

Double Resonance Spectroscopy of isolated DNA bases and base pairs: Structure and Photochemistry

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Intrinsic properties of isolated biomolecules and large parts of their energy landscape can be investigated by high resolution laser spectroscopy in molecular beams and directly compared to theory. Different tautomers and electronic states of Adenine as well as Adenine-Thymine and Adenine-Adenine and their methyl substituted derivatives are observed and assigned based on resonant two photon ionisation and IR-UV and UV-UV double resonance experiments in a supersonic jet. Expansion conditions were chosen to preferentially form small clusters. The IR-UV spectrum in the range of the NH stretch vibrations fits cluster structures with $\text{HNH}\cdots\text{O}=\text{C}/\text{N}\cdots\text{HN}$ hydrogen bonding based on the comparison with the A and T monomer IR spectra and with ab initio calculated vibrational spectra of the most stable A-T isomers. The Watson-Crick A-T base pair is not the most stable base pair structure at different ab initio levels and its vibrational spectrum is not in agreement with the observed experimental spectrum. The Adenindimer shows $\text{HNH}\cdots\text{N}/\text{N}\cdots\text{HN}$ hydrogen bonding. 9-Methyladenine – adenine has a stacked structure and exhibits extremely efficient hydrogen transfer upon electronic excitation. Adenine shows H atom dissociation upon UV excitation as exhibited by 2+1-REMPI at 243 nm.

The results show that isolated AT and GC do not form the Watson-Crick structures. Probably the special orientation of the DNA backbone forces these structures. The photochemical stability of the DNA bases and bases pairs and their mechanism of conversion of electronic excitation to the ground state is critically discussed based on our experimental results of hydrogen transfer and N-H photodissociation.