TAUTOMERISM OF THE DNA BASE GUANINE AND ITS METHYLATED DERIVATIVES AS STUDIED BY GAS-PHASE IR AND UV SPECTROSCOPY

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Calculations suggest that only four tautomeric forms of the guanine DNA base should be significantly populated in the gas phase. Because of the fragility of the molecule only a few expermental studies have been dedicated to the gas-phase molecule so far and only three species have been identified. The present IR-UV depletion spectroscopic study, carried out in a supersonic expansion coupled to a desorption device, extends the recent data of literature by providing evidence for the existence of a fourth form of guanine in the gas phase. The comparison of the UV and IR signatures of the four forms together with those of the 7- and 9-methylated derivatives allows us to build up a new assignment in terms of enol/keto and 7/9NH tautomerisms. From this complete picture, it turns out that the UV spectroscopy of free guanine is mainly controlled by the 7/9NH tautomerism: both 7NH tautomers observed are red shifted compared to the 9NH ones, with the following origin transition order, from red to blue: 7NH enol (32864 +/-5 cm^{-1}), 7NH keto (+405 cm^{-1}), 9NH keto (+1046 cm^{-1}) and 9NH enol (+1891 cm^{-1}); 7-, 9- or 1-methylations are found to cause only moderate red shifts (less than 400 cm^{-1}). The opposite trend is observed for the IR spectroscopy, which appears to be essentially controlled by the enol/keto tautomerism. This study exemplifies the need for cross-checked experimental approaches, namely the IR/UV depletion spectroscopy or the study of relevant methylated species, in order to reach a global and consistent assignment, even in rather simple biological systems such as purine bases.

Additional spectroscopic data, namely fluorescence spectra and lifetimes measurements, provide evidence for the fluorescent character of first near UV electronic state of all tautomers, in contrast to the short lifetimes reported in solution.