Gas-Phase Chemistry of Polycyclic Aromatic Hydrocarbon Anions

Nicholas J. Demarais,[1,*] Zhibo Yang,[1] Oscar Martinez Jr.,[1,4] Nadine Wehres,[1,2]
Theodore P. Snow,[2,3] and Veronica M. Bierbaum[1,2]

[1] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[2] Center for Astrophysical and Space Astronomy, University of Colorado, Boulder, CO, USA
[3] Department of Astrophysical and Planetary Sciences, University of Colorado, Boulder, CO, USA
[4] Current Address: Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA
* Corresponding author: Nicholas.Demarais@Colorado.edu

Ion-neutral chemistry is an integral component in determining the evolution of the interstellar medium (ISM). The detection of anions in the ISM in the past decade highlights the importance of their inclusion in models of this environment. The inclusion of polycyclic aromatic hydrocarbons (PAHs) in models of dense clouds has dramatic consequences. However, a problem with including PAH anions in models of interstellar clouds is that very little work has been done. Experimental and computational studies have been carried out to investigate reactions of polycyclic aromatic hydrocarbon anions with H atom and neutral species of interstellar relevance. The rate constants, mechanisms, and products observed provide insight into the chemistry of PAH anions in the ISM.

The experiments were carried out using a flowing afterglow-selected ion flow tube (FA-SIFT) Mass Spectrometer.(1) PAHs were introduced into the gas-phase through their vapor pressure or laser induced acoustic desorption (LIAD).(2) PAH anions were generated by chemical ionization, mass selected by a quadrupole mass filter, and injected into the reaction flow tube. Subsequently, reagent molecules of known concentration were introduced into the reaction flow tube and allowed to react. Hydrogen atoms were produced by thermal dissociation of H_2. Ion signal intensities were measured using a quadrupole mass filter coupled to an electron multiplier. Reaction rates and product distributions were determined by monitoring the ion signal intensity as a function of atom concentration or reaction distance.

Reactions of small dehydrogenated PAH anions were considered in this work due to their stability compared to the parent PAH anions. The gas phase reactivity of phenide with molecules of interstellar relevance has been studied. In addition, reactions of deprotonated naphthalene and anthracene with H atoms were investigated. Reactions of phenide with neutral molecules proceed through multiple mechanisms including proton abstraction, atom abstraction, and S_N2 processes. Reactions of the dehydrogenated PAH anions with hydrogen atom proceed exclusively through an associative detachment channel. The reaction rate constants and branching ratios measured in the current study provide reaction mechanisms and critical parameters for astrochemical modeling.

Ab initio calculations were carried out at the CCSD(T)/aug-cc-pVTZ level of theory for reactions involving open shell species such as molecular oxygen, and B3LYP/aug-cc-pVTZ level of theory for reactions with closed shell species. Theoretical calculations have provided further insight into the measured rate constants, mechanisms, and products.

Lastly, LIAD has been successfully implemented on an FA-SIFT mass spectrometer. Large, non-volatile PAH molecules have been successfully introduced into the gas-phase using the LIAD technique and sufficient ion densities have been attained to probe reactions with natural, interstellar species. These preliminary results will also be presented

Experimental and theoretical studies of PAH anions with interstellar have been instigated. The rate constants measured for these reactions can be included in chemical models to give insight into the evolution of astrophysical environments. In addition, reactions observed can suggest the existence of previously undetected molecules and influence their possible detection the ISM.