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Ph.D. DISSERTATION DEFENSE

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Title: Investigation of Gas-Phase Ion Neutral Interactions by Ion Mobility Separation Technique and Mass Spectrometry

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ABSTRACT

Gas phase ion-neutral reactions that occur under mass spectrometric conditions have been extensively explored to probe molecular structures and differentiate isomeric radical ions. Neutral molecules interact with gas phase ions in two primary ways: by forming adducts through chemical association or by influencing the internal energy of the ions through collisional interactions without forming an association. A well-known phenomenon in this context is gas phase intramolecular proton transfer, where a proton is transferred from one site to another within a molecule, resulting in the formation of isomeric structures. These isomeric forms can be separated by ion mobility. Generally, these isomeric exhibit different fragmentation spectra. Understanding intramolecular proton transfer mechanisms is crucial for accurate qualitative and quantitative analysis, as it aids in the proper interpretation of mass spectrometric data.

In this study, both associative and non-associative interactions of gas phase ions and neutrals were investigated to understand their impact on intramolecular proton transfers. Specifically, the effect solvent molecules on intramolecular proton transfers in protonated Michler's ketone, which has two electron rich sites: the carbonyl (*O*-protomer) and the amine group (*N*-protomer) were investigated. We found that vapors from protic molecules such as methanol or ammonia vapors can associate with the *N*-protomer in the gas phase, forming a proton-shared bridge and facilitating the transport of the proton from the *N*-protomer to the *O*-protomer.

Moreover, for monofunctional compounds such as aromatic amines, intramolecular proton transfer can occur from the amine group to a ring site, without any external assistance. Our study demonstrated that neutral gases could retard the intramolecular proton transfer by reducing the internal energy of the ion. Most notably, it was shown that exposing the ions to virtually any solvent vapor, irrespective of its chemical nature, can decelerate intramolecular proton transfers, through collisional cooling.

Furthermore, gas phase ions can interact with neutrals molecules to form adducts, providing additional structural information. Researchers have long debated whether the gas-phase naphthyl cation exists as a singlet or triplet ground state. The formation of an adduct between the naphthyl cation and carbon dioxide confirmed that the naphthyl cation exists in a singlet ground state. Additionally, associative ion neutral interaction can be isomer specific. The reactivities of deprotonated *ortho*-, *meta*-, and *para*-hydroxybenzyl alcohols toward CO_2 and water were studied to elucidate the fragmentation pathway of these isomers.