

Proton transfer driven by excess electrons in bound anionic states

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I will discuss bound anionic states in nucleic acid bases and amino acids. In hydrogen bonded complexes the excess electron attachment can induce intermolecular proton transfer, which leads to formation of radicals of hydrogenated species. These radicals are characterized by quite large electron affinities and may trigger further chemical transformations, such as strand breaks in DNA. The excess electron can also trigger intramolecular proton transfer, i.e., a tautomerization. New tautomers of nucleic acid bases will be discussed which result from proton transfer from a nitrogen site to a carbon site. These new tautomers are the most stable among valence anionic nucleic acid bases and some of them are adiabatically bound with respect to the corresponding canonical neutral. Possible formations pathways for these new tautomers will be discussed. The new anionic tautomers are characterized by quite large vertical electron detachment energies ($1.0 \text{ eV} < \text{VDE} < 2.5 \text{ eV}$). When only canonical tautomers of nucleic acid bases are considered the ordering of nucleic acid bases based on their excess electron affinity is: $\text{U} (\sim 0 \text{ eV}) > \text{T} (-0.09 \text{ eV}) > \text{C} (-0.19 \text{ eV}) > \text{G} (-0.46 \text{ eV}) > \text{A} (\text{vertically unbound})$. On the other hand, when all biologically relevant tautomers are considered the ordering becomes: $\text{G} (0.37 \text{ eV}) > \text{U} (-0.05 \text{ eV}) > \text{T} (-0.09 \text{ eV}) > \text{C} (-0.09 \text{ eV}) > \text{A} (-0.32 \text{ eV})$. Evolution of amino acids from canonical to zwitterionic tautomers upon hydration and electron attachment will be discussed.