



BILKENT UNIVERSITY

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FACULTY OF SCIENCE

MATERIALS SCIENCE and NANOTECHNOLOGY

GRADUATE PROGRAM SEMINAR

“Infrared Multiple Photon Dissociation Spectroscopy, Guided Ion Beam and Theoretical Study of Alkali Metal Interactions with Histidine”

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The interactions between histidine (His) with the alkali metal cations (Na^+ and K^+) have been investigated using guided ion beam mass spectrometry. Bond energies are determined using threshold collision-induced dissociation of the $\text{M}^+(\text{His})$ complexes with xenon in a guided ion beam mass spectrometer. In order to assign ground state conformations of these and related complexes more definitively, the gas-phase structures of cationized His, including complexes with Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ , as well as protonated His, are examined by infrared multiple photon dissociation (IRMPD) action spectroscopy utilizing light generated by a free electron laser (FELIX), in conjunction with quantum-chemical calculations. To identify the structures present in the experimental studies, measured IRMPD spectra are compared to spectra calculated at B3LYP/6-311+G(d,p) (H^+ , Li^+ , Na^+ , and K^+ complexes) and B3LYP/HW*/6-311+G(d,p) (Rb^+ and Cs^+ complexes) levels of theory, where HW* indicates that the Hay-Wadt effective core potential with additional polarization functions was used on the metals. Single point energy calculations were carried out at the B3LYP, B3P86, and MP2(full) levels using the 6-311+G(2d,2p) basis set. On the basis of these experiments and calculations, the only conformation that reproduces the IRMPD action spectra for the complexes of the smaller alkali metal cations, $\text{Li}^+(\text{His})$ and $\text{Na}^+(\text{His})$, is a charge-solvated, tridentate structure where the metal cation binds to the nitrogen atom of the imidazole side chain and the amine and carbonyl groups of the amino acid backbone and the nitrogen atom of the side chain, $[\text{N}_1, \text{N}_\square, \text{CO}]$, in agreement with the predicted ground states of these complexes. For the larger alkali metal cation complexes, $\text{K}^+(\text{His})$, $\text{Rb}^+(\text{His})$, and $\text{Cs}^+(\text{His})$, the spectra have very similar spectral features that are considerably more complex than the IRMPD spectra of $\text{Li}^+(\text{His})$ and $\text{Na}^+(\text{His})$. For these complexes, the bidentate $[\text{N}_1, \text{CO}]$ conformer, in which the metal cation binds to the nitrogen atom of the imidazole side chain and backbone carbonyl oxygen, is a dominant contributor, although features associated with the tridentate $[\text{N}_1, \text{N}_\square, \text{CO}]$ conformer remain and those for the zwitterionic $[\text{CO}_2^-]$ conformer are also clearly present. Theoretical results for $\text{Rb}^+(\text{His})$, and $\text{Cs}^+(\text{His})$ indicate that both $[\text{N}_1, \text{CO}]$ and $[\text{CO}_2^-]$ conformers are low-energy structures, with different levels of theory predicting different ground conformers. For $\text{H}^+(\text{His})$, the IRMPD action spectrum is reproduced by $[\text{N}_1, \text{N}_\square]$ conformers, in which the protonated nitrogen atom hydrogen bonds to the backbone amino nitrogen.

Dr. Murat Citir received his B.S. degree from Bogazici University in 2001 and earned his Ph.D. from the University of Massachusetts Amherst in 2007. His Ph.D. studies have focused on photo fragment studies of carbon-oxygen and carbon-hydrogen bond activation by transition metal cations using a laser ablation source coupled to a dual time-of-flight mass spectrometer. Dr. Citir is currently postdoctoral fellow at the University of Utah and his research is intended to provide a detailed understanding of the thermochemistry, kinetics, and dynamics of simple and complex chemical reactions by using the guided ion beam tandem mass spectrometer. Of particular interest is elucidation of the intrinsic reactivity and thermochemistry of transition metals, metal-ligand complexes, metal-clusters, and metallated molecules of biological relevance. He also applies ab initio theory to provide structures, molecular parameters, and bond energies for use in the analysis and interpretation of experimental results.

Date : April 22, 2011 (Friday)

Time : 10:40

Place : Faculty of Science Building, A Block, Seminar Room (SA 240)