

## Activities:

Last year we reported that there have been several drawbacks. “These drawbacks were substantial and numerous. Given that the instrument had yet to be tested in negative ion mode, it was discovered early on that the software would not allow the proper high voltages to be applied and arcing resulted which caused damage to several components which needed to be returned for repair. After several attempts to prevent arcing due to software (each of which caused the same components to be damaged) a final protected software mode was designed. Then it was discovered that there was a physical-mechanical arcing in the system. After several weeks of troubleshooting, it was deemed necessary that the experts make an on-site repair.

A few design problems also caused problems, such as incorrect flow reactor – TOF coupling measurement, a missing bias potential means, and others. But most recently and significantly, it was discovered that no reagent ions were making it into the RTOF region and was due to a missing ion focusing mechanism to guide the ions into the pulsing region. The design of the instrument was such that ions were produced by electron impact or laser photionization inside the chamber close to the extraction region. In the new arrangement using electron attachment following alpha particle bombardment, ion production took place outside and the ions entering the chamber were lost before they reach extraction region.”

A new steering mechanism for ions consisting of ion lenses close to the effusive source is now built, and being installed and tested. Following the installation of the ion lenses we expected a smooth ride.

However there is a persistent problem with the detector circuit in the negative mode which kept blowing amplifiers and damaging more electronics in the system. There were still two major problems that prevented us from collecting data in the negative ion mode. The persistent problem that damaged amplifiers and other electronics was getting to costly and frustrating. In an attempt to identify the electronic problem responsible for damaging amplifiers, the detector was shipped to Atom Sciences for replacement of capacitors. In return shipping, the detector was severely damaged, including an expensive piece of mounting ceramic and micro channel plates. This did not fix the problem.

Several months were spent testing and troubleshooting for a problem that was damaging electronic components in the signal amplifier. It was finally determined that the problem was localized to somewhere within the *reflectron* detector. The detector was removed and shipped the detector back to the vendor for repair. After a careful and through trouble shooting by the manufacturers, it was determined that the **incorrect rated capacitors installed in the detectors were the cause of the amplifier damage**. While the system is now operational in negative ion mode with the replacement of the capacitors, attempts to obtain useful ion signal for reagent ions flowing through the Polonium source was found to be a challenge.

We have now determined that the ions are lost in the walls of the flow tube because the flow tube was at ground potential. The flow tube is now being fitted with the necessary power supply to add a voltage to bias the flow tube so the ions can drift through and reach the repeller region of

the time of flight instrument. *However during the long down times in the lab, we tried to take advantage of the working Cavity ring down system that we developed in our labs to carry out complimentary and atmospherically relevant studies using carboxylic acid samples.*

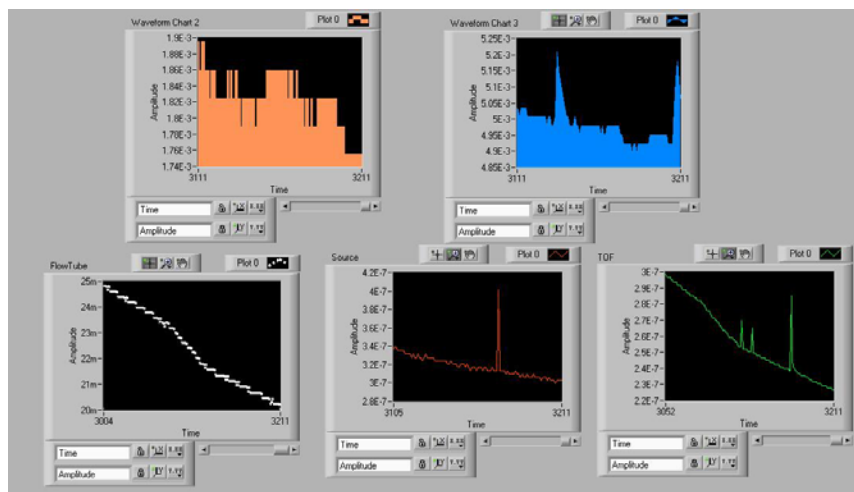
The vibrational O-H overtone absorption cross section of carboxylic acids is a necessary quantity to calculate the photochemical reaction rate ( $J$ ) for reactions initiated by the excitation of the OH overtone. These reactions have been shown to include unimolecular reactions such as decarboxylation and photodissociation. An experimental setup consisting of a Cavity Ring-Down Spectroscopy (CRDS) instrument and a Ultra-Violet Absorption Spectroscopy (UV-Abs) instrument was built, calibrated, tested and used to measure the fourth O-H overtone absorption cross sections of **acetic acid** and **peracetic acid**.

**The major activities during this period were therefore twofold:**

1. Work with the Reflectron Mass Spectrometer, gas flow system
2. Vibrational O-H overtone absorption spectroscopy of carboxylic acids using CRD

### **1. Work with the Reflectron Mass Spectrometer, gas flow system**

A compact gas flow control scheme which will control the carrier and dilution gases necessary to mix the proper amounts of reagent and gases in the flow reactor was designed. The controllers are mounted neatly on a rack adjacent to the spectrometer which minimizes the amount of Teflon plumbing necessary. This makes the time needed between sample changes much shorter. Numerous additions to the data monitoring scheme were added. The example shown below is the addition of a panel created in the LabView programming environment which charts the 5 critical pressure environments of the mass spectrometer. A similar panel was created for the 8 high voltage settings. These panels are necessary for both controlling the values as well as monitoring them for any abnormal changes or fluctuations during data collection. The data from these charts can also be stored for later analysis.



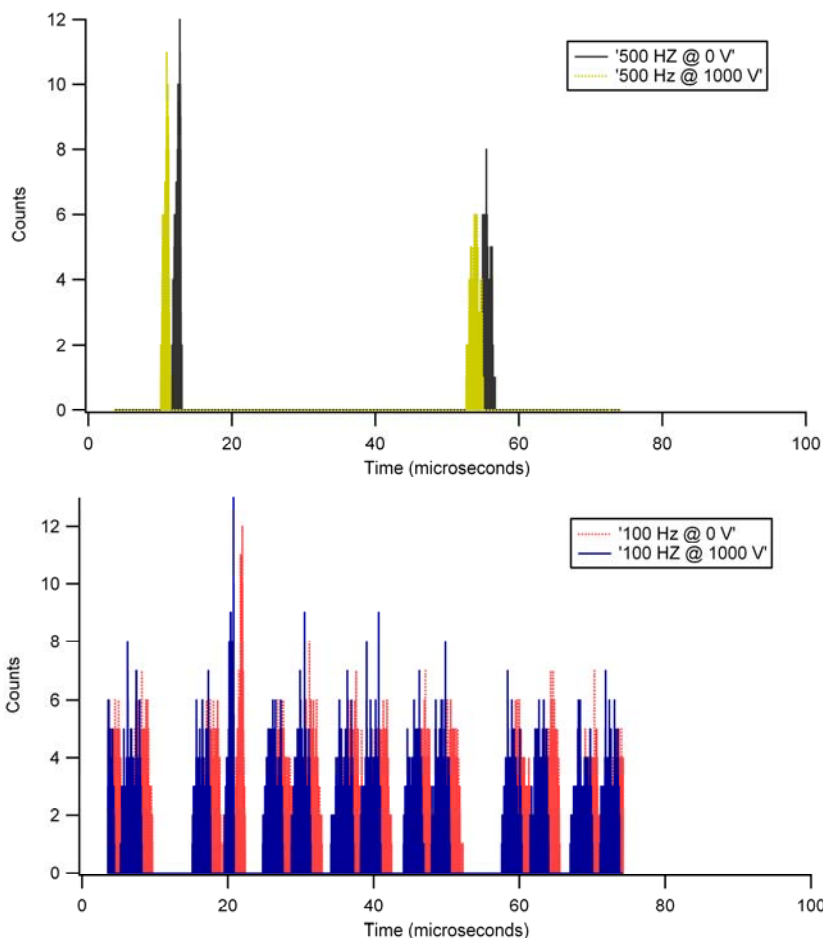
A PID temperature controller was acquired and it was successfully wired and tested. It will be used to control heat to both the permeation tube samples as well as inlet tubing.

A high capacity pump installed and tested. This pump is connected directly to the flow reactor and allows for increased reagent flow into the reactor in order to facilitate more proton transfer reactions.

### ***Performance and Characterization Data***

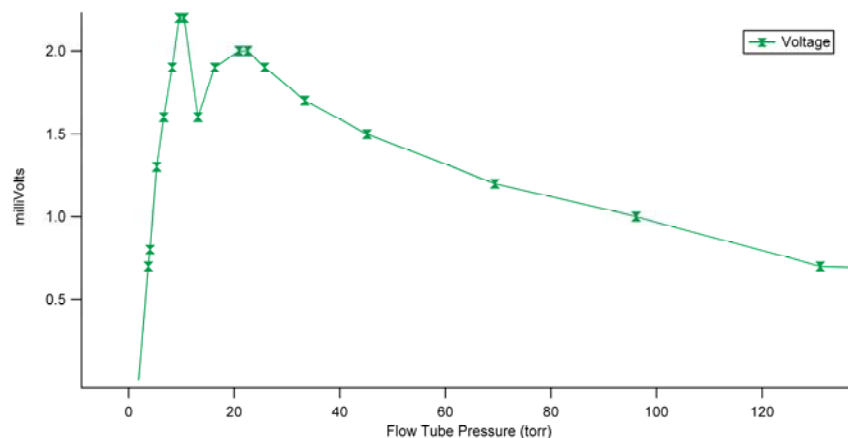
#### *a) low frequency artifacts*

It was discovered early on that the time of flight repeller rate of operation was limited due to mysterious artifacts that appeared in the data. It was deduced that the problem was electronic in nature given the periodicity and reproducibility of the artifacts. Numerous frequency measurements were taken at various voltages in order to characterize the issue and establish limits of operation. The two plots below show examples of the data collected, which were taken with no sample in the system. No voltages were applied other than that of the repeller itself. It was determined that the lowest frequency to operate at is 1.639 KHz and the upper limit is 3.325 KHz.



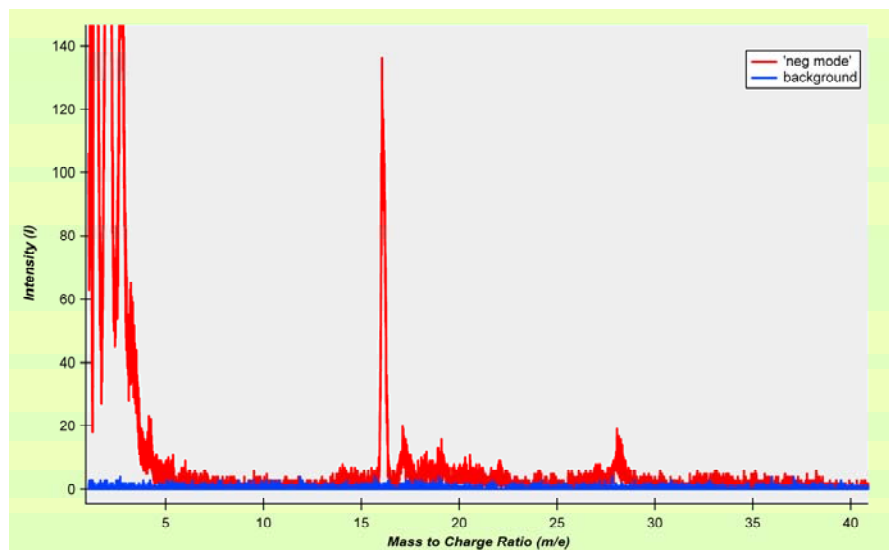
Early on, attempts were made to detect ions in the spectrometer from “soft” ionization. In order to verify that soft ions were being created by alpha particle ionization from polonium-210 radioactive decay (as opposed to the “hard” ions from electron impact), it was attempted to

measure the ion current at the pinhole exit of the flow reactor. This was accomplished by connecting a digital meter to the BNC feed through connector connected to the pinhole. The results are shown below and characterize nicely the dependence of the ion creation on the flow tube pressure. The optimal operating pressure can easily be extracted from a similar graph when the final instrumental configuration is chosen.



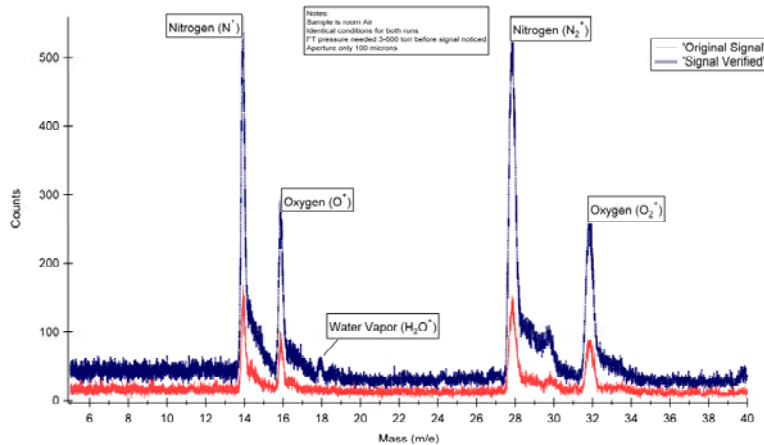
*b) system calibration*

The electron impact ionization source was used to generate the first negative ion spectrum from a sample of ambient air. This spectrum is not calibrated, but several peaks can easily be seen and need to be identified. Calibration and parameter optimization is needed in order to convert the flight time to mass properly. The background shown in blue is of the same collection time and is negligible. This shows the excellent signal to noise ratio for electron impact. The large peaks seen below mass 5 are not from ions but likely from electronic noise from one of several or a combination of voltage or time settings.

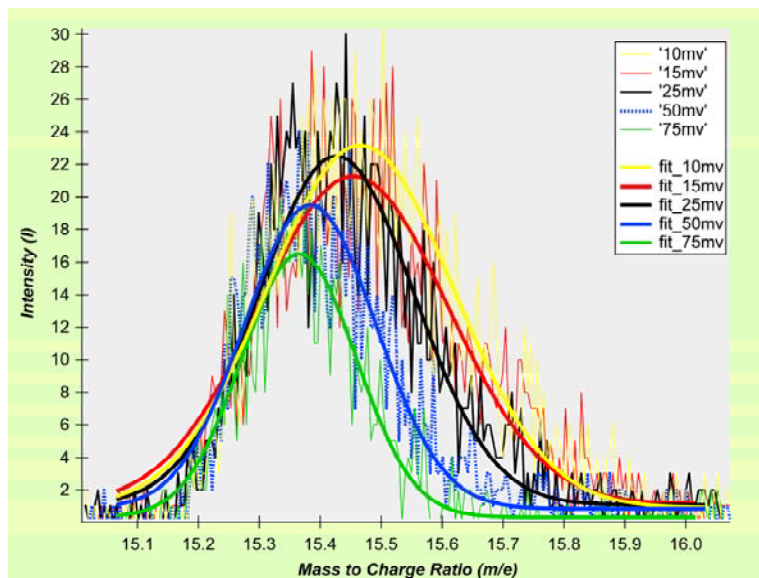


c) *Negative ions using polonium source*

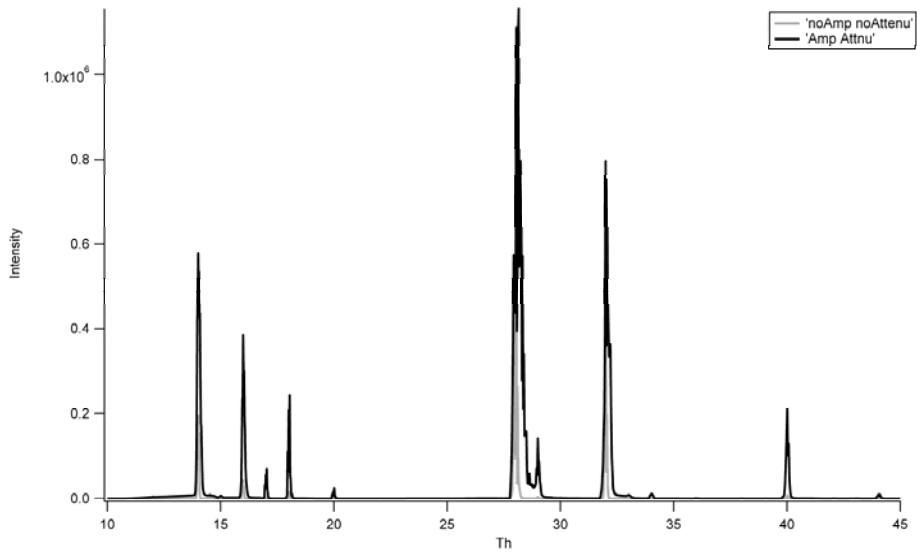
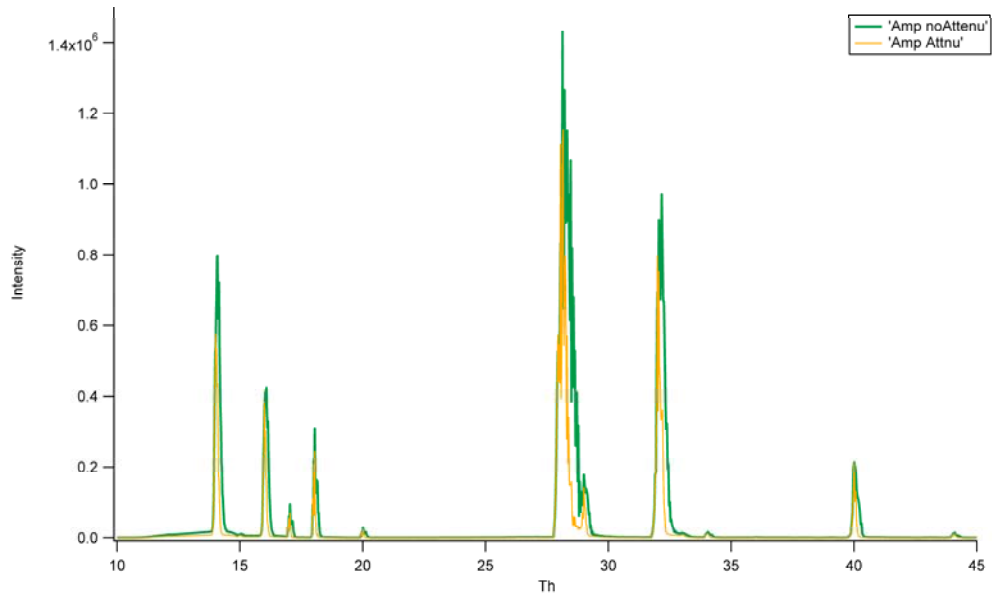
The first ions from polonium-21 were detected after discovering that a reflection voltage setting was not at the optimal value. Then new attempts were made and at about the operational pressure limits of the system, counts were seen that could not be attributed to random background ions. The graph below shows the original signal of ambient air (red) and a longer collection time spectrum (blue) was collected to verify the signal and shows additional peaks. The mass accuracy and abundance were accurate and finally verified that ions (in this case positive) could be transported from the flow reactor to the detector.



The threshold value is the minimum detector voltage signal measured that will be counted as an ion event. The lower the threshold, more noise is introduced into the spectrum, but the higher the threshold, the cleaner the signal, but it is lower in intensity. It was necessary to determine the extent of the effect of the choice of threshold on the data and attempt to find the ideal threshold with both good intensity and low noise. The figure below is data from short collection times with various threshold values (electron impact, positive ion mode) and actually shows an unexpected effect of varying threshold values. The right sides of the peaks actually stretch out as you decrease the threshold value. The Gaussian peak fits show this best. There are more counts in the lower threshold peaks, but the resolution is degraded and leads to less certainty of the actual mass.



Given the numerous problems with the signal amplifier, there was a need to know the benefit of using the amplifier and the impact of using an attenuator to protect the amplifier if necessary. There is about a 19% signal loss when using the attenuator (first figure below), but the final figure shows clearly that an amplified signal that has an attenuator attached, is still much better than running with no amplifier at all.



## Vibrational O-H overtone Spectroscopy of Carboxylic Acids Using CRDS

- A simple cavity was constructed using a 1/2" Teflon tube of approximately 50 cm in length. The Teflon tube was placed inside a rigid copper pipe of the same length to keep the ring-down cell stable.
- The CRDS setup was tested by measuring water vapor absorption coefficient and comparing the measurement with a spectrum generated from HITRAN spectroscopic database.
- The HITRAN spectrum was generated by applying a Lorentzian line shape on the line intensities in the database. This analysis was carried out by executing an algorithm written in IgorPro software.
- The widely tunable dye laser wavelength for the CRDS setup was calibrated in a similar manner measuring water vapor absorption and comparing the measurement with a spectrum generated from HITRAN database.
- The CRDS instrument furnishes the absorption coefficient for the sample; this quantity is the product of the number density and the absorption cross section. Therefore, in order to extract the absorption cross section from the data a separate way of measuring the number density was needed. A relative humidity probe (RH probe) or a hygrometer (VWR Scientific) was incorporated into the setup to calculate number density from RH and temperature measurement and saturation vapor pressure of water.
- A UV-Abs instrument was put together to determine the number density of the gas flowing through the RDC for the carboxylic acid measurements. The instrument consists of Zn Lamp, a glass absorption cell and a UV detector.
- Several circuit designs to operate the UV detector (a phototube, Hamamatsu) were tested and the circuit with the optimal signal was used.
- The absorption cross section for **acetic acid and per acetic acid** was measured by scanning the dye laser initially across a wide spectral window (600 – 650 nm) at a resolution of 0.05 nm and later on focusing on the fourth O-H vibrational overtone (610 – 625 nm) at a higher resolution of 0.01 nm.

### The major educational activity was

1. Weekly group meetings involving undergraduate and graduate students involving short presentations, literature review and discussions of problems related to experiments.
2. Mentoring of undergraduates by graduate students
3. Training of students in the use of lasers, laser alignment, cavity ring down techniques, LabView programming.
4. Attending seminars on related topics