Time of Flight Mass Spectroscopy and Velocity Map Imaging

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January 26, 2013

Velocity map imaging (VMI) is used to study the dynamics of various dissociative electron attachment (DEA) processes by finding the kinetic energies and angular distribution of the products. In this project a VMI mass spectrometer was used as a Time of Flight Mass Spectrometer (ToFMS). ToFMS can be used to measure the absolute cross section of the ions. The voltage conditions for the best mass resolution was determined for electron impact ionization which produces positive ions, so that it could be used in similar conditions for the negative ions just by changing the polarity of the electric fields. A calibration of the spectrometer was also attempted to convert the time of flight of various ions to their $m/q$ ratio. Then the spectrometer was studied in the VMI mode and optimized for best imaging conditions. Thus the spectrometer can be used both in ToFMS mode to get the absolute cross section and VMI mode to get angular distribution and K.E. of DEA.

1 Time of Flight Mass Spectroscopy

1.1 Introduction

A time of flight mass spectrum for positive ions can be obtained as discussed in the seminal paper by Wiley et. al. [4]. It can be used to identify the ions formed in the process and measure the absolute cross-section of these ions. In this project an attempt was made to optimize the resolution of the ToFMS which differed in the spectrometer of [4] by an additional lens and to calibrate the spectrometer to convert the time of flight of various ions detected to their respective $m/q$ ratios. Positive ions formed by the dissociative ionization of Air was used for this purpose. The positive ions have a high count rate making them easy to detect. The mass spectrum due to electron ionization of various molecules is well documented by the NIST website. This can be used as a reference during calibration. The voltage conditions then can be reversed for use with negative ions formed by DEA. Positive ions produced from the electron impact ionization of Air molecules were used in the calibration. Finally the mass spectrum due to electron impact ionization of Acetone was recorded and the $m/q$ ratio of various ions calculated.
1.2 Experimental Setup

The experiment was carried out in a vacuum of few times $10^{-8}$ Torr which was achieved using a combination of turbo and scroll pumps. Such high vacuum was needed to ensure a single molecule collision with the electron by decreasing the pressure and thus increasing the mean free path. It also helped to prevent the oxidization of the electron gun and also ensured that no stray molecules were taking part in the ionization process. A schematic experimental setup shown in Figure 1 lists the main parts of the spectrometer. A tungsten filament electron gun was used to produce an electron beam. A Pierce geometry cathode was used for focusing of the electrons. Two coils placed in a Helmholtz configuration mounted outside the vacuum chamber helped in collimating the electrons by providing a constant field along the beam direction. A Faraday cup placed opposite to the gun was used for measuring the electron current. An effusive molecular beam was introduced perpendicularly to the electron beam and along the axis of the spectrometer using a capillary array. The collision took place in the interaction region between the pusher and puller. The ions produced in the interaction region were transported to the detector using an ion optics arrangement which consisted of the pusher, puller, lens and flight tube (FT). The puller, lens and the opening of FT had an aperture of diameter 20mm. The other end of FT had a aperture of 40mm diameter. The distance between pusher-puller was 10mm, between puller-lens and lens-FT was 5mm. Length of the FT was 50mm. The ions at the end of the FT were incident on the position sensitive detector (PSD). The PSD consisted of 3 Micro Channel Plates (MCP) placed in the Z-stack configuration. It was followed by a germanium layer and a wedge and strip anode which is shown in Figure 2. When an ion is incident on the MCP a secondary electron is produced which gets successively multiplied finally forming a charge cloud on the germanium layer. The image charge is picked up by the wedge and strip anode. The output signals of these anodes are then amplified by a fast amplifier and
fed to the constant fraction discriminator (CFD). The output of CFD was fed to a P-7888 card to obtain the ToF spectrum. Figure 3 shows a schematic of the data acquisition system for ToFMS.

Figure 2: Structural representation of the Wedge-and-Strip anode. (a): the anode coated with Ge-Layer and facing the MCP, (b): the side view of the detector and (c): the main structural form of the Wedge-and-Strip anode.

Figure 3: A Schematic of the Data Acquisition system used for the ToFMS.

1.3 Interaction, Transport and Detection

The electron beam was restrained by placing a grid of negative potential w.r.t the electron gun in front of it. This grid was overridden with positive pulses of duration 100ns from a master pulser. The ions were produced in this duration. The pusher was also connected to the master pulser but with a delay of 150ns, so that the ions move freely for 50ns after their formation. This helps in time lag focusing as discussed in [4]. Another main advantage of pulsed extraction is that the interaction region is field free while the ions are being created. A 1µs duration of the pusher pulse ensures that all the ions cross the puller during this time thus giving them equal K.E. Figure 4 shows the various delays.

The voltages of the Pusher, lens and FT were adjusted to get the best resolution possible. The detector output after going through a pre-amplifier was amplified using a fast amplifier and then
fed to the CFD, which sent a stop to the P-7888 card every time an ion was detected. The P-7888 card can record multiple stops and thus the mass spectrum was obtained. The start for the P-7888 was obtained from the master pulser after a delay.

1.4 Calibration, Results and Discussions

Molecular beams of Air and Acetone were made to interact with the electron beam at right angles in a background pressure of about 10^{-6} Torr. The voltage conditions for the best resolution was determined by systematically varying one of the voltages while the others were held constant. Figure 5 shows the change in resolution as a function of FT voltage when others were kept constant.

From the design of the spectrometer it was seen that there existed a linear relation between $t^2$ and $m/q$. Two of the known $(m/q)$ peaks of Air were selected and a linear fit was done between $t^2$ and $m/q$. The slope and intercept thus found were used to calculate the $m/q$ ratio of the peaks in the acetone spectrum. The acetone spectrum peaks are shown in Figure 6. The mass spectrum obtained showed a very good match with the data on NIST website. Figure 7 shows the mass spectrum of acetone as published in the NIST website.
Figure 5: Resolution of the ToFMS as a function of FT voltage
Figure 6: Mass spectrum of Acetone

Figure 7: Mass spectrum of Acetone as published on the NIST website
2 Velocity Map Imaging

2.1 Dissociative Electron Attachment (DEA)

When an electron-molecule collision takes place at low energies (of $\leq 15 \, \text{eV}$), depending on the electron energy and the molecular species, a resonant negative ion is formed. This short lived negative ion decomposes either by auto-detachment or by DEA as shown in Figure 8. The DEA process can be considered to be a two step process, namely formation of negative ion resonant (NIR) state and its dissociation. The dynamics of the DEA processes could be obtained from the kinetic energies and angular distribution of the fragment ions. The angular distribution measurements are particularly important for the case of DEA, due to the selection rules, which connects the states of the neutral molecule to the negative ion resonant states and the orientation of the neutral molecule with respect to the incoming electron momentum vector. Thus the angular distribution contains information on the symmetry of the negative ion state and the angular momentum of the electron that was captured. Note that this is under the assumption that the molecule does not rotate in the dissociation time, i.e from the time it attaches the electron till it dissociates. Velocity map imaging technique as discussed in Section 2.2 was used to determine the angular distribution of the products.

2.2 Velocity Map Imaging

An outline of the experimental steps for the velocity map imaging in the photo-dissociation studies is depicted in Figure 9. Photo-dissociation is the process for which VMI has been done extensively. The VMI techniques used in the analysis of this process [5] can be extended to VMI of DEA process. The steps in VMI of photo-dissociation are as follows: (a) creation of the Newton spheres by photo-dissociation; (b) conversion of photo-fragments to ions by laser ionization; (c) projection
of the ionic Newton spheres onto a 2D position sensitive detector; and (d) recovery of the three dimensional information from the 2D image in order to get the central slice through the Newton’s sphere, either by using an inversion procedure or keeping the detector active during a small time window. In this experiment the ionic Newton sphere is created due to the interaction of electron beam with the molecular beam. Thus there is only one step instead of steps (a) and (b). The procedure for recording the ion cloud and obtaining appropriate slice of the Newton sphere also differs from steps (c) and (d).

Figure 9: Schematic of the experimental steps used in the photo-fragment imaging from photo-dissociation. In our experiments the Newton spheres are produced due to collision of electron beam with molecular beam. Thus the direction of the electric field of the dissociating laser will be replaced by the electron momentum vector in our experiment. The recording of the Newton sphere and retrieval of the 3D slice were also different in this experiment.

In this experiment, time slicing technique was used with some modifications. A pulsed extraction was used to extract the ions formed in the interaction region. Pulsed extraction was needed to avoid disturbance to the electron beam by the ion extraction field. A PSD with a wedge-and-strip arrangement was used for recording the position information. The use of Wedge and Strip detector allowed recording of the time of arrival of individual ions at the detector along with its position. Since the events were recorded separately, it was feasible to separate them out according to their time of arrival and position during off-line analysis after the experiment was over and thus the necessary ‘slicing’ was carried out.
2.3 Experimental Setup

The experimental setup is similar to the ToFMS setup as discussed earlier in Section 1.2. The only difference is in the voltages applied at various stages of the ion optics and the data acquisition system. In VMI the position information has to be extracted. A voltage of +170 V was applied to the MCP front for negative ion detection. The MCP back was held at 2800 V. When an ion hit the MCP, a secondary electron was created. After getting multiplied through the MCP, an electron cloud was formed. This electron cloud was incident on the Ge layer. The three segments of the anode which were at a potential of about 50 V higher than the MCP back picked up the image charge created on them when the electron cloud was incident on the Ge-layer. The pulse heights of the signals obtained from strip and wedge electrodes were proportional to the X and Y co-ordinate of the center of the charge cloud. The pulse height from meander electrode was used to normalize all readings. The signals from each of the three structures were amplified by a set of charge sensitive preamplifiers followed by spectroscopic amplifiers. The three voltage signals were then processed using an Analog-to-Digital Converter (ADC) and given to the computer for monitoring and storing in the list mode using specially built Linux Advanced Multi Parameter System (LAMPS) software.

2.4 Data Acquisition System

A schematic of the Data Acquisition System is shown in Figure 10.

![Figure 10: Block diagram of data acquisition system used in Velocity Map Imaging](image)

Signals from the wedge-and-strip anode were capacitatively coupled to the charge sensitive preamplifiers (CASTA, RoentDek). The ac coupling isolated the charge amplifiers from the high voltage supply connected to the anode of the detector. A fast timing amplifier was used to amplify the
timing signal derived from the output of the channel plates. After discrimination, this signal was used as a STOP pulse of the TAC used for ToF determination. A ADC which measured the peak height of the positive input signals, was used for data acquisition. The conversion was initiated by external fast NIM strobe input, which was generated from the time outputs of the pre - amplifiers. A gate width was generated, triggered by the same external strobe signal. During the gate width the peak value of all four inputs were detected and stretched. It was monitored that the peak position of all inputs lied within the gate signal. The ADC and the controller module were held in a CAMAC mini crate (Kinetic System, Model: 1507) connected to a PCI card via a CC 2000 crate controller. Once the charge signal was digitized, the impact position of the ions onto the detector could be calculated from simple standard expressions:

\[
X = \frac{S}{S + W + M}
\]

\[
Y = \frac{W}{S + W + M}
\]

where S, W, and M refer the charge signals measured from strip, wedge, and meander respectively.

2.5 Results and Discussions

DEA to \(O_2\) produces \(O^-\) which is a resonant process peaking at 6.5eV. The bond dissociation energy of oxygen is 5.1 eV, electron affinity of oxygen atom is 1.4eV and since the incoming electron has an energy of 6.5 eV, conservation of energy and momentum gives 1.4 eV as kinetic energy of the fragments. The excitation function obtained by sweeping the electron energy from 0 to 10eV is shown in Figure 11.

The voltages of the Pusher, Lens and flight tube were determined by running Simion simulations after creating a nearly same model of the real spectrometer in the simulation and systematically varying the voltages till the best resolution was achieved. The ‘slicing’ was done using a matlab code. Figure 12 shows the resolution as a function of different voltages. It can be seen that in the solutions the best resolution was for a lens voltage of 0V.

After setting the electron energy to 6.5ev, the velocity map images were taken. However it was found that the the voltage conditions for the best resolution obtained by simulations was not the same for the real spectrometer. The optimal lens voltage was not zero. Figure 13 shows the plot of resolution vs various voltages that were obtained. Though we see an increase in the resolution as the FT voltage goes beyond 180V, the ion count had really reduced and hence this increase was neglected. The voltages corresponding to the maximum resolution were finally used.

Figure 14 shows the images obtained for 3 different energies, 5eV, 6.5eV and 8eV. The images obtained were then analyzed to get the Angular distribution of the ions.

The angular distribution of \(O^-\) from \(O_2\) is known to have 4 peaks as shown in Figure 16. The presence of only two peaks obtained in this project could be attributed to the limited resolution of the electron gun used in the spectrometer which translated into poor image resolution.
Figure 11: A plot of count of $O^-$ ions vs the electron energy. A resonance can be clearly seen.

Figure 14: Images obtained at different energies. The red arrow indicates the direction of the electron beam.
(a) Varying FT voltage.  
(b) Varying Lens voltage.

Figure 12: Resolution as a function of different voltages in simulation.

(a) Image at 5eV  
(b) Image at 6.5eV 
(c) Image at 8eV 

Figure 15: Angular Distribution at different energies.
Figure 13: Graphs of resolution vs different voltages for the real spectrometer. When one voltage was varied the others were kept constant.

Figure 16: Angular distribution of $O^-$ from $O_2$ as reported by [1]. The squares, circles, and triangles are the data at electron energies of 5.0, 6.5, and 8.0 eV respectively.
Acknowledgement

I would like to thank Vishvesh. Without his help this project would not have seen completion. I would also like to thank Yogesh and Satej for their timely help and Krishnendu for his friendly advice. Finally, I express my gratitude to Dr. Vaibhav for allowing me to work in his lab, for showing me the flavor of experimental research and for always coming to the lab whenever I called him.

References


