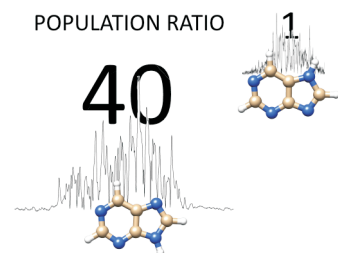


SOLVING THE TAUTOMERIC EQUILIBRIUM OF PURINE THROUGH THE ANALYSIS OF THE COMPLEX HYPERFINE STRUCTURE OF THE FOUR ^{14}N NUCLEI

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Microwave spectroscopy has been restricted to the investigation of small molecules in the last years. However, with the advent of FTMW^{a,b} and CP-FTMW^c spectroscopies coupled with laser vaporization techniques^d it has turned into a very competitive methodology in the studies of moderate-size biomolecules.

Here, we present the study of purine, characterized by two aromatic rings, one six- and one five-membered, fused together to give a planar aromatic bicycle. Biologically, it is the mainframe of two of the five nucleobases of DNA and RNA. Two tautomers were observed by FTMW spectroscopy coupled to UV ultrafast laser vaporization system. The population ratio of the two main tautomers [N(7)H]/[N(9)H] is about 1/40 in the gas phase. It contrasts with the solid state where only the N(7)H species is present, or in solution where a mixture of both tautomers is observed. For both species, a full quadrupolar hyperfine analysis has been performed. This has led to the determination of the full sets of diagonal quadrupole coupling constants of the four ^{14}N atoms, which have provided crucial information for the unambiguous identification of both species.

^a T. J. Balle and W. H. Flygare *Rev. Sci. Instrum.* **52**, 33-45, 1981.

^b J.-U. Grabow, W. Stahl and H. Dreizler *Rev. Sci. Instrum.* **67**, 4072-4084, 1996.

^c G. G. Brown, B. D. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman and B. H. Pate *Rev. Sci. Instrum.* **79**, 0531031/1-053103/13, 2008.

^d E. J. Cocinero, A. Lesarri, P. Écija, F. J. Basterretxea, J. U. Grabow, J. A. Fernández and F. Castaño *Angew. Chem. Int. Ed.* **51**, 3119-3124, 2012.