The Pennsylvania State University

The Graduate School

Department of Chemistry

BIMETALLIC CLUSTERS:

INSIGHTS INTO REACTIONS OF SUBNANOSCALE SURFACES

A Research Report in

Chemistry

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

May 1997

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ABSTRACT

Reactivities of bimetallic clusters can be controlled by varying their composition, making them potentially useful as catalysts and valuable for use in elucidating the reactivities of such subnanoscale surfaces. A new dual rod laser vaporization source coupled to a fast flow reactor is developed for the study of bimetallic clusters and their reactions. In order to establish the versatility of the technique, the results of studies are presented in which Nb/Al clusters are formed in two plasmas induced by the second harmonic (532 nm photons) of a single Nd:YAG laser and then detected by a quadrupole mass spectrometer. The beam from the laser is split and then focused on to each rod, allowing the mixing ratio within the cluster to vary by altering the laser fluence on each rod. With a low fluence on the Nb rod and a high fluence on the Al rod, an Al rich cluster distribution is formed: $NbAl_m^-$ (m = 2-20), and Al_m^- (m = 5-31). By increasing the fluence on the Nb rod, and decreasing the fluence on the Al rod, a Nb rich cluster distribution is formed: $Nb_nAl_m^-$ (n = 3-8 and m = 1-3), $Nb_nOAl_m^-$ (n = 3-8 and m = 1-5), and Nb_nO^- (n = 3-8). Additional characterization is also performed on V/Al clusters.

TABLE OF CONTENTS

LIST OF FIGURES

Figure Page

ACKNOWLEDGEMENTS

First of all I would like to acknowledge my gratitude and indebtedness to Dr. A. W. Castleman, Jr. His open mind and willingness to let me explore my ideas, and not tie me down, has lead to the accomplishment of this research. Without his insight, patience and understanding, my ideas for a research project would still just be thoughts in my mind and on paper.

Special thanks goes out to Walter Vann for his patience in teaching me how to use the experimental apparatus and for giving me insights on how to fine tune my ideas. I wish to thank Jess Ford for the great friend that his is. He has encouraged me through the bad times and has celebrated with me in the good times. I wish also to thank the present and former members of the Castleman Group. Each has been instrumental in keeping me sane and, more importantly, developing me as a scientist.

My deepest, and most heart felt thanks and appreciation, goes out to my wife, Loralee. Military life has brought it's ups and downs; from long hours at the flight line, deployment to Desert Storm, handling the death of one of my soldiers, to the murder of a soldier's wife. The stress that my wife has had to endure is unmeasurable. Through it all, she has stood by me with little or no complaint. I thank her for her patience, kindness, love and understanding. Not many women can endure what she has.

Thanks goes out to each of my children, Celia-Ann and Brian, for their love and patience during the long separations, many moves, and having to leave friends and family. Through it all, I know they have grown, and that these experiences will be with them forever.

Finally, I thank my parents. Without their love and understanding, I wouldn't be the person I am. They have endured a lot, from not seeing their grandchildren but every 3-4 years to wondering if their son would return from Desert Storm. Although we are separated by thousands of miles their prayers and support for me have been unfailing.

CHAPTER 1

INTRODUCTION

Over the past 15 years, investigation of the bulk physical and structural properties of bimetallic clusters has been the focus of several research groups because of their role in the processes of chemisorption and catalysis. Bimetallic clusters (alloys) used as catalysts represent one of the most promising avenues towards new catalytic systems.[1] It has been known for many years that metal mixing (alloying) can significantly modify the catalytic activity and selectivity of a metal.[2,3] Many questions are still unanswered on how alloying modifies catalytic behavior. Does it just change the distribution of islands of a given metal which otherwise retains its reactivity (ensemble effect),[2,3,4] or does it change the local bonding geometry (structure effect),[5] or modify the reactivity of the metal atoms (electronic or ligand effect)?[6,7] The primary benefit of using bimetallic clusters is the variability of their composition allowing the cluster reactivity to be tailored to each individual application.[8] Furthermore, by determining the reactivities of small bimetallic particles it is possible to increase our understanding of the development of bulk behavior, especially concerning the electronic and geometric makeup in metallic entities of finite dimensions. [9,10,11]

Another role of bimetallic clusters is their use as building blocks. It is possible that a new class of materials with tailored properties can be produced starting with clusters as building blocks.[12,13,14,15] The possibility for additional materials is unlimited, since, in principle there is no limit to the size and composition of bimetallic clusters. It

is not unreasonable to expect bimetallic cluster-assembled materials to exhibit unique properties.

Various methods of producing bimetallic clusters have been employed; a single rod (utilizing a binary alloy rod) laser vaporization source,[16] a dual rod/dual laser vaporization source,[17] and a rotating disc source composed of pressed mixed metal powders and carbides[18] to name a few. Possible difficulties with these bimetallic cluster sources include the inability to find suitable powder combinations for the disc source, timing difficulties associated with the synchronization of two lasers and a pulse nozzle in the dual rod dual laser arrangement, and finally the lack of tunability of the mixing ratio in the cluster formation process for a single bimetallic alloy rod. This paper deals with a new dual rod laser vaporization source developed for the study of bimetallic clusters and their reactions. This source is mounted to a fast flow reactor and employs the second harmonic (532 nm photons) of a single Nd:YAG laser to form clusters. The clusters are then detected by a quadrupole mass spectrometer.

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CHAPTER 2

APPARATUS

2.1 Introduction

This chapter describes the flow tube apparatus and the new dual rod laser vaporization (LAVA) source developed as part of the MS research, enabling the facile and efficient production of bimetallic clusters. In order to study the reaction kinetics, the new source is combined with a flow tube reactor. Ferguson, Fehsenfeld, and Schmeltekopf[1] successfully reported the first flow tube experiments in the late 1960's. Following these early experiments several important developments were made. Among these developments were new methods of producing ions. Perhaps the most important development in the study of metal clusters was the advent of the LAVA source. Laser vaporization was used successfully by the groups of Smalley and Bondeybey[2,3] in the early 1980's, to produce neutral metal clusters in a pulsed molecular beam. The ability to create metal clusters using laser vaporization with a continuous gas flow was reported by Riley and co-workers[4], in 1984.

With regard to bimetallic clusters, there are various methods[5,6] being used to generate and study these clusters. This chapter outlines the technical development of a new dual rod LAVA source for the study of bimetallic clusters. A description of the major elements of the flow tube apparatus are also presented.

The fast-flow reactor which has been used in our laboratory for a number of years[7,8,9], is based on the flowing afterglow system of Ferguson and co-workers. The apparatus can be divided into four major sections: the flow tube (7.2 cm id., 104 cm long), the differentially pumped ion sampling/detection region, the electronics, and the ion source (oriented at a 45^{o} angle to the flow tube).

2.2 LAVA Source

In earlier work, a variety of ion sources have been affixed to the reactor enabling a study of the reaction rates of a number of ions and cluster ions. In order to enable the study of the reactions of bimetallic clusters, the development of a new source was undertaken. In this new arrangement, it has been established that bimetallic clusters can be produced by irradiation of two independent metal rods, in a laser vaporization (LAVA) source, with the second harmonic (532 nm) of a single Nd:YAG laser (Spectra-Physics Lasers, Inc., Mountain View, CA, Model GCR-150-30) at a repetition rate of 30 Hz. Prior to entering the lava source, the laser beam is attenuated, split and focused; see *Figure 2-1*. Attenuation is accomplished by a split vertical transverse stage; see *Figure 2-2*. This is done to control the laser fluence on each target rod. A 1 in. diameter circular mirror, cut in half, serves to split the laser beam. The beam is then focused by a 20 cm focal length lens before entering the LAVA source.

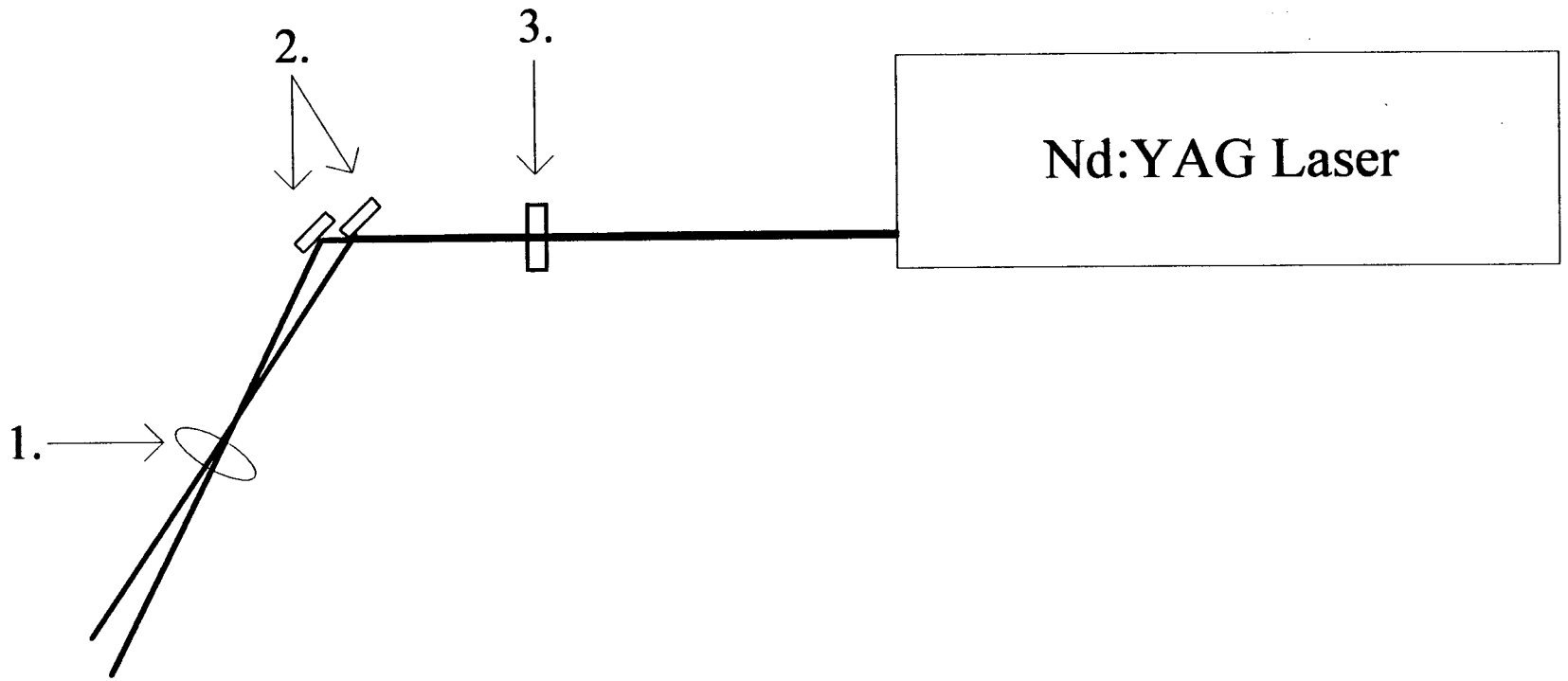

Figure 2-1: Schematic of laser beam attenuation, splitting, and focusing. (1) 20 cm focal length lens. (2) 1 in. dia. circular mirror cut in half. (3) Attenuating split transverse stage.

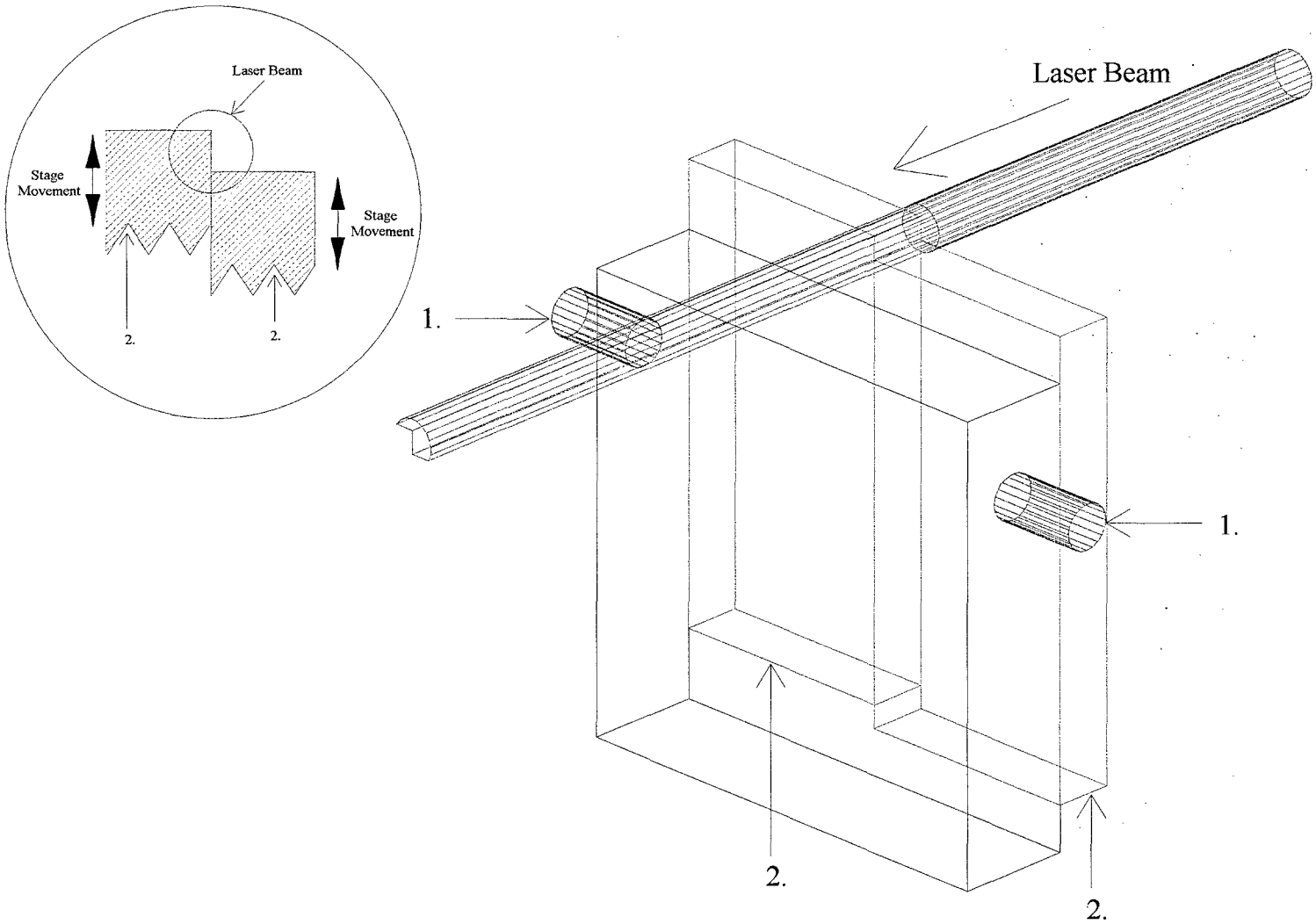

Figure 2-2: Attenuating split transverse stage. (1) Adjustment knobs. (2) Split stage. Each knob adjusts half the stage either up or down to attenuate half of the laser beam.

The new dual rod laser vaporization source is somewhat similar in design to those previously reported.[10,11], with major differences being a continuous flow of carrier gas and the use of two target rods. The source is made from an aluminum block, machined and lathed to specification, shown in *Figure 2-3*. The front (flow tube side) of the source is turned down to 2.9 in. diameter, 0.3125 in. in from the front, for mounting purposes. Four 0.3125 in. diameter holes 1.6750 in. apart are drilled to receive four 1/4x20 bolts for mounting the source to the flow tube. A 0.3750 in. diameter hole 3.0 in. long is drilled, centered on one side, for use as the laser beam channel. Two 0.25 in. holes 2.5 in long, 0.0200 in. apart and opposite each other, are drilled to accommodate the target rods. A 1/8 in. pipe thread (PT) hole is drilled in the center of the front to accommodate a Teflon nozzle. On the back side, a 1/8 in. PT hole is drilled for the carrier gas inlet. Finally a 1.95 in. O.D. and 1.625 in. I.D. grove is cut to accommodate an o-ring.

A horizontal cross section and front view schematic drawing is shown in *Figure 2-4*. A Nd:YAG (532nm) laser beam, split and focused, enters the source via a 0.3750 in. dia., 3.0 in. long channel which also serves to funnel the carrier gas onto the target rods. The laser beam channel is continuous through the source, and sealed at each end with an optical grade fused silica window. The windows are affixed with low vapor pressure silicon rubber to maintain vacuum. Two 0.25 in. target rods, 0.020 in. apart and opposite each other, perpendicularly bisect the laser beam channel 40 mm down stream from the carrier gas inlet (see *Figure 2-4*). Each target rod is attached to a 1 RPM high torque synchronous instrument motor (Hurs Mfg. Corp., Princeton, IN,

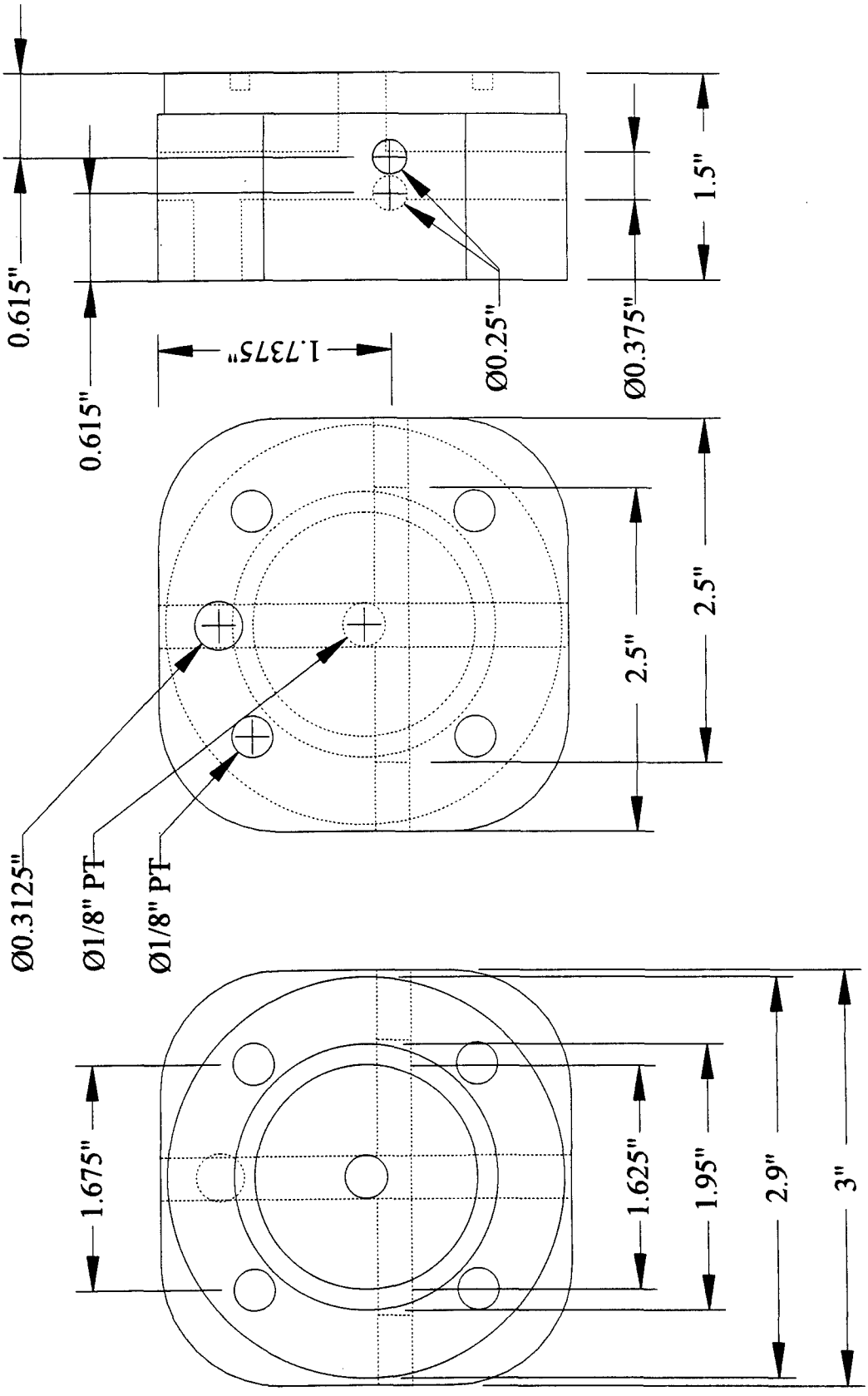

Figure 2-3: Dual rod LAVA source specification diagram.

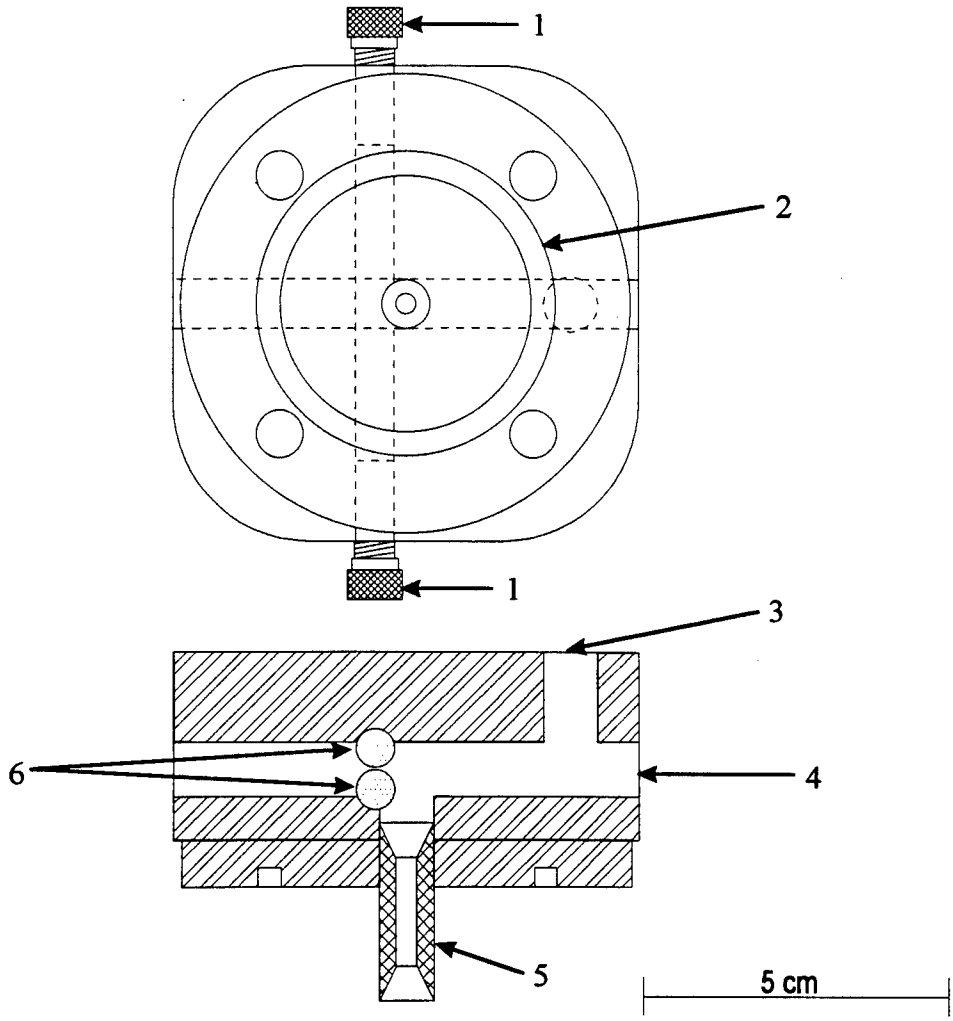

Figure 2-4: Horizontal cross section and front view of the new dual rod LAVA source. (1) Ultra-Torr fittings housing the target rods and allowing for rotation while maintaining vacuum. (2) O-ring grove. (3) Carrier gas inlet. (4) Laser beam channel. (5) Teflon nozzle with a 1/8 in. dia. bore. (6) Target rods, 0.0200 in. apart.

Model A), which rotates and translates each rod in order to provide a fresh surface for laser ablation. Each rod passes through a CAJON Ultra-Torr fitting (Pittsburgh Valve & Fitting, Co., Pittsburgh, PA, SS-4-UT-1-4) to maintain vacuum. A Teflon nozzle, with a 1/8 in. bore, mounted on the front of the source, provides a smooth transition from the laser ablation region into the flow tube. The LAVA source is mounted on a 4.5 in. non-rotatable flange, attached to the flow tube, with an o-ring seal.

2.3 Flow Tube

The most important purpose of the flow tube is to provide a physical container by which the mixture of ions, neutrals, and carrier gas are contained. Other vitally important features are well defined hydrodynamics enabling kinetic measurements and the ability of the flow tube to allow a smooth transition from turbulent to laminar flow before the ions interact with a neutral reactant gas. The flow tube used in our lab has an inner diameter of 7.2 cm and is 104 cm in length and is fabricated from stainless steel. Diagnosis and flow control are accomplished through several stainless steel ports attached to the flow tube.

A schematic drawing of the apparatus is shown in *Figure 2-5*. The LAVA source, which can be removed and/or repaired quickly and easily, is attached at the right ('Y' end of drawing) and the ion detection region is on the left. The source is oriented at a 45 degree angle with respect to the flow tube. The direction of ion flow is from the LAVA source to the detection region, viewed right to left in this diagram.

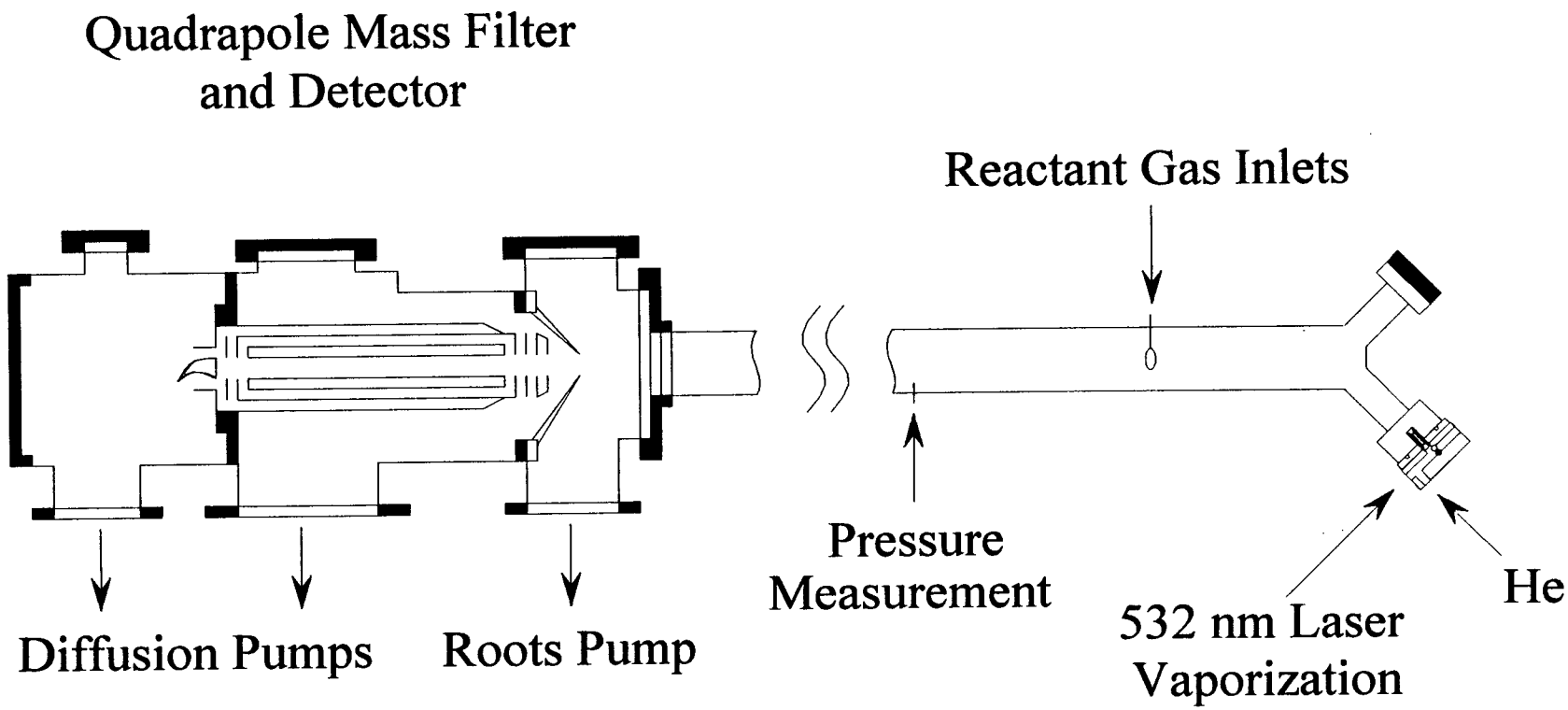

Figure 2-5: Schematic drawing of fast flow tube.

The other side of the 'Y' end is capped for future use.

Bimetallic clusters are produced by laser vaporization (described in Section 2.2). The source is attached to the flow tube via a 4.5 in. non-rotatable flange, with an o-ring seal. The overall physical arrangement at this part of the flow tube is narrower by about 2 cm and then widens to 7.2 cm at the 'Y' intersection. This aids in dampening shock waves induced at the entrance, as well as assits in a smooth transition to laminar flow. Transport of the ions into the flow tube is accomplished by a continuous flow of high purity helium buffer gas (Air Produces Specialty Gas, Creighton, PA, 99.995%) passing through the LAVA source at 9000 sccm (standard cubic centimeters per minute). The flow rate is maintained by a 20,000 sccm flow controller (MKS, Andover, MA, Model 259) and the pressure is measured by a 1 Torr Baratron pressure head (MKS, Andover, MA, Model 626A). The flow tube pressure is maintained by a fast Roots pump (Stokers Pennwalt model 1721) at $\approx$ 0.3 Torr.

To remove trace contaminants, like water, prior to passing through the source and before entering the flow tube, the helium is passed through a series of molecular sieves, 3, 5, and 10 angstrom, respectively (Union Carbide, South Plainfield, NJ, MS-1014, MS-1192, and MS-1341, 1/16 in. pellets) which are immersed in liquid nitrogen.

A neutral reactant gas can be introduced through a reactant gas inlet (RGI) and allowed to react with the cluster ions before the flow mixture is sampled (see *Figure 2-5*). A schematic drawing showing the shape of the RGI is shown in *Figure 2-6.* The RGI is made of 0.0625 in. (1.59 mm) stainless steel tubing bent in a circle containing

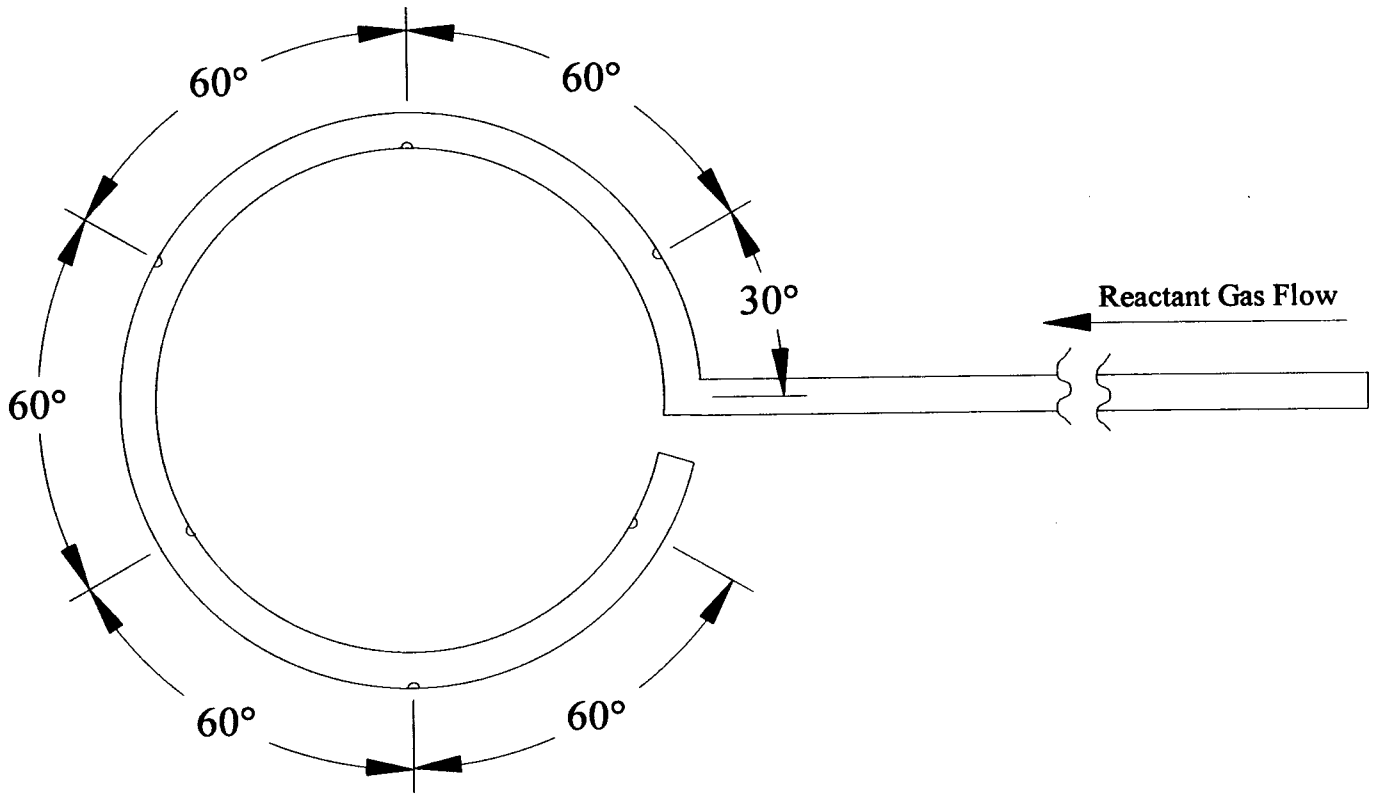

Figure 2-6: Schematic drawing of the reactant gas inlet (RGI). Each 0.4 mm hole is located 60° apart. Three holes point radially inward and three holes point radially outward.

6 equally spaced 0.0156 in. (0.4 mm) diameter holes. Each hole is spaced 60° apart around the circumference of the circle, with three holes pointing radially inward and three hole pointing radially outward. The RGI passes through a 1/16 in. Ultra-Torr fitting (Pittsburgh Valve & Fitting, Co., Pittsburgh, PA, SS-1-UT-1-2), which is mounted to a 2-3/8 in. non-rotatable flange (MDC, Vacuum Products Corp., Hayward, CA, F275000), before entering the flow tube. The diameter of the RGI circle is 3/8 the diameter of the flow tube's inner diameter. It is located 74 cm upstream from the sampling orifice and is positioned perpendicular to the axis of the flow tube. Details of this RGI have been reported previously.[12]

The flow tube is physically attached to the sampling/detection region via a large six-way chamber. A blank flange which contains six BNC electrical feedthroughs (Ceramaseal Inc., #807B7007-1), is mounted on one of the side ports; it allows potentials to be applied to the sampling and focusing electronics. The other side port connects the ion sampling and detection chambers via a manually actuated gate valve, to facilitate efficient pumping of the entire system when not in operation. The top port is capped with a 1/2 in. thick glass blank, used for visual inspection and observation of the ion sampling optics. The bottom port is connected, via a long bellows tube, to a high capacity (37000 cubic liter per minute) Roots pump (Stokes-Pennwalt, Philadelphia, PA, model 1721). Located between the system and the Roots pump is a pneumatically actuated gate valve (VAT Inc., Woburn, MA, model #11415U) which isolates the system when the flow tube is not in operation. The last port, opposite the flow tube, attaches the reactor to the sampling/detection chambers.

2.4 Ion Sampling and Detection Region

A brief description of the ion sampling and detection region and components is presented in this section. The external electronics associated with this region is presented in Section 2.5. The low pressure ion sampling/detection system consists of the sampling chamber and the detection chamber, which are physically distinct. The main purpose of this system is to collect a representative ion distribution sample from the flow tube, efficiently focus, mass select, and electronically detect the ions. The sampling chamber is attached, opposite the flow tube, to a six-way chamber. This chamber allows for extraction of a small sample of ions from the flow tube. The detection chamber houses a quadrupole mass analyzer (Extrel Mass Spectrometry, Pittsburgh, PA, part #4-162-8, 0.95 cm diameter rods) used for selection, and a channeltron electron multiplier (Galileo Elctro-optics Corp., Strubridge, MA, Model 4830) used for detection.

A schematic cross-section of the ion sampling region is shown in *Figure 2-7*. Three electrostatic elements are used for sampling: orifice plate, shield, and nose-cone. Machinable insulators (Envex 1000) are used to electrically and physically isolate these elements. In order to draw cluster ions into the low pressure detection region small potentials are applied to these elements. Typical potentials, used for anions detection, on the orifice, shield, and cone are ≈15, ≈ -9, and ≈8 volts dc, respectively. The polarity is reversed for positive ions. Sampling occurs via the orifice plate which is

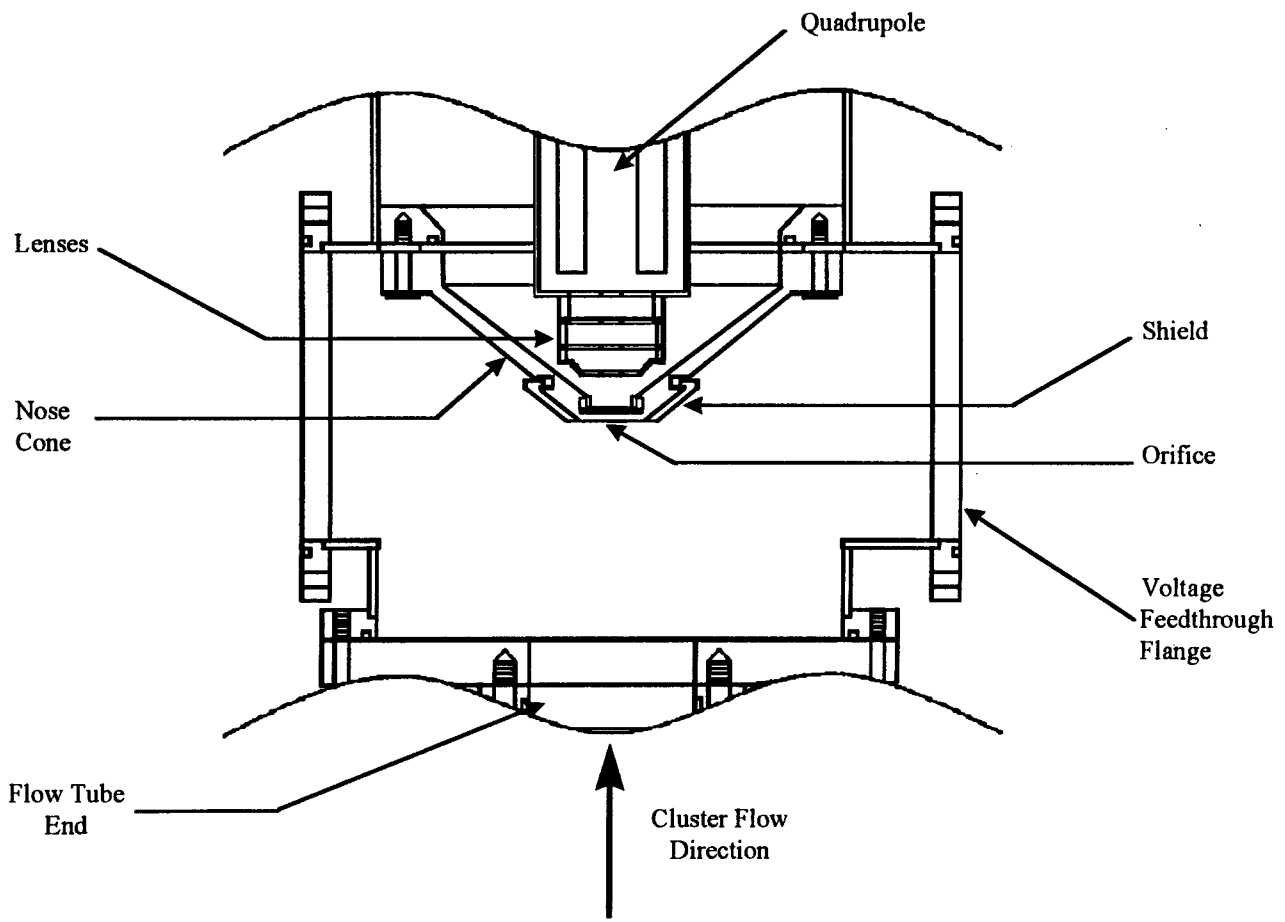

Figure 2-7: Schematic cross section of the ion sampling region.

fabricated out of a platinum disk, with a 0.75 mm orifice hole, welded to a stainless steel plate.

After the ions are sampled they are focused by three thin molybdenum (EINZEL) lenses (L1, L2, and L3) mounted in front of the lens attached at the entrance of the quadrupole (L4). Typical potentials for L1, L2, L3, and L4 are ≈16, ≈13, ≈60, and ≈13 volts dc for negative ions, respectively. The polarity is reversed for positive ions. Once the ions pass through the electrostatic lenses they enter the detection chamber, where the quadrupole and channeltron are housed. The only access between the detection chamber and the sampling chamber is a 1 cm hole in the front plate of the quadrupole. The quadrupole has a mass selection range of 4000 amu. A DC pole bias potential of around 35 volts for cations and 25 volts for anions is typically applied. The pole bias used depends on resolution versus signal intensity desired. Lower voltages increase resolution but decrease signal intensity, where as higher voltages produce the opposite effect.

The sampling and detection chambers are differentially pumped with a 650 *l/s* (Alcatel Crystal 160) and a 300 *l*/s (Alcatel Crystal 100) diffusion pumps, respectively, which maintain an operating pressure of ≈1 x 10^{-6} Torr. The need for a larger pump in the sampling chamber is due to the greater volume of gas that must be handled. Both diffusion pumps are backed by a single mechanical pump (Sargent-Welch, Anaheim, CA, Model 1397). The mechanical pump is also used to rough the entire system to pressures below 0.02 Torr before employing the diffusion pumps. Pneumatic butterfly

valves are used to isolate the diffusion pumps from the sampling and detection chambers, when opening the chamber.

2.5 Electronics

The electronics associated with data acquisition and manipulation are: the channeltron, preamplifier-amplifier-discriminator (PAD) (Mechtronics Inc., Addison, IL, model 509), MCS II multichannel scaler card (Oxford Instruments Inc., Oak Ridge, TN), and a Gateway 2000 DX2-66 PC computer. Mass selected cluster ions emerging from the quadrupole are accelerated to the channeltron. Both cations and anions can be detected by the channeltron. To detect cations a potential voltage of -3.0 kV is applied to the front dynode of the channeltron to attract the ions and the rear dynode is set to ground. For detection of anions, through a voltage divider circuit, a potential voltage of 3.6 kV is applied to the front dynode and 1.4 kV is applied to the rear dynode.

The PAD processes the current pulses that emerge from the channeltron. To eliminate noise the PAD threshold discriminates the input current before it is amplified. The discriminated output (5 volt pulses) is connected, via a T-coupling, to a ratemeter (Mechtronics Inc., Addison, IL, model 777) and to the MCS II multichannel scaler card. The ratemeter is used to optimize signal.

The MCS II card is physically installed into the computer. The output from the PAD, fed into the MCS II card, is quantitatively converted from a voltage pulse signal

into an analog signal. This signal is then converted, via software, to an intensity versus amu display on the computer screen. The MCS II card has 8192 channel acquisition memory and can be selected, in binary increments, from 256 channels to 8192 channels. Each channel has a maximum memory capacity of 16,77,215 counts. The dwell times (channel widths) may be selected between 2 μsec and 325 days. These parameters and various others are adjustable through the software provided by the manufacturer. The normal dwell time and channels used are 30 μsec and 1024, respectively.

The binary data stored in memory is saved as an ASCII (SPM) file format. These data are then converted, via a software (mcsconvert) program written by Dr. Steven Buzza, to another ASCII (SPC) file format. The SPC file format is used for data analysis. The software used is Grams/32 Spectral Notebase Version 4.02 Level I (Galactic Industries Corp., Salem, NH). Calibration of the data, within Grams/32, is accomplished by a calibration program (macro), specifically written for this type of data and this program, see Appendix A.

Data acquisition and analysis is done by using a Gateway 2000 DX2-66 personnel computer with a math co-processor. The system has 16 Mbytes of random access memory (RAM), 540 Mbyte hard drive, 3-1/2" and 5-1/4" floppy disk drives, and a CD ROM drive. The operating system used is Windows 95.

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CHAPTER 3

CHARACTERIZATION OF A NEW DUAL ROD LASER VAPERIZATION SOURCE

3.1 Introduction

The new dual rod LAVA source is characterized by studying two bimetallic systems, Nb/Al and V/Al. Both Nb/Al and V/Al clusters are formed in two plasmas induced by the second harmonic (532 nm photons) of a single pulsed Nd:YAG laser. By altering the laser fluence on one or both rods, the mixing ratio within the cluster can be varied. The laser fluence is varied between 3 and 17 mJ/cm^2 depending on the material and the cluster distribution desired. It is essential to have a good focus on each rod to achieve high cluster ion intensities and good mixing ratios. Cluster intensity and mixing ratios are monitored and analyzed with the quadrupole mass filter located at the terminus of the fast flow reactor; it can be used to detect both anions and cations. The characterization study only deals with anions.

3.2 Results/Characterization

Two Nb/Al anion mass spectra are shown in *Figure 3-1* and *Figure 3-2*, each with a different cluster distribution. *Figure 3-1* shows a Nb rich cluster distribution which is produced with laser fluences of 2 mJ/cm^2 and 8 mJ/cm^2 on the Nb and Al rods, respectively. Niobium's high reactivity with O_2 is the cause for the observation

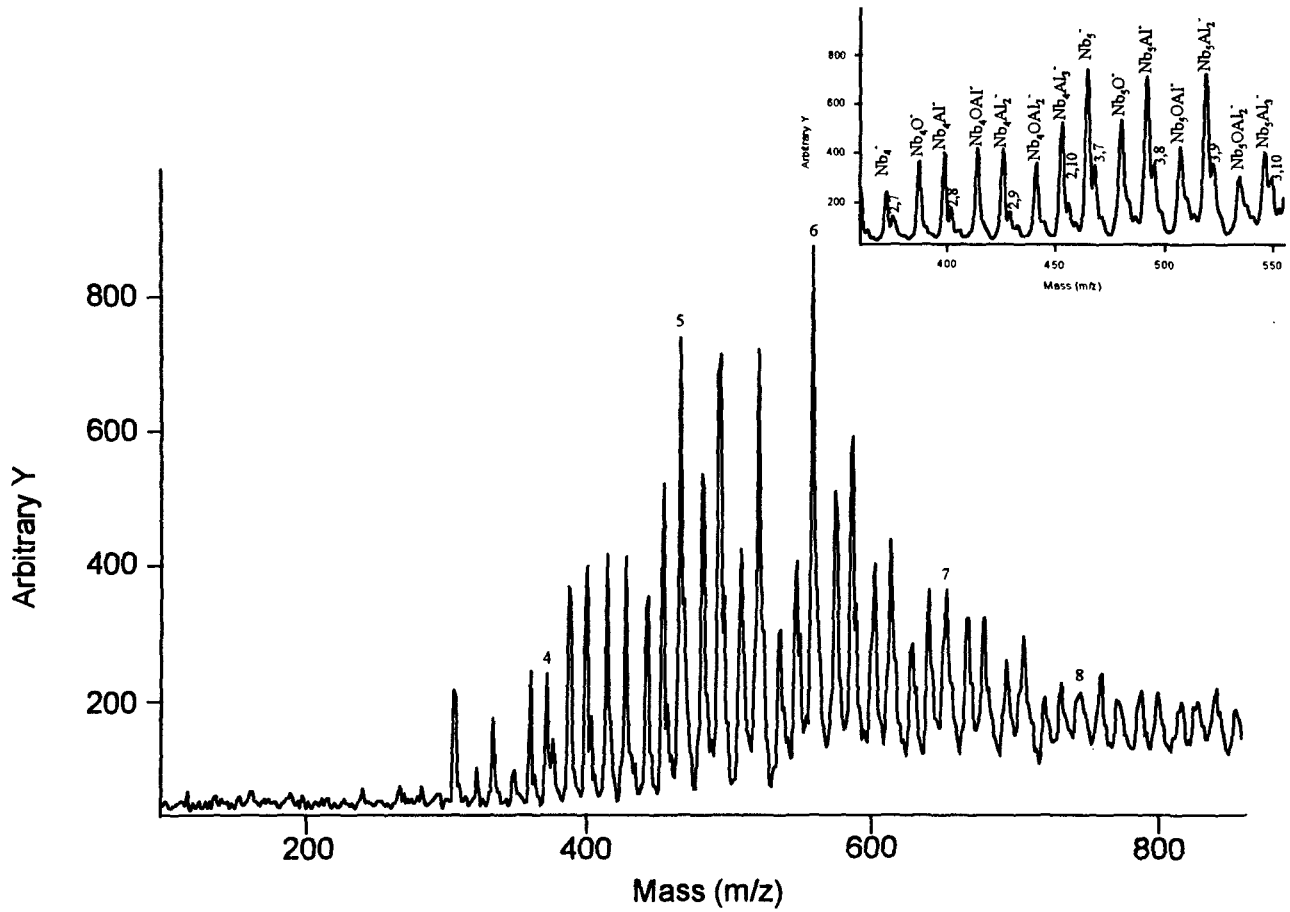

Figure 3-1: Nb rich cluster distribution. Laser fluence on the Nb/Al rods are 2 mJ/cm^2 and 8 mJ/cm^2, respectively. Numbered peaks in the spectrum correspond to pure Nb peaks. Numbered peaks in the insert (2,7) correspond to $Nb_nAl_m^-$ peaks.

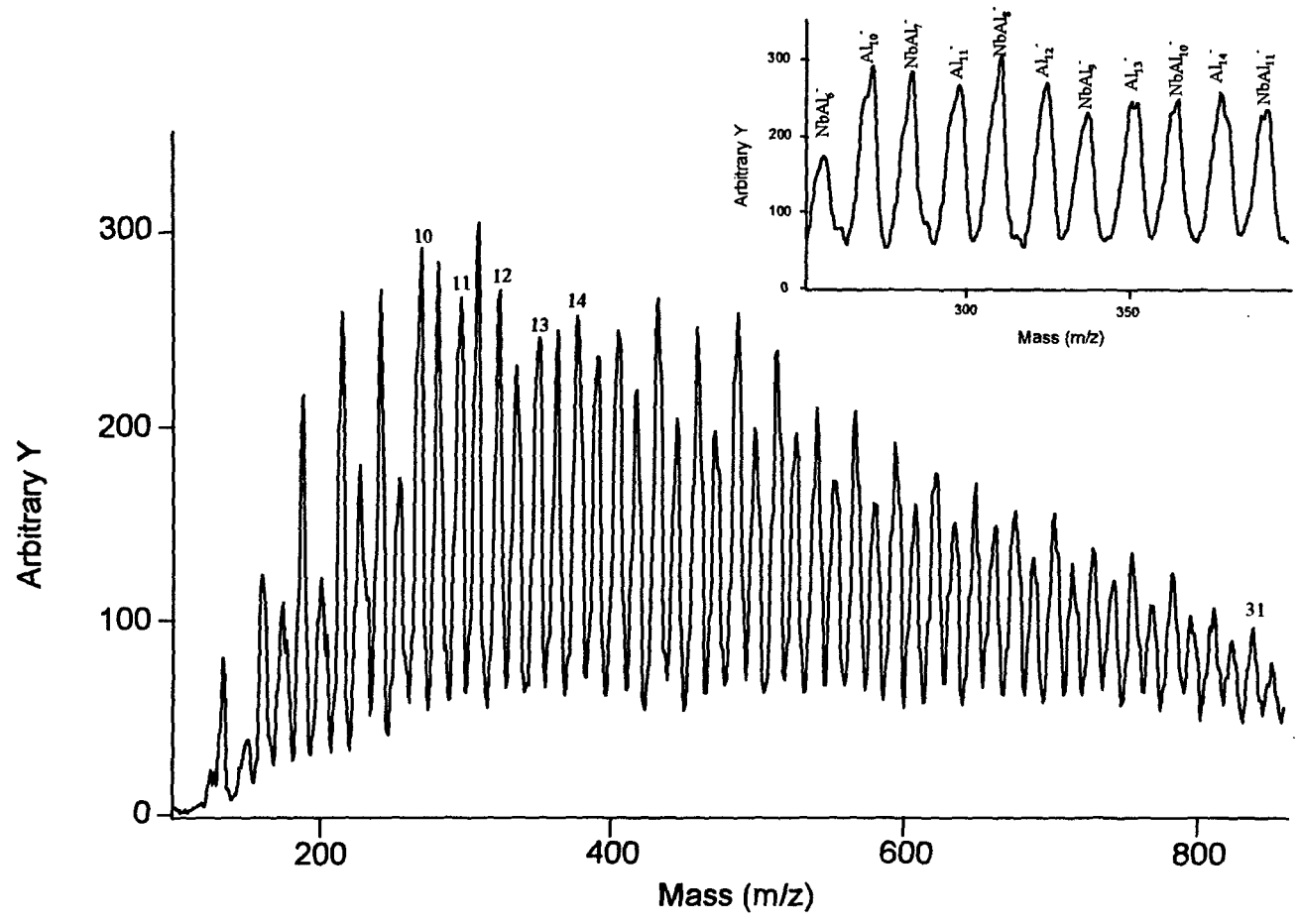

Figure 3-2: Al rich cluster distribution. Laser fluence on the Nb/Al rods are 3 mJ/cm^2 and 17 mJ/cm^2, respectively. Numbered peaks in spectrum correspond to pure Al^- peaks.

of niobium oxides in the spectrum. Each pure Nb cluster has associated with it $Nb_{n-2}Al_m^-$. (n = 3-8 and m = 7-10), $Nb_nOAl_m^-$ (n = 3-8 and m = 0-2), and $Nb_nAl_m^-$ (n = 3-8 and m = 1-3), e.g. Nb_4^- has associated with it $Nb_2Al_7^-$, Nb_4O^-, Nb_4Al^-, $Nb_2Al_8^-$, Nb_4OAl^-, $Nb_4Al_2^-$, $Nb_2Al_9^-$, $Nb_4OAl_2^-$, $Nb_4Al_3^-$, and $Nb_2Al_{10}^-$ as shown in the insert of *Figure 3-1*. The cluster distribution in *Figure 3-1* is similar to the cluster distribution observed by Kaya and co-workers, using their dual rod dual laser LAVA source.[1] The Al rod is in the position closest to the flow tube. Test experiments made with the apparatus reveal that the position of the rods, relative to the flow tube, has no effect on the cluster distribution. By altering the laser fluence on both the Nb and Al rods, an Al rich cluster distribution is formed, $NbAl_m^-$ (m = 2-28) and Al_m^- (m = 5-31); see *Figure 3-2*. The laser fluences are 3 mJ/cm^2 and 17 mJ/cm^2 on the Nb and Al rods, respectively. Pure Al clusters and mixed clusters alternate, e.g. Al_{10}^-, $NbAl_7^-$, Al_{11}^-, $NbAl_8^-$ as shown in the insert of *Figure 3-2*.

In order to validate that the new source can be used with a variety of materials, the Nb rod is replaced by a V rod. V/Al clusters are produced with the same conditions as in the Nb/Al experiments. *Figure 3-3* and *Figure 3-4* show two V/Al mass spectrum differing only in laser fluence on the V rod. The Al rod is still in the position closest to the flow tube. *Figure 3-3* shows the V/Al spectrum with a laser fluence of 2 mJ/cm^2 on the V rod and 10 mJ/cm^2 on the Al rod. The predominate peaks are Al_m^- (m = 5-29). As part of the peak manifold including the Al_m^- peak, there is a series of peaks of the form $V_nAl_{m-2n}^-$, as shown in the insert of *Figure 3-3*. These clusters may be produced in one of many ways. Two of possibilities are direct

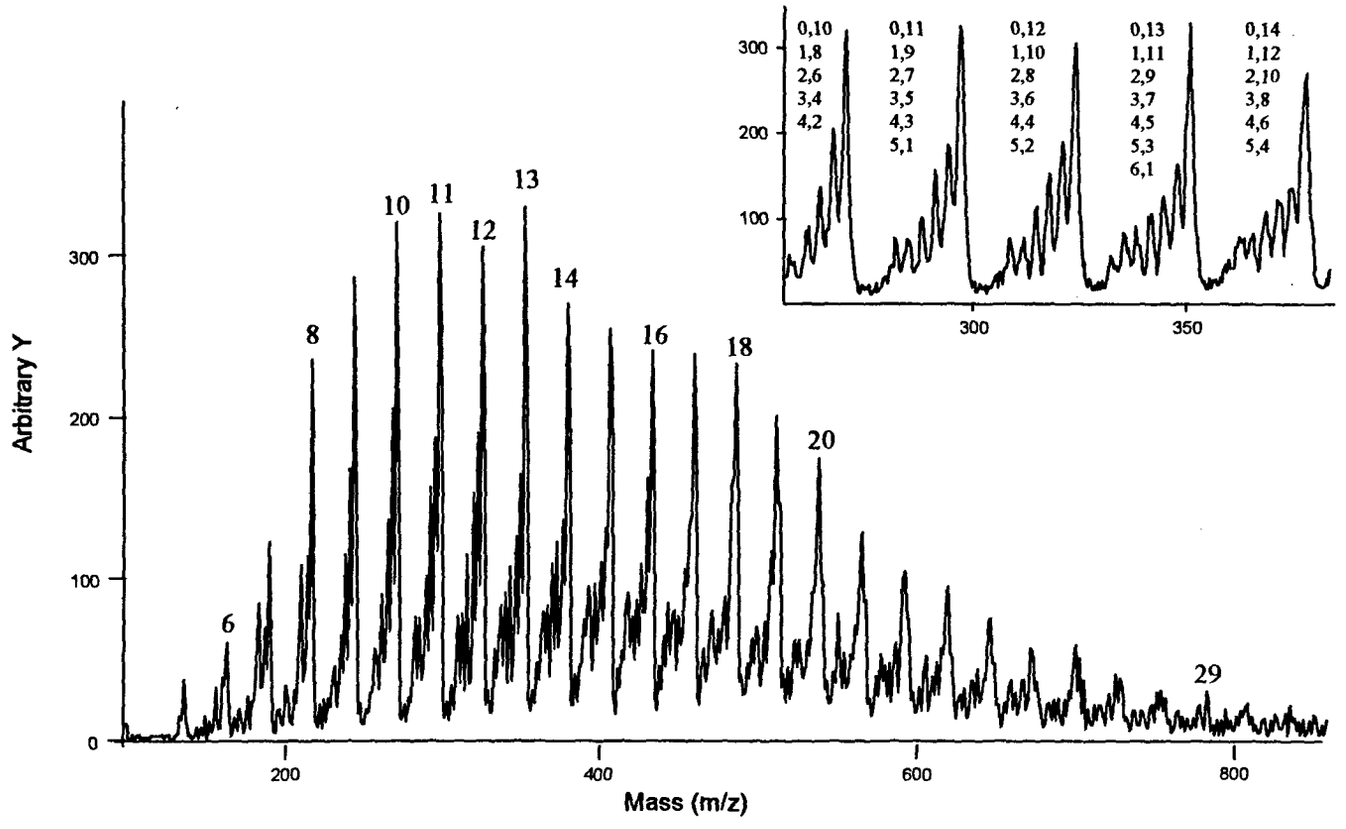

Figure 3-3: $V_nAl_m^-$ mass spectrum with n = 1-6 and m = 6-29. Laser fluence on the V/Al rods are 2 mJ/cm^2 and 10 mJ/cm^2, respectively. Numbered peaks in spectrum correspond to pure Al peaks. Numbered peaks in the insert correspond to $V_nAl_m^-$.

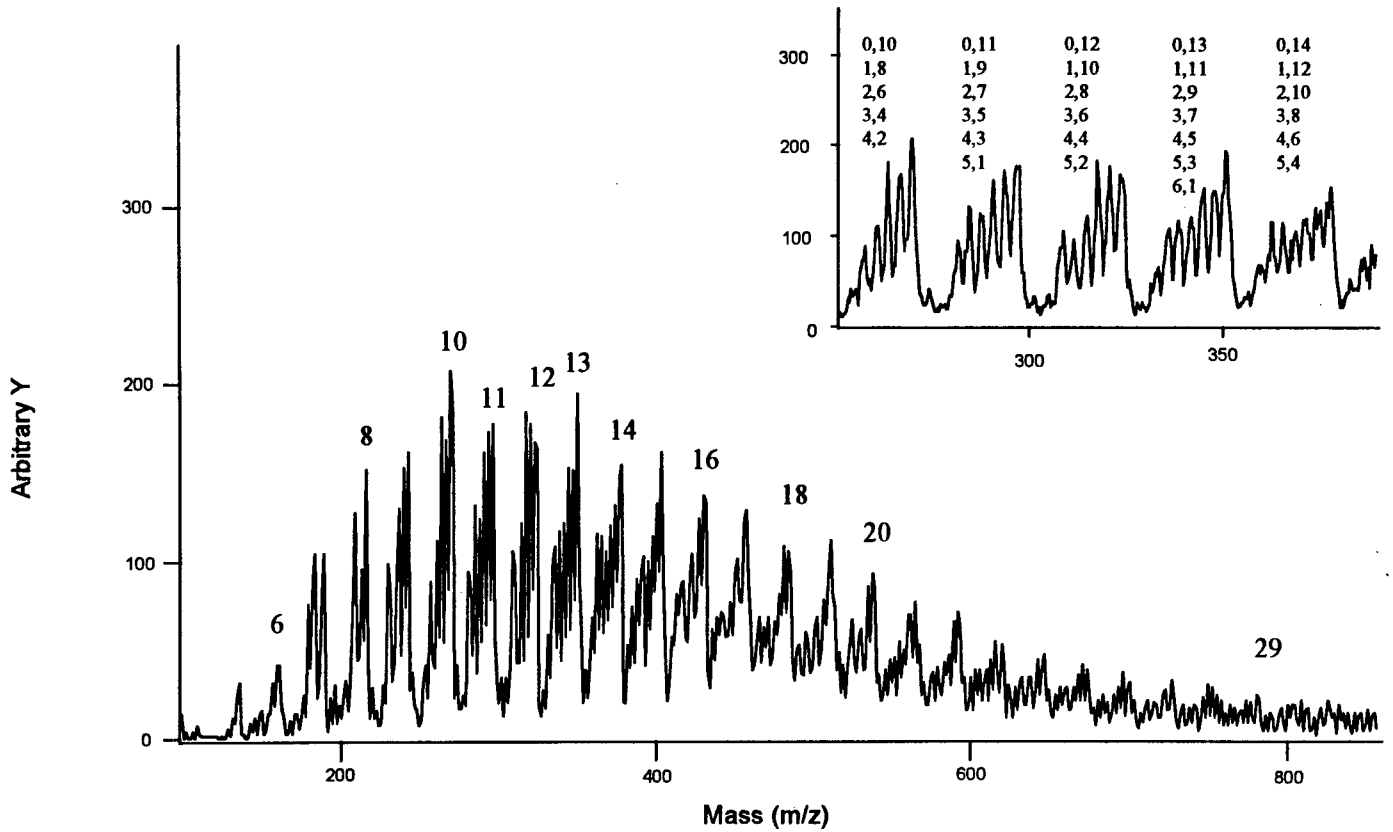

Figure 3-4: $V_nAl_m^-$ mass spectrum with n = 1-6 and m = 6-29. Laser fluence on the V/Al rods are 4 mJ/cm^2 and 10 mJ/cm^2, respectively. Numbered peaks in spectrum correspond to pure Al peaks. Numbered peaks in the insert correspond to $V_nAl_m^-$.

substitution of V into the pure Cluster of Al with subsequent losses of Al atoms and/or addition of Al atoms to V monomer or V clusters. However, the experimental operation of our instrument precludes the determination of which mechanism is occurring. *Figure 3-4* shows the same V/Al cluster distribution and pattern as, the only difference being the cluster intensity. In *Figure 3-4* the laser fluence on the V rod is 4 mJ/cm^2 and 10 mJ/cm^2 on the Al rod. Under these conditions, pure Al_m^- cluster peaks decreased in intensity and some $V_nAl_m^-$ cluster peaks increased in intensity.

3.3 Conclusion

The design and operation of this new dual rod LAVA source simplifies the production of bimetallic clusters. The use of a single laser for vaporization and a continuous flow of carrier gas eliminates the need to properly synchronize the gas pulse and the vaporization pulse, used by other sources, simplifying set up and operation. It provides a new source of bimetallic clusters especially suitable for conducting studies of cluster reactions. Laser fluence and focusing of the laser beam on each target rod are the most critical parameters for cluster production. Laser fluence influences cluster intensity as well as the cluster distribution. On the other hand, rod placement, front or rear, has no effect on cluster distributions. Trace amounts of O_2, whether in the carrier gas or from a small leak, is the cause for the niobium oxides present in the Nb rich cluster distribution. This new dual rod LAVA source has proven to be capable of making a variety of bimetallic clusters.

3.4 References

[1] S. Nonose, Y. Sone, K. Onodera, S. Sudo and K. Kaya, *Chem. Phys. Letters* **164** (4), 427 (1989).

CHAPTER 4

Future Directions

Now that a new dual rod LAVA source has been developed and found to be able to produce bimetallic clusters, there are many systems that can be studied. Regarding these systems many questions arise. Some of the questions I would like to answer in my future research are: (1) What properties change, if any, when substituting elements within a group? (2) Is the jellium model[1,2,3] applicable to alloys of metals whose pure systems are in accord with the model? (3) What types of bimetallic clusters will form a stable jellium model? (4) What effects do environmentally relevant species have on various bimetallic clusters? (5) How do changes in size and cluster composition change catalytic properties?

One way we could answer some of these questions is to substitute the base metal with another metal from the same group. One such substitution would be the substitution of In for Al and using Nb or V as the secondary metal. This should establish if there is a size dependence of the cluster formation process.

Various clusters when reacted with O_2 produce a jellium model cluster. For example, reacting O_2 with Al anion clusters, through an etching action, forms Al_{13}^- and Al_{23}^- as major products, which fits into the jellium model. Reacting O_2 with Nb/Al, V/Al, Nb/In and V/In systems should produce $NbAl_4^-$, VAl_4^-, $NbIn_4^-$, VIn_4^- type clusters, if they adhere to the jellium model. This may not be the case in that the jellium model does not always explain reactivity behavior.[4,5]

An important area of catalysis research is how clusters react with environmentally relevant species. To test the catalytic properties of the above systems I propose to react them with several environmentally relevant species, e.g. H_2O, NO, H_2SO_4, and SO_2. To be able to discern if changes in size and/or cluster composition change catalytic properties it is imperative to be able to mass select a certain size/composition cluster with which to investigate reactivities. This can be accomplished with a selective ion flow tube (SIFT). We believe that this new bimetallic cluster source, coupled with a SIFT, will enable us to answer many questions regarding catalysis and reactivity in relation to cluster size and electronic structure.

4.1 References

[1] W. D. Knight, K. Clemenger, W. de Heer, W. Saunders, M. Chou, and M. Cohen, *Phys. Rev. Lett.* **52**, 2141 (1984).

[2] M. Chou, A. Cleland, and M. Cohen, *Solid State Commun.* **52**, 645 (1984).

[3] M. Chou, and M. Cohen, *Phys. Lett. A* **113**, 420 (1986).

[4] R. E. Leuchtner, A. C. Harms, and A. W. Castleman, Jr., *J. Chem. Phys.* **91** (4), 2753 (1989).

[5] D. M. Cox, D. J. Trevor, R. L. Whitten, and A. Kaldor, *J. Phys. Chem.* **92**, 421 (1988).

APPENDIX

CALIBRATION PROGRAM

A.1 Introduction

The original calibration program (macro) was written in October 1991 by Adrian Selinger. This program was written specifically for a program called LabCalc (Galactic Industries Corp., Salem, NH), a DOS based program. In July 1996 our research group acquired the new generation software, from Galactic Industries Corp., Grams/32. Grams/32 is a new 16 and 32 bit data analysis program written for Windows 3.11 and Windows 95. Since LabCalc is a DOS based program, the calibration program would not run in Grams/32; therefore it was rewritten to run in Grams/32. The basic calculations are the same but the language is different. The macro in Grams/32 is called calmas2. A listing is provided below.

A.2 Program

```
' Calibrate a Mass Spectrum by Data Points or Reference Spectrum

' (c) Adrian Selinger October 1991
' (c) Rewritten for Grams/32 July 1996 by Raymond L. Wagner
10      free : pauseon
        dim sname(30),rname(30)
        portout -44,-1
        pauseoff
        dialogon "CaliMass"
        print " "
```

```
      print "   ===== PLEASE NOTE : ==================== "
      print "   'CALIMASS' needs your cooperation.                    "
      print "   - first activate the file you want to calibrate.          "
      print "   - then find a reference spectrum with the desired scale OR  "
      print "   - pick two old x-values (i. e. channel or old calibration)  "
      print "     and assign new values (i. e. mass or size) to them.       "
      print "   ================================================ "
      dialogoff

      if getsfile() < > 0 goto 100
      beep:dialogon "File Error"
      print "No Trace in Memory"
      dialogoff
      end


100    string sname,-1
      onerror 900
      dialogon "Calabration Factor"
      dialogask i,4,400,150, "Data_points  Reference"
      dialogoff
150    onerror -1

      onerror 900
      refname "Choose a File"
      string rname,-2:
      dialogon "Reference File"
      print "File ";$sname;" will be calibrated using ";$rname;" !!"
      dialogask i,4,200,100, "Okay Change"
      dialogoff
200    onerror -1
      leftx=freq(#r(0))
      rightx=freq(#r(1023))
      goto 450

400    onerror 900
      dialogon "Peak Input"
      dialogask fdx,0,0,0,"Old X(1) : "
      dialogask sdx,0,0,0,"Old X(2) : "
      dialogask fms,0,0,0,"New X(1) : "
      dialogask sms,0,0,0,"New X(2) : "
      dialogoff
      onerror -1
```

```
      factor=(sms-fms)/(sdx-fdx)
      leftx=fms-factor*(fdx-getffp())
      rightx=fms+factor*(getflp()-fdx)

450    onerror 900
      dialogon "New Scale"
      print "Range ";leftx;" to ";rightx
      dialogask i,4,500,100,"Okay Change"
      dialogoff
500    onerror -1

      setxtype 9
      setffp leftx,rightx
      onerror 900
      dialogon "Save File to Disc?"
      dialogask i,4,600,900,"Yes  No"
      dialogoff
600    dialogon "Use Same File Name?"
      dialogask i,4,650,700,"Yes No"
      dialogoff
650    onerror -1
      i = index0(sname - 46)              'find . in string
      sname(i) = 0                        'set it to null terminator

      onerror 760
      openspc $sname
      dialogon "File Already Exists"
      dialogask i,4,760,660,"Replace  Change"
      dialogoff
660    onerror -1
700    menufile sname, "Enter_spectrum_name: "
760    savespc $sname
      closespc $sname

900    end
```

VITA

Raymond Lee Wagner [redacted].

CPT Wagner attended Klamath Union High School and graduated in June of 1977. After serving a 2 year mission in Japan for his church, CPT Wagner attended Brigham Young University (Provo, Utah) and graduated with a B.A. (Chemistry) in April of 1984. After serving eight years in the United States Army, he was accepted into the Advanced Civil Schooling Program and began his graduate work in Chemistry at Penn State (1995). CPT Wagner is a member of the Army Aviation Association of America (AAAA), the Aircraft Owner and Pilots Association (AOPA), the American Chemical Society (ACS) and the Sigma Xi, The Scientific Research Society. He married Loralee Piersall in [redacted] of 1987. They have two children, Celia-[redacted] and Brian [redacted]