Final Technical Report

Title: Capturing Ultrafast Electron Driven Chemical Reactions in Molecules

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Program Scope

The goals of this project, are to develop experimental tools to investigate the dynamics of dissociative electron attachment (DEA) reactions in real time. In a DEA reaction, the attachment of a low energy electron to a molecule results in bond breaking and the fragmentation of the molecule. A new instrument has been designed and is under construction to perform time-resolved photoelectron and photo-fragment spectroscopy following electron transfer from an iodide anion to a molecule within a mass-selected molecular dimer. Iodide binds only weakly through the dipole interaction with many polar molecules, and such molecules forming a dimer with iodide undergo only small changes from the equilibrium geometry in isolation. When the electron is transferred from the iodide, the iodine atom is no longer bound, so the electron transfer step can be considered analogous to electron attachment and brings the key advantage of ultrafast timing precision. The experiments proposed here will establish the experimental tools to interrogate the dynamics of dissociative electron attachment on the fundamental timescales of the nuclear motion, by simultaneously probing the valence electronic structure and the fragmentation pathways.

Introduction

Low energy (few eV) electrons are readily generated in the interaction of radiation with matter, and these electrons can in turn interact with molecules and drive a large number of chemical processes in atmospheric, radiation and plasma chemistry. One of these fundamental processes is dissociative electron attachment, where a low energy electron attaches to a molecule, forming a transient anion that dissociates. The metastable transient anion system evolves from the electronic continuum, so dissociation competes with autodetachment. These reactions can take place on femtosecond time scales and exhibit strong coupling between electronic and nuclear motion. The breakdown of the Born-Oppenheimer approximation makes it highly challenging to accurately describe the dynamics with existing quantum chemistry methods. It is also very challenging to observe these reactions experimentally on the relevant timescale, due to the difficulty in delivering few-eV electron pulses on a sample to trigger the reaction with femtosecond resolution.

We are developing a new instrument to do momentum- and time-resolved measurements of dissociative electron attachment reactions by combining two experimental methodologies: time resolved photoelectron imaging spectroscopy and coincidence momentum imaging of the photoelectron and the mass-resolved reaction fragments. The experiments proposed here will establish the required tools to interrogate these dynamics on the fundamental timescales of the nuclear motion. Initial experiments will focus on anion fragment mass spectrometry and fragment momentum imaging, followed by time resolved photoelectron spectroscopic measurements of photodetached electrons. Near-future developments include momentum imaging experiments of both photoelectrons and neutral fragments in coincidence. The coincidence measurements will allow us to assign the measured valence electron binding energies to specific fragmentation channels. The experiments will be supported by theoretical calculations of the electron attachment and dissociation processes.

Year 1

Work in the first year of the project focused on the design and construction of a new experimental apparatus. The setup comprises three modular systems: The anion source chamber, the time of flight (TOF) module, to mass-select target anions, and the velocity map imaging (VMI) and detector chamber. The design of the different elements has been guided by numerical simulations of charged particle trajectories and by the literature on mass-selected anion beam instrumentation. Figure 1 shows a CAD drawing of the three connected modular systems. The first chamber (A in Fig. 1) will produce an anion beam by intersecting an electron beam with a molecular beam formed by a supersonic co-expansion of a noble gas and the target molecule. At the connection between the first and second chambers there is a skimmer and steering optics to guide the beam towards the accelerating electrodes in the TOF module (second chamber, labeled B in Fig. 1). The TOF uses pulsed electrodes to accelerate the anions to an energy of a few keV, followed by steering and focusing ion optics (see inset in Fig. 1). A mass gate will be implemented at the temporal focus of the TOF to select the anions of interest, which will pass through to the laser interaction region (C in Fig. 1). At the laser interaction region, a VMI spectrometer will be installed to measure detached electrons. This VMI will serve a dual purpose. First, we will use it to perform photo-detachment spectroscopy of mass-selected anions to measure the electronic structure. Second, we will use it for time-resolved photodetachment spectroscopy of the transient anion complex in order to map the changes in the potential energy surface during the dissociation reaction. A second TOF spectrometer and position-sensitive detector will be used to measure the momentum of mass-resolved anion fragments and energetic neutral fragments resulting from the laser interaction. In the following, we describe the progress so far in the design, fabrication and testing of all the components.

A. Source Chamber. The design and fabrication of the source chamber has been completed. Figure 2(a) shows a photograph of the source (A) and TOF (B) chambers in the laboratory. In the source chamber, an electron beam intersects a molecular beam to generate the desired anion beam. Figure 2(b) shows a top view of the chamber showing the electron gun (C), the nozzle assembly (D), Faraday cups to measure the electron and ion beam currents (E) and a connection point for a liquid nitrogen cooled cold finger. We have designed and fabricated a continuous electron gun to produce an electron beam with tunable energy up to 2 keV. This will allow us to tune the energy to optimize the desired anion formation channel. The electron gun is differentially pumped to maintain a high vacuum when the nozzle is in operation. We have tested the differential pumping to produce a two orders of magnitude pressure difference between the electron gun and source chambers. On first test, the electron gun has produced a beam current of more than 250 microA, which is sufficient for our purposes. Currently we are testing the optimal focusing and steering parameters of the gun.

The gun has so far only been tested for beam energies up to 240 eV and it will operate at up to 2 keV once we receive the appropriate power supply within the next few weeks. A pair of concentric faraday cups was built to characterize and optimize the electron beam. The target gas will be introduced with a pulsed valve (Even-Lavie) which operates at a repetition rate of up to 1 kHz, which matches the repetition rate of the laser system. The position and direction of the nozzle can be adjusted manually from outside during operation, without breaking vacuum. The nozzle has been installed and is currently being tested. A cold finger has been designed and fabricated to cool the nozzle down to the optimal temperature to form the clusters that produce the anions. The nozzle is connected through braided copper wire to a copper cold finger. The cold finger is thermally connected to a liquid nitrogen reservoir outside the chamber.

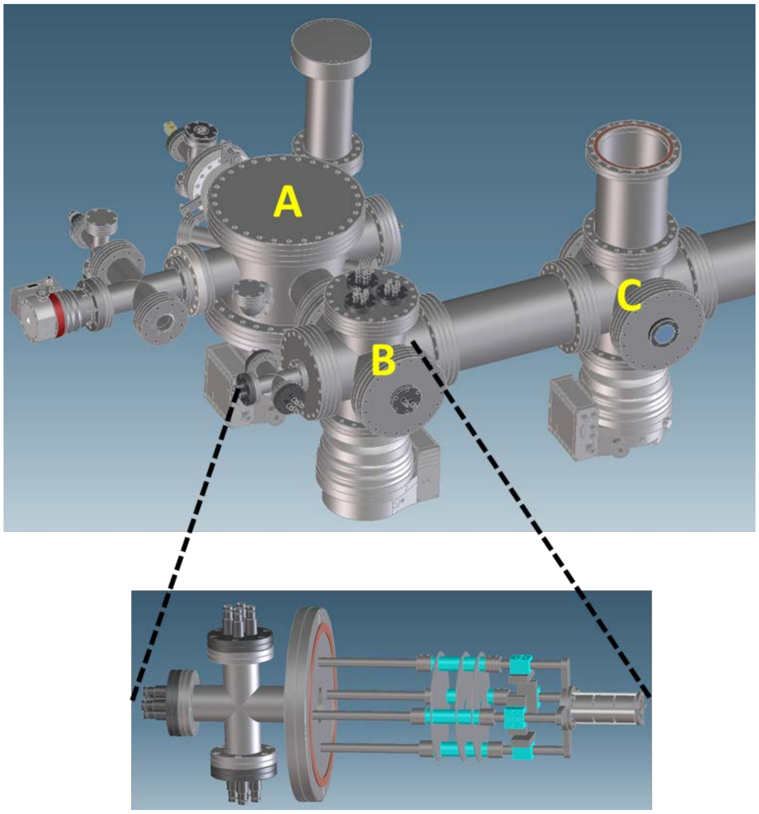

Figure 1. CAD design of the setup with three modular chambers. A: Source chamber, B: TOF module, C: Detector and VMI. The inset below shows the design of the TOF electrodes and the following focusing and steering electrodes with everything mounted on a single flange.

B. Time of flight (TOF) spectrometer. The TOF chamber includes three sets of electrodes, the first are to steer and focus the anion beam onto the acceleration region, the second are the TOF electrodes to accelerate the beam, and finally a second set of steering and focusing electrodes. The inset in Figure 1 shows the acceleration electrodes followed by the focusing and steering electrodes, which are all mounted as a single assembly. The TOF chamber has been purchased and is in the process of assembly in the laboratory (labeled B in Figure 2(a)). The first set of steering and focusing electrodes has been designed and is currently being fabricated. The design of the

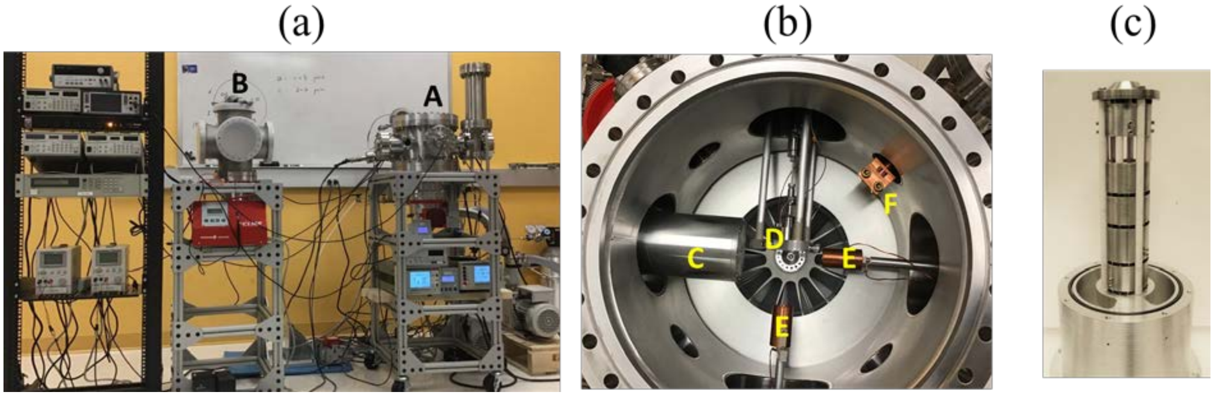

Figure 2. (a) Source chamber (A) and TOF chamber (B). b) Top view of the source chamber showing the compact electron gun (C), gas nozzle (D), Faraday cup (E) and connection for the cold finger. (c) The home-made electron gun.

electrodes for the TOF has been finalized, while the last set of steering and focusing electrodes is currently being optimized to deliver the appropriate beam waist at the interaction region.

C. VMI and detector chamber. The third module is still in the design phase. A first design for the VMI has been produced but needs to be optimized after the final parameter of the anion beam are known. A channel electron multiplier detector will be used initially to capture the anion fragments to analyze the constituents of the anion beam by their TOF mass spectra. The detector mount and electronics are currently being designed and tested.

Year 2

We have successfully characterized the ion beam using cations and anions formed in electron collisions with carbon dioxide, installed and tested the time of flight (TOF) electrodes and channeltron detector, and designed and constructed a mass selector and a reflectron mass spectrometer. We have constructed the gas delivery system to deliver the gas mixtures needed to produce iodide-molecule clusters. In addition, significant simulation work has been carried out on the performance of the TOF mass selecting system and the reflectron mass spectrometer module to analyze charged fragments following the intra-dimer electron transfer by a laser pulse.

Anion source: The anion source has been designed and tested using carbon dioxide as a test gas. This chamber contains a pulsed gas nozzle to generate the desired clusters, an electron beam to generate anions through collisions, and a skimmer to select and transport the central part of the beam to the time of flight electrodes. A continuous electron gun is used to ionize the gas coming out of the nozzle. In order to produce the iodide-molecule clusters for our experiment, a gas jet with a mixture of three gases will be intersected by the electron beam. For first experiments, the gases will be Argon, CF_3I or CH_3I, and nitromethane (CH_3NO_2). The argon gas, upon impact, generates a large number of low energy electrons by ionization. The iodine-containing molecules break up upon electron impact and provide the iodide anions, which attach to the nitromethane as the iodide-nitromethane anion cluster. We have constructed a sample delivery system to produce the required gas mixtures, which is based on two bubblers where the different chemicals can be stored and have high pressure argon flow through. The sample delivery system has been installed and leak tested.

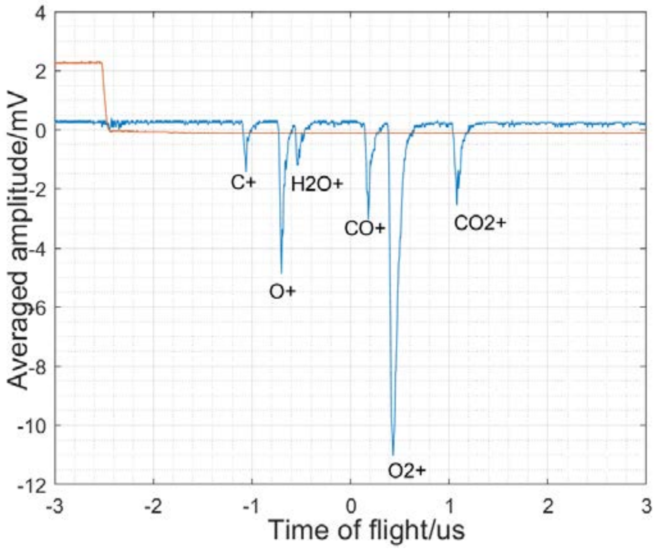

Figure 3. Time of flight trace of cation fragments produced by electron impact ionization of CO_2. The figure shows the voltage response decoupled from the channeltron detector, without amplification. The water peak is attributed to contamination of the sample line. We have used this to optimize the temporal focusing of the TOF. The TOF spectrum of the fragments was simulated using SIMION and found to be in good agreement with the measurement.

<u>Time-of-flight (TOF)</u>: The anions generated in the source pass through a skimmer to enter into the TOF chamber. Steering and focusing electrodes have been installed to guide the anion beam into the TOF region. First experiments were done with CO_2 as a test sample. Cation and anion beams have been generated and transported to the TOF chamber. The beam current is measured and optimized using a Faraday cup that sits after the TOF electrodes, such that with the TOF electrodes grounded the beam passes through into the Faraday cup. With this measurement we have optimized the direction and focusing of the electron beam and the opening time of the gas nozzle time. The Faraday cup was also used to measure the travel time of the ion packets from the source to the TOF region, such that the time of the extraction field pulse applied to the TOF electrodes can be synchronized with the time of arrival of the ions. The TOF system comprises three electrodes, the third of which is kept grounded. The first two are switched on using a high voltage pulse at the time when the ions reach the center of the electrodes. The maximum voltage determines the final energy of the ions after acceleration, while the difference in voltage between the first two electrodes determines the position of the temporal focus of the packet. We have successfully tested the TOF using CO_2 gas. Figure 3 shows the trace from the first successful test of our TOF, using a beam of CO_2 cations produced by electron impact ionization, with the assignments for different fragments. The experimental results are in good agreement with simulations. The performance of the TOF was simulated using the SIMION software package. The simulations were used to optimize the TOF voltages such that the temporal focus overlaps with the detector, and to calculate the time or arrival of the different fragments.

Detection: The detection chamber will include three devices: a mass gate to select a single anion from the incoming anion beam, a reflectron mass spectrometer that will measure the fragments produced by the photoattachment-dissociation reactions and a VMI spectrometer to study photodetachment by one or two laser pulses. First experiments will be performed with a single laser pulse to measure charged fragments with the reflectron, and in the second phase the VMI will be installed for pump-probe time-resolved experiments. Simulations were carried out to inform the design of the mass selected anion beam (consisting of a time-of-flight spectrometer and a mass gate), reflectron and VMI spectrometer.

A mass selector will be used to select the desired anion clusters, and reject the rest of the beam. The mass selector consists of a set of electrodes which are normally held at a high (negative) voltage to reject the incoming ion beam. A voltage pulse applied on the mass selector electrodes will be timed to allow only a selected fragment to pass. The selected ions will be excited by a laser pulse, and the fragmentation will initially be studied using a simple and compact reflectron spectrometer to analyze the anion fragment. The performance of the system comprising the TOF and the reflectron has been simulated using SIMION, and shows that a mass resolution of approximately 2% of the mass of the fragment can be achieved. The reflectron uses six electrodes, with the voltages optimized using two parameters, a linear and a quadratic component to the voltage step between electrodes. This allows for a simple configuration of the device. The time resolution can be optimized for low or high masses simply by changing the maximum voltage of the device. The design of the reflectron, aided by simulations, has been completed, and the reflectron spectrometer has been constructed (see Figure 4). The reflectron is mounted at an angle of six degrees with respect to the incoming anion beam. The performance of the device is very sensitive to the angle of incidence of the anions, so it is mounted on a rotational feedthrough to allow for fine tunning of the angle. While the reflectron will capture the fragmentation products, a velocity map imaging (VMI) detector will capture the electrons produced in the competing processes of photodetachment. A first design for the VMI has been produced but needs to be optimized after the final parameters of the anion beam are measured.

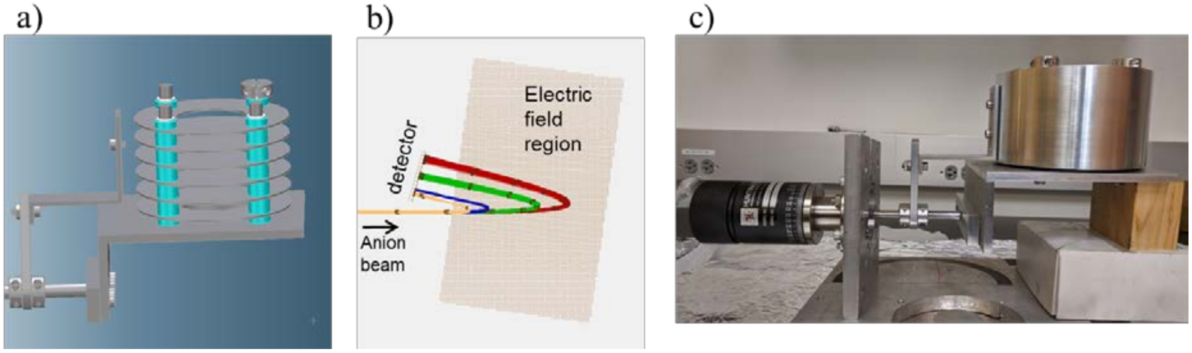

Figure 4. a) CAD design of the reflectron time of flight spectrometer containing six parallel electrodes. b) SIMION simulated trajectories of parent anion $I^-.CH_3NO_2$ and the fragments I^-, CNO^- and O^- through the electric fields. All fragments can be well resolved in the simulations c) The fabricated device, with a shield around the electrodes to prevent stray fields from interfering with the incoming anion beam.

Year 3

We have successfully completed the construction and testing of an experimental apparatus including a mass-selecting anion cluster source, comprising a pulsed nozzle, a time-of-flight spectrometer with mass selector, a reflectron mass spectrometer and ion detector. We have also improved the stability and count rates of each anion species produced by the source, and constructed the laser beam line and timing and synchronization system to temporally and spatially overlap the laser and anion pulses. Figure 5 shows the experimental setup. With this setup, measurements of laser triggered fragmentation of iodide-molecule clusters are ongoing, where we will soon investigate the fragmentation pattern as a function of the wavelength of the excitation laser. We will compare these fragmentation channels with those produced by direct interaction with an electron beam with a narrow energy distribution, using the existing DEA reaction microscope at LBNL. The setup for the time-of-flight experiments is completed, the VMI for the time-resolved photoelectron measurements has been designed but not yet installed.

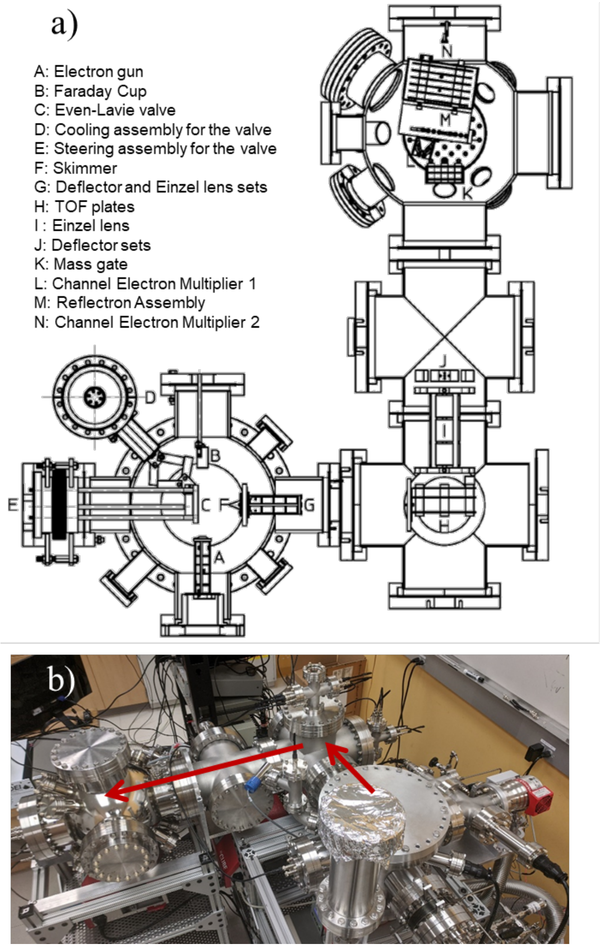

Figure 5. a) CAD design of the source, TOF spectrometer and target chambers. b) Photograph of the constructed setup, the red arrow indicate the path of the anions from the nozzle to the detector.

Anion source: The anion source comprises a pulsed valve through which a mixture of gases is flown, an electron gun with tunable energy to generate a high density of anions (and cations) at the exit of the nozzle. The anions are transferred through a small aperture to a second chamber where they are accelerated by a set of electrodes in a time-of-flight (TOF) configuration, and detected using a channeltron. The source has been tested using a mixture of nitromethane, CF_3I and argon, and we have successfully produced high yields of the nitromethane-iodide dimer, along with atomic iodide and other anions. The relative pressures of the three gases were adjusted to optimize the production of the desired cluster. A recent improvement in the setup was introducing an additional pressure regulator to keep the relative pressure of argon constant during the experiment, which keeps the signal levels steady over several hours.

Figure 6a shows a typical TOF spectrum showing I-, and nitromethane anions and the nitromethane-I- clusters.

Mass selection. Experiments will require the selection of a single anion for photoexcitation. We have implemented a mass selector for this purpose. The mass selector is composed of three concentric circular electrodes that are held at a voltage to repel all anions. At the time the anion of interest reaches the vicinity of the first electrode, a voltage pulse is applied to lower the barrier and let only the selected anion pass. The mass selector was successfully installed and tested. Figure 6b shows a TOF spectrum with the mass selector tuned to the nitromethane-iodide cluster. The selected cluster is transmitted with an efficiency of more than 50% and the surrounding anion peaks are completed blocked (below the noise floor of the measurement).

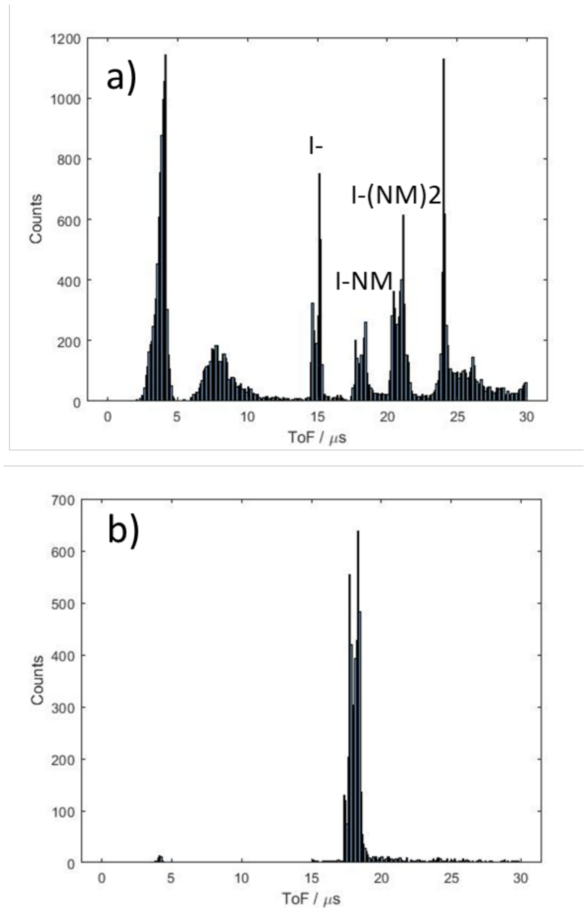

Figure 6. a) TOF spectrum measured on the reflectron spectrometer. The species of interest are iodide (I-), the iodide nitromethane cluster (I-NM) and a cluster of iodide with two nitromethane molecules (I-(NM)2). b) The TOF spectrum with the mass selector tuned to pass only the I-NM clusters.

Reflectron spectrometer. In our setup, a laser pulse will be used to transfer an electron from the iodide to the molecule. A reflectron spectrometer will be used to capture the anion fragments produced by the electron attachment. A reflectron was designed using SIMION to optimize the mass separation to the range of interest. The reflectron consists of a set of electrodes with different static voltages, which can be adjusted to target different mass ranges. The potentials can be adjusted to reach a temporal focus on the detector for different target masses. Based on the simulations, we expect that a mass resolution of approximately 5% of the mass of the target fragment when operated over a large mass range, which will allow us to resolve unit mass (single H atom) changes in small fragments. With this we expect to be able to determine the fragmentation pattern of the parent anion. The reflectron spectrometer can be operated with considerably higher mass resolution for a limited range of masses, which will allow heavier fragments to be precisely identified, even if they are only a single or a few Da different in mass. The detection is done by a pair of rectangular channeltron detectors, which were chosen based on the spatial distribution of the mass dispersed anions after the laser interaction in the SIMION simulations. The reflectron has been successfully tested and shown to produce similar count rates to the single channeltron at the end of the TOF setup.

Laser beamline. We have constructed a laser beam line to transport the ultraviolet beam from the laser lab (next door) to the target chamber. The laser is transported through a beam tube connecting the two laboratories through the wall, and guided and focused onto the anion beam using a set of mirrors and lens. The laser pulses are monitored at the output of the chamber with a fast photodiode to determine time of arrival and power stability.

Laser timing and synchronization. The arrival of the laser pulses and the anion packets has to be synchronized to better than the duration of the anions packets, which is ~ 500 ns. We use the laser trigger signal to operate the pulsed nozzle in the source, the laser photodiode signal, and a set of delays to ensure the temporal overlap of the laser and anion packets. The synchronization system has been built and will be tested in the immediate future.

Data acquisition. We have completed the data acquisition setup to record interleaved data where the pump laser is ON/OFF for every other shot. This will allow us to accurately subtract background counts and look for small signals. The signal from the channeltron is recorded for each shot, along with the laser trigger signal. The laser is run at a repetition rate of 100 Hz, and the nozzle is run at a repetition of 200 Hz. The 200 Hz signal is created by copying and delaying the 100 Hz signal, such that the laser and the pulsed nozzle are synchronized. This creates an interleaved data stream with shots with and without the pump laser. The recorded trigger signal is used to identify and ON and OFF shots.