CORE LEVEL SPECTROSCOPY AND TAUTOMERISM OF KEY BIOMOLECULES IN THE GAS PHASE

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The nucleobases cytosine, thymine and uracil are pyrimidine derivatives. They pair with their complementary purines, guanine and adenine, through hydrogen bonding to form DNA and RNA chains. The tautomeric forms of DNA bases are capable of unusual base pairing like thymine-guanine and cytosine-adenine and create mutations, which are the precursors of some molecular-based diseases. Low energy spectroscopies such as microwave, laser and infrared techniques are commonly used as methods to investigate the conformatonal and tautomeric equilibria of biomolecules, while the high energy technique of x-ray photoemission spectroscopy (XPS) has yielded a smaller amount of significant structural information about biomolecules in the gas phase. In the present studies we successfully apply XPS to the study of five nucleic acid base tautomers, as well as the prototypical system 2-hydroxypyridimine and the related molecules S-methyl-2-thiouracil and 2-thiouracil in the vapor phase. XPS is a quantitative technique, allowing the experimental determination of the populations of keto and enol tautomers at known equilibrium temperatures: it is difficult to obtain this information otherwise. The effect of different substituents on stability of tautomers has been revealed. Quantum chemistry calculations have been carried out in order to obtain information about the structure, relative stability and difference in populations of the tautomers and conformers under study.