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Advances on the identification of DNA bases specific isomers via high accuracy single photon ionization and ab initio computations

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DNA/RNA bases and amino acids are building blocks of life. The spectroscopy and stability of their ionic forms are relevant to their survival rate under interstellar conditions, and to the field of radiation damage, where ionizing radiation can lead to DNA/RNA strand breaking and production of hazardous by-products through processes involving nucleobases.
Several experimental works at BESSY II, Advanced Light Source and synchrotron SOLEIL were devoted to unveil the structure and the spectroscopy of the cationic species of DNA bases and amino acids and analogues [1]. Since they possess numerous tautomers and isomers that lie close in energy, the experimental characterization of a unique tautomer is challenging.
At present, we apply single photon VUV synchrotron based experiments combined with state-of-the-art ab initio methodology to determine the adiabatic ionization energies (AIE) of specific gas phase DNA bases tautomers produced in a molecular beam. The experiments were performed at the undulator-based DESIRS beamline of the French synchrotron facility SOLEIL in connection with its 6.65 m normal incidence monochromator and the double imaging photoelectron photoion coincidence (i2PEPICO) spectrometer DELICIOUS3. [2] The coincidence scheme allows the photoelectron images to be filtered as a function of mass and ion kinetic energy in a multiplex manner. Treatment of such photoelectron images as a function of the photon energy leads to the threshold / slow photo electron spectroscopy of the selected masses [3,4].
Theoretically, the structures and the energetics of neutral and cationic DNA bases tautomers were determined using either explicitly correlated methods or density functional theory –explicitly correlated approaches composite schemes, where we consider core-valence (CV), scalar relativistic (SR) and zero point energy (ZPE) corrections. The atoms are described using the aug-cc-pVTZ basis sets. These computations are carried out using Gaussian 09 and MOLPRO suites of programs [5,6].
The experimental spectra of jet cooled DNA bases correspond to well resolved bands that are attributable to the specific contribution of a unique or several neutral tautomers of DNA bases prior to ionization. Their AIEs are experimentally determined for the first time with an accuracy of 0.003 eV. A good agreement with theoretical values is also observed.
Our work can be generalized to other molecular entities presenting a dense pattern of isomeric and tautomeric forms in their spectra that can be investigated to understand the charge redistribution in these species upon ionization. Several examples will be presented [7-10].

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Summary

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