Photoelectron-photofragment coincidence studies of tert-butoxide with a cryogenically cooled electrostatic ion beam trap

Ben B. Shen[1], Christopher J. Johnson*, Berwyck L.J. Poad , and Robert E. Continetti [2]

Department of Chemistry and Biochemistry and Department of Physics*,
University of California, San Diego, La Jolla, California, 92093-0340, USA

A cryogenically cooled electrostatic ion beam trap[1] (CEIBT) has been integrated with a fast ion beam translational spectrometer and used to perform photoelectron-photofragment coincidence (PPC) experiments[2]. PPC spectroscopy is a kinematically complete experiment in which dissociative neutral intermediates of known internal energy are created by photodetachment of a stable molecular anion. By collecting all resultant neutral fragments from the dissociation event in coincidence with the detached electron using time- and position-sensitive detectors, the correlated momenta and energies of all products can be determined. Incorporation of the CEIBT allows for the use of low duty cycle ion sources, allowing the production of colder anions, and permits radiative cooling of the anions in the trap as well. This has improved sensitivity and resolution while maintaining the high duty cycle required for coincidence experiments. Ions oscillating inside the CEIBT are phase locked and bunched by applying a low amplitude RF waveform synchronized with the Ti:Sapphire regenerative amplifier used for photodetachment. Photodetached electrons are ejected into a velocity map imaging electron detector at the center of the trap while neutral species recoil out of the trap to a multi-particle neutral detector. Ion beams can be trapped at pressures of ~6 x 10^{-11} torr for periods of many seconds.

The kinetic energy and angular resolution for studying dissociation processes in PPC spectroscopy is dependent on the distribution of trajectories of neutral particles exiting the trap. The highest precision measurements are obtained when the recoiling center-of-mass trajectory distribution is small, which requires the ion beam to remain collimated over the entire trapping period. For a given ion beam energy, the mirror and lens voltages, bunching RF phase and voltage all affect the neutral fragment trajectories. Characterization of the effect of these parameters on the neutral fragment trajectories will be presented.

Experiments conducted using the CEIBT on the $C_4H_9O^-$ anion produced from tert-butanol will be presented. Both stable and dissociative photodetachment processes are observed, consistent with production of both the tert-butoxide anion and a carbanion isomer. Improving on earlier experiments carried out without the CEIBT, it has been found that the dissociative process involves elimination of a methyl radical, consistent with dissociative photodetachment of a carbanion. These results will be discussed in the context of *ab initio* calculations at the UMP2/6-311G++(d,p) level of theory.

This work was supported by the U.S. Department of Energy under grant number DE-FG03-98ER14879.

References

[1]M. Dahan, *et al*., Rev. Sci. Instrum. **69**, 76 (1998).
[2] C. J. Johnson and R. E. Continetti, J. Phys. Chem. Lett. **1**, 1895 (2010).

[1,] E-mail: bbshen@ucsd.edu

[2] E-mail: rcontinetti@ucsd.edu