ESF Scientific Report
Stephen Walker SIMLI Grant

Purpose of Visit

My stay in Braunschweig, Germany, made possible by the SIMLI grant funded through the ESF, allowed me to study and work with Dr. Cristof Maul in his 3-D velocity map imaging lab. I was working alongside another PhD. student of Dr. Maul's, Mr. Mikhail Proboskey, to help adapt the current apparatus such that it can analyse both positive and negative ions. The eventual goal of this research is to create a machine able to study the photodynamics of reaction processes following exposure to laser fields. This is done by analyzing the velocities of both cations and anions formed simultaneously or through collisions. My part in the project was to assist in the set-up and initial tests of the system and collect the first sets of data using this apparatus. The system in Braunschweig is similar to the one we developed in our lab at Queen's University but with several key differences. They use a 3-D detector, a much smaller flight tube and a molecular beam to introduce their samples. The fundamental principles, however, are the same. Additionally, many of the instruments used in Braunschweig are the same make and model as the ones at Queen's. This proved to be invaluable as I was able to assist in the lab immediately upon arriving. The second purpose of my stay was to share my PhD research in a semi-formal setting through lab group presentations. This helped to forge a new relationship between our two groups, and set a platform for collaborations that will allow longer exchange trips for future students within the two groups.

Theory

Velocity Map Imaging (VMI) has developed into a very useful tool for studying the dynamics of many types of reactions including photo dissociation, bimolecular collisions and photoionization. The concept stems from the idea that if one can detect the kinetic energy (velocity) of one of the product fragments. Then by using the conservation of momentum and energy, one can obtain internal electronic, vibrational and rotational energy states of not only the detected fragment but also the co-fragment. See figure 1.

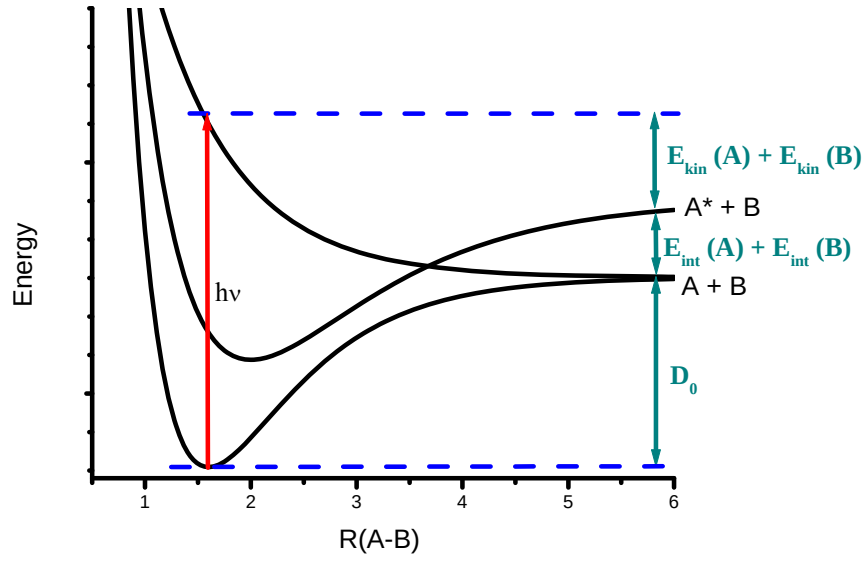

FIG. 1 Sketch of a simple diatomic following photodissociation. If the initial state is well defined and the energy applied is well known, then by conservation of momentum and mass imaging one fragment will provide the information about the second species.

$E_{photon} = h\nu = D_0 + E_{int}(A) + E_{int}(B) + E_{kin}(A) + E_{kin}(B)$

VMI experiments are conducted either by reacting two molecular beams for studying bimolecular collisions or by exposing the molecules to a laser field in order to study photodissociation. The molecules are then ionized and propagate as a cloud of ions in the direction given by their initial kinetic energy.

In practice ionization is usually done through an intense laser field using resonance enhanced multiphoton ionization (REMPI) which allows for state selective ionization. Using ring electrodes the ions are accelerated down the time of flight mass spectrometer without changing the initial velocities in the other two perpendicular directions. At the end of the time of flight, these ions strike a multichannel plate cascading electrons towards a phosphor screen. This generates light which are mapped using a CCD camera or in the case of 3-D imaging a delay line detector.

In order to achieve the needed certainty of the initial energy states of the molecules usually cold molecular beams are used. The other restriction is that the deposited energy needs to be well defined. This is usually done using monochromatic laser fields, REMPI is preformed done using monochromatic lasers.

The high level of resolution of images has been made possible by the work of Parker and Eppink[i] who replaced the grid electrodes previously used to accelerate the ions with an Einzel lens. This drastically increased the resolution allowing one to resolve the different velocities of the fragments. The second innovation by Chan[ii] improved the resolution of the images even further. They analyzed each spot detected by the CCD camera which represented a burst of electrons causing several pixels to be excited. This would create a blur in the image and eliminated this problem by introducing real-time event counting. The highest intensity pixel was selected and stored for each ion that struck the phosphor screen and the final pixel value then corresponded to the number of ions detected at each position. A third technique known as DC slicing has also been used to decrease blurring of the image pioneered by Suits et al.[iii] In this technique the ion cloud is allowed to expand while in the acceleration region giving the ions a large Δt of arrival times at the detector. The detector is then gated on the center part of the time interval. This allows for only the equatorial part of the image to be obtained without the need for inverting the image as only the center is obtained.

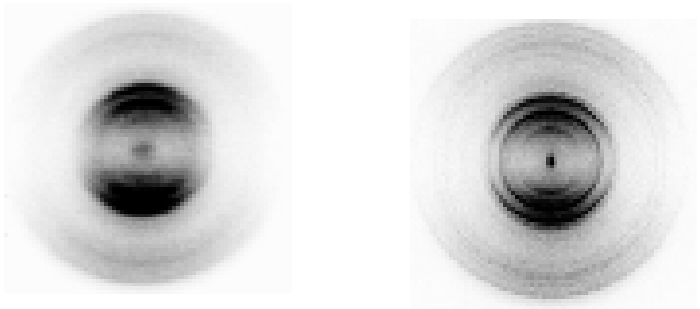

FIG.2. Comparison between images of O^+ ions from the photolysis of molecular oxygen at 225 nm.
Reproduced from Eppink and Parker. [i]

Resonance Enhanced MultiPhoton Ionization (REMPI)

This section follows the description of REMPI given by Telle.[iv] The technique commonly used to selectively ionize the different molecules formed after photolysis is REMPI. The ionization process in REMPI is a multiphoton technique, whereby the first photon excites the molecule to an excited state, and the absorption of a second photon leads to ionization of the molecule. The ability to state-selectively access the excited state is what leads to the advantage of REMPI over traditional multiphoton techniques. Alternatively, if one were to use single photon ionization, the energies needed for most applications would be well within the vacuum ultraviolet, greatly increasing the complexity of the apparatus. The resonance absorption into the excited state is governed by spectroscopic selection rules and ground state population. This leads to a distinct spectrum with identifiable vibration and rotational levels when monitoring either the electron or ion current. When describing a given REMPI process it is common to use the notation of (m+n) for single colour REMPI processes and (m+n') for two-colour processes. Here, m is the number of photons at the wavelength used to pump the fragment to the resonance state, and n is the number of photons used to ionize the resonant state. When n and m have different energies, n' is used. Figure 10 describes the different REMPI processes.

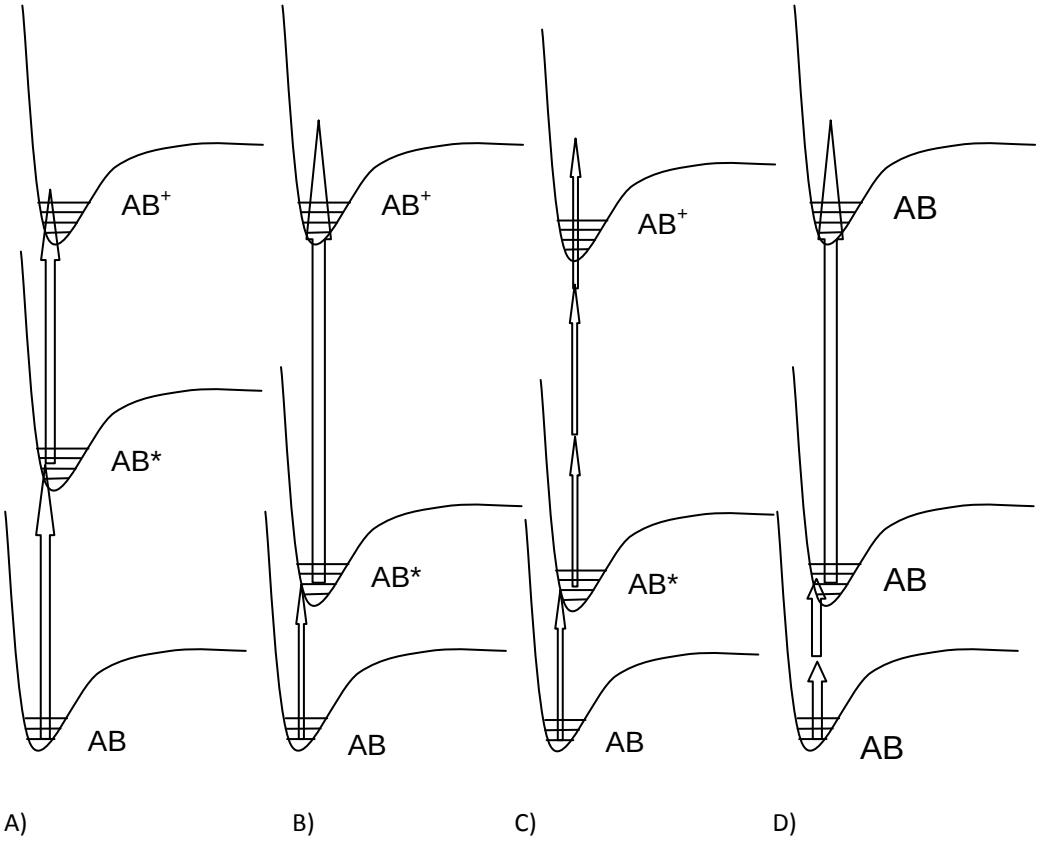

Figure 3: Description of four different REMPI process for a hypothetical diatomic AB;
A) (1+1), B) (1+1'), C) (1+3), and D) (2+1')

3-D imaging of ions

The description is based on chapter 6 of Imaging in Molecular Dynamics Technology and Applications, the chapter itself is written by members of the group that I visited in Braunschweig.[v]

In traditional 2-D imaging, it is not possible to obtain the full 3-D velocities of the molecules directly from the data obtained at the detector. This is because the image formed

on the detector is actually a 2-D representation of the original 3-D cloud. In order to obtain the full information from the data, one needs to use a mathematical treatment known as the Abel transform to rebuild the original 3-D velocity information. There are, however, some complications when the ion cloud is not ideal: the Abel transform magnifies noise found in the image and there is a singularity in the calculation of the Fourier Transform that is used in the calculation[vi].

3-D Imaging techniques can be used in order to avoid some of these problems. In this technique instead of imaging a 2-D representation of the ion cloud, the x-y positions of the ions are detected along with the time at which they reach the detector. This provides the three dimensions, two in space and one in time. In order to obtain the time resolution needed to perform this task, the group uses a Delay Line Detector (DLD), which is made from a delay-line anode wrapped around a copper plate. In a helical wire delay line, two wires are wrapped perpendicular to each other, giving four ends of wires where information is obtained. When a signal is induced from the electrons hitting the wire, the signal propagates in both directions. By measuring the difference in time it takes for the signal to reach the ends of the wire, one can obtain both the impact position and the time at which it hit to a great degree of accuracy. In most 3-D imaging techniques, the ions are accelerated towards the detector by using ring electrodes such that the ions do not focus to one plane this preserves the ion cloud shape and allows the ions to be imaged properly. The three dimensional imaging technique is new and interesting field within the imaging community. The set-up can be slightly more complicated than traditional 2-D imaging; however, both methods have their pros and cons and are consequently still both found in the literature today.

Project description

I will first describe the project instrumentation here and then discuss my role in its development.

The 3-D velocity map imaging apparatus consists of a high vacuum chamber with a time of flight chamber, along with a molecular beam valve and a delay line detector. The system is pumped by a turbo molecular pump (Pfeiffer) which is forepumped by either a small turbo molecular pump coupled with a membrane pump, or a rotary vane pump.

Molecules of interest are pulsed through the beam valve into the reaction chamber perpendicular to the time of flight (TOF) access. The excitation laser then intersects the beam again perpendicular to both the molecular beam and the TOF. The time of flight chamber consists of an acceleration region and a field free drift region; the acceleration region is made up of ten ring electrodes to accelerate the ion cloud towards the detector. These ring electrodes are separated by glass rods 1 mm thick, with the molecular beam and laser entering between the 5th and 6th electrode. The ring electrodes can be charged in two different ways to achieve either ion imaging or velocity map imaging configurations. If all 10 electrodes are charged a near homogenous field is generated allowing for ion imaging. If, however, plates 1 and 10 are connected and charged and 7 and 9 are also charged, then plates 7,8,9 will form an Einzel lens increasing the resolution for velocity map imaging. The plates are charged on the order of a1000V difference between back and front plates using a Stanford research systems PS350 power supply, and are connected with resistors.

A Spectra Physics Scanmate 2 dye laser pumped by an infinity Nd-YAG laser was doubled using a BBO crystal; it is pumped by an Infinity Nd-YAG laser. All told the Scanmate produced ultraviolet light at a power of about 250 μJ. Dye lasers are very convenient as they allow for very narrow bandwidth resolution on the order of 0.2 cm^{-1} and this allows the group to use REMPI. This is what is used to state-selectively ionize the molecules after the reaction has occurred. While I was at Braunschweig, I conducted one-colour experiments using this dye laser to induce the reaction, and ionize the products. Once the ions were created the ring electrodes accelerated them towards the drift region and finally to the detector 10 cm away. A commercial 3D imaging detector made up of a dual MCP detector and a Delay line from Roentdek was used to capture the image for later analysis.

Shortly before my arrival, the group in Braunschweig added a second time of flight chamber in the opposite direction of the imaging TOF with a pseudo delay line. This will allow the group to image either the cation or the anion and detect the other at the same time. This is the start of this ambitious project which eventually will lead to the group being able to detect both ions in coincidence with each other.

My part in the project was to help with the initial setup and testing of this new appendage of the apparatus. The initial set up tests involved checking that photons were flying along a line of sight and are detected by the MCP. Then using the pulsed valve we introduced HCl in Ar 5% such that the positive ions can be imaged and that the negative ions are detected. From there more controlled studies could be performed with the intention of publication of possible results. Unfortunately my work began not with detecting light on the MCP but from helping to align the dye laser used to produce the photo dissociation event. The whole system needed to be realigned from the Nd-YAG pump beam. This took several days to complete. After fixing the dye laser into an operational state we were able to double the beam using a BBO crystal, this allowed us to test the electronics of the new assembly. It was here found that there was another error as only 3 signals from the delay line were present. After some time we were then able to trace the problem to the differential amplifier. This gave 4 strong signals from the delay line detector there however, was still another problem. The laser seemed to be lasing over a large number of wavelengths as tuning the laser did not change the strength of the doubled beam which is a clear indicator that the laser is actually emitting as fluorescence rather than from the grating in the dye oscillator chamber. Thus the laser was not aligned perfectly and while it was operational it was far from ideal and needed to be attended to. As discussed above the resolution of the laser must be very fine as a requirement for proper REMPI. If the beam is broadband then it will excite several states or no states at all. We worked for several days to rectify this but we were unable to obtain sufficient line width at high enough power to allow for excitation at which point my time in Braunschweig had come to an end. Now the system has come along a far way and is very close to being fully functional.

The other major part of my trip was to discuss the work of our group in Canada and how our two groups could work together in the future. This was done both in a casual atmosphere relating the similarities and differences between our groups and in a more, formal setting where I gave a presentation on my PhD. work in Canada. In Kingston we are building an apparatus in order to study the photo dissociation reaction dynamics of solid ice systems using two dimensional velocity map imaging. Once our set up is complete we should be able to perform similar experiments to the group in Germany attempts. However, we will be able

to study condensed phase materials such as water ice or methanol ices. My talk involved a brief description of 2-D VMI which is the original form upon which 3-D imaging is based and then described the reasons for studying the reaction dynamics of condensed phase matter and the technical challenges. This discussion following my seminar I hope my talk allowed both groups to appreciate the similarities and differences between the two approaches. I believe my presentation was well received by the German group.

While it was somewhat unfortunate that I was unable to obtain any publishable data in the short 15 day period I was in Germany, this was not my main goal of the visit. I was certainly able to learn a large amount on 3-D imaging and on technical issues on the experiment. Additionally my visit it helped pave the way for a future visit possible future neutral exchanges from either group, possibly for longer periods of time would allow for the accumulation of publishable data. I would strongly appreciative of the ESF for making it possible for me to visit the lab in Germany and I would recommend the ESF to other students or project supervisors for this type of opportunity.

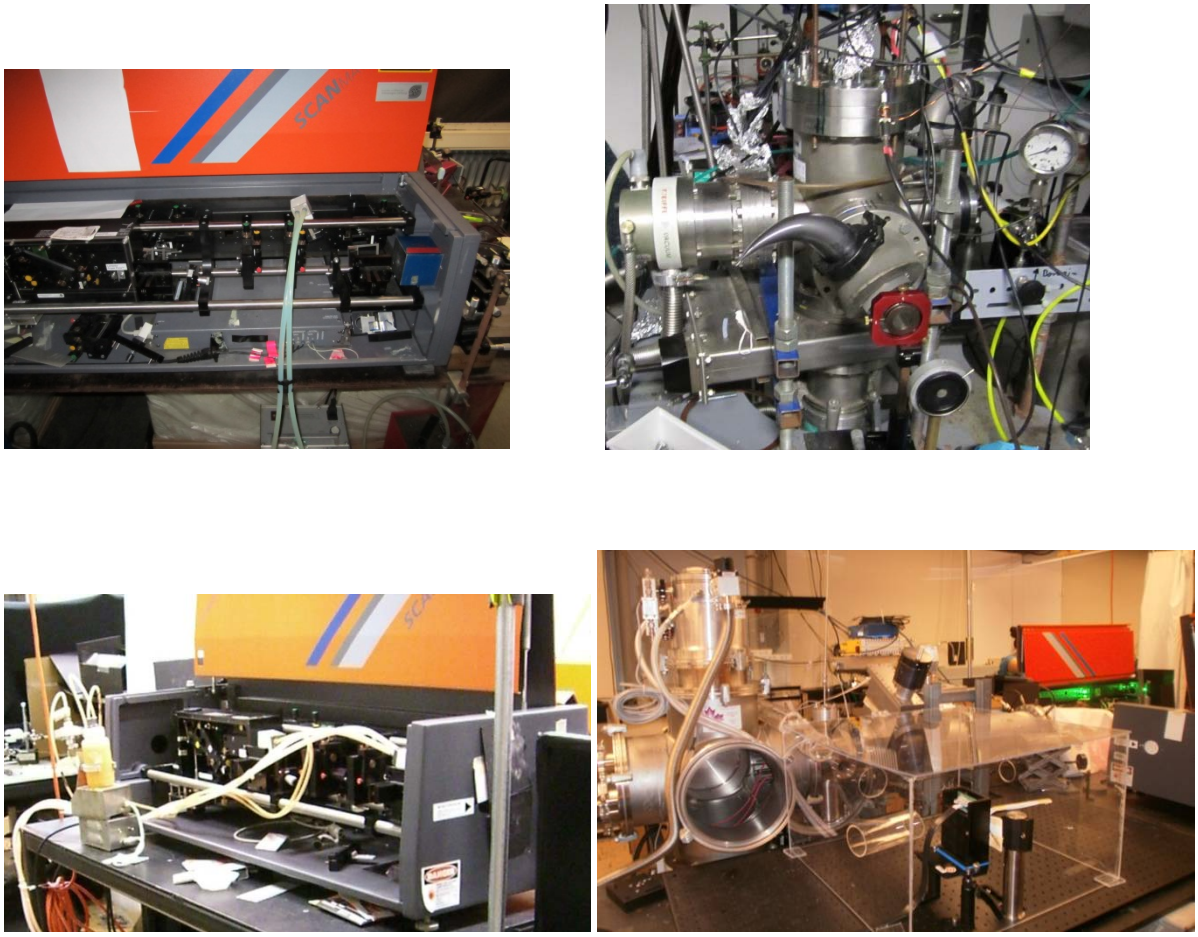

Fig 3) Scanmate 2 dye laser in Braunschweig (top left), 3-D VMI apparatus Braunschweig (top right), Scanmate 2 dye laser in Kingston, Canada (bottom left) and 2-D VMI apparatus for the study of condensed phase matter Kingston (bottom right)

[i] A. T. J. B. Eppink, and D. H. Parker, Rev. Sci. Instrum. **68**, 9 (1997).
[ii] B. Y. Chang, R. C. Hoetzlein, J. A. Mueller, J. D. Geiser, and P. L. Houston, Rev. Sci. Instrum. **69**, 1665 (1998).
[iii] D. Townsend, M. P. Minitti, A.G. Suits; Rev. Sci. Instrum. **74**, 4, 2530 (2003).
[iv] H. H. Telle, A. G. Urena, R.J. Donovan; Laser Chemistry, Spectroscopy, Dynamics and Applications, Wiley, West Sussex, (2007).
[v] A. Chichinin, T.S Einfeld, K.H Gericke, and C. Maul, Chapter 6, Imaging in Molecular Dynamics: Technology and Applications, B. J. Whitaker, Cambridge University Press, New York, (2003).
[vi] A.T.J.B. Eppink, S.M Wu, B.J Whitaker, Chapter 3, Imaging in Molecular Dynamics: Technology and Applications, B. J. Whitaker, Cambridge University Press, New York, (2003).