Electronic and Vibrational Spectroscopy of 1-Methylthymine and its Water Clusters: The Dark State Survives Hydration


Electronic and vibrational gas phase spectra of 1-methylthymine (1MT) and 1-methyluracil (1MU) and their clusters with water are presented. Mass selective IR/UV double resonance spectra confirm the formation of pyrimidine-water clusters and are compared to calculated vibrational spectra obtained from ab initio calculations. In contrast to Y. He, C. Wu, W. Kong; J. Phys. Chem. A, 2004, 108, 94 we are able to detect 1MT/1MU and their water clusters via resonant two-photon delayed ionization under careful control of the applied water-vapor pressure. The long-living dark electronic state of 1MT and 1MU detected by delayed ionization, survives hydration and the photostability of 1MT/1MU cannot be attributed solely to hydration. Oxygen coexpansions and crossed-beam experiments indicate that the triplet state population is probably small compared to the \(^{1}n\pi^{*}\) and/or hot electronic ground state population. Ab initio theory shows that solvation of 1MT by water does not lead to a substantial modification of the electronic relaxation and quenching of the \(^{1}n\pi^{*}\) state. Relaxation pathways via \(^{1}\pi\pi^{*}\rightarrow n\pi^{*}\) and \(^{1}\pi\pi^{*}\rightarrow S_{0}\) conical intersections and barriers have been identified, but are not significantly altered by hydration.