

DETAILS OF THE EXCITED STATE POTENTIAL ENERGY SURFACES AND EXCITATION SPECTRA OF ADENINE BY COUPLED-CLUSTER TECHNIQUES

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The potential energy surfaces of excited states of adenine, one of the building blocks of DNA, were investigated by coupled-cluster methods. Calculations on the four lowest singlet excited states of the canonical tautomer were performed using the CCSD and CC2 methods with cc-pVDZ basis set. In the equilibrium structure of the S_1 state, which has an $n - \pi^*$ character, an out-of-plane distortion of the six-membered ring can be observed. It seems that the two $\pi - \pi^*$ states (S_2 and S_3) do not have minima in the region that affects the relaxation dynamics. During the geometry optimization of the S_2 state, the molecule relaxes to the S_1 minima after a change of character. Energy minimization of the S_3 state leads to the immediate vicinity of a three-state conical intersection of the S_1 , S_2 , and S_3 states.

In order to understand the topology of the potential energy surfaces, different cuts of the surfaces were obtained. These indicate that the S_1 - S_2 crossing takes place close to the ground state minima, and has an energy lower than the vertical excitations.

Searches for the minima on the crossing seams lead to two- and three-state conical intersections. The intersection between the S_1 and S_2 states is located at an energy lower than the vertical excitation energies and the crossings estimated from the PES cuts. In the S_1 - S_2 - S_3 three-state intersection, the energy is comparable to the vertical excitation energy of the first state. The geometry is planar in both intersections, with significant changes in the bond lengths of the six-membered ring.

Finally, the excitation spectra of adenine including five excited states have been simulated and compared to experiment. In the case of the UV absorption spectrum excellent agreement between the calculated and the matrix UV (measured also in our laboratory) spectra could be found, which indicates high accuracy of the calculated (EOM-CCSD(T)) data. Low energy part of the calculated spectrum was also compared to experiment (R2PI and similar techniques). Here our results seem to resolve some long debated assignment issues.