light-absorbing components of DNA, is characterized by short lifetimes of several picoseconds or less. However, recent experiments by Kohler et al. show that the excess electronic energy relaxes one or two orders of magnitude more slowly in a series of diribonucleoside monophosphates ApA, ApG, ApC, ApU and CpG. [1]

The potential energy surface of ApU in water (see below) has been calculated at QM/MM level, using ONIOM(CASPT2//CASSCF/6-31+g(d):Amber) method. We have located four different exciplex minima ((AA^*), (UU^*), $(AU)^*$, and (A^+U^-)) which can be used to explain the experimental observations quite well. The characteristic of these four exciplex minima and their deactivation processes are discussed in detail.





[1] Takaya, T.; Su, C.; Harpe, K. d. L.; Crespo-Hernández, C. E.; Kohler, B. *Proc. Nat. Acad. Sci.* 2008, *105*, 10285-10290.