Molecular Ion Dissociation Processes in a Partially Cooled Electrostatic Trap

C. R. Vane*1, M. E. Bannister1, and S. Deng1, M. Fogle2, and R. D. Thomas3

1Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
2Department of Physics, Auburn University, Auburn, AL
3Department of Physics, AlbaNova, Stockholm University, SE-106 91, Stockholm, Sweden
E-mail: vanecr@ornl.gov

Abstract. An experimental capability being developed at the Oak Ridge National Laboratory Multi-Charged Ion Research Facility (ORNL MIRF) is described that enables stored cooling and state characterization of atomic and molecular ions of essentially any mass. Ions selected from a variety of available (hot and cold) sources are injected into a 1.5 meter long electrostatic mirror trap, in which excited internal states decay by radiative cooling. Ion lifetime studies or direct measurements of ‘in-trap’ interactions of molecular ions with electrons or atomic targets are accomplished with either a crossed electron beam or atomic beam (with recoil ion detection) located in the field-free region of the ion-trap, coupled with product velocity imaging. Similarly, extraction of trap-cooled ions can be used ‘out-of-trap’ for near state-specific electron capture (EC) and dissociative charge exchange (DCE) studies employing higher resolution COLTRIMS techniques coupled with fragment imaging.

1. Introduction
Dissociative interactions of molecular ions with electrons, atoms, and other molecules are important in a wide variety of environments, generating reactive fragments (e.g., free radicals) that often play significant roles in initiating and driving the dominant chemistries. Examples range from cool plasma interactions at fusion near-edge regions, to enhanced chemical vapor deposition plasmas, to planetary upper atmospheres and interstellar clouds, and to molecular breakup phenomena used in mass spectroscopic techniques for investigating the structures of heavy (e.g., biological) molecules. The interactions involved are complex and any hope of untangling the underlying many-body processes and of developing a fundamental understanding of observable charge and energy evolution will require reliable detailed data arising from extreme control of the interacting species’ quantum states and environments. One method for achieving such significant control involves storage of molecular ions in an innocuous environment (e.g., low EM field, ultrahigh vacuum, low wall temperature) until radiative decay provides a near ground-state population for direct interaction measurements with a similarly identified target species, or for subsequent excited-state preparation preceding such measurements. Often heavy molecular ions are stored as energetic beams to benefit from kinematic advantages in detection and analysis of products. A number of laboratories are centering their research on enhanced capabilities of intrinsically mass independent all-electrostatic storage traps and rings that are relatively small and therefore cheaper to construct and operate (especially at cryogenic temperatures) than magnetic rings that have been employed so successfully, for example, in exploring and elucidating details of the dissociative recombination processes.

At ORNL we are developing a broad potential experimental capability for detailed, near state-specific studies of dissociation processes occurring for interactions of molecular ions with free electrons and atomic targets, based on a linear electrostatic mirror trap, similar to the design of Zajfman et al [1]. Our research is concentrated on dissociation of O2+, O3+, and XH2+, to complement our dissociative recombination (DR) studies at CRYRING. The MIRF Ion Cooling and Characterization Endstation Trap (ICCE TRAP) has been designed to store atomic and molecular species from a number of ion sources (ranging from internally hot ions produced in a permanent magnet ECR ion source, to heavy biomolecular...
ions from an electrospray ion source), permit them to radiatively cool, interact them with crossed electron and atomic targets, and measure dissociation fragments using imaging techniques. The linear trap (with 40 mm mirror element aperture) is similar in scale to the Cryogenic Trap for Fast ion beams being developed Max-Planck-Institut für Kernphysik at Heidelberg [2], except that the ORNL trap is designed to operate primarily at room temperature. Unique features of the ICCE TRAP’s design enabling a variety of both ion-electron and ion-atom interaction studies include use of side-injection of ions to avoid fast switching of high voltages permitting operation over a wide range of stored ion energies (up to 16 keV per charge), and instrumentation with an intense crossed-beam (5-100 eV) electron target and an ‘in-trap’ atomic beam target with recoil ion detection.

Figure 1. Layout of the ICCE TRAP at the ORNL MIRF. Ions enter from the top right port and are injected along the trap axis to Mirror (A) at the bottom left using pulsed electrostatic deflectors.

A schematic of the apparatus is shown in Figure 1. Atomic and molecular ions enter from the top right and are injected onto the linear trap axis through combination of a 32° cylindrical deflector and a pulsed 13° parallel plate deflector. The ions oscillate between two electrostatic mirrors (A) and (B), the latter designed to operate inside a copper shroud cryo-cooled to ~ 20 K. The trap is pumped by three cryopumps, one titanium sublimation pump, and one getter pump. Typical background pressure over the 1.5 m long mirror to mirror trap length is < 1 x 10^{-10} Torr. Transverse magnetic fields along the axis are reduced to less than 100 mG using a pair of Helmholtz-like coils mounted above and below the trap axis. Stored ions interact with either a low-energy (5-100 eV) crossed electron beam target or an atomic or molecular beam target, LN cooled to ~ 80 K, mounted between the mirrors. IR laser reheating of trapped, cooled molecular ions is also planned through an access port located at the ion turn around point in mirror (A). A 78 mm diameter imaging detector based on a triple-MCP, Z-stack followed by a P46 phosphor screen is located at one end approximately 1 m beyond mirror (A) for measurements of neutral product fragments from molecular ions interacting with the targets, while the other mirror (B) will be instrumented with an a pulsed, field-modifying electrode for extended slow extraction of stored ions to ‘out-of-trap’ measurements. The imaging detector phosphor light pulses are also focused onto a segmented PMT for timing and particle multiplicity gating. Two dimensional images of multi-fragment hit data are stored on a fast, multi-frame capable camera and the data analyzed real-time. The imaging
detector can also function as a position-sensitive detector of charge-reduced atomic ions formed by electron capture (EC) in the atomic target when multi-charged atomic ions are stored in the trap. These ions readily escape the trap along its axis, and a secondary electrostatic deflector (not shown in Figure 1) mounted between mirror (A) and the detector is used to spatially separate ions and neutrals.

Ion loading of the trap is accomplished from the side by switching on the 13° parallel plate deflector, and then rapidly switching off the deflector steering potential prior to return the ion pulse as it is reflected from the first mirror (A). The trap is then filled to a maximum of about 40% of its length by an ion bunch that oscillates between the mirrors. Long term (seconds) trapping is accomplished by tuning the potentials on elements of the mirrors and on Einzel lenses at the entrance to each mirror. Optimization is obtained by tuning two sets of horizontal and vertical ‘trim’ plates, also located at the entrance to each mirror. The mirror potentials, the highest of which must exceed the energy of the trapped ions divided their charge, are then held static during trap operation, avoiding any fast switching of potentials greater than a few kV even for ion energies up to tens of keV. Exact timing and pulse width for the 13° injection deflector depends on the velocity of the ions being injected, but is typically about 10 µs wide for light ions, permitting loading of approximately $6 \times 10^4$ ions per particle nA of beam current.

The number of stored ions can be monitored as a function of time after injection via three separate methods, two non-destructive and one destructive. In the first, a capacitive pickup (19 mm dia x 19 mm long) mounted inside the atomic target grounded shield can be used to measure the relative intensity of beam pulses when the ions are bunched and to infer stored ion mass distribution from Fourier analysis.

In the second method, neutrals formed from electron capture, dissociative charge exchange, collisional dissociation (CD), or other neutral fragment-producing dissociation processes – such as dissociative excitation (DE), escape the trap and are detected in the imaging detector. Instantaneous neutrals rates are proportional to the number of stored ions. Figure 2 displays neutral counts (from C, O, and CO) versus trap time (after injection) for 10 keV CO$^+$ ions stored at 1 x 10$^{-10}$ Torr background chamber pressure (~90% H$_2$), and the effect of adding CO target gas.

**Figure 2.** Lifetime curves from measured neutrals for 10 keV CO$^+$ ions, for background and with approximately 1x10$^{-10}$ Torr (indicated ion gauge pressure) added CO gas.
An atomic beam target is located 22 cm from one of the mirrors and 139 cm from a 78 mm diameter imaging detector. Electron capture generated target recoil ions are extracted by a weak electric field (< 50 V/cm) perpendicular to the trap axis and transported to a fast discrete dynode electron multiplier detector to provide the ‘start’ signal for time-of-flight (TOF) measurement. Arrival timing of the neutrals made with respect to trap injection, especially when gated with coincidently detected target recoil ions, can be used to represent the time evolution of spatial distribution of the ions in the trap. Under certain mirror element biasing conditions, trapped ions can be automatically retained in narrow (few µs) bunches for hundreds of milliseconds [3]. Example data from a storage oscilloscope for stored 10 keV O⁺ ions interacting with an O₂ gas target are displayed in Figure 3 indicating detection timing of neutral fragments and recoil target ions after injection. Signals with a period of 9.7 µs arriving from a 1.4 µs wide ion bunch passing through the target toward the neutral detector are clearly visible, as well as correlated signals from O₂⁺ recoil ions created in charge exchange events in each direction of the ion’s motion.

![Storage oscilloscope screen shot of signals from neutral O atoms (black) and O₂⁺ recoil ions (gray) for trapped 10 keV O⁺ ions.](image)

The time-of-flight TOF delay spectral data – [recoil ion = ‘TAC start’, neutral = ‘TAC stop’], can be used to uniquely identify EC or DCE from a particular target atom at the atomic beam target position on an event-by-event basis. An example is shown in Figure 4 for 10 keV O₂⁺ ions undergoing EC and DCE with background H₂ and H₂O, and with a small amount of added Ar. By gating data on a selected recoil-

![Measured TOF spectra for O and O₂ neutrals from DCE and EC by trapped 10 keV O₂⁺ ions detected in coincidence with correlated recoil target ions. Events arising from EC from background gas (mainly H₂O and H₂) are indicated by the dotted line, data from added argon are indicated by the solid line.](image)
neutral TOF delay, measurements can be accumulated for specific ion-atom combinations and as a function of cooling time for ions stored in the trap. For example, imaging of DCE-generated fragments can be simultaneously selected according to trap cooling time of the molecular ion and the target atom element contributing the active electron. Even more specific selection of events permitting identification of initial and recoil final states can be accomplished using high resolution COLTRIMS techniques. But these are presently restricted to external or ‘out-of-trap’ measurements using extracted ions due to the complexity of the COLTRIMS apparatus required for high resolution.

A third, destructive method being developed for determining the trap lifetime curve for a given ion, energy, and trap tune is based on measurement of total stored ion energy. Ions are injected and stored for a given variable time, then dumped in one cycle onto a calibrated solid-state detector (International Radiation Detectors Inc., IRD) by appropriate synchronized pulsing of the 13° deflector. For bunched ions where the deflector can be switched on during a period in which the ion bunch is completely located within a ‘turn-around’ in mirror (B), the signal directly represents the total number of ions multiplied by the energy per ion. For un-bunched ions more nearly filling the trap, the IRD detector signal represents a fraction of the stored ions. The advantage of this method is its potential absolute nature (IRD available absolute detector energy calibration and on-line calibration using ion pulses directly from the source) and its relative independence from ion-cooling effects on the details of the measurement.

The ICCE Trap is also used as a metastable atomic ion fraction diagnostic employing stored-ion decay curve measurements for selected singly- and multiply-charged atomic ion beams from the ECR ion source. These are especially of interest for ion species used in merged ion-neutral beams experiments in which significant metastable fractions are expected, e.g., He-like, Be-like, and Mg-like ions. Lifetimes of interesting atomic ions with electric dipole forbidden transitions (mainly M1) range from microseconds to tens of seconds. ICCE Trap ion storage lifetime measurements permit determinations of populations of some metastable ions with lifetimes ranging from milliseconds to seconds [4,5]. These ‘in-trap’ metastable fraction determinations are possible for stored-ion species for which electron transfer rates from specific targets (e.g., He) depend strongly on the ion’s initial internal electronic state, leading to trapped ion overall decay rates that systematically change with the evolving metastable state population. For example, C\(^{2+}\) ions from the ORNL MIRF permanent magnet ECR ion source are expected to have a substantial metastable C\(^{2+}(1s^22s2p\,^3P)\) population, with component lifetimes of 9.7 and 190 ms [6]. Electron capture by these metastable ions is known to proceed with cross sections about 3-7 times larger than for ground state C\(^{2+}\) ions [7]. Initial analysis of lifetime data versus He pressure yield a C\(^{2+}(^3P)\) metastable fraction of approximately 45%. Similar techniques can be applied to molecular ion dissociation studies, for example DCE, if rates are sufficiently state-dependent to significantly affect the pace of neutral fragment production.

More detailed measurements, leading to identification of the particular metastable quantum states involved, can be performed in ‘out-of-Trap’ charge-changing measurements using timed-extraction of ions from the trap and COLTRIMS-based high resolution experimental techniques as described in references [8,9] for molecular ions. The main disadvantage to this ‘out-of-trap’ method is unavoidably low data acquisition efficiency due to relatively poor duty cycle. The ORNL COLTRIMS apparatus configured for measurements of DCE of molecular ions on gas targets is displayed in Figure 5. Molecular ions from any of the available ion sources will first be injected and cooled (or prepared via laser or electron interactions) in the ICCE TRAP. After a suitable time, atomic or molecular ions can be extracted from the trap through mirror (B) over an extended number of oscillations using a mirror field-modifying
technique we have developed using SIMION ion-optics simulations. The extracted ions are then directed into the COLTRIMS apparatus where they interact with a cold atomic beam target. Standard COLTRIMS techniques are then used to provide high resolution recoil ion momentum analysis and to derive the collision Q-value for each event. Charge-changed products, including neutral fragments in the case of DCE of molecular ions, are detected in coincidence with recoils using an imaging detector 1.5 m downstream of the COLTRIMS target. Values of Kinetic Energy of Release (KER) are determined from the imaging data, and can be correlated with the recoil data to identify initial and final states [6,7].

Acknowledgements
Research sponsored by the U.S. DOE, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

*Author SD gratefully acknowledges support from the ORNL Postdoctoral Research Associates Program administered jointly by Oak Ridge Institute for Science Education and ORNL.

References
[1] Zajfman, D., et al, 1997 Phys. Rev. A 55, R1577 - R1580
[2] Lange, M., et al, Rev. Sci. Instrum. 81, 055105 (2010)
[3] Pedersen, H. B., et al, Phys. Rev. Lett 87, 055001 (2001).
[4] Trabert, E., Physica Scripta 61, 257 (2000).
[5] Fardi, A., Cederquist, H., and Schmidt, H. T., Hyperfine Interactions 127, 247 (2000).
[6] Fogle, M. et al., Astrophys. J. Supp. Ser. 175, 543 (2008), and references therein.
[7] Ishii, K., Itoh, A., & Okuno, K., Phys. Rev. A, 70, 042716 (2004).
[8] Schmidt, L. Ph. H., Phys. Rev. Lett. 101, 173202 (2008).
[9] Johnson, N. G., J.Phys: Conf. Ser. 194, 102004 and 102019 (2009), and Johnson, N. G., unpublished thesis, Kansas State University 2010.