

Details of the Excited State Potential Energy Surfaces of Adenine by Coupled-Cluster Techniques

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To understand what happens with DNA after UV irradiation, the most logical route, both theoretically and experimentally, should start with the investigation of the nucleobases, the principal building blocks of DNA responsible for the absorbance of UV photons.

Theoretical results for the nucleobases are found to be highly dependent on the method and as a consequence, the interpretation of the measured spectra and the proposed decay paths can differ significantly. High level quantum chemical calculations are needed to understand more about the ordering of excited states and the location of conical intersections.

In this study the ultrafast deactivation of adenine was investigated using Coupled-Cluster methods. Calculations on the three lowest singlet excited states (two $\pi \rightarrow \pi^*$ and an $n \rightarrow \pi^*$ state) of the canonical tautomer were performed using the EOM-CCSD and the iterative LR-CC2 methods with cc-pVDZ basis set.

Equilibrium structure could only be obtained for the S_1 state which has $n \rightarrow \pi^*$ character. It was shown that no minimum for the S_2 and S_3 states exists in the Frank-Condon region due to conical intersections between these low lying states. To understand the topology of the surfaces, relevant cuts of the potential energy surfaces have also been calculated and conical intersections have been located. Even a three-fold intersection was found between the three lowest excited states. These crossings can be reached barrierlessly from the bright $\pi \rightarrow \pi^*$ state, without major change in the geometry. Therefore the conical intersections found here might play an important role in the ultrafast deactivation of adenine.