SPECTROSCOPY AND MOLECULAR STRUCTURES OF Al AND Li COMPLEXES OF DNA AND RNA BASES

SERGIY KRASNOKUTSKI, JUNG SUP LEE, and DONG-SHENG YANG, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*.

1:1 M-L (M = Al, Li; L = cytosine, uracil, thymine, adenine, guanine) complexes were produced by laser vaporization of a rod made of the metal and nucleobase powders in molecular beams. The ionization thresholds of these complexes were measured with photoionization efficiency spectroscopy. Vibrationally resolved spectra of the uracil, thymine, and adenine complexes were obtained with pulsed field ionization-zero electron kinetic energy (ZEKE) spectroscopy. The ZEKE spectra display strong transitions between the zero vibrational levels of the ground electronic states of the neutral molecule and ion and several metal-ligand and ligand-based vibrational excitations. The adiabatic ionization energies of Al-uracil, Al-thymine, Li-uracil, Li-thymine, and Li-adenine were measured to be 43064, 42322, 33908, 33384, and 32240 cm^{-1}, respectively, with an uncertainty of about 5 cm^{-1}. The lowest-energy isomers of the cytosine, uracil, and thymine complexes are planar with metal binding to the O2 and N3 atoms of cytosine or the O4 atom of uracil and thymine. The preferred structures of the adenine complexes are also planar with Li binding to the N7 atom in the imidazole ring and the nitrogen atom of the amino group. The structures of the guanine complexes are different from others, where the imidazole ring is no longer planar and the primary metal binding site is the O6 atom. Additionally, the metal-ligand bond dissociation energies of several neutral complexes were derived from thermochemical cycles.