Electronic structure of the ionized DNA bases clusters: the effects of H-bonding and stacking interactions.

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Electron hole formation is the primary step of DNA oxidative damage and charge transfer causing distant mutations in the DNA sequence. Ionization energies of the nucleic-acid bases (NAB) in their natural environment are decreased in comparison to those of isolated bases due to stabilization of open-shell cation through hydrogen bonds formation, stacking interaction with neighboring bases and electrostatic interactions. Isolated dimers of the A, T bases and $(AT)_2$ tetramer are considered as model systems. The influence of the H-bonding and stacking interactions on the vertical ionization energies of the NAB monomers and dimers, electronic structure of produced cations is analyzed using equation-of-motion coupled-cluster (EOM-IP-CCSD). IP-CISD and DFT methods are employed to study ionization of the $(AT)_2$ tetramer. It is shown that inter-fragment interactions affect ionized states of the NAB dimers via two distinct mechanisms: hole delocalization and electrostatic interactions. H-bonding and stacking interactions have profound impact on ionization energies of NAB in dimers: ionization energies in dimers can be decreased by as much as 0.4-0.5 eV. Both factors are also found to contribute to the strong decrease in ionization energy of the tetramer. The hole is found to be delocalized over two A bases, which results in 0.45 eV decrease of the ionization energy. H-bonding between AA and TT stacked pairs leads to further stabilization of the ionized state by 0.24 eV.