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I am submitting herewith a thesis written by James M. Chenault entitled "Gas Phase Diagnostics of CVD Diamond Growth From Chloromethane and Chloroform." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Charles S. Feigerle, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

Gas Phase Diagnostics of CVD Diamond Growth From Chloromethane and Chloroform

A Thesis
Presented for the
Master of Science Degree

The University of Tennessee, Knoxville

James M. Chenault
December, 1998

Dedication

This thesis is dedicated to

My wife, Debbie, whose worth *is* beyond diamonds

My children, with whom I am blessed

My friends, for all their encouragement

My mom, just because she is

and to

My teachers for taking the time to teach

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Abstract

Low energy electron impact ionization (LEEII) time of flight mass spectrometry (TOFMS) has been used to interrogate gases sampled through an orifice from a diamond growth surface. Methane, chloromethane and chloroform precursor gases were examined to produce electron energy plots of the fragment ions that occur using LEEII. Filament temperature studies were completed covering temperatures from room temperature to over 2000 °C, and the results were compared to the LEEII plots. The monochloromethyl radical has been detected in the experiments using chloroform and the effect of a pretreatment with this radical present has been shown to enhance diamond nucleation. Scanning electron microscopy (SEM) and Raman spectroscopy have been used to confirm diamond growth.

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1.0 Introduction

1.1 Why Diamond?

People throughout the world desire diamond for many different reasons. Diamond is the hardest material known to man, has excellent optical, thermal and electrical properties, and is a very desirable gemstone. Typical industrial uses of diamond include drilling, grinding, polishing and cutting. Routine uses of diamond include dies for drawing wire, guides for thread in textile mills, nozzles for very high pressure spraying systems, elements in flat panel video displays, heat sinks for electronic chips and lenses for optical systems. Research is developing bearing surfaces and semiconductor devices from diamond. Easing the production costs of diamond or improving the quality of produced diamond will certainly lead to more uses.

A means of lowering the economic cost of diamond is to lower the temperature required for diamond growth. This would increase the range of materials diamond can be grown upon. Thin film diamond may find use in the shipping industry, as a protective coating on

large cargo ships, to slow or prevent the attachment of barnacles to the hulls of ships, thus saving considerable money in cleaning the hulls alone. Diamond frying pans would behave as a teflon coated pan would, but would not wear out as quickly. Diamond films can be used as a coating to protect delicate components from hazardous environments or to help with heat transfer. As a coating in a turbine engine, diamond films may help transfer heat from engine components to the air moving through the system, or vice versa, improving the general efficiency of the turbine and allowing use of new alloys in different parts of the engine.

Manufactured diamond is superior to mined diamonds for many industrial purposes. Diamond can be made to order, with control over morphology and size affecting the final properties of the material produced. In 1997, manufacturing produced more than 90% of the diamond used by industry.[1] The development of chemical vapor deposition (CVD) methods of diamond growth has added control over the properties of the finished product and will continue to do so.

1.2 Chemical Description of Diamond

The known allotropes of carbon are: fullerenes, including carbon nanotubes, graphite and diamond, including lonsdaleite. Fullerenes are "soccer ball" forms of carbon, with sp^2 hybridized bonding in alternating five and six member rings forming the shell of a sphere. Graphite is the most stable form of carbon, consisting of sp^2 hybridized carbons joined in a planar configuration of six membered rings, which form sheets. The sheets are joined by weaker bonds from the pi orbitals of the carbons in the rings. Diamond is made from six member rings also, but with sp^3 bonding and it is 1.56 times as dense as graphite. The rings formed in diamond are in the chair configuration of the cyclohexane molecule, with each carbon being a member of 12 separate rings in the crystal lattice and with all carbon bonds in the staggered configuration. The rings form stacked layers, and the connecting bonds between the layers form more chair configuration rings. In the lonsdaleite form of diamond, the rings in the layers are in the chair configuration, but those that connect the layers are in the boat configuration with eclipsed bonds.

The bond lengths in diamond are all 1.54 angstroms, while in graphite, bond lengths of 1.42 angstroms and 3.35 angstroms are found, with the longer bonds connecting the sheets of rings. Diamonds have a face centered cubic structure, and the direction along any bond is normal to a <111> surface.[2] Diamond and graphite are hydrogen terminated and for the most part are chemically inert.

1.3 Diamond Synthesis

The ultimate goal of diamond research is to produce pure single crystal diamonds in usable quantities to take advantage of the unique properties of this material. Diamond can be manufactured in either bulk or film form. Currently, single crystal films have not been produced, but near perfect crystals of up to nine carats have been produced by high pressure, high temperature (HPHT) methods. Bulk crystals are made by HPHT methods while films are made by CVD methods. A few miscellaneous methods that defy these two broad classifications, but which produce films and crystals will also be mentioned.

1.3.1 Bulk Crystal Synthesis

The first successful manufacture of diamonds through use of a HPHT method was by General Electric Corporation researcher F. P. Bundy and his group on December 16, 1954.[3] The method relied on the solubilities of graphite and diamond in nickel and iron solutions at high pressures (100,000 bars) and high temperatures (>1,000 °C). Under these conditions, graphite is more soluble than diamond, and diamond precipitates out of solution on diamond seed crystals. Bundy *et al.* also noted that diamond crystals would form without seeding. The melt compositions, reaction times, pressures, temperatures and other parameters for these growths are closely guarded commercial secrets.

The shock wave method of producing diamond is fully commercialized and in use. A mix of powdered graphite and copper is placed in a steel tube. The steel tube is surrounded by an explosive. A spacing is required between the steel tube and the graphite/copper mix for this method to work. The explosive is set off, and diamonds are produced from the resulting heat and pressure very quickly. The

copper is required to keep the formed diamond from reverting back to graphite.[3] Diamonds produced by this method are used as grit.

In another HPHT method, nanometer size diamond crystals have been found in the soot from the detonation of TNT and other explosives in an argon atmosphere.[4] Diamond has also been grown in hydrothermal systems by sealing seed diamond crystals in gold canisters with glassy carbon and water and heating to between 600 and 1000 °C. It is of interest that this method did not work when platinum canisters were used, presumably because hydrogen diffuses easily through platinum, but not through gold, lending credence to the theory that hydrogen atoms are crucial to the growth of diamond under these conditions.[5]

1.3.2 Film Synthesis

W. G. Eversole of the Union Carbide Corporation succeeded in producing diamond growth on diamond seeds by CVD in late 1952 from CO_2.[6] This date would make Eversole the first researcher to successfully grow diamond of any type. Since then, many groups have attempted to grow diamond films by CVD methods. Other methods

have more recently produced diamond films also. One such method is the "reduction-pyrolysis-catalysis" synthesis, in which diamond is made via the Wurtz reaction as follows from a sodium melt containing CCl_4.[7,8]

1) $$R^1X + R^2X + 2Na \dashrightarrow R^1R^2 + 2\ NaX$$

In another method diamond was grown using ion beams to deposit carbon atoms of specific energies on the surface, providing good control over morphology of the grown film.[9]

All CVD methods have several common features as shown in Figure 1.1. First, a source of carbon must be present in the gas phase. Second, there must be some way to initiate the radical chemistry that occurs in the activation region. And third, a substrate must be present and suitable to grow diamond upon. The transport of radicals from the activation region to the growth surface is usually diffusion controlled.

In most CVD systems, the carbon source is in the gas phase, hence, the vapor in chemical vapor deposition. Films have been grown from a variety of precursor gases, including C_3F_8, CH_4, C_2H_2, benzene, most of the halogenated methane series, the entire chlorinated methane series, and C_2H_5Cl. Most systems use around

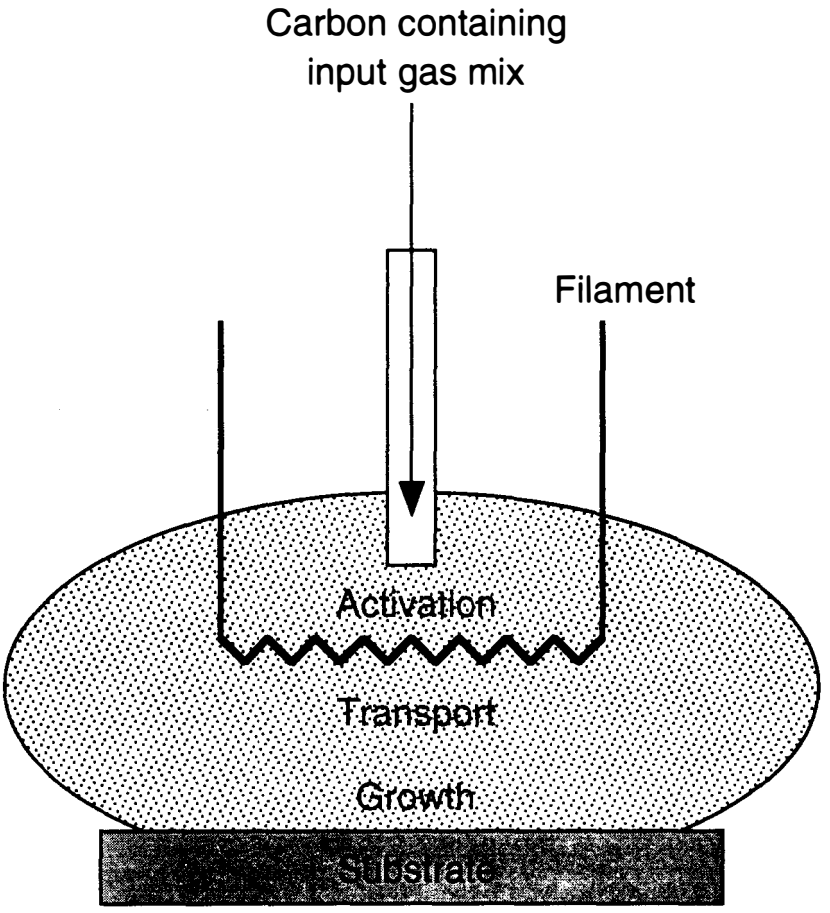


Figure 1.1 Diagram of Basic CVD Growth Process

1-2% carbon mole fraction in the source gas in an atmosphere consisting mostly of hydrogen gas. Sometimes, a noble gas is used to provide a known reference in mass spectrometric measurements. Usually only one carbon containing species is present, but, in some isotopic studies, multiple sources of carbon have been used.[10]

Initiation of the free radical chemistry begins with activation (dissociation) of hydrogen gas. This can be accomplished by heating the input gas to at least 1400°C with either thermal or plasma methods. Many different plasma types have been studied. A short list would include DC, RF, and microwave plasmas. Thermal methods can also be used to create hydrogen radicals, the most common of these being hot filaments at low pressures, and acetylene torches at atmospheric pressure.

Diamond has been grown on many different substrate materials. The most common heteroepitaxial material being silicon, due to the near crystal lattice match involved, but, diamond has been grown on molybdenum, tungsten, copper, quartz and platinum substrates also. Sometimes, the substrate may be prepared by using a diamond suspension to scratch the surface. This may be accomplished either by hand rubbing two substrate surfaces

together with diamond suspension as a lubricant, or by treatment in an ultrasonic bath of diamond suspension. It has been suggested that preparing the substrate surface with diamond suspension leaves behind traces of diamond, which form the seed crystals for diamond growth.[11] However, since diamond will form on non-scratched surfaces, and on surfaces scratched with BN or other hard materials, many researchers believe that diamond seed crystals left behind after cleaning the scratched substrate are not required for nucleation. These researchers believe that the type of damage caused by scratching forms high energy sites (craters) in which diamond may readily nucleate.[12] Angus *et al.* have indicated that diamond nucleates and grows from the action of atomic hydrogen on a layer of graphitic (sp^2) carbon continually formed on the growth surface.[13] A diamond seed would not be necessary for diamond growth using this theory.

1.4 Methane Based CVD Diamond Growth Mechanisms

The current theory of CVD diamond growth from methane in a hydrogen gas atmosphere indicates that carbon atoms are added one

at a time to the diamond lattice. It is believed that this occurs via the methyl radical, $CH_3\bullet$, bonding to an active site on the diamond surface. As hydrogen gas is activated, it will dissociate to form hydrogen atoms.[14] These atoms can find a methane molecule, and abstract a hydrogen from the molecule in the following reaction.

2) $CH_4 + H\bullet \text{---> } CH_3\bullet + H_2$

An alternative route to methyl radical production exists, namely

3) $CH_4 \text{---> } CH_3\bullet + H\bullet$

which can also take place during activation. In either case, the methyl radical can then find an active site, and add to the diamond lattice. The active site is produced on the surface when a hydrogen atom abstracts a hydrogen from the surface reforming hydrogen gas by the following reaction.

4) $C_{(d)}H_x + H\bullet \text{---> } C_{(d)}H_{x-1}\bullet + H_2$

$C_{(d)}$ is a terminating carbon atom on the diamond surface and x is the number needed to give that atom four bonds. It is well known that two methyl radicals colliding in the gas phase can create ethane, which is reduced to acetylene by hydrogen abstractions as follows under growth conditions.[15]

5) $CH_3\bullet + CH_3\bullet \text{---> } C_2H_6$

6) $C_2H_6 + H^\bullet \text{---> } C_2H_5^\bullet + H_2$

7) $C_2H_5^\bullet + H^\bullet \text{---> } C_2H_4 + H_2$

8) $C_2H_4 + H^\bullet \text{---> } C_2H_3^\bullet + H_2$

9) $C_2H_3^\bullet + H^\bullet \text{---> } C_2H_2 + H_2$

Acetylene production is a necessary but not sufficient condition for diamond growth. An alternative route would be loss of hydrogen molecules.

10) $C_2H_6 \text{---> } C_2H_4 + H_2$

11) $C_2H_4 \text{---> } C_2H_2 + H_2$

Any of the carbon radicals listed in above could add to the growth surface also, however they are not usually detected in the growth gases. The hydrogen atom also plays a role in etching away any graphitic carbon faster than it etches away diamond carbon. Thus enhancing diamond growth by insuring that only diamond survives.[16]

The reactions that involve the $C_{(d)}$ species listed above are considered surface phase reactions and are dependent on the substrate temperature used, the rest are gas phase reactions dependent on the temperature used to activate the gas. It has been shown that the limiting step in diamond growth involves the

breaking of a C-H bond.[17] Hydrogen abstraction from the surface is required for diamond growth to take place, and this is a surface reaction, dependent on the substrate temperature.

1.5 CVD Activation Methods

As mentioned in section 1.3.2, all CVD methods require activation of the gases present to initiate the radical chemistry required for diamond growth. There are many ways to do this, and some of the more popular ones are described in the following paragraphs with advantages, disadvantages and typical growth rates along with special considerations listed for each. See the review article by Bachmann *et al.* for more details.[18]

1.5.1 Plasmas

Several types of plasmas, including DC arc, microwave, and RF have led to diamond growth. The DC plasma method is the simplest of these. An electrical discharge created between an anode and a cathode in a low pressure gas creates a plasma. Plasmas created in

this fashion are not hot enough to grow diamond by themselves however, and additional heat must be supplied. The substrate must be mounted to the anode in this method, and the resulting diamonds are of poor quality, have a large hydrogen content, and have low growth rates (.01 -.1 micrometers per hour). Areas of up to 70 cm^2 of uniform films have been grown this way. Only diamond-like carbon is deposited if the substrate is the cathode.

In a microwave plasma system, the plasma is generated by subjecting the gas mix to microwave radiation. The growth species are present in the gas mix, and thus activation is achieved. The films produced are of good quality, but the growth rate of three micrometers per hour needs improvement. Large areas, up to 100 cm^2 have been covered by this approach.

Rf plasma systems are almost identical to microwave plasma systems in that the growth species are present in a gas mix, however radio waves are used to excite the gas mix. The growth rates of .1 micrometers per hour and the low quality of the grown films are major drawbacks. Coverage is only three cm^2, but, this is the easiest method to scale up to full industrial production so interest is high in this area.

All of the plasma methods discussed so far were considered from a low pressure point of view. As the pressure is increased, the growth rate increases, while the deposition area decreases rapidly. In some plasma systems the quality of the film increases, and in some it decreases with pressure change.

1.5.2 Acetylene Torches

The use of acetylene torches to initiate the gas phase chemistry has provided fair quality diamond over small areas (two cm^2) at high growth rates (100 micrometers per hour). However, it is very simple and is accomplished at atmospheric pressure. The substrate is usually copper in this method and is sometimes water cooled. Crystals up to 300 micrometers have been seen in growth by torches. Ethylene, methane, propane, methanol and ethanol have also been used as source gases.

1.5.3 Hot Filaments

The hot filament method can produce good quality growth over an area greater than 250 cm^2 at growth rates over ten micrometers per hour. Hot filament methods have been adapted to coat three dimensional objects with diamond.[19] It is a simple method, but has some drawbacks. Filament metal contaminates the diamond film, and little or no oxygen can be present while the filament is on. The shape of the filament produces a temperature gradient on the substrate surface due to differing substrate-filament distances. This gradient can cause changes in the morphology of the diamond film grown which are dependent on those distances.

1.6 Chlorine Addition to HFCVD

Chlorine addition to the gas mix has demonstrated growth of diamond at lower substrate temperatures.[20-24] Presumably the lower temperature required is due to the weakness of the C-Cl bond compared to the H-H and C-H bonds as shown in Appendix A-1. Rego

et al. have shown that there is little difference in the concentrations of HCl, CH_4 and C_2H_2 based on the choice of gas used to introduce the chlorine into the system.[21] That is, chlorine gas and the chlorinated methanes all produced about the same concentrations for these species. The HCl concentration of course varied with the chlorine substitution as would be expected. HCl is the only chlorine containing species detected in the exhaust gases from these experiments.

Pan *et al.* predict the presence of the monochloromethyl radical under growth conditions and indicate that it is responsible for changes in growth rates observed.[22] An isotopic study, using carbon-13 labeled methane and carbon-12 labeled halomethanes showed that when the halogen used was chlorine, the ratio of carbon-12 to carbon-13 incorporated in the grown diamond increased.[10] This study also suggested the monochloromethyl radical as a growth species of importance. The monochloromethyl radical has also been suggested to play a role in assisting diamond growth by dehydrohalogenation of the surface.[20,25]

Typical chlorine assisted hot filament chemical vapor deposition (CA-HFCVD) of diamond produces better quality diamond

than HFCVD of methane if the temperatures are the same in both cases. If the temperature is lowered, a temperature can be reached at which diamond will not grow from methane (without chlorine gas), but still grows from the chlorinated precursor.[26] Wu *et al.* have also shown an increased growth rate from chlorinated precursors in one study using laser reflective interferometry.[27] Current studies show that the greatest benefit of chlorine addition to diamond growth is either enhanced nucleation[20,26] or the protection of diamond seeds left behind during surface preparation.[11] In a study by Wu *et al.* the nucleation density of diamond was studied on pretreated and non-treated substrates.[11] More diamond nucleation sites were found on the pretreated substrate.

1.7 Molecular Beam Mass Spectrometry

The method of molecular beam mass spectrometry (MBMS) has been applied to study the growth of diamond from methane by several groups.[21, 28-30] The main advantage is the ability to observe many different masses at the same time. Coupled with orifice

sampling, MBMS provides a unique tool to study the composition of the gas phase close to the growth surface. The main disadvantage is the complexity of the system required.

1.8 Conclusion

Diamond is much desired throughout the world for its excellent material properties and beauty. Many uses for diamond have already been found, and it is expected that more uses will be found as manufacturing methods improve due to research into the mechanism of CVD diamond growth. Chlorine has been shown to allow diamond growth at lower substrate temperatures and to increase the nucleation density of diamond on substrate surfaces. The growth of films at lower temperatures will increase the range of materials that could be coated with diamond, thus increasing the range of use of this material.

HPHT and CVD are the two major methods of growing man-made diamond, although some miscellaneous methods have also produced diamond. HPHT methods produce bulk crystal while CVD methods produce films of diamond. All CVD methods require

activation of the gas phase chemistry, carbon in the gas phase, and a suitable substrate to grow upon.

The chemistry of growth is only partially understood, even in the simple system using only CH_4. This chemistry is believed to be started by radical formation in the gas phase which is achieved by any of several methods including plasmas, torches, and hot filaments. Each of these methods has complicating factors when considered for industrial use. Much more research into these areas is needed.

2.0 Experimental Section

2.1 System Overview

A HFCVD diamond growth chamber was incorporated into a high vacuum system to allow monitoring of near surface growth gases by *in situ* time of flight mass spectrometry (TOFMS). Figure 2.1 shows an overview of the system. The gases from the chamber were sampled through an orifice in the substrate holder so as to cause minimal disruption of the growth conditions during monitoring and to allow interrogation of the gas composition directly above the growth surface. The flow of gas through the orifice forms a molecular beam which is collimated by the skimmer and analyzed by the TOFMS. The system includes two stages of differential pumping to reduce the pressure from the growth chamber, typically 20 torr, to the pressure required in the TOF region, typically 4E-6 torr.

The experimental apparatus can be broken down into the growth chamber, the substrate holder, the molecular beam, the TOFMS and several, sometimes overlapping, subsystems. These subsystems are heating and temperature measurement, gas input,

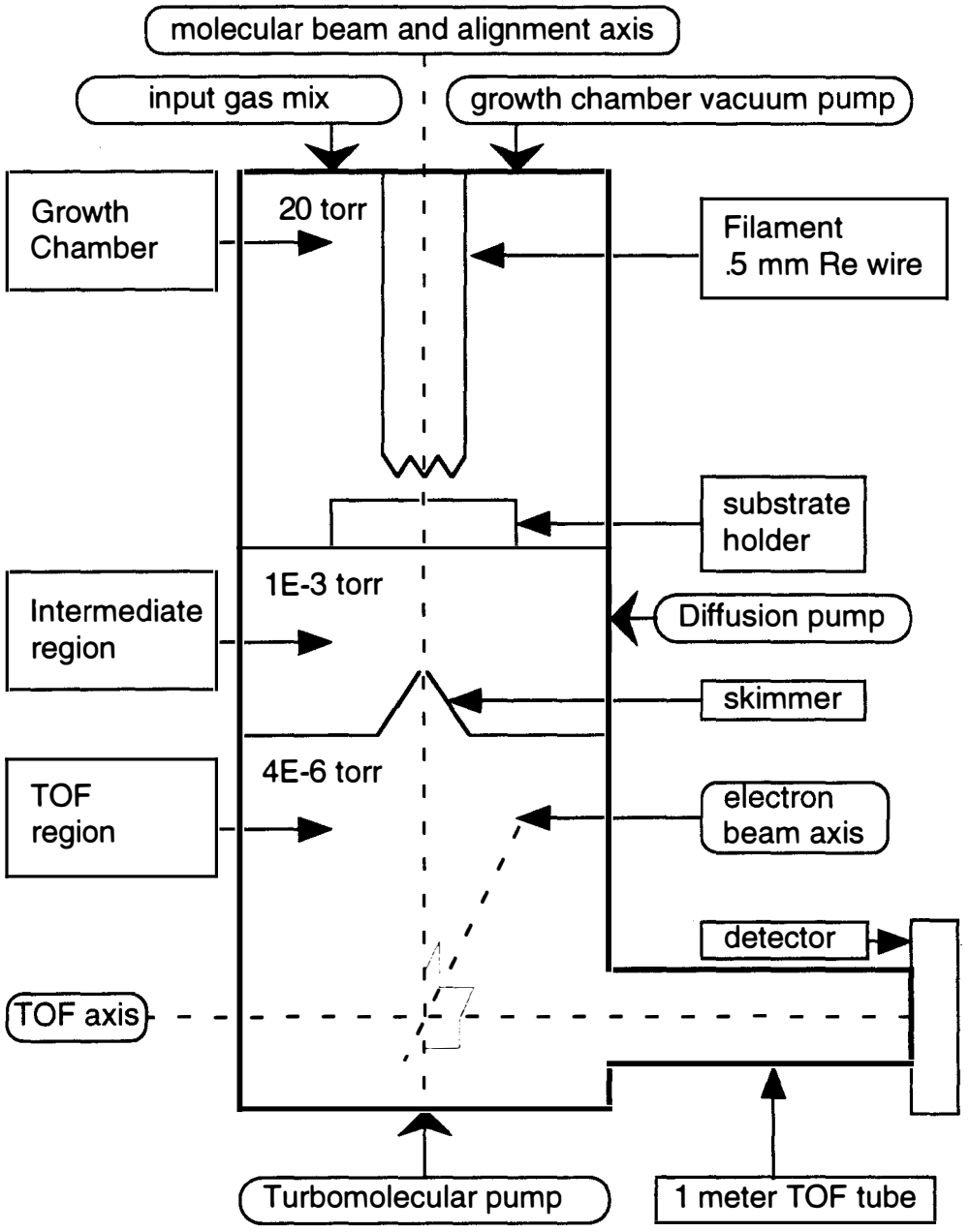


Figure 2.1 Overall System Schematic

substrate, vacuum, and data collection. The first sections here will present only a description of these systems. Discussion of operation will be presented after these are complete.

2.1.1 The Growth Chamber

A custom made quartz tube, 76 mm in diameter and 280 mm long, was used as the growth chamber and housed the filament, the substrate holder and the substrate. The quartz tube was held in place by a silicone O-ring that was compressed between a stainless steel cap and the top flange of the system. Three nylon tipped screws aligned the molecular beam by positioning the quartz tube. The cap provided the connections for growth chamber vacuum pump, input gases, the growth chamber vacuum gauge, and filament power. The top flange provided connections for substrate heater power and for the substrate thermocouple. A 6.35 mm diameter hole was drilled in the bottom of the quartz tube to provide registration for the substrate holder.

2.1.2 The Substrate Holder

Figure 2.2 shows the molybdenum substrate holder which incorporated facilities for substrate mounting, supplemental substrate heating, and substrate temperature measurement. The holder was designed to accept a 200 micron diameter press fit molybdenum electron microscope aperture that provided an orifice for growth gas sampling. A thermocouple well was provided next to the substrate and a heater coil was wound on the substrate holder. A shield (not shown), made from molybdenum sheet, held the thermocouple in place on the substrate holder surface by direct contact, shielded the growth gases from the substrate heater coils and shielded the thermocouple from radiative heating processes in the system.

2.1.3 The Molecular Beam

Gases directly above the substrate were sampled through the 200 micron diameter orifice in the substrate holder. Differential

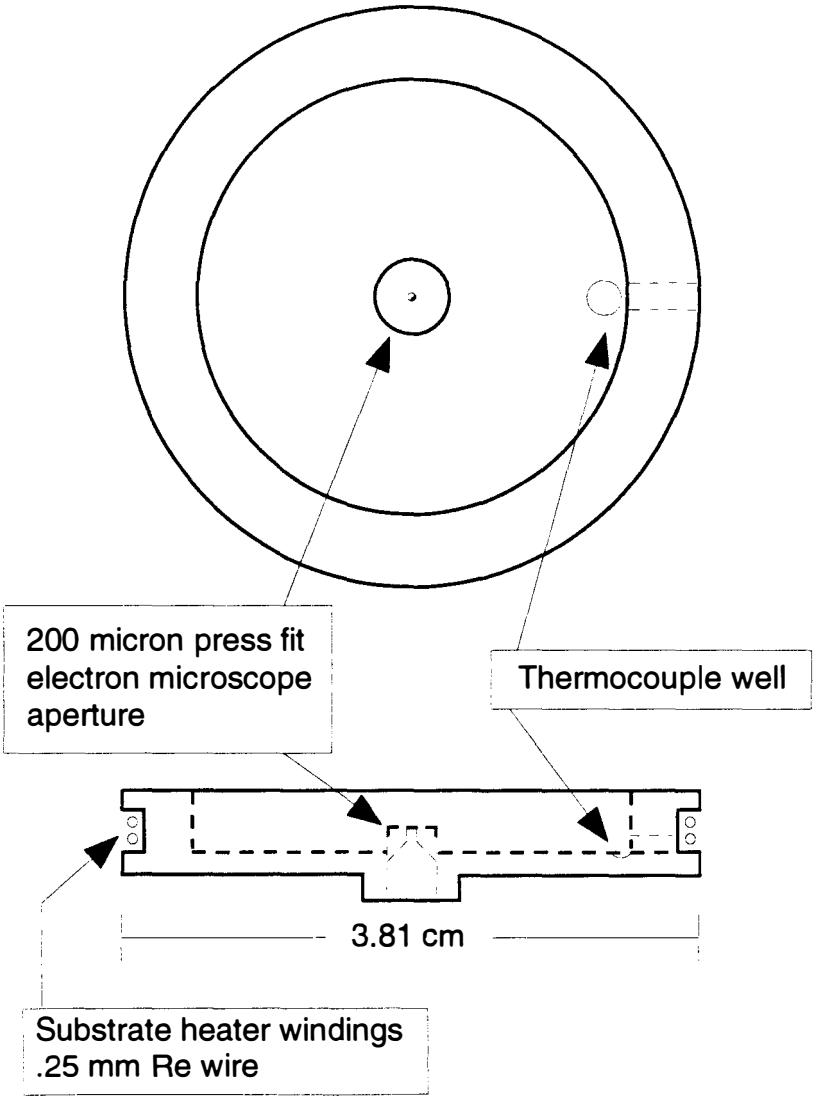


Figure 2.2 Substrate Holder

pumping between the growth chamber and the expansion region created a continuum flow of growth gases into the expansion region. This flow of molecules, atoms and radical species from the growth chamber formed the origin of the molecular beam. After 3-6 mm, the species from the orifice encountered a 500 micron diameter stainless steel skimmer. Differential pumping across the skimmer defined the molecular beam by selecting the central portion of the continuum flow from the orifice. The region between the orifice and the skimmer was pumped to around one millitorr by a diffusion pump. The molecular beam path was aligned by use of a diffraction pattern produced from a He/Ne laser shone through the orifice and the skimmer. When the diffraction pattern was as symmetrical and bright as possible, and when the beam was centered on a removable target in the TOF ion source, the beam was considered aligned. A more detailed analysis of this molecular beam was done by L. L. Jones.[31]

2.1.4 The Time Of Flight Mass Spectrometer

The R. M. Jordan company of Grass Valley, Ca., manufactured the TOF apparatus described by the block diagram in Figure 2.3. The electron gun produced electrons which ionized the gases in the molecular beam, producing positive ions by the following reaction.[2]

1) $X + e^- \rightarrow X^+ + 2e^-$

All singly charged positive ions formed are given the same kinetic energy as they are accelerated down the flight tube. This allows for their masses to be determined from their time-of-flight in the flight tube. The TOF region was pumped by the turbomolecular pump to around 4E-6 torr during normal operation.

The electron gun irradiated the TOF ion source with electrons at all times except during ion extraction. Pulsing the extraction grid caused positive ions to be extracted from the ion source into the acceleration region. The extraction grid was pulsed at 1 KHz. The TOF tube was one meter long, and two 19-mm diameter multichannel plates were used for the detector. The detector output was fed through two stages of an EG&C Ortec model AN302/N quad

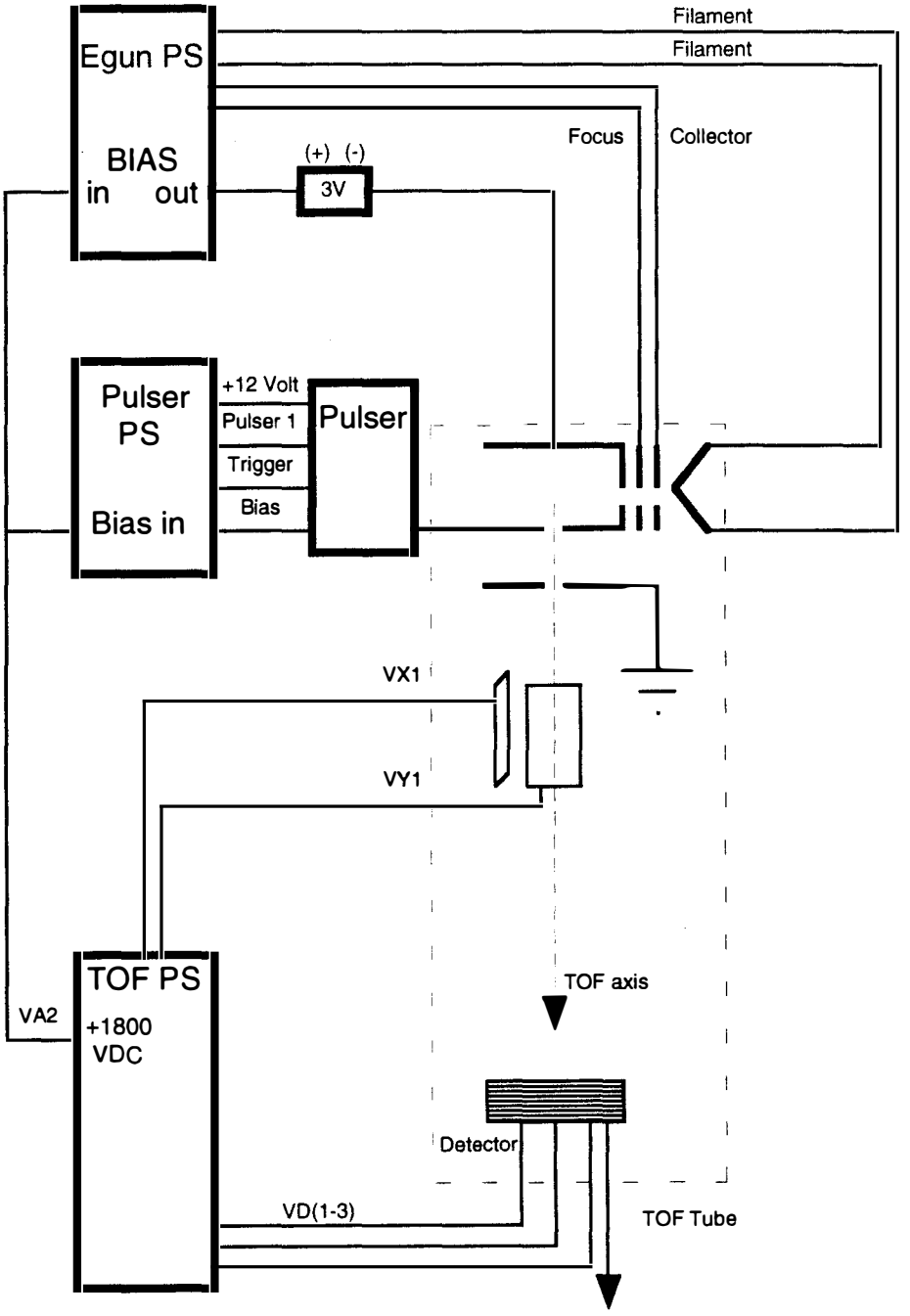


Figure 2.3 Basic Time-of-Flight (TOF) Electronics

preamplifier with 4.5 X gain per stage for a total gain of about 20.

As shown in Figure 2.4, the original design of the TOF system was modified by adding three batteries (4.5V, 9V, and 30V) and a switch to allow for low energy electron impact ionization (LEEII) experiments. The batteries were necessary because the original electron gun power supply could not produce electron energies below 40 eV. With the battery and switch setup, electron energies as low as zero eV could be reached. Using the battery and switch setup allowed experiments to be run at electron energies differing by the battery voltage selected. Since the electron gun power supply was designed to draw minimal current from the bias voltage power supply, the drain on the batteries was on the order of microamps. The switch setup allowed very precise reproduction of electron energies by eliminating the error due to resetting the analog electron energy voltage control during single experiment sets. All electron energy experiments were done at room temperature.

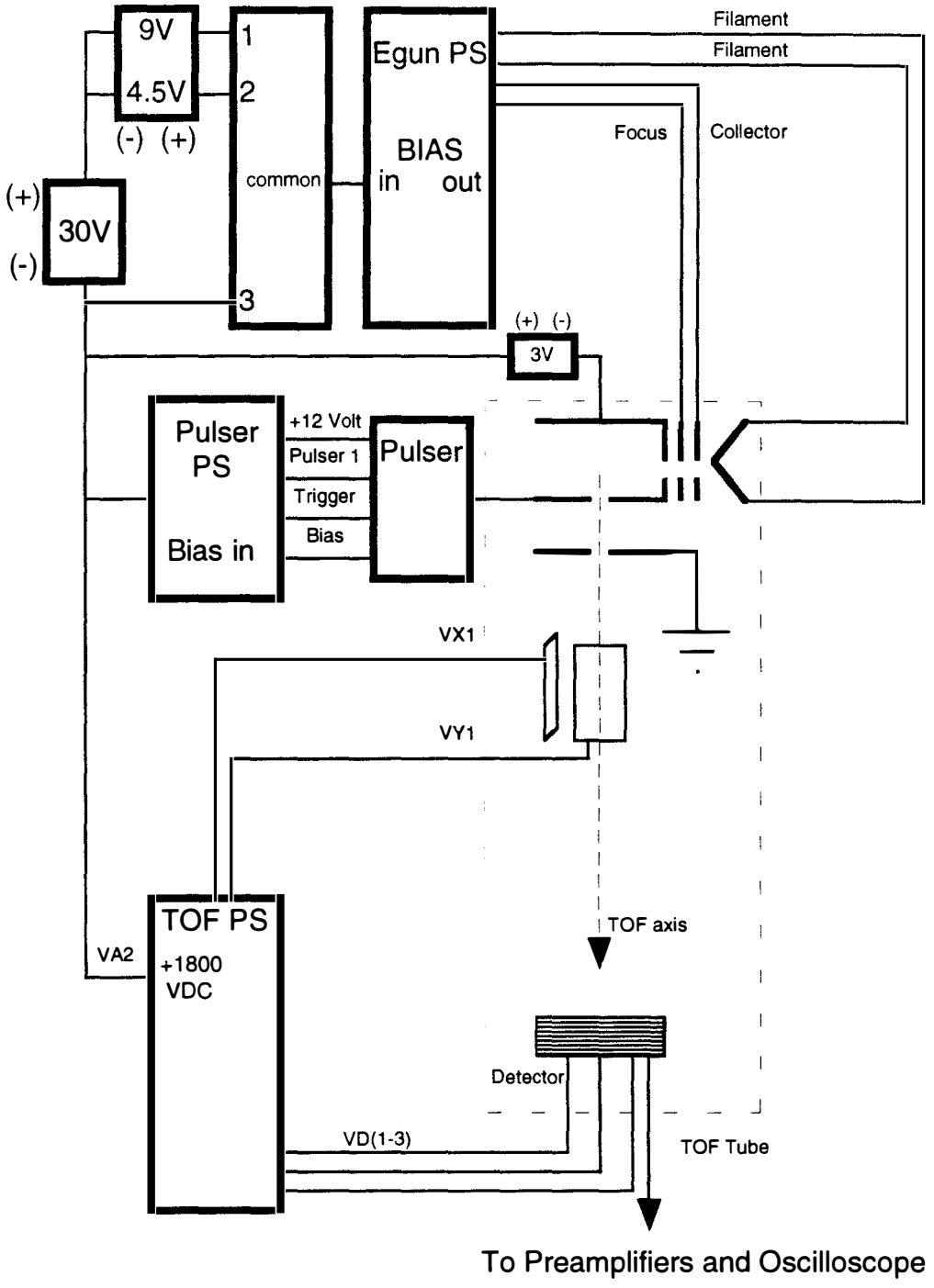


Figure 2.4 LEEII TOF Electronics

2.1.5 Heating/Temperature Measurement Subsystems

The filament (.5 mm) and the substrate heater coil (.25 mm) were both wound using rhenium wire from Rhenium Alloys of Elyria, OH. The filament was eight turns of wire wound around a decking screw to produce a four mm outside diameter coil. The leads of the filament were attached by molybdenum screw connectors to the tungsten rods from feedthroughs on the growth chamber cap. The filament was powered by a Sorensen 40-40B power supply operating in current regulation mode to control the filament temperature. The filament temperature was measured using a single color pyrometer from The Pyrometer Instrument Company, Inc. The filament-substrate distance was kept close to four mm. The substrate heater coil was two wraps of wire around the substrate holder. These coils were held in place by alumina beads, each with two parallel holes, cut for this purpose. The leads of the substrate heater were spot welded to tungsten rods that attached to connectors on the flange. Power was supplied to the substrate heater through two 120V AC variacs connected in series to allow for more precise control of the

substrate temperature when additional heat was required during substrate temperature experiments. The substrate temperature was monitored using a type S (Pt/Pt-10%Rh) thermocouple connected to an Omega, type DP460 readout, and could be controlled to within five degrees.

2.1.6 The Gas Input System

Figure 2.5 details the gas control system used. Gas was introduced to the system via three model 2259C mass flow controllers. These were controlled in turn by a model 147B multichannel gas controller from the MKS Corporation. This controller was programmed with calculated gas correction factors for each gas mix used. The gas mixes used were combinations of three components, the base gas, the noble gas mix, and the precursor of choice. The base gas was research grade hydrogen, the noble gas mix was 10.0% argon, 10.0% neon, 10.1% helium and 69.9% hydrogen. Both of these were from Air Liquide company of Oak Ridge, TN. The precursor gas was either a mix of 4.999% methane in hydrogen from Air Liquide or a mix of 5.0% chloromethane and 3.0% krypton in

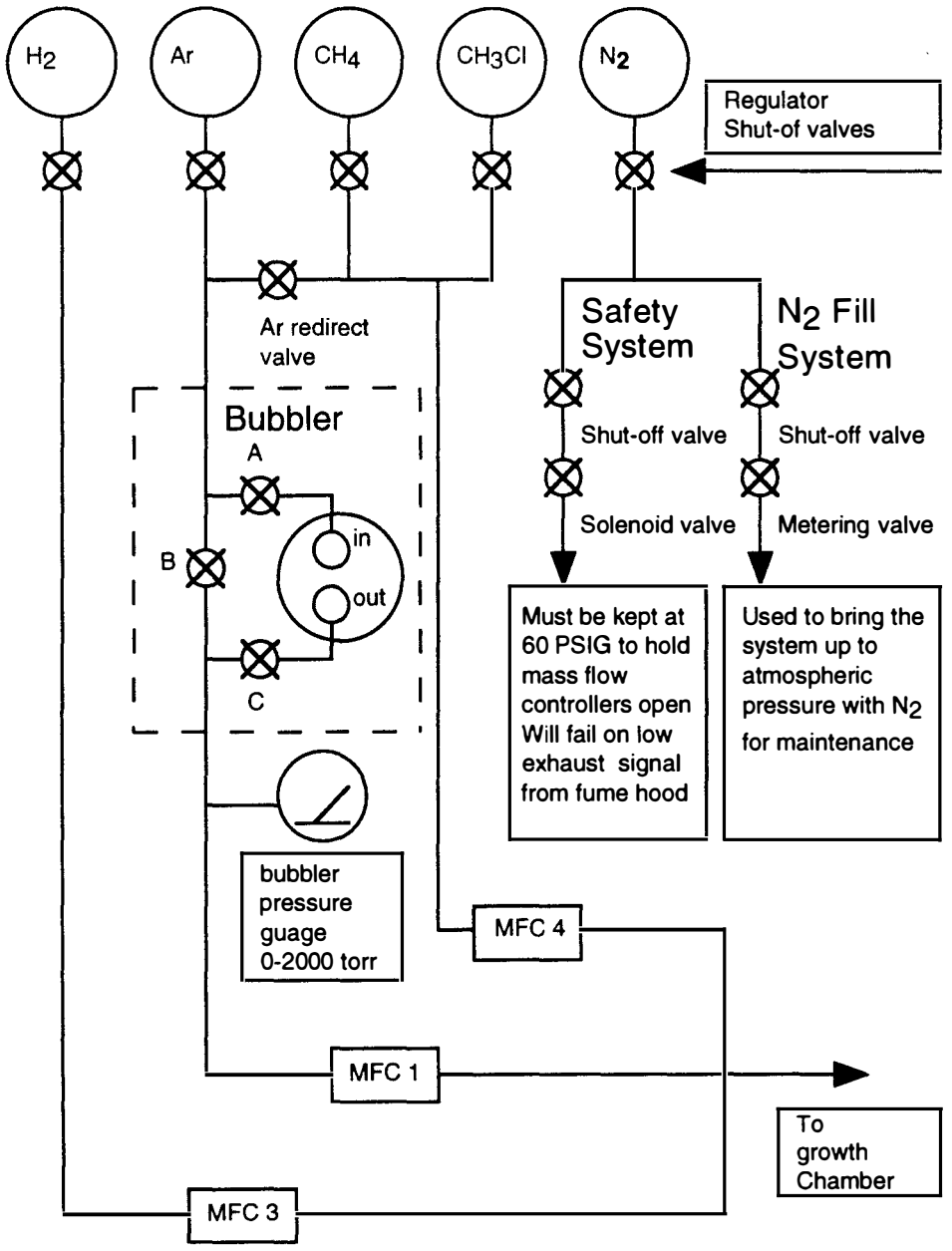


Figure 2.5 Gas Control System

hydrogen from Spectra Gases of Irvington, NJ. HPLC grade chloroform from Burdick and Jackson was introduced by bubbling the noble gas mix through the liquid in the bubbler (Figure 2.6).

The flow rate was 100 sccm total of the base, the noble gas mix and the precursor mixed together. The carbon content of the precursor gas was kept at 1% for all experiments reported except the growth and electron energy study using CH_4. The carbon content was 0.25% for these two experiments and they were done at 60 torr growth chamber pressure. This was five sccm of the 5% methane/hydrogen mix, five sccm of the noble gas mix and 90 sccm hydrogen (gas mix #1). All other experiments used 1% carbon content and 20 torr growth chamber pressure. For all the chloromethane experiments, 20 sccm precursor gas (chloromethane gas mix), five sccm noble gas mix and 75 sccm hydrogen were used (gas mix #2). When using the bubbler to pick up chloroform, the carbon content was determined from the room temperature vapor pressure of chloroform (195 torr) and the reading from the bubbler pressure gauge (980 torr). The mixture at the exit of the bubbler contained 20% chloroform, 8% each of argon, neon and helium, and 56% hydrogen (gas mix #3). The carbon content of the chloroform gas

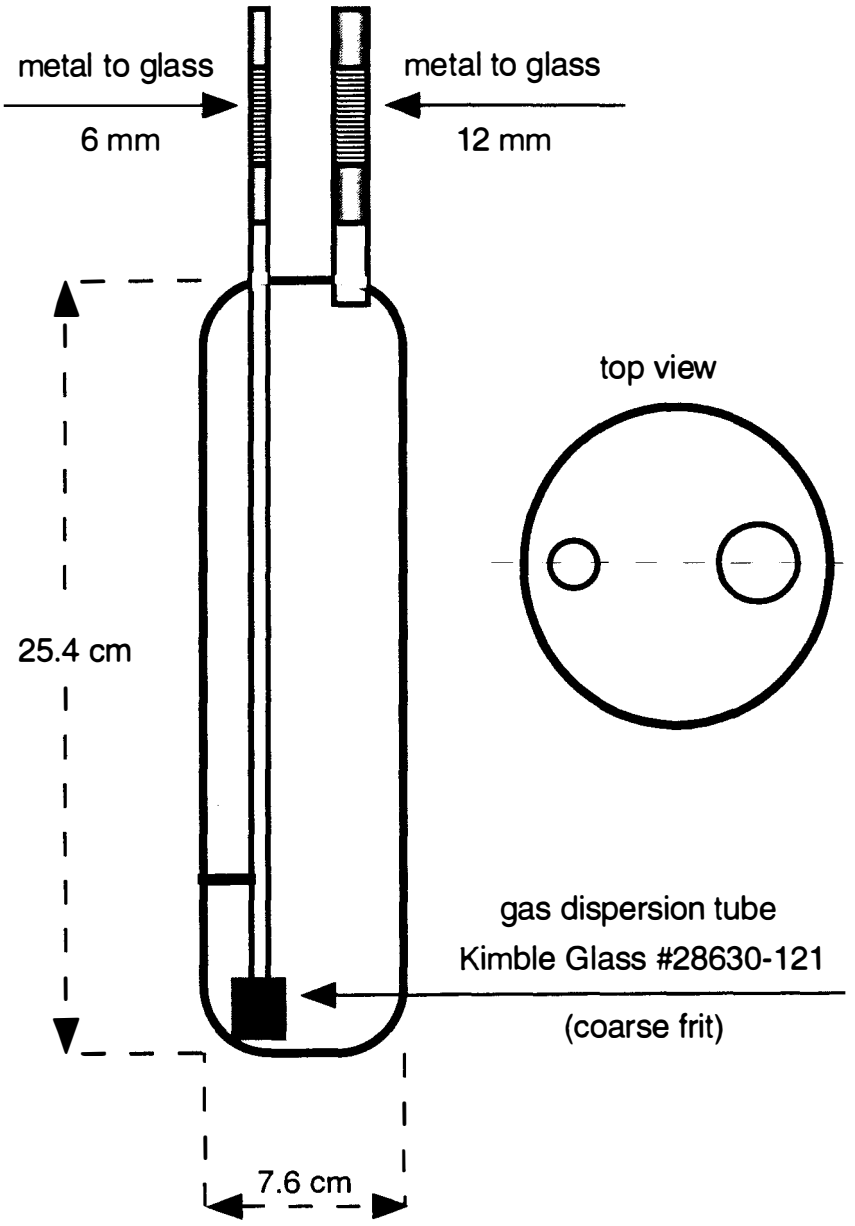


Figure 2.6 Gas Bubbler

mix was adjustable by varying the regulator pressure on the noble gas tank when using the bubbler. Five sccm was allowed to flow through the bubbler. The sums of all the carbon containing peaks at room temperature from spectra generated using gas mix #2 and gas mix #3 were compared and found to be within 25% of each other without taking ionization cross sections into account.

The pressure in the growth chamber was maintained by use of an electrically controlled throttle valve connected to a type 250 controller from MKS. The type 250 controller was in turn connected to an MKS PDR-C-2C readout monitoring the growth chamber pressure via an MKS vacuum gauge (1-100 torr, type 127) attached to the chamber cap. This feedback loop provided pressure control to within .05 torr.

2.1.7 Substrates

The substrates were cut by hand to 10 mm by 20 mm rectangles from the <111> surface of semiconductor grade silicon wafers. A registration hole 3.175 mm diameter was ground through the center using nine micron diamond suspension. One micron

diamond suspension was used to burnish half of the upper surface of the substrate (the scratched side) to enhance diamond growth on that portion. Both suspensions were from South Bay Technology (San Clemente, CA). The scratched side is easily covered with a diamond film during deposition. The unscrached side provides an indication of diamond nucleation density. After burnishing, the substrates were sonicated using GC grade methanol for twenty minutes at 40 °C. Records were kept of the growth conditions for each substrate, and each was stored in a separate numbered container for later analysis.

2.1.8 The Vacuum Systems

Vacuum for the growth chamber was provided by a 60 L/min belt driven roughing pump. The intermediate chamber was pumped on by a Varian VHS-6 diffusion pump with a water cooled baffle. This pump had a pumping speed of 2400 L/sec and was backed up by a 360 L/min mechanical rough pump (Varian SD450). The pressure in this region was monitored by use of a Varian model 843 vacuum ionization readout connected to a type 0531 thermocouple gauge and an Electron Technology 4336P ion gauge. A 0-1 torr vacuum gauge

(MKS type 127) was also available for measuring the pressure in this region via the PDR-C-2C readout. The TOF region was pumped a Leybold-Heraeus Turbovac-450 turbomolecular pump controlled by the NT-450 controller from the same company. This was backed up by another SD450 rough pump. Pressure in this region was monitored by another type 0531 thermocouple gauge and a Varian ion gauge through the same model 843 readout.

2.1.9 Data Collection systems

Data were collected from the detector of the TOFMS in the form of an oscilloscope waveform which was transferred to a 486-33DX (IBM clone) running MSDOS 6.20. The initial stages of this experiment were conducted using a Tektronix 2324 oscilloscope connected through a GPIB interface to this computer. This oscilloscope was replaced with a Tektronix TDS524A near the end of the experiment. When the 2324 was used, a series of programs, known as QMASPx.x (written by Prof. Ling Jun Wang and modified by Prof. Xiaming Han) were used to capture the data, calibrate the mass axis, and produce a compilation file from data sets thus stored in

the computer. When the TDS524A was introduced, the QMASP series was replaced by the program MASPEC which produced the same compatible compilation file from the disk file data sets of the new oscilloscope. The compilation data files were processed using the program COMPSORT which produced a spreadsheet file importable into the Kaleidagraph graphing program running on a power Macintosh 8100/80 that was used to produce the graphs of the data used in this thesis. All of the custom programs were written in Quickbasic version 4.5, and listings of the MASPEC and COMPSORT programs are provided in Appendix A-7 and A-8 with instructions for their use in Appendix A-9.

With the 2324 oscilloscope, 256 acquisitions were averaged to produce a trace on the screen. This was changed to 2500 averages with the TDS524A. In both cases, a minimum of three data sets were obtained for each point produced on the graphs. The data sets were averaged together by the COMPSORT program and standard deviations were calculated and used as error bars when desired. The 2324 could store record lengths of up to 1000 points. This caused problems with normalization since in order to obtain usable signals, limited mass ranges had to be used. Thus, some data sets were

normalized using neon, others using argon, and others using krypton. The introduction of the TDS524A allowed record lengths of 150,000 points which covered the entire mass range desired. Data sets taken with this oscilloscope were normalized to argon or krypton.

2.1.10 Raman Analysis

A Dilor XY Raman spectrometer with a CCD detector and a microscope attachment was used to examine diamond films produced in these experiments. A magnification of 80X was used with 100mW of 514.5 nm excitation to obtain spectra. The Raman instrument was calibrated to the 1332.2 cm^{-1} line of single crystal natural diamond before analyzing samples.

2.2 Overview of Operation

The experimental procedure listed in Appendix A-2 provides the basic system operation sequence. The gas mix of choice was input into the growth chamber above the Re filament. The filament initiated dissociation of the gases present by thermal and possibly

catalytic decomposition at the filament surface. The radicals thus formed, interacted in the gas phase, and made their way to the substrate surface. These gases were sampled through the orifice. Only gases near the surface are sampled as long as the mean free path of the gases is much less than the orifice diameter.[29] The sampled gases then pass the skimmer and form a molecular beam which was aligned on the TOF ion source. LEEII was used to ionize the species present, and TOFMS was used to determine the near substrate surface gas composition.

2.3 Discussion of Errors

The following sections detail the major sources of error present in the system. Explanations of the methods used to deal with these errors are also presented.

2.3.1 Molecular Beam

Gases could escape the growth chamber by passing under the substrate holder, which simply sat on the quartz tube bottom.

Previous measurements have indicated that between 30% and 40% of the gases in the growth chamber escape the chamber through the orifice and/or under the substrate holder at room temperature.[31] The use of the skimmer helps preclude inclusion of gases escaping under the substrate holder into the molecular beam.

A flow dependent mass discrimination error is present in molecular beams. Heavier masses tend to stay in the center of the molecular beam, while lighter masses tend to be diffuse from the center. This error has been discussed fully in the literature.[29] Normalization using a noble gas signal eliminates the flow dependence of this error, but does not eliminate the mass discrimination.

2.3.2 Electron Gun Energy Spread

There is an error in the system due to the electron energy spread from the electron gun. For our system this value was estimated to be about 1.0 eV due to the voltage drop accross the electron gun filament.[32] The analog meter which reported electron gun energy could be read to within about one eV. This set a limit on

electron energy scale calibration between data sets with this system. Within any particular set of data, however, by using the batteries and switch installed, the ionization potentials could be calibrated with a known value and then reported to within 0.5 eV.[33] The ionization potential of Ar is 15.8 eV, and that of Kr is 14.0 eV. The spread of the electron gun energy was determined from a study of these two gases, shown in Figure 2.7, to be about 1.5 to 2 eV. There is also the possibility that the flux of electrons used for ionization changes with a change in electron energy. More electrons would produce a larger signal, fewer, a smaller one.

2.3.3 Ionization Cross Sections

Some of the species in this experiment have known electron impact ionization cross sections. These are H_2, H, Ar, CH_4 ,CH_3, CH_2, CH, C, and C_2H_2.[34] No literature was found on the cross sections of the chlorinated species used. Although cross sections vary rapidly near the threshold of ionization, it was assumed that all species behaved in the same manner about this region. A small change in electron energy in this region could produce a large change in the

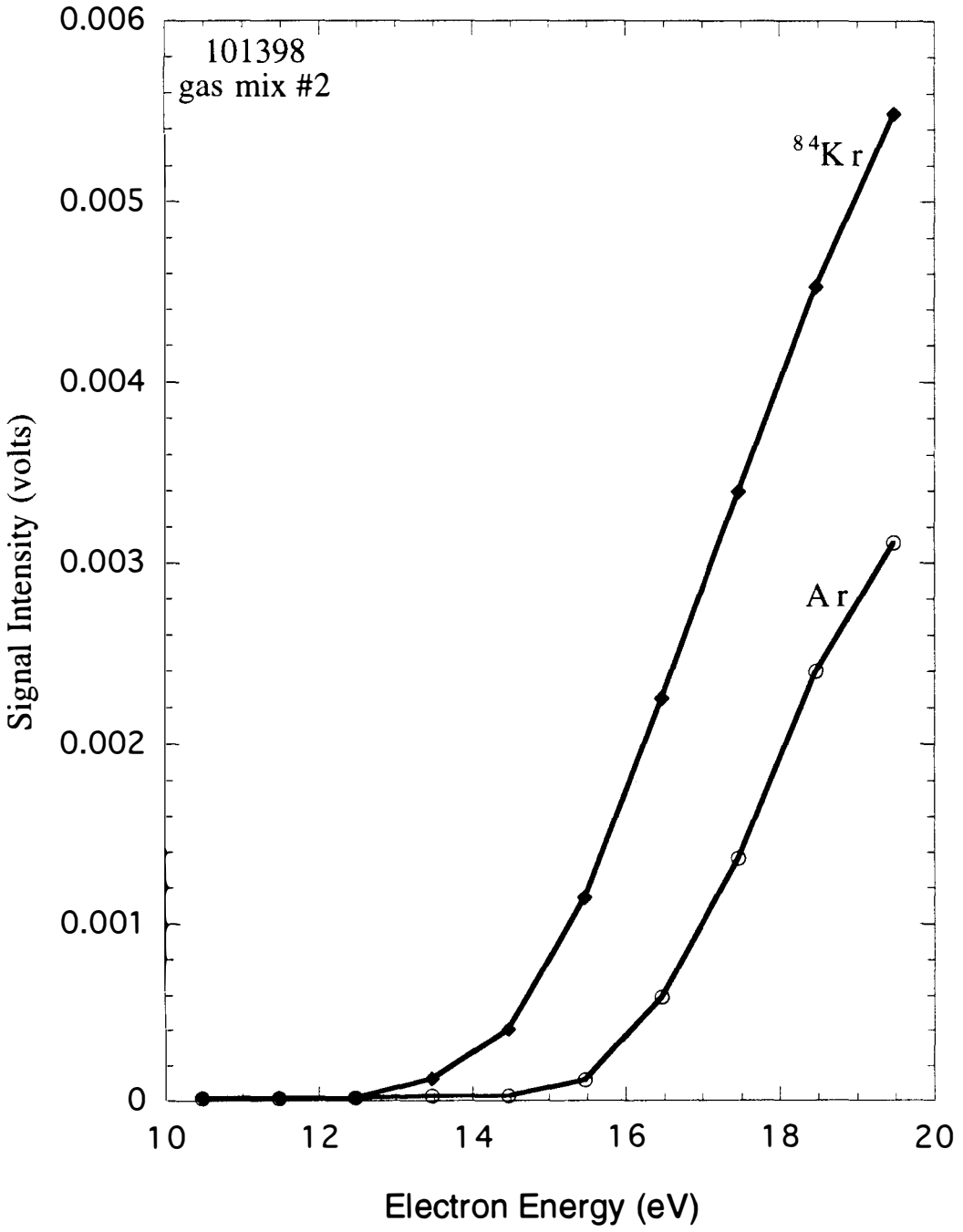


Figure 2.7 Argon and Krypton Signals

signals obtained. The battery and switch system helped eliminate this error. Uncertainty due to resetting the electron energy control was avoided by this method. The Ar signal used for normalization of the data was usually taken at a higher electron energy (60 eV) than the energy used in taking the data. This was done at all times in the later experiments so as to provide a strong normalizing signal, and in experiments which required electron energies less than the ionization potential of argon it was essential.

2.3.4 Ion source Electrons

An interference was caused by electrons in the volume of the ion source being accelerated to the repeller plate during the extraction cycle of the TOFMS. Because the extraction grid was dipped by 180 volts during extraction, electrons in the TOF ion source were accelerated to an average of 90 eV in line with and directly away from the detector. These electrons could then ionize any molecules or atoms present at a much higher electron energy than was expected, and each of those ionized species would be in line with the detector and thus detected. This effect caused a signal

to be present for H+ and other species at electron impact energies below their appearance potential. Figure 2.8 shows this effect for some of the weaker signals in the system. Although this was most noticeable for H+, the daughter from H_2, this signal is not shown so that the smaller signals may be seen. The H+ signal will be discussed further in Section 3.2.

2.3.5 Double Ionization

At higher electron energies doubly ionized mass 28 and 32 would contribute to the signals at mass 14 and 16. This effect can be ignored when using low energy electrons due to the high second ionization potentials of most species, but must be kept in mind when looking at data obtained using high ionization energies. See Appendix A-4 for a table of ionization potentials. The main result of this effect was seen in the doubly ionized krypton peaks at masses 41, 41.5, 42 and 43 due to the low second ionization potential of krypton (24.4 eV).

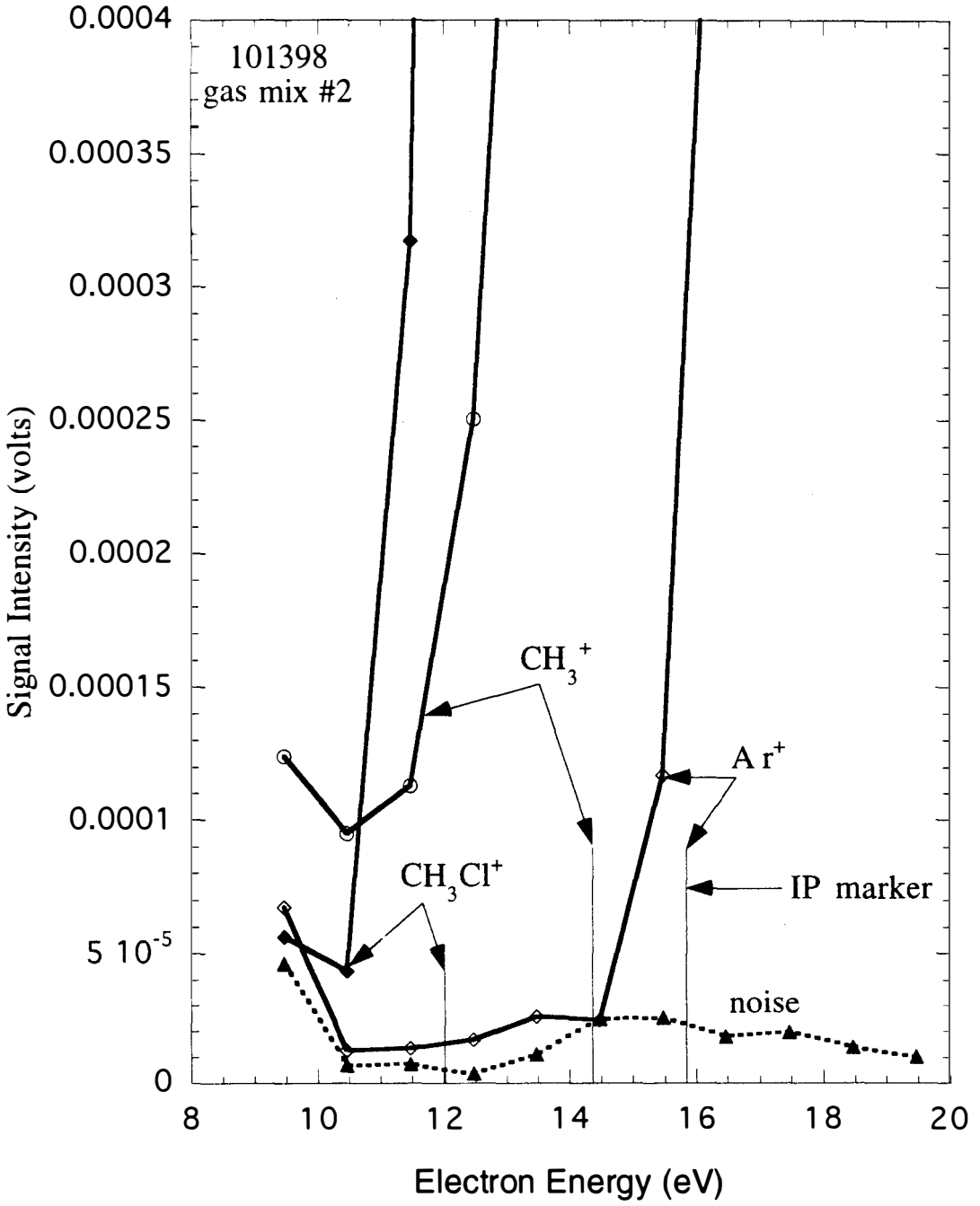


Figure 2.8 Signal Contribution from Ion Source Electrons

2.3.6 Baseline Evaluation

The program set that was developed for this experiment helped to eliminate human error, and provided a standard method of peak height calculation. A typical mass spectrum is shown in Figure 2.9. The size of the H_2^+ signal produces the ringing seen from overdriving the preamps. Furthermore, groups of signals close together in mass rest on pedestals. The pedestals are believed to be caused by residual gas in the flight tube. These artifacts dictated the choice of suitable areas for baseline determinations. After It was observed that the spectra had several regions in which no mass signals were ever present, these regions were used for baseline calculation. The waveform in the baseline calculation region closest to the peak of interest was summed and averaged to produce the baseline for that peak. See the subroutine BASELINE listing in program MASPEC starting on page 121 for the set of baseline areas and assignments used to calculate peak heights. The peak heights reported also require an explanation. The program MASPEC defines the peak height as the largest signal present in a range (+/- .2 amu) around the mass

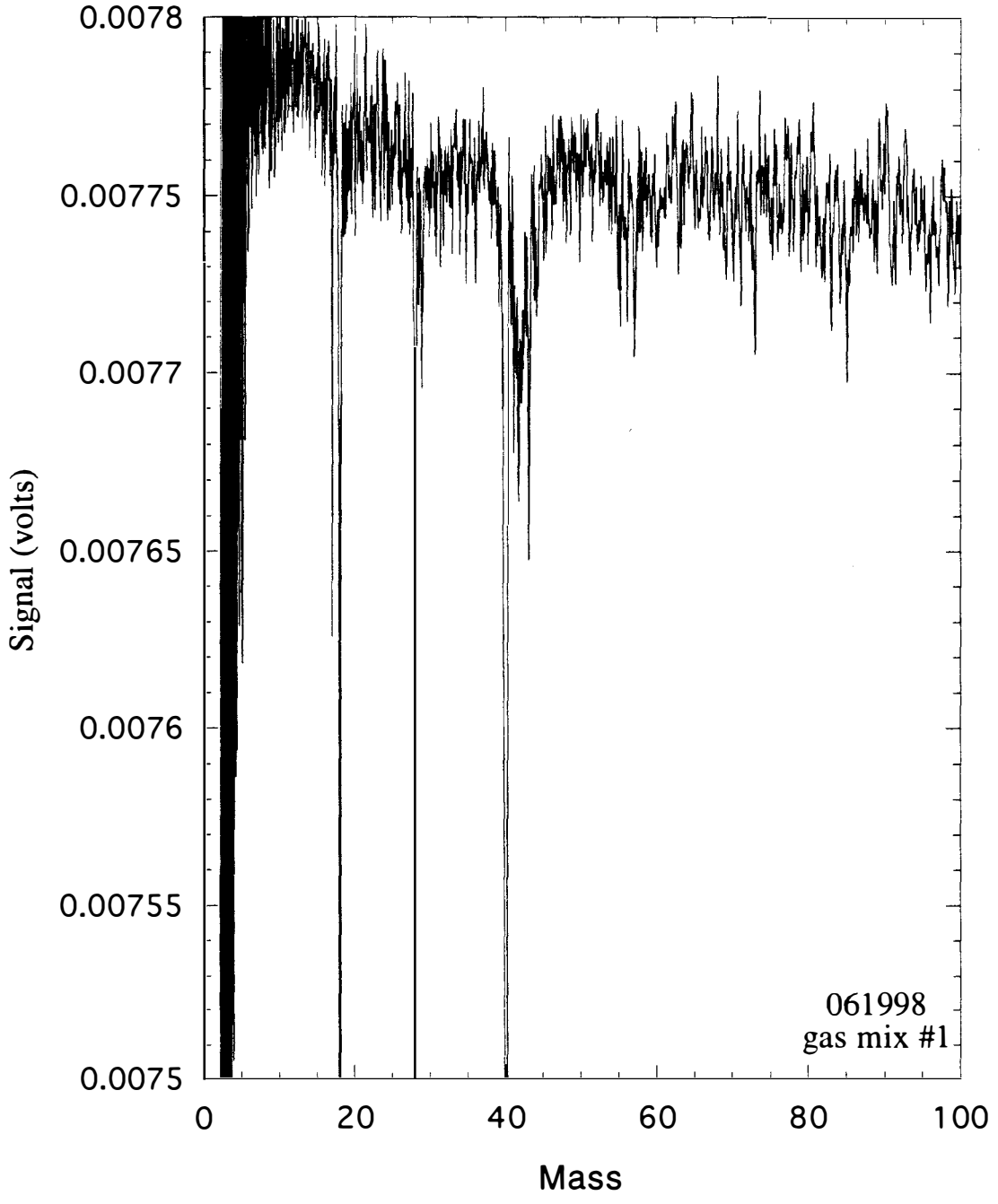


Figure 2.9 Typical Mass Spectrum

chosen. This means that a peak height measurement on a baseline calculation region will not report a zero signal, but will report the largest noise peak in that area. This was used as an indication of the noise in the system.

2.3.7 Temperature Measurement Errors

Errors could be introduced into the temperature measurments from several sources. The first of these involves the pyrometer, the second involves the thermal contact and shielding of the thermocouple, and the third involves the filament.

Single color pyrometry is a well established method for measuring unknown filament temperatures[35]. The pyrometer used was calibrated to within one percent by the Instrumentation and Controls Shop at ORNL using a tungsten filament traceable to NIST. There were three corrections, pyrometer calibration, rhenium emissivity and quartz tube absorpton, that were necessary for the temperature readings for the rhenium filament in this system. A linear regression of the pyrometer calibration data produced the first correction formula. A second correction formula was developed

for the emissivity of rhenium (.40 was used as the emissivity). A type 7447, 12VDC automobile tail light was used to measure the pyrometer error due to absorption by the quartz tube and inspection windows. Measurements were taken inside and outside the chamber at various currents. A linear regression of the data provided the third correction of the pyrometer reading which corrected for differences in transmission through the quartz tube and glass view port due to cleanliness. Appendix A-5 lists these corrections. All filament temperatures reported in this work have been corrected as described therein.

The second temperature error was introduced by rebuilding the substrate heater coil. This involved removing the shield that held the thermocouple in place, and thus there is no guarantee that the contact between the thermocouple, shield, and substrate holder was equivalent in all cases. It was, however, equivalent for any set of data taken between rebuilds.

The last thermometry issue involves filament replacement. These were made by hand. Human errors in making and installing the filament cannot be avoided, only minimized. The placement of the filament affects the filament substrate temperature relationship

since a closer filament would heat the substrate differently. Also, the filament-substrate distance is known to be an important factor in determining the radical concentration at the surface of the substrate.[23] Care was taken to minimize this contribution, but it cannot be eliminated, however, it only affects the the relationship between the temperature scales for experiments with different filaments.

3.0 Results and Discussion

First, a description of the experiments completed will be given and then a discussion of the results of the experiments will be presented. During the discussion, literature examples will be compared with the results obtained during these experiments to show how they expand the general knowledge in the area of CA-HFCVD.

3.1 Experiments Undertaken

Four different, but related sets of experiments were attempted using the system available at ORNL. The first set of experiments used low energy electrons to ionize the species present in the molecular beam to understand in more detail the processes taking place in the growth chamber. The second set of experiments was a filament temperature dependence study of gas mixes #1, #2, and #3 (Section 2.1.6). The third set of experiments was a series of substrate temperature dependencies of species present at selected filament temperatures with gas mix #2. The fourth set of

experiments involved growing diamond films at points of interest seen in the previous experiments and characterizing those films using scanning electron microscopy (SEM) and Raman spectroscopy.

3.2 Low Energy Electron Impact Ionization (LEEII)

Experiments were undertaken to understand the room temperature LEEII of the species present in the system in order to demonstrate that the signals obtained under growth conditions indeed reflected the species produced in the growth chamber from thermal reactions. In the early experiments, before the use of LEEII in the TOFMS system, the mass spectra contained components from the thermal chemistry of the growth chamber and from the electron impact ionization process within the TOFMS. Both of these sources could cause fragmentation of the parent species that would lead to signals in the TOFMS. The use of a threshold ionization method allows for a separation of these effects.[29, 36] To this end, plots of mass spectral signal intensity *vs* ionization electron energy for precursor gases at room temperature were produced. Appendix A-3 presents a tabulation of known appearance potential values

compared to values derived from these experiments. This table uses the term appearance potential to define the onset of positive ions from the corresponding neutral species listed. In this sense, ionization potentials are just the energy at which the parent ion appears during the ionization process.

Since the appearance potential of a charged daughter species is usually about two to three eV higher than the appearance potential of the charged parent species, an electron energy window in which the parent may be observed without producing the daughter species from electron impact is typically available. Since the ionization potential of a daughter radical is usually lower than that of the parent species, any radical produced in the growth process should be detectable below the appearance potential of the parent ion.[36] The ability to separate the parent and daughter appearances is limited by the electron energy spread discussed in Section 2.3.2.

Figure 3.1 shows an example of low and high energy electron impact ionization of the methane growth mix to illustrate signal intensity complications introduced by choice of electron energy. In this figure, the 12.5 eV trace was scaled and shifted as indicated. Because the appearance potential of CH_3+ from CH_4 is 14.3 eV, the

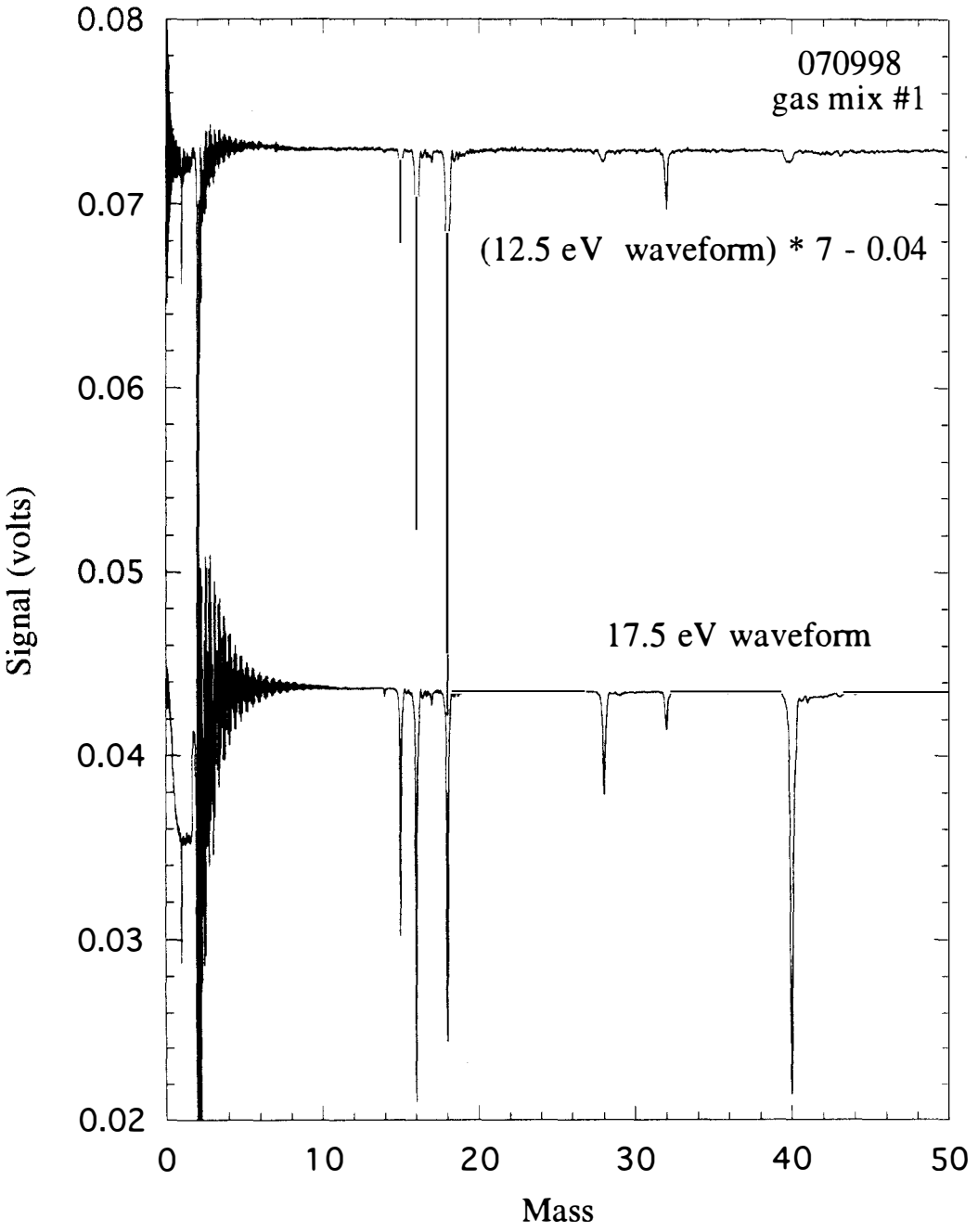


Figure 3.1 Methane Waveforms at 17.5 and 12.5 eV

CH_3+ signal should be absent in the 12.5 eV electron waveform. It is present due to the electron gun energy spread. Due to the high ionization potential of argon, 15.8 eV, only a small peak is observed in the 12.5 eV electron trace, indicating an upper limit on the electron gun energy spread of 3.3 eV (HWHM). The relationship between the O_2+ and N_2+ signals further illustrates this point. Also present is the mass/charge (m/z) = 1 peak assigned to H+ (AP = 18.6 eV). At 12.5 eV, this should not be present, even given the energy spread of electrons in this system. This peak is due to the ion source electron problem described in Section 2.3.4.

3.2.1 Chloromethane

Four unambiguous m/z signals at masses 47, 48, 51 and 52 ($C^{35}Cl$+, $CH^{35}Cl$+, $CH_2{}^{37}Cl$+ and $CH_3{}^{37}Cl$+) helped in assigning the peaks at masses 49 and 50. The m/z 49 signal could be either $CH_2{}^{35}Cl$+ or $C^{37}Cl$+ and m/z 50 signal could be either $CH_3{}^{35}Cl$+ or $CH^{37}Cl$+. The isotopic abundance of chlorine provided the additional information needed to assign the peaks to the proper species.

Figure 3.2 shows the appearance of some of the ions of

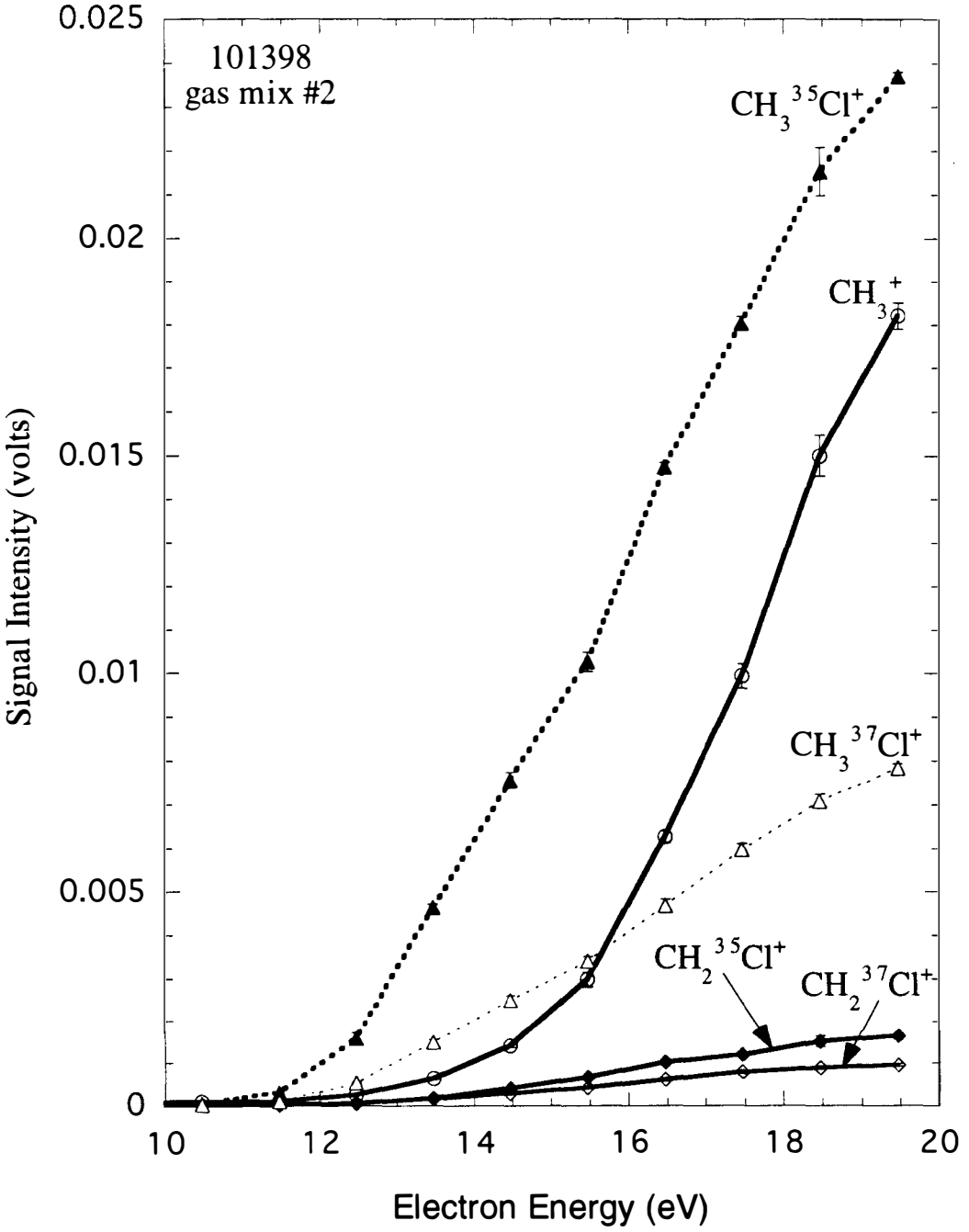


Figure 3.2 Electron Energy Study for CH_3Cl

interest from ionization of chloromethane. In this figure, the isotopic abundance ratio of chlorine was used to assign $CH_3{}^{35}Cl+$ as the mass 50 peak since it follows the $CH_3{}^{37}Cl+$ peak at a ratio of about 3:1. The methyl radical signal appears at a higher electron energy (13 eV) than that needed to produce the parent CH_3Cl+ peak (12eV). From Appendix A-4, the ionization potential of the methyl radical is 9.8 eV. Any methyl radical produced in the CVD chemistry should be discernable in an ionization energy window between 9.8 and 13 eV. The monochloromethyl radical appears at an even higher electron energy than the methyl radical in Figure 3.2. This is to be expected, as the carbon-hydrogen bond (103 kcal/mol) is stronger than the carbon-chlorine bond (78 kcal/mol).[26] Thus, one would predict the loss of chlorine before the loss of hydrogen in this case. The CH_2Cl+ signals appear last in this graph and roughly follow isotopic abundance as well.

An examination of the weaker peaks from the experiment of Figure 3.2 is provided in Figure 3.3. Note that the CH_4+ signal is about 1/50 of the CH_3+ signal in Figure 3.2. This could be due to carbon-13 or deuterium substitution, as methane should not be found in this system. The unambiguous, but small, $CH^{35}Cl+$ signal indicates

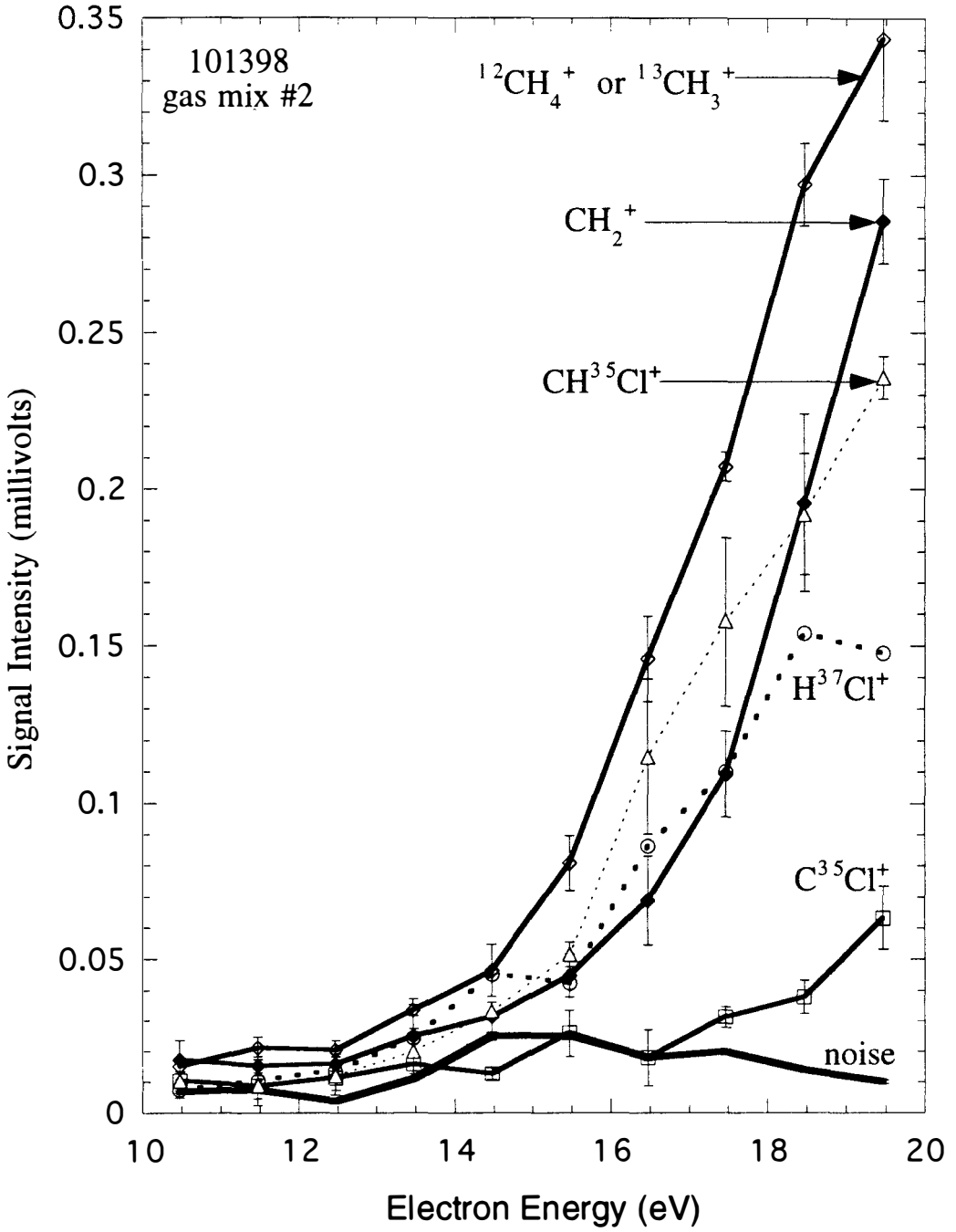


Figure 3.3 Electron Energy Study for CH_3Cl, Smaller Signals

the contribution of $CH^{37}Cl^+$ to the m/z 50 peak ($CH_3{}^{35}Cl^+$) of Figure 3.2 is small. Also, since the unambiguous $C^{35}Cl^+$ signal is small in Figure 3.3, there is little contribution from $C^{37}Cl^+$ to the $CH_2{}^{35}Cl^+$ signal of Figure 3.2. This shows that the expected CH_3Cl^+/CH_2Cl^+ ratios in Figure 3.1 are of the order of 10:1 for electron impact processes at low energies from the chloromethane precursor.

3.2.2 Chloroform

Figure 3.4 shows the electron energy dependence of the ion yeild for chloroform. The chloroform molecule is very susceptible to loss of Cl (or Cl^-) by electron impact ionization as can be seen from the size of the $CH^{35}Cl_3{}^+$ peak compared to the size of the $CH^{37}Cl_2{}^+$ peak plotted. The species containing two chlorine atoms were followed as an indication of precursor concentration because of this. That $H^{35}Cl^+$ appears early on in the graph indicates that chloroform can lose this species in electron impact. $H^{37}Cl^+$ was not plotted, but followed the expected 3:1 ratio. Isotopic ratios are followed between the $C^{35}Cl^+$ and $C^{37}Cl^+$ signals, as well as between the $CH^{35}Cl^+$ and $CH^{37}Cl^+$ signals. All peak sizes for the CH_2Cl^+ and CH_3Cl^+

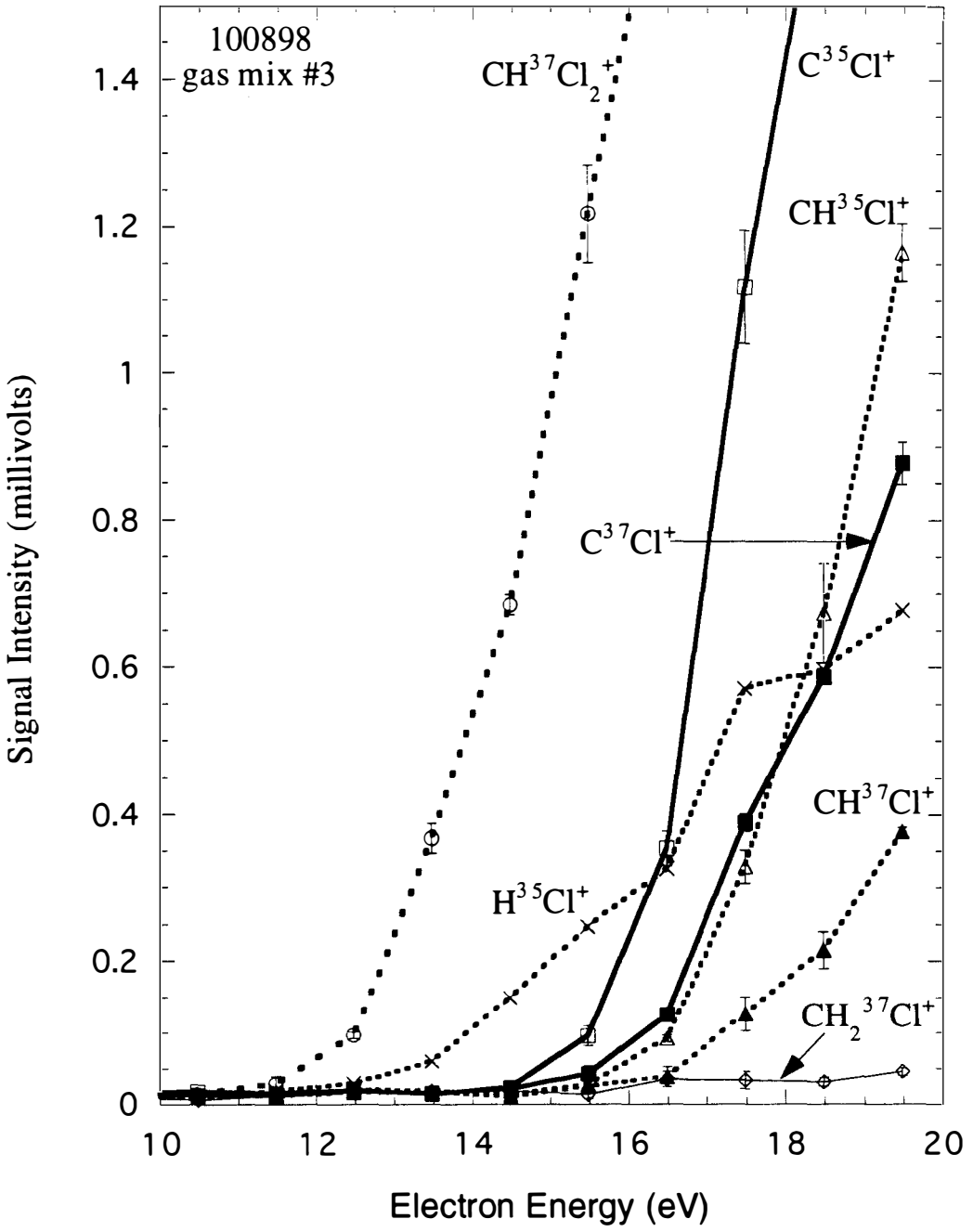


Figure 3.4 Electron Energy Study for $CHCl_3$

species were confined to the order of the noise in the system. The $CH_2{}^{37}Cl^+$ signal shown should be one third of the $CH_2{}^{35}Cl^+$ signal, which should be the largest of the CH_2Cl^+ or CH_3Cl^+ signals. As seen, there is no (or very little) production of CH_2Cl^+ or CH_3Cl^+ from the electron impact ionization of chloroform. Thus, there is very little interference from the fragments produced by ionization of chloroform to the detection of the monochloromethyl radical produced by CVD chemistry.

3.3 Temperature Ramping

In order to understand the temperature dependence of the reactor chemistry, filament temperature studies were conducted on the CH_4, CH_3Cl and $CHCl_3$ gas mixtures described in Section 2.1.6. Filament temperatures from room temperature to over 2000 °C were explored. In order to avoid any gradual effects of changing the filament temperature in one direction, the experiments were conducted by randomly ordering filament temperatures in the range explored. Typically, a complete set of these measurements was made in one day so as to avoid any error from turning the equipment off

and on.

In the filament temperature experiments, the substrate heater was not used. Rather, the reported substrate temperature is due to heating of the substrate by the filament, and the graphs showing filament temperature studies have all been put on the same substrate temperature scale. This was done to eliminate the need for separate filament temperature scale corrections to each graph due to the deterioration of the transmission of the quartz reactor tube. In some cases the state of the tube changed severely over the course of an experiment making pyrometric measurements of the filament temperature unreliable. The plotted filament temperature scale is a linear extrapolation of the filament temperature against the substrate temperature determined using a clean quartz tube. See Appendix A-5 for a list of temperature calibration corrections.

3.3.1 Methane

Figure 3.5 shows the filament temperature dependance of the CH_3^+, CH_4^+ and $C_2H_2^+$ signals from gas mix #1 using 12.5eV electrons for ionization. This figure demonstrates that the acetylene is not

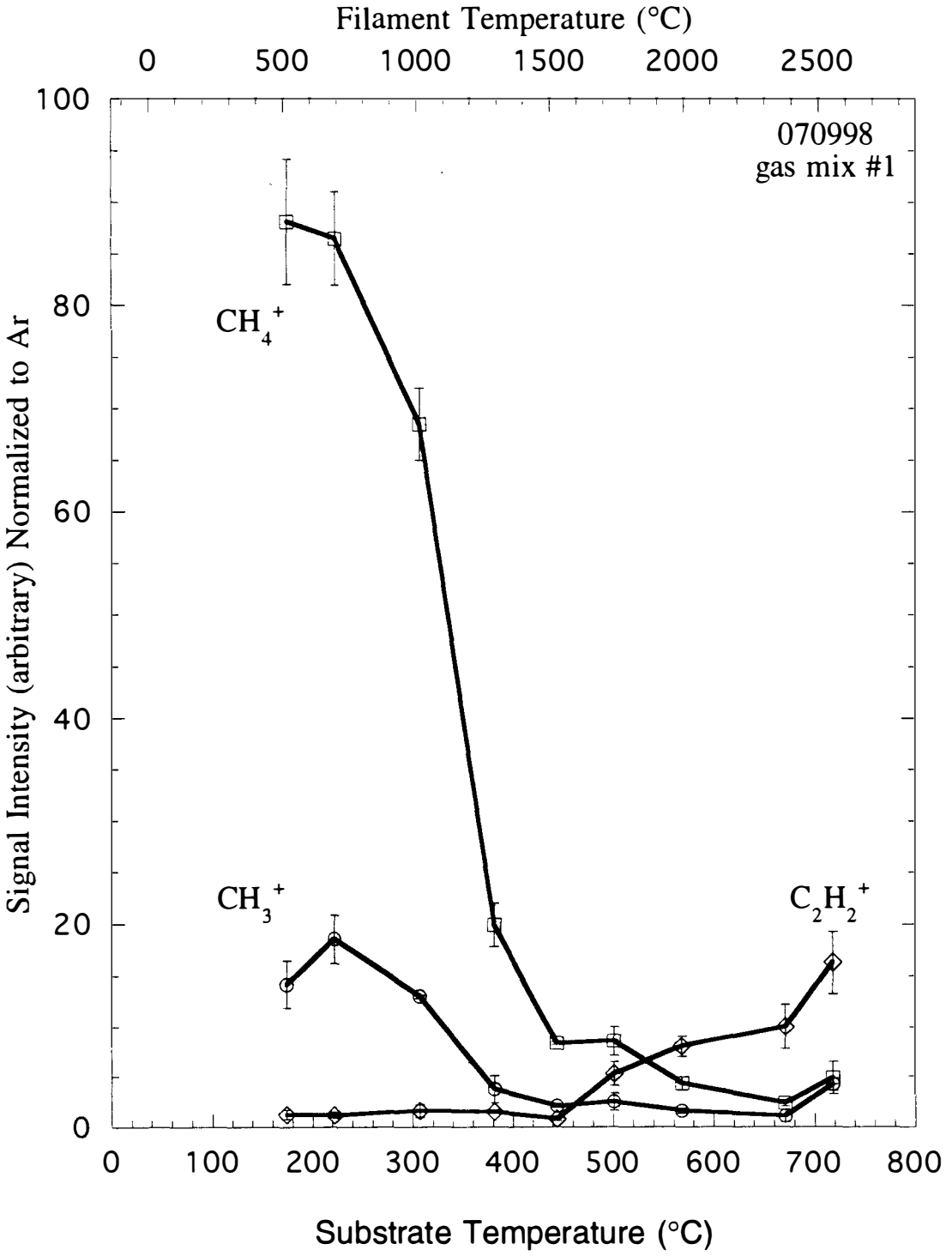


Figure 3.5 Filament Temperature Study of CH_4/H_2 Mix Using 17.5 eV Electrons

produced from gas mix #1 until a substrate temperature around 450 °C is reached. In this case, this production must be due to the production of atomic hydrogen at the filament. In this experiment, the CH_3^+ signal is seen to track the CH_4^+ signal, identifying it as a daughter fragment ion in the electron impact ionization of CH_4. Methyl radical from the growth chamber is masked by the strong fragment ion signal from the electron impact process.

3.3.2 Chloromethane

As shown in Figure 3.6, the results from a filament temperature experiment using gas mix #2 and 16 eV electron energy show little change in the precursor concentration detected until a substrate temperature of 350°C is reached. Prior to this temperature, the CH_3^+ signal follows the precursor signal due to loss of Cl during ionization in the TOF source. At 350 °C, the precursor signal decreases and the HCl^+ and CH_4^+ signals increase sharply. The methane is probably formed by the loss of Cl from CH_3Cl at or near the filament followed by hydrogen abstraction from H_2 as follows.

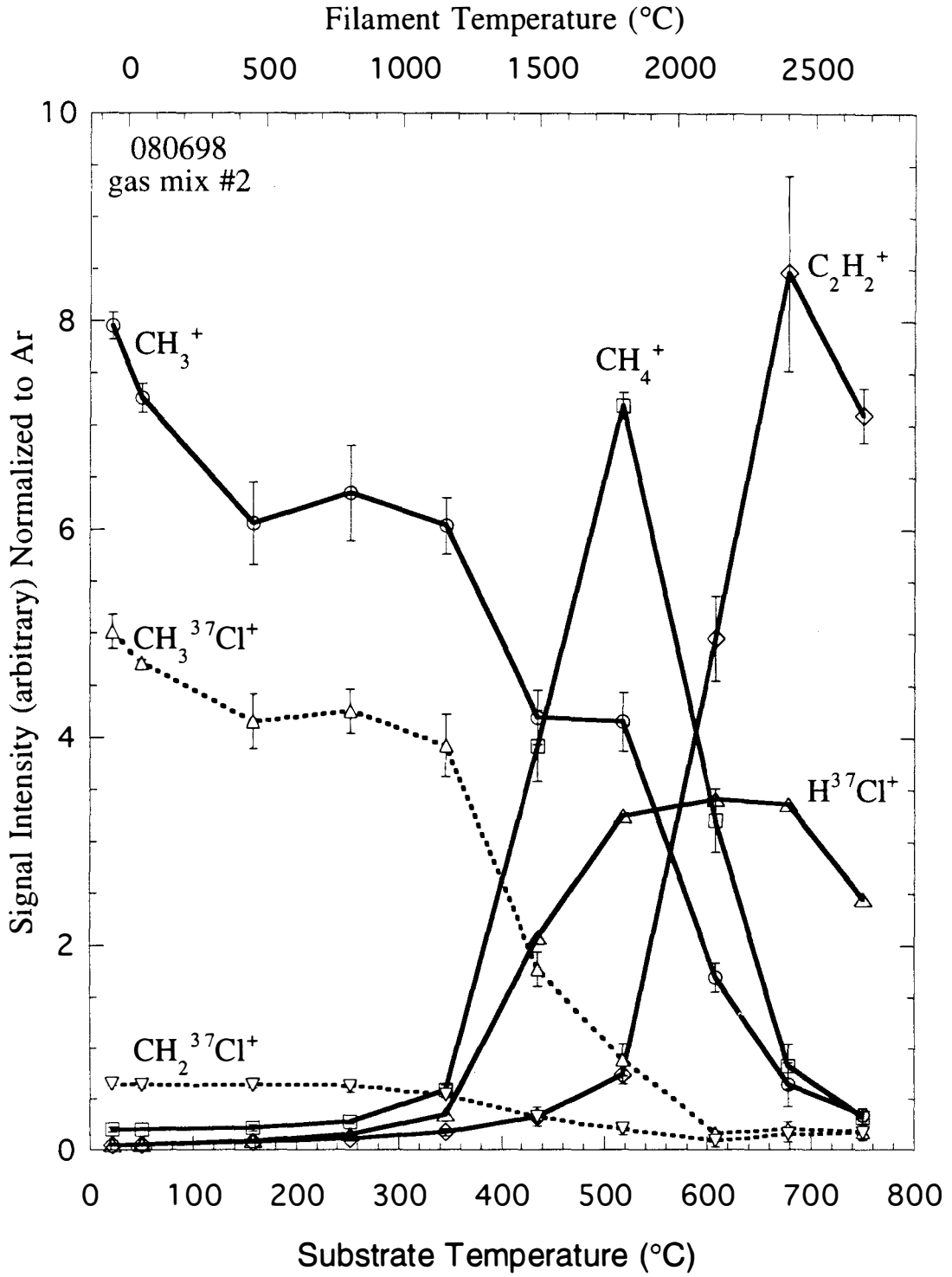


Figure 3.6 Filament Temperature Study of CH_3Cl/H_2 Mix Using 16 eV Electrons

1) $CH_3Cl + heat \rightarrow CH_3^{\bullet} + Cl^{\bullet}$

2) $CH_3^{\bullet} + H_2 \rightarrow CH_4 + H^{\bullet}$

Note that the CH_3^+ signal now contains a contribution due to the loss of hydrogen (in the ionization process) from the methane produced in the thermal process. These trends continue until 500 °C substrate temperature at which point acetylene is formed by the combination of methyl radicals and dehydrogenation (Section 1.4). The production of acetylene and the following sharp decrease in methane signal coincide with the large increase in hydrogen atom production expected from hydrogen dissociation at the corresponding filament temperature.[16,31] Thus, due to the high concentration of hydrogen in the system, the hydrogen radical dominates the chemistry once it is produced. Methyl radical is produced by reactions of H· with CH_3Cl and CH_4 as follows.

3) $CH_3Cl + H^{\bullet} \rightarrow CH_3^{\bullet} + HCl$

4) $CH_4 + H^{\bullet} \rightarrow CH_3^{\bullet} + H_2$

With an abundance of methyl radical around, the production of acetylene as described in Section 1.4 is increased sharply.

3.3.3 Chloroform

Figure 3.7 shows the filament temperature dependence of reactor gas composition for gas mix #3 when using 16 eV electrons for ionization. The precursor is represented in this graph by the $CHCl_2^+$ signals instead of the $CHCl_3^+$ signal because the precursor dissociates easily during electron impact ionization as previously mentioned (Section 3.2.2). The loss of chlorine in these signals is due to electron impact. Thermal processes destroy the precursor completely by 550 °C. The two HCl^+ signals increase rapidly after 300 °C is reached and the chlorine isotopic ratio of about 3:1 is maintained during the ascent. The CH_4^+ signal increases around 400 °C, peaks at 550 °C, and the CH_3^+ signal tracks this behavior. The production of methane and methyl radical is described by the following reaction series

5) $CHCl_3 + \text{heat} \rightarrow CHCl_2^{\bullet} + Cl^{\bullet}$

6a) $CHCl_2^{\bullet} + H_2 \rightarrow CH_2Cl^{\bullet} + HCl$

6b) $CHCl_2^{\bullet} + H_2 \rightarrow CH_2Cl_2 + H^{\bullet}$

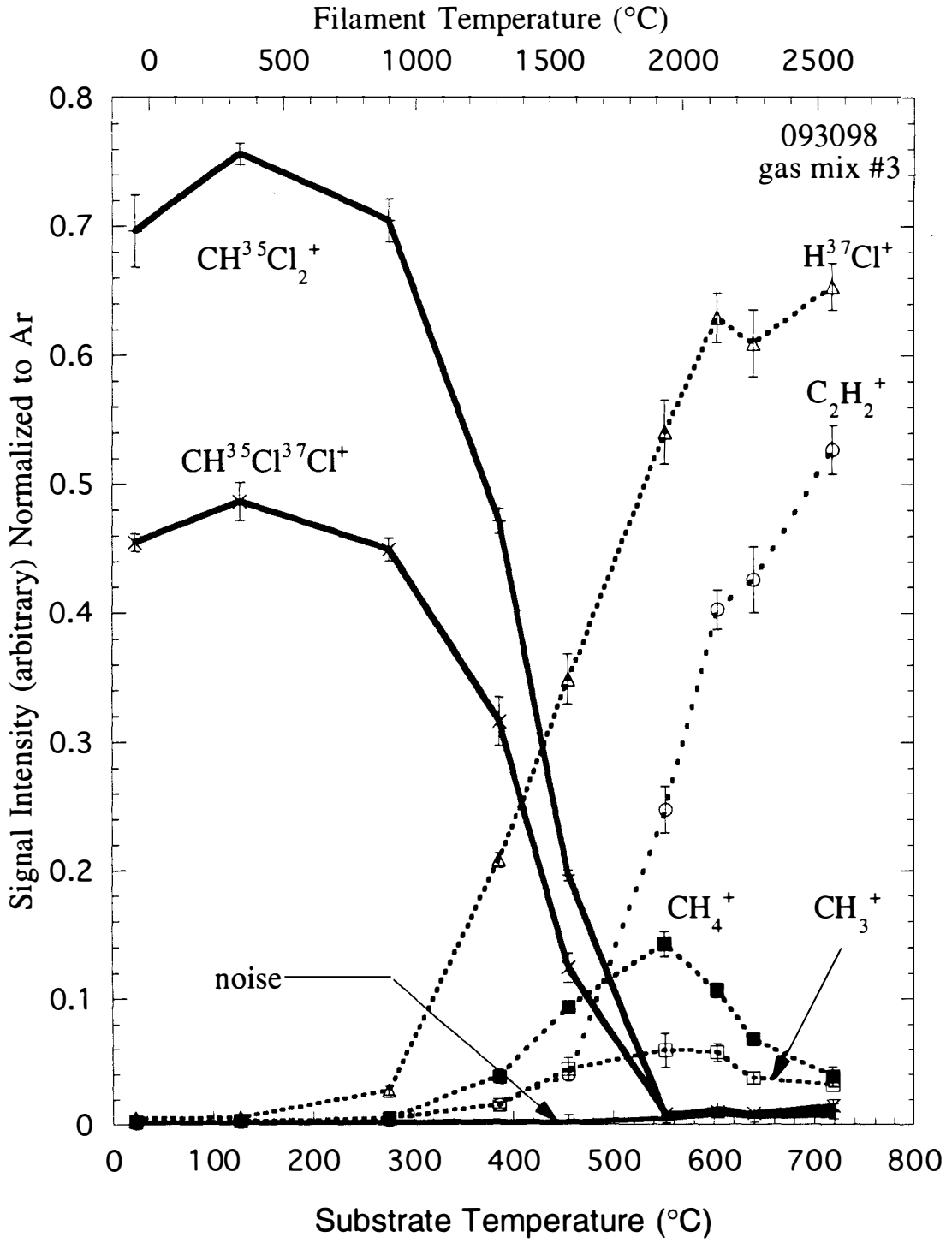


Figure 3.7 Filament Temperature Study of $CHCl_3/H_2$ Mix Using 16 eV Electrons

7) CH_2Cl_2 + heat ---> $CH_2Cl^\bullet$ + $H^\bullet$

8) $CH_2Cl^\bullet$ + H_2 ---> $CH_3^\bullet$ + HCl

9) $CH_3^\bullet$ + H_2 ---> CH_4 + $H^\bullet$

The production of acetylene can be from the recombination of any of the radicals in 5 through 9, followed by loss of HCl, H_2 or Cl_2 as required, a mechanism analogous to that in Section 1.4.

Figure 3.8 shows some less abundant ions in the experiment not shown in Figure 3.7. The CH_3^+ signal is shown for comparison. Note that the waveforms of the chlorinated species all peak prior to the CH_3^+ signal peak. Also, these chlorinated signals disappear as the CH_4^+ and CH_3^+ signals peak. This is expected from the bond strengths involved. In this figure, clear ratios of 1:1 are observed for the CH_3Cl^+ and CH_2Cl^+ signals for each chlorine isotope. These sets of peaks roughly follow the chlorine isotopic ratio. This was not the case seen in the room temperature CH_3Cl electron impact data of Figure 3.2 where the chloromethyl to chloromethane ratios were observed to be on the order of 1:10. In Figure 3.4, no significant signal was observed for either species starting with $CHCl_3$. This ratio change indicates the production of the monochloromethyl

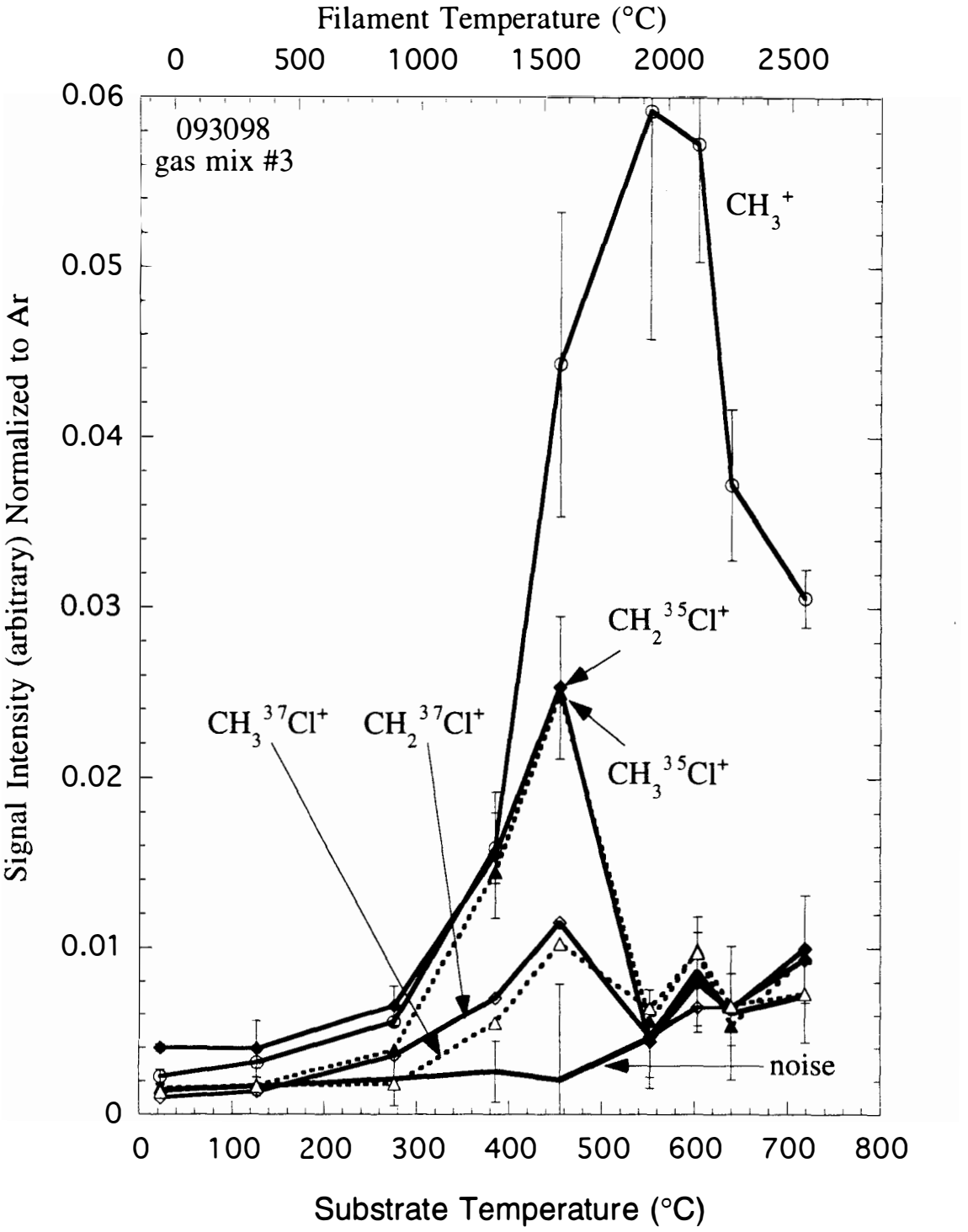


Figure 3.8 Filament Temperature Study of $CHCl_3/H_2$ Mix
Smaller Signals not shown on Figure 3.7

radical in the gases sampled from the substrate surface in the growth chamber. This provides the first known detection of CH_2Cl· which has been predicted to play a role in CVD diamond growth (Section 1.6). Figure 3.9 is a repeat of the filament temperature study seen in Figure 3.7 but using 20 eV electrons for ionization to improve the signal sizes observed and with smaller temperature intervals taken near the temperatures of interest. The signals plotted follow almost exactly the same behavior as for the 16 eV electron case (Figure 3.7), but are larger.

One notable exception is the amplitude of the CH_4^+ peak relative to the C_2H_2 signal. In Figure 3.6, the methane signal peaks just as the acetylene signal begins to increase and is much larger than the acetylene signal is at that point. In Figure 3.7, the methane signal has peaked while still smaller than the acetylene signal. Also, in Figure 3.7, the methane signal peaks as the acetylene signal reaches about half of its maximum value. In Figure 3.9, the methane signal peak is larger that the acetylene signal, but still peaks as the acetylene signal reaches about half its maximum value. The difference between figures 3.7 and 3.9 may be due to the magnitude of the electron ionization cross sections and the rate at which they

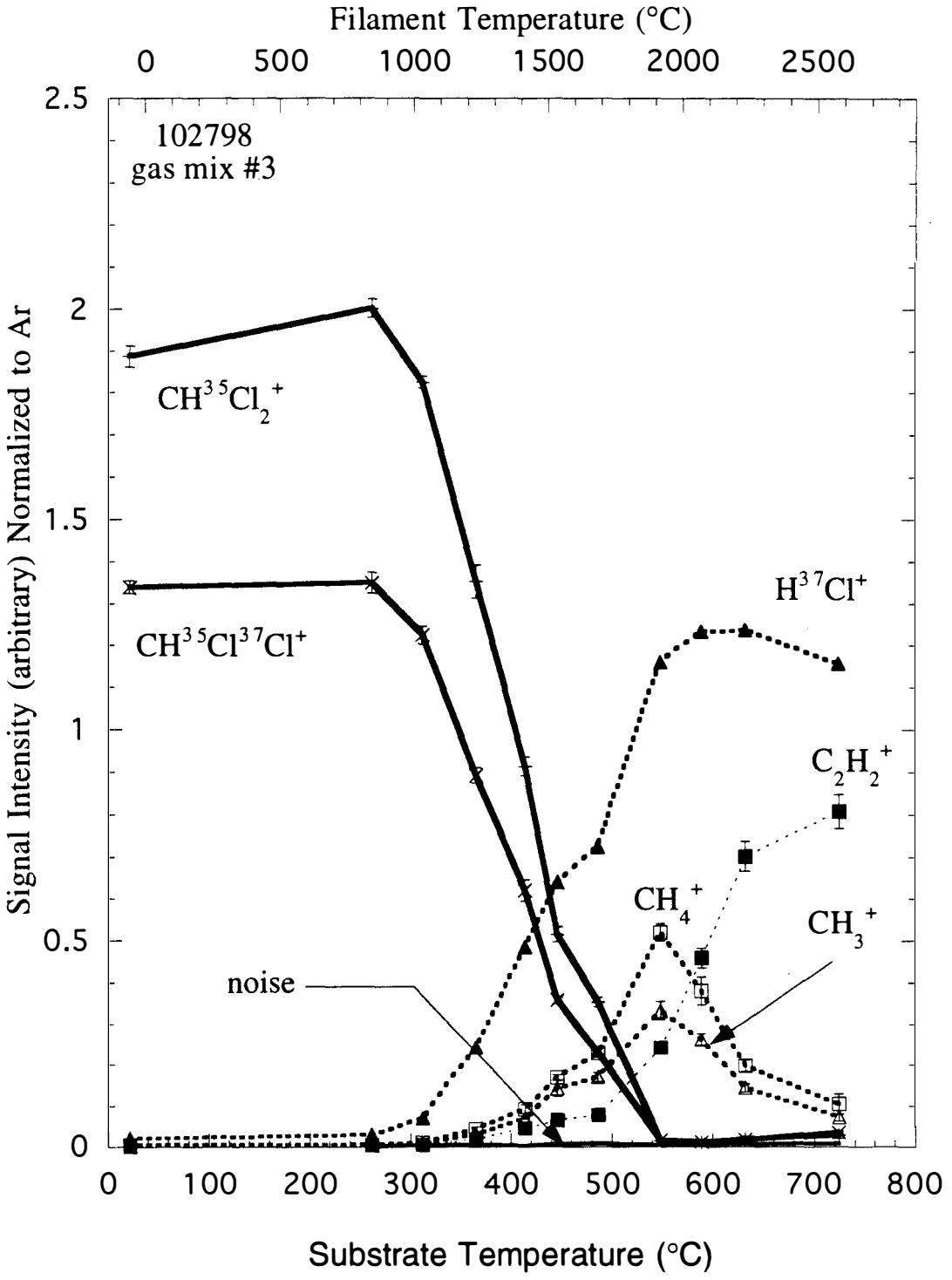


Figure 3.9 Filament Temperature Study of $CHCl_3/H_2$ Mix Using 20 eV Electrons

change for acetylene and methane with varying electron energy. The difference between Figure 3.6 and 3.7 must be attributed to the chemistry that is taking place in the growth chamber.

Figure 3.10 shows smaller peaks not shown in Figure 3.9 keeping the CH_3+ peak to relate the scales. A y-axis enlargement of Figure 3.10, seen in Figure 3.11, shows the electron impact contribution to the $C^{37}Cl$+ and $CH^{37}Cl$+ signals. The ratio of these signals at room temperature matches very well to the ratio of the same signals in Figure 3.4 at 20 eV. In Figure 3.11, the $C^{37}Cl$+ and $CH^{37}Cl$+ signals represent the $C^{37}Cl$+ and $CH^{37}Cl$+ fragments from the electron impact processes. At higher temperatures they represent $CH_2{}^{35}Cl$· and $CH_3{}^{35}Cl$ produced by the chemical processes in the growth chamber. This is reflected in the $CH_2{}^{37}Cl$+ and $CH_3{}^{37}Cl$+ signals. Once again, the $CH_2{}^{37}Cl$+/$CH_3{}^{37}Cl$+ ratio indicates that the monochloromethyl radical was detected. However, if the data had been taken at higher electron energy, these signals may have been lost due to the larger expected signal size.

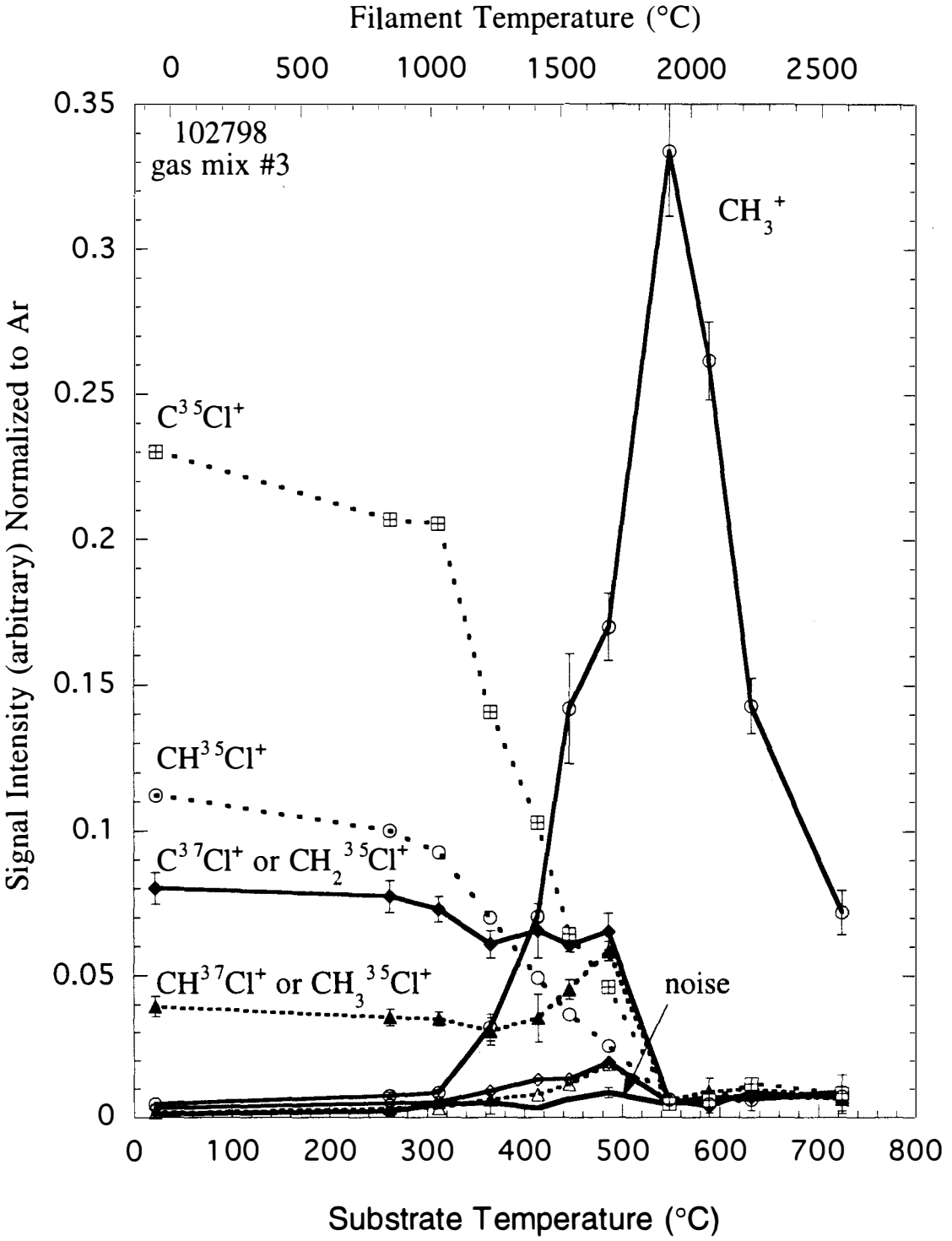


Figure 3.10 Filament Temperature Study of $CHCl_3/H_2$ Mix
Smaller Signals not shown on Figure 3.9

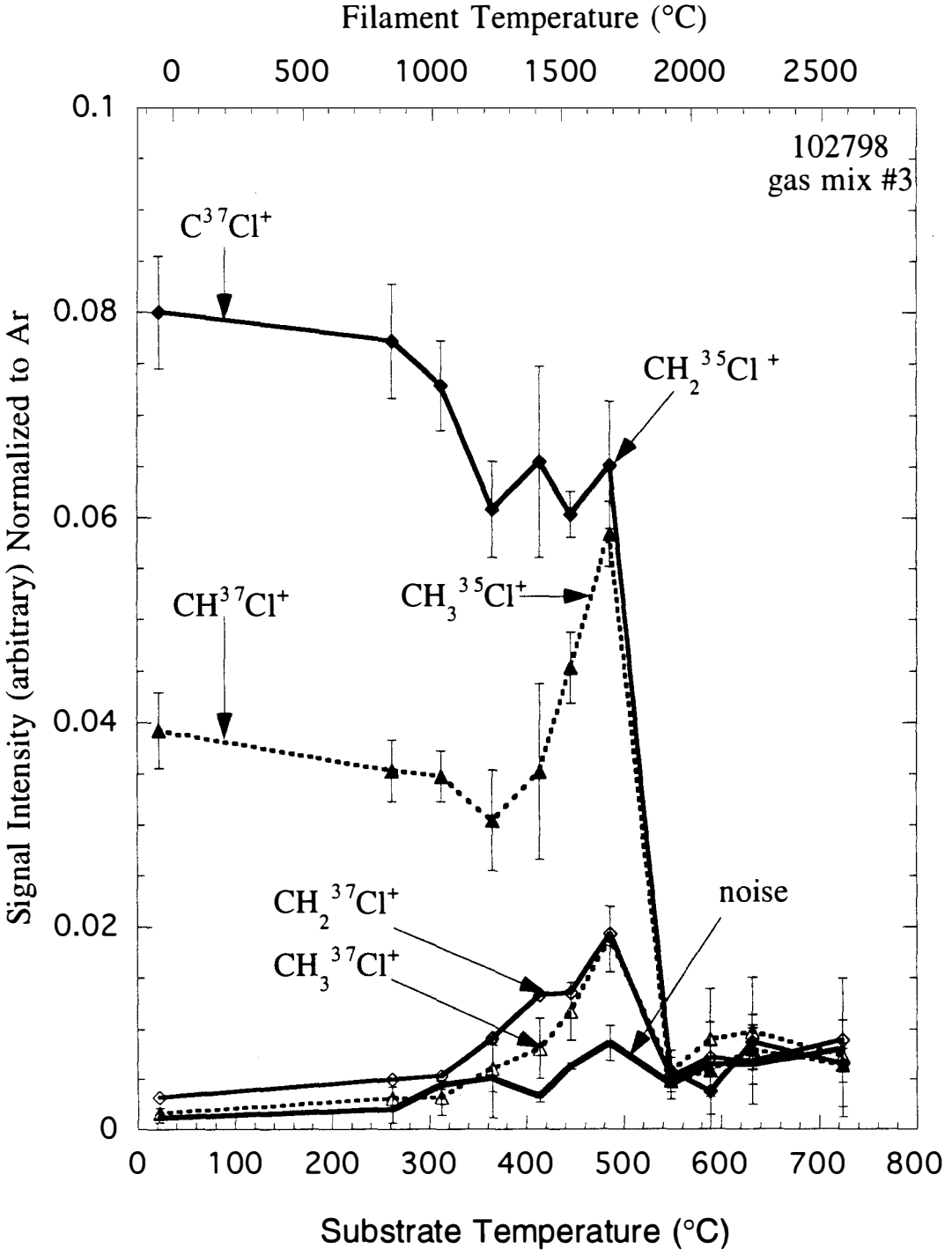


Figure 3.11 Filament Temperature Study of $CHCl_3/H_2$ Mix
Smaller Signals seen on Figure 3.10

3.4 Substrate Temperature Dependencies

The dependence of mass spectrum peak heights while varying the substrate temperature, but holding the filament temperature constant was also examined. If a species had been shown to be substrate temperature dependent, then the production or consumption of that species could be tied to a surface phenomenon. Data were obtained for constant filament temperatures of 1225, 1297, 1425, 1486, 1546 and 1725 °C with CH_3Cl. In this set of experiments, the filament temperature was held constant while the substrate temperature was varied by use of the substrate heater. Figure 3.12 shows the data set taken at 1425 °C. The only dependence seen in this set of experiments matches the dependence seen in the filament temperature experiments in Section 3.3 and can be attributed to the leads of the substrate heater glowing as hot as the filament. Figure 3.6 shows similar behavior for the species plotted. This closely follows the results obtained by Corat *et al* who showed no substrate dependence on species other than $CH_3\cdot$ in a similar experiment.[37]

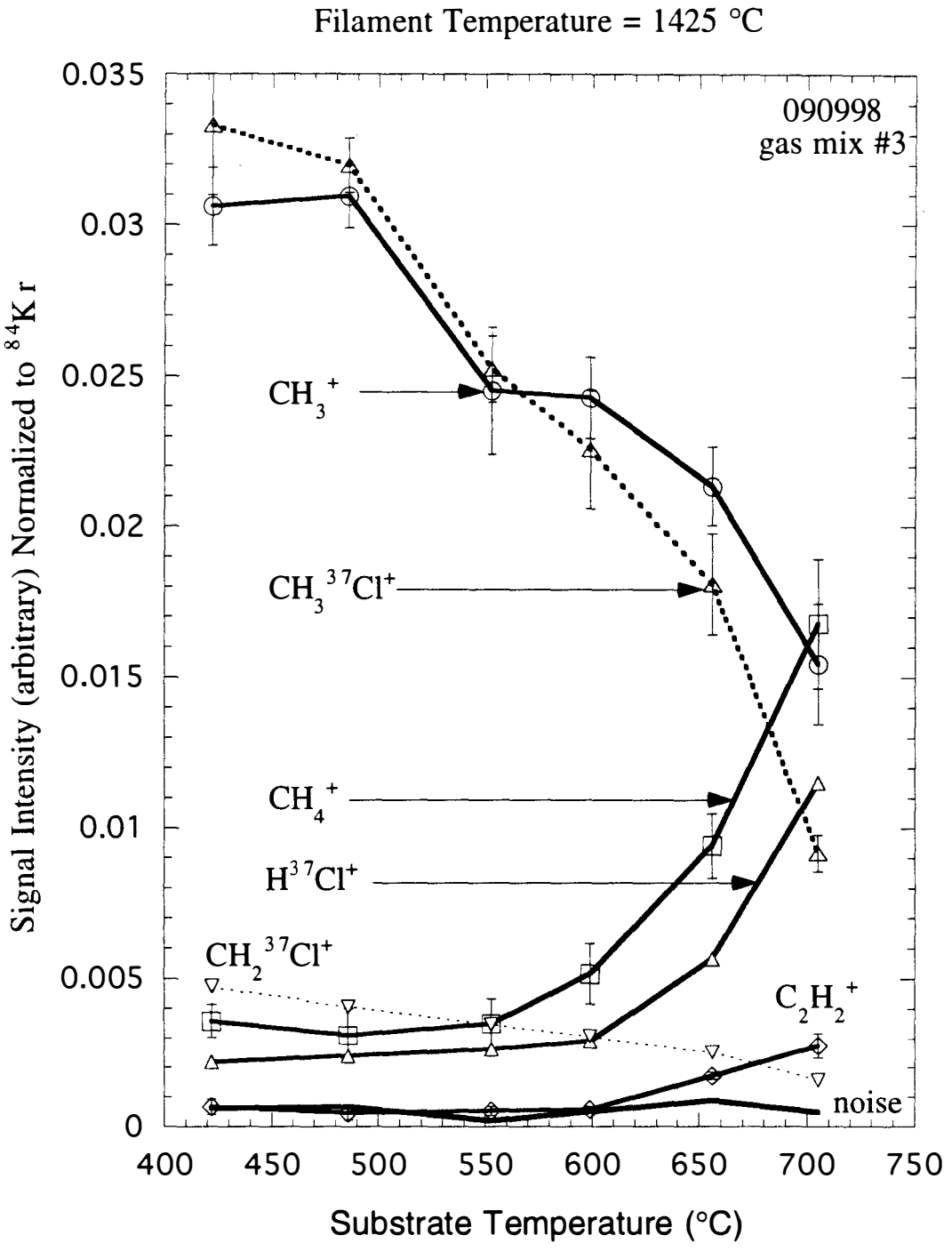


Figure 3.12 Substrate Temperature Study of CH_3Cl/H_2 Mix Using 16 eV Electrons

3.5 Film Growths

Film growths were completed in order to show that the system did in fact grow diamond from chlorinated precursors. These were analyzed by use of SEM and Raman spectroscopy. The substrate surface was prepared with a scratched and an unscratched area (half of the growth surface was scratched). Comparisons between scratched area film coverage, unscratched area nucleation density and diamond quality were obtained from SEM images. Diamond quality was then verified using micro-Raman spectroscopy. Appendix A-6 shows the results of these growths. Gas mix one was used as the for the first film grown. This film was completed as a non-chlorinated precursor benchmark. Film growth at filament temperatures of 1225, 1320, 1546, and 1725 °C using CH_3Cl precursor and a substrate temperature of 700 °C was attempted. After it was seen that only ball like diamond was produced, and that only at the higher two filament temperatures, another growth was attempted using a filament temperature of 1700 °C and a substrate temperature of 800 °C. This growth resulted in complete coverage of

the scratched substrate area, but still only ball-like diamond was grown.

Two diamond films were grown using $CHCl_3$ to illustrate the effect of the monochloromethyl radical in diamond growth. In each growth, well-faceted diamond was grown, and no ball-like diamond was seen in the SEM images. The first growth was subjected to a pretreatment period of ten minutes at 450 °C substrate temperature (1540 °C filament) with $CHCl_3$. The temperature used in the pretreatment corresponds to the maximum production of the CH_2Cl radical observed in the filament temperature studies (Section 3.3). Prior to the pretreatment, only hydrogen gas was admitted into the system. The second $CHCl_3$ growth had no such pretreatment applied; instead, the filament temperature was raised to growth temperature in a hydrogen atmosphere and then the $CHCl_3$ was admitted. The pretreated growth produced a nucleation density of 44,300 sites/mm^2 on the unscratched side (Figure 3.13), and covered 100% of the scratched side (Figure 3.14). The untreated growth produced 4,330 sites/mm^2 on the unscratched side (Figure 3.15) and 70% coverage of the scratched side (Figure 3.16). The figures shown are the first images taken from each area. The nucleation density was

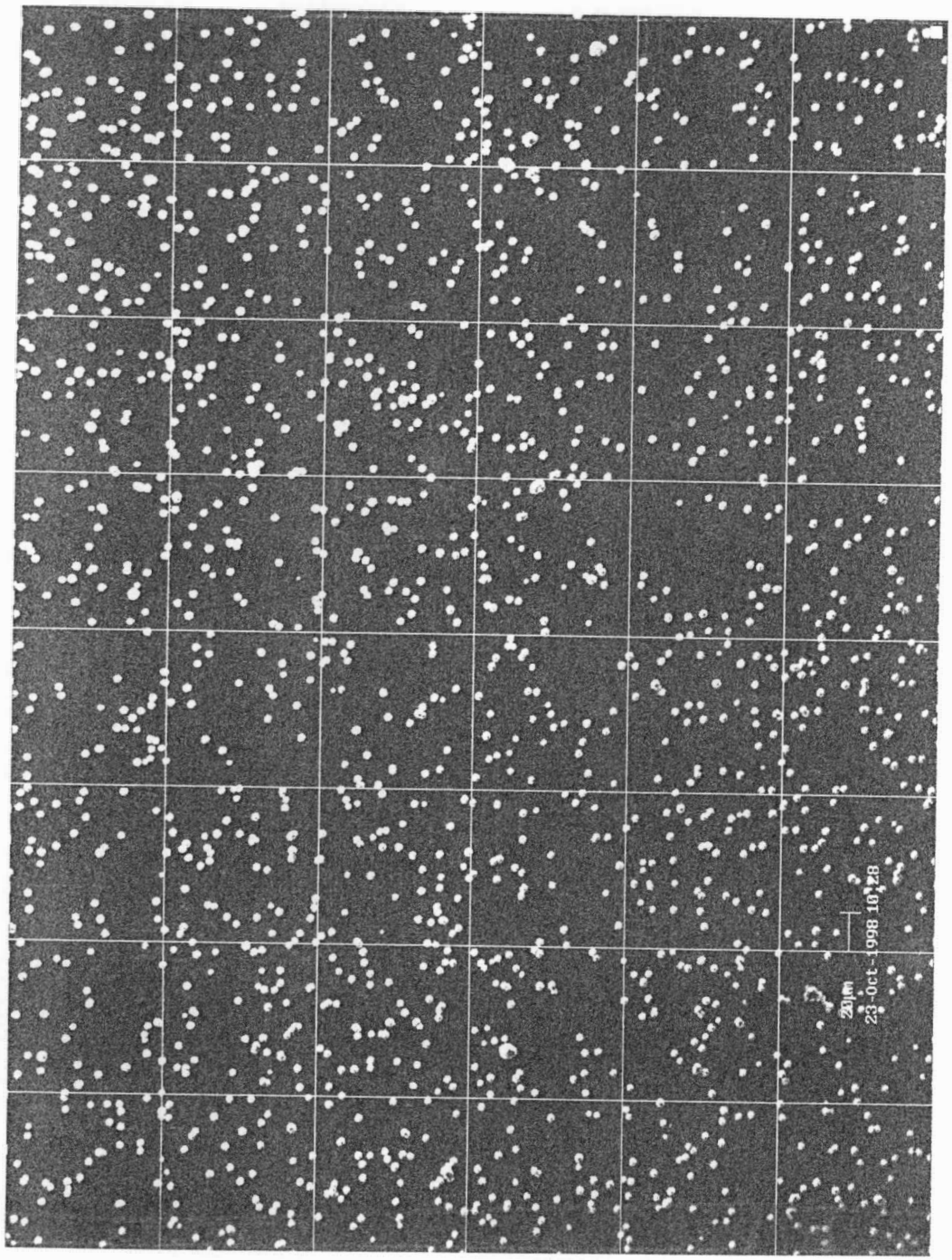


Figure 3.13 Pretreated Substrate Unscratched Area

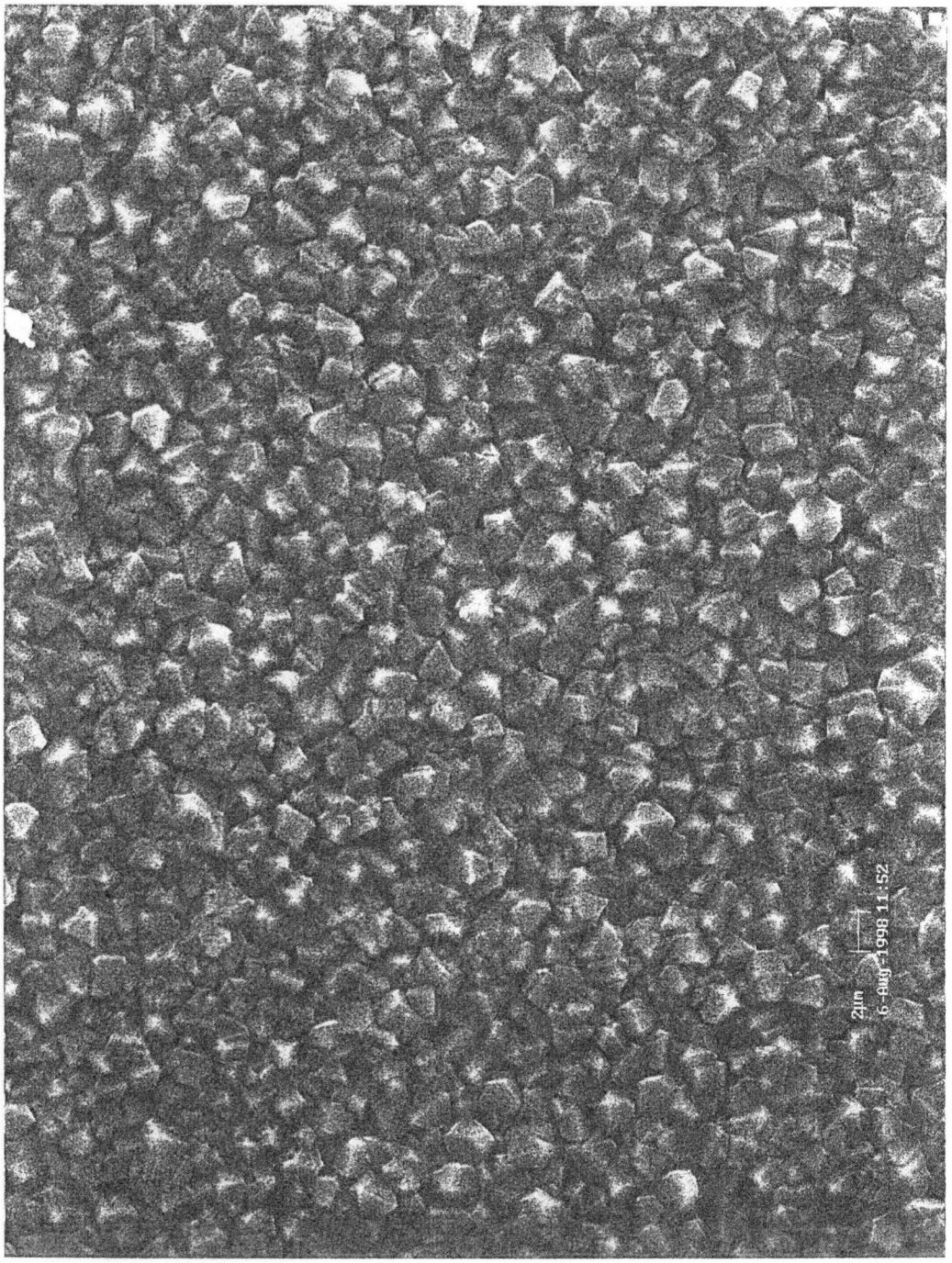


Figure 3.14 Pretreated Substrate Scratched Area

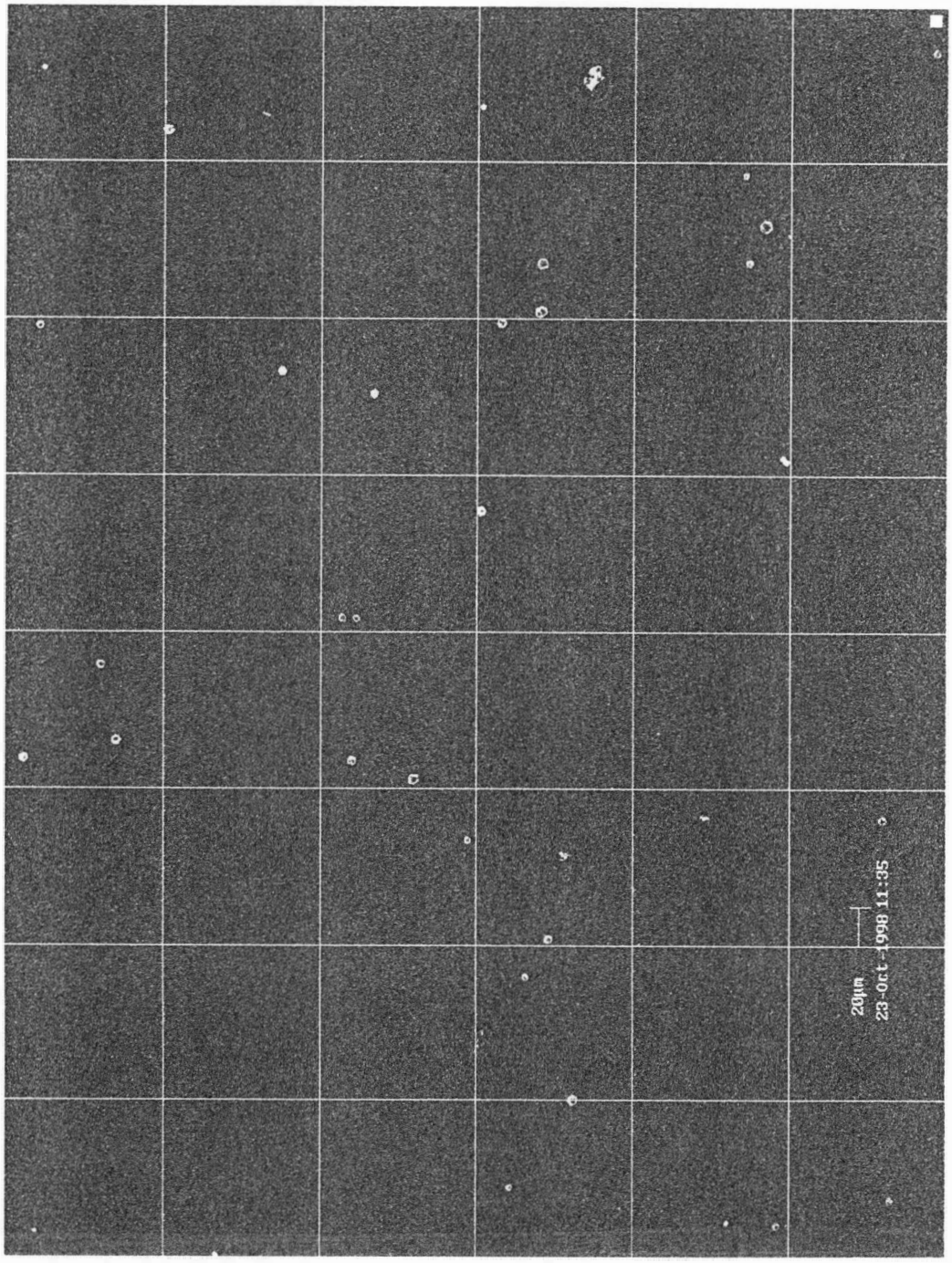


Figure 3.15 Untreated Substrate Unscratched Area

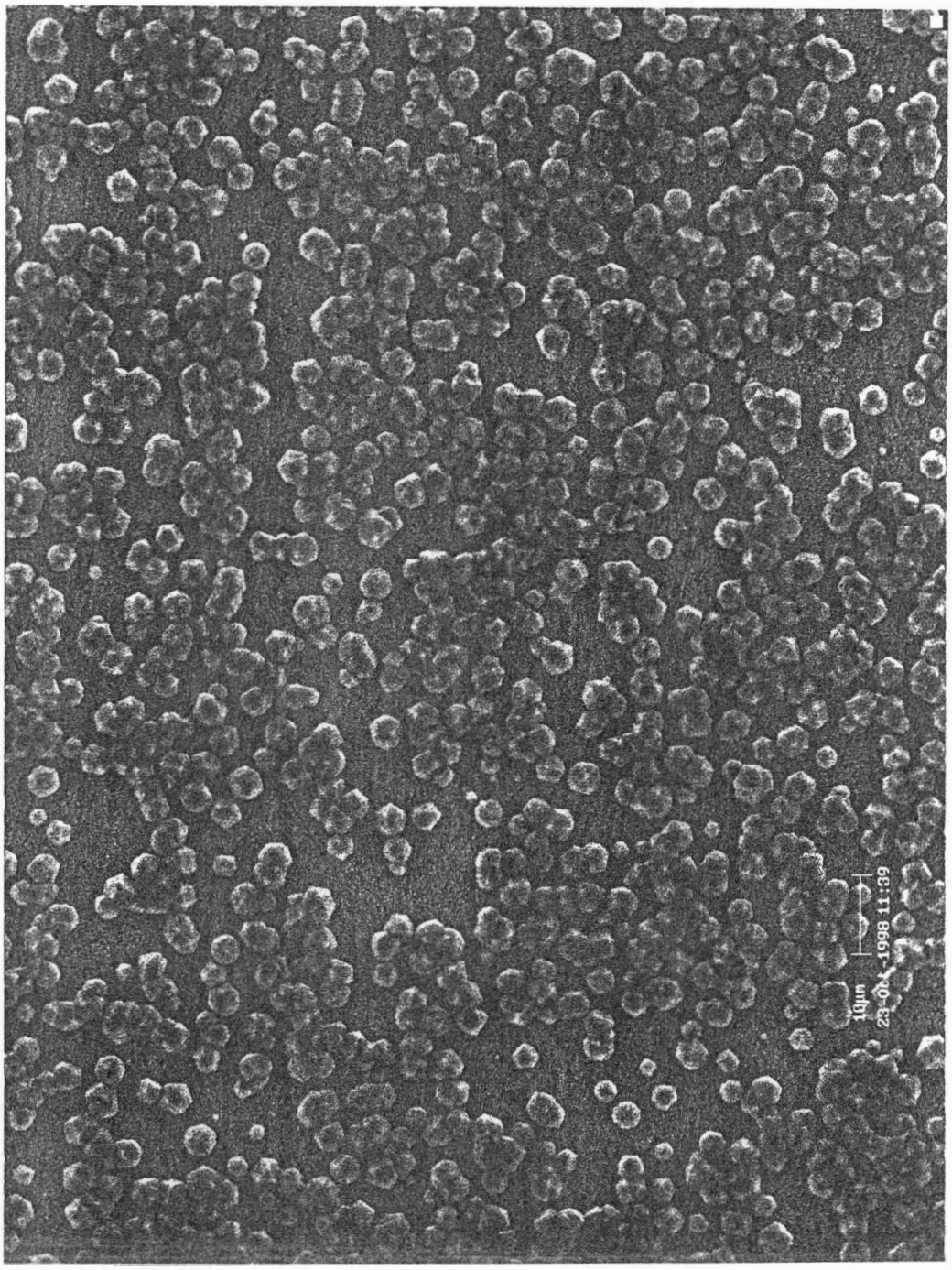


Figure 3.16 Untreated Substrate Scratched Area

calculated by manually counting the seeds in three of the grid squares and multiplying by eight to provide an estimate of the 24 grid squares which were available. When appropriate, all seeds in the 24 grids were counted. Ten separate images were counted and averaged, and the result scaled to 1 mm^2 to produce the nucleation density reported. The difference in nucleation density reported by Wu *et al* can be explained in terms of this experiment.[11] In that experiment, diamond nucleation density was measured as a function of precursor gas being present or not present as the filament was heated from room temperature to growth temperature. The nucleation density was reported higher with the precursor present. This is due to crossing the temperature range reported in this work, thereby producing the monochloromethyl radical for a period of time. It is likely that other researchers have not noticed this radical because they have not looked at what happens to the precursors as the filament temperature is raised to growth temperature and because it would not be seen using high energy electrons to ionize the samples taken.

3.6 Raman

A Raman spectrum of the film grown on the pretreated substrate scratched area is shown in Figure 3.17 and that of the untreated substrate scratched area in Figure 3.18. The Raman spectra were taken on the scratched sides of each sample. The peak at 1333.69 wavenumbers in the Raman spectrum (Figure 3.17) of diamond grown with the pretreatment indicates good quality diamond was grown. Figure 3.18, the spectrum of the untreated growth, shows that diamond was grown. The shift further away from the 1332 wavenumber peak of natural diamond indicates that the quality of the diamond is reduced in this sample. This may have been in part to the incomplete coverage of this sample.

Finally, it should be noted that when the system was left for any length of time more than about 10 minutes at the 450 °C substrate temperature condition with $CHCl_3$ precursor gas, the quartz tube quickly became blackened by an unknown deposit. An attempt to do a substrate temperature dependence study under these conditions resulted in a darkening of the tube until it looked like

Figure 3.17 Raman Spectrum of Pretreated Growth

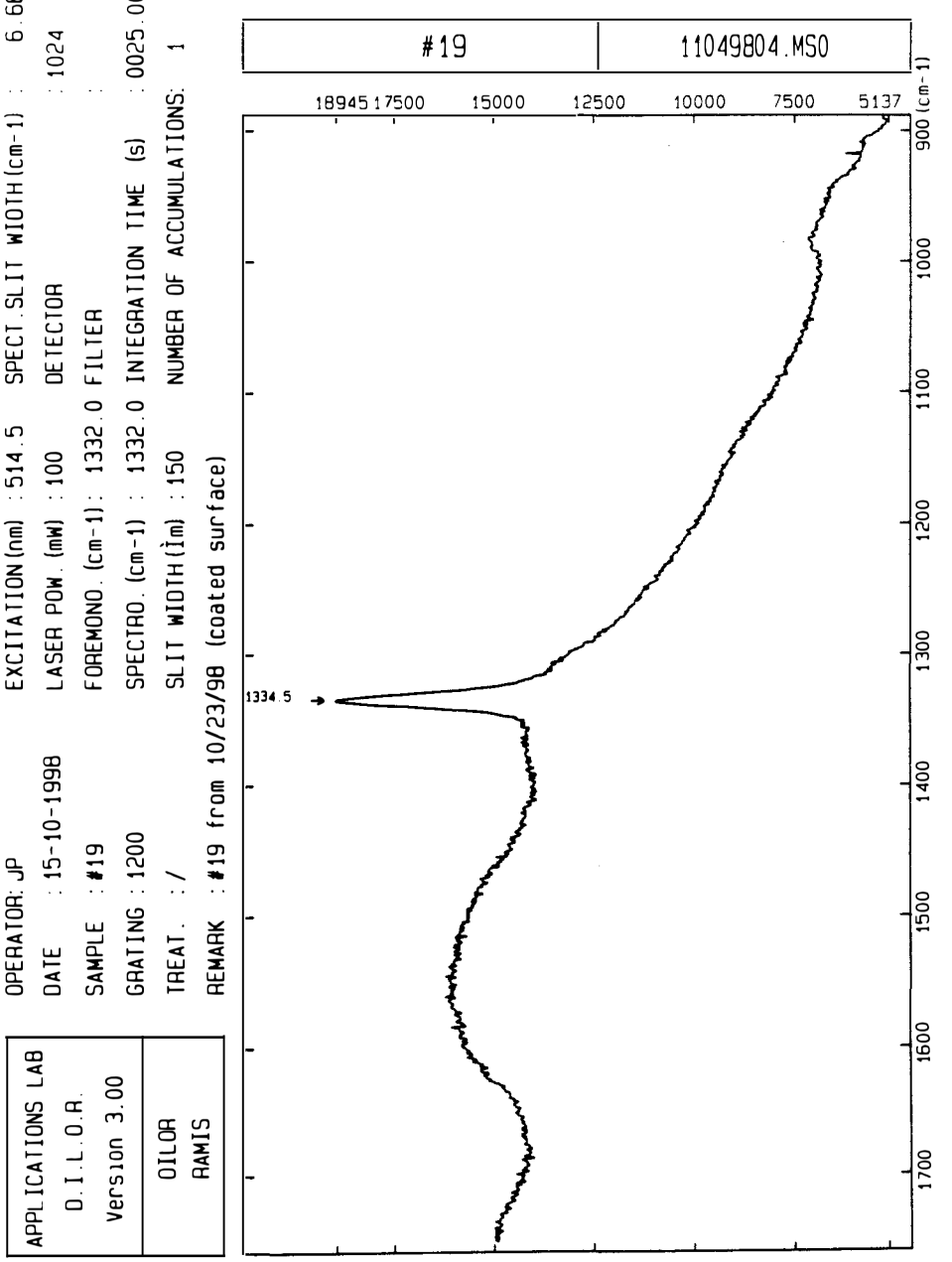


Figure 3.18 Raman Spectrum of Untreated Growth

welders glass. There was a working substrate in the chamber at the time, and a Raman spectrum of the surface was seen in figure 3.19. This unknown film may be a graphitic carbon film. Several researchers have suggested that diamond is produced by the action of hydrogen radicals on sp^2 carbon.[13, 38, 39]

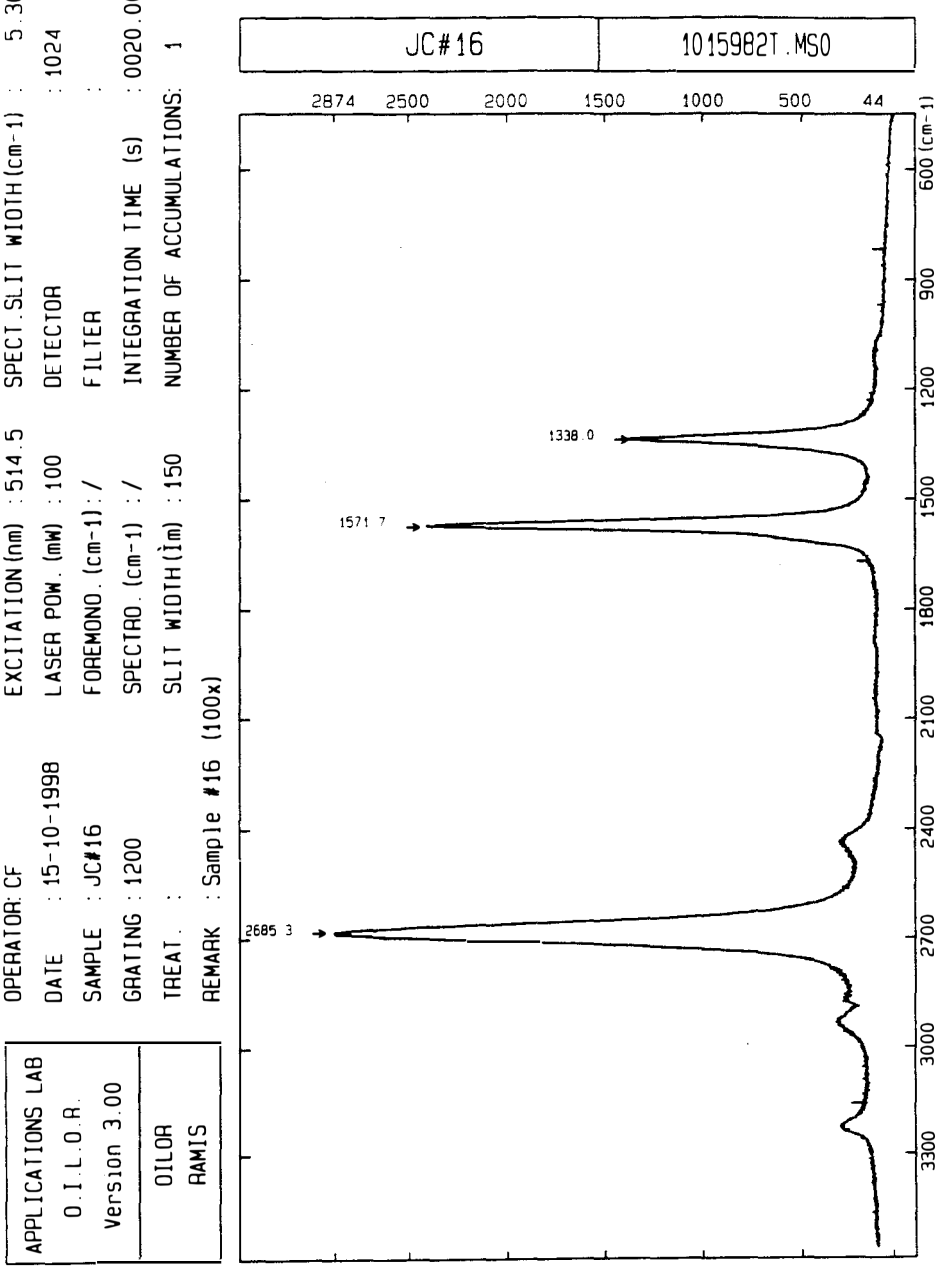


Figure 3.19 Raman Spectrum of Substrate with Unknown Deposit from 450 °C Substrate Temperature

4.0 Conclusions

The studies completed have provided new data on diamond growth. Researchers have shown that chlorinated precursors enhance diamond growth, and have predicted that the monochloromethyl radical would play an important role in the process. The CH_2Cl radical has now been detected from the results of electron impact and filament temperature studies using chloroform in a hot filament diamond growth reactor. Higher diamond nucleation density has been demonstrated from a pretreatment under the conditions which produce the monochloromethyl radical. The results of this study fit well with the predictions of other researchers.

The detection of the radical was made possible by use of LEEII TOFMS. At higher electron energies the radical signal would be masked by strong contributions from fragmentation products in the ionization chamber. The choice of precursor is also important. There is no interference for the monochloromethyl signal from the electron impact fragmentation of chloroform. Any signal seen for this radical must come from the growth processes. With the use of chloromethane as a precursor, the monochloromethyl ion is produced

from electron impact fragmentation and this fragment masks the detection of the radical from the growth processes. This does not mean that monochloromethyl radical does not exist in the growth process with chloromethane precursor, but only that it would not be detectable in the system used by LEEII TOFMS.

The appearance and disappearance of the monochloromethyl signal in the filament temperature studies over a temperature range of only a few hundred degrees indicates that either the radical does not survive the higher temperatures required for diamond growth or that the chemistry changes at the higher temperatures, preventing the production of or enhancing the destruction of the radical. However, knowing this range of temperatures provides a window for further investigation. Substrates can now be pretreated, improving nucleation density on the surface and decreasing the time needed to reach 100% film coverage. This increased nucleation density may be the result of an unknown material that was deposited on all surfaces in the reactor during a study at the filament temperature which produces the chloromethyl radical. Further study is needed on this deposited material.

The system on which these studies was conducted has been

improved by the use of new software which allows fast data extraction from multiple data sets, by the added LEEII capability which allows use of threshold ionization techniques for species determination, and by addition of a bubbler system which allows liquid precursors to be introduced into the system.

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Appendix

A-1 Bond Strengths

Hong *et al* printed the following table.[26]

Bond type	Bond strength (kcal/mol)	
H - H	104	
H - Cl	103	
H - CH_3	105	
H - $CHCl_2$	101	
H - CCl_3	96	
Cl - CH_2Cl	78	
Cl - $CHCl_2$	79	
Cl - CCl_3	73	
Cl - Cl	59	
Cl - CH_3	84	reference 21

A-2 Experimental Procedure (TDS524A)

1. Pump system down to operating pressure
2. Choose and setup gas mixture (gas correction factor)
3. Setup the oscilloscope (mmddyy??.wfm for file name)
4. Fill the system with the gas of choice
5. Choose the desired parameter (temperature or electron energy)
6. Wait for stable temperature if required (<1 °C/5 min)
7. Hit acquire on scope to start acquisition
8. Wait for 2500 acquisitions (make note of parameter and file number)
9. Save file as mmddyy??.wfm (?? represents sequential file numbering)
10. Repeat 7-9 at least 3 times
11. Repeat 5-10 until experiment is finished
12. Begin system shutdown by turning off heat
13. Turn off gas input and vacuum pumps
14. Transfer .WFM files to computer using MOVEWFM command
15. Start MASPEC, select a file for mass calibration
16. Calibrate mass axis and check several masses to be sure

17. Enter automatic data mode to produce compilation file

18. Start COMPSORT, select the compilation file

19. Transfer output of COMPSORT to computer with spreadsheet

20. Open spreadsheet file and produce graph

21. Analyze graph and decide on next experiment

A-3 Appearance Potentials

Positive Ion	Parent Species	This Work* (eV)	Published Value[33] (eV)
H^+	H_2	18.6	17.3, 18.0[29]
H_2^+	H_2	15.9	15.4
Ar^+	Ar	15.8	15.8
Kr^+	Kr	14.1	14.0
N_2^+	N_2	15.1	15.6
CH^+	CH_3Cl	- - - -	22.5
CH^+	$CHCl_3$	- - - -	23.9
CH_2^+	CH_4	20.4	15.2
CH_2^+	CH_3Cl	15.1	14.6
CH_3^+	CH_4	13.5	14.3
CH_3^+	CH_3Cl	14.4	13.9
CH_4^+	CH_4	11.2	12.7
HCl^+	CH_3Cl	15.0	- - - -
HCl^+	$CHCl_3$	13.0	- - - -
CCl^+	$CHCl_3$	16.0	- - - -
$CHCl^+$	CH_3Cl	14.0	- - - -
$CHCl^+$	$CHCl_3$	16.4	17.5
CH_2Cl^+	CH_3Cl	12.3	13.0
CH_2Cl^+	$CHCl_3$	16.1	- - - -
CH_3Cl^+	CH_3Cl	12.0	11.3
$CHCl_2^+$	$CHCl_3$	12.6	- - - -
$CHCl_3^+$	$CHCl_3$	12.4	- - - -

*These values were determined from a linear regression of the points of the trace in the electron impact study for the species of interest which were off the baseline, excluding the point closest to but off of the baseline.

A-4 Ionization Potentials

By Species Type

	Species	Ionization potential (eV)
Atom	H	13.6
	He	24.6
	C	11.3
	N	14.5
	O	13.6
	Ne	21.6
	Cl	13.0
	Ar	15.8
	Kr	14.0
Mol	H2	15.4
	OH	11.1
	CH2	10.4
	CH3	9.8
	CH4	12.6
	C2H2	11.4
	N2	15.6
	O2	12.1
	OH	13.2
	H2O	12.6
Cl	HCl	12.7
	Cl2	11.5
	CCl3	8.8
	CHCl2	9.3
	CCl4	11.5
	CHCl3	11.4
	CH2Cl2	11.4
	CH3Cl	11.3
	CH2Cl	9.3

By ionization potential

Species	Ionization potential (eV)
CCl3	8.8
CH2Cl	9.3
CHCl2	9.3
CH3	9.8
CH2	10.4
OH	11.1
C	11.3
CH3Cl	11.3
C2H2	11.4
CHCl3	11.4
CH2Cl2	11.4
Cl2	11.5
CCl4	11.5
O2	12.1
CH4	12.6
H2O	12.6
HCl	12.7
Cl	13.0
OH	13.2
H	13.6
O	13.6
Kr	14.0
N	14.5
H2	15.4
N2	15.6
Ar	15.8
Ne	21.6
He	24.6

A-5 Pyrometer Corrections

Quartz tube correction:

actual temperature = -13.254 + 1.0344 * measured temperature
R = .99981

Rhenium brightness correction:

actual temperature = -76.187 + 1.1496 * measured temperature
R = .99986

Pyrometer calibration correction:

actual temperature = -46.619 + 1.1086 * measured temperature
R = .9996

Fit of substrate / filament temperatures with clean quartz tube:

filament temperature = 6.7647 + 2.844 * substrate temperature
R = .9957

Final correction form:

filament temperature = -147.5 + 1.3183 measured temperature

filament temperature (scale) = -138.6 + 3.75 substrate temperature

A-6 Growth Table

Table of growth observations. Tf = filament temperature. Ts = substrate temperature

precursor	Tf	Ts	growth	coverage	substrate number	growth time	comments
CH_4	2020	850	faceted	100%	2	35 h	
CH_3Cl	1225	700	no	---	12	11 h	
	1320	700	no	---	15	7 h	
	1546	700	ball	---	13	13 h	sparse
	1725	700	ball	90%	14	11 h	
	1706	800	ball	100%	17	9 h	
$CHCl_3$	2021	750	faceted	60%	18	8 h	not pretreated
	2021	750	faceted	100%	19	8 h	pretreated

A-7 MASPEC

```
DECLARE FUNCTION mainhelp! ()
DECLARE FUNCTION helpgraphics! (msf!)
DECLARE FUNCTION stdev! (mass1!, mass2!, average!)
DECLARE FUNCTION sumrange! (begin!, ending!)
DECLARE FUNCTION baslinavg! (peak!)
DECLARE FUNCTION peakheight! (peak!)
DECLARE FUNCTION mainmenu! (y!)
DECLARE FUNCTION setup! ()

10  'initialization  block
errorflag1 = 0  '1 means error checking is on  0 means off

maxintmass = 50    'maximum number of masses of interest
maxautosize = 120  'maximum number of files to handle in automatic
mode
maxarraysize = 15050
maxrecord = maxarraysize
zoom = 1
psv = 0      'pixel shift value
scrnh = 300 'screen height
scrstrt = 0
flagspi = 1
cursor = 100
time1 = -1
time2 = -1
mascalflag = 0
fileout1$ = "&  #####  "
mask1$ = "Time     = ##.####^^^^ channel = ##### "
mask2$ = "Mass     = ###.#### "
mask3$ = "Signal  = ##.####^^^^ pixel   =   ###"
mask4$ = "peak    = ##.####^^^^ "
mask5$ = "Mass ###.###  Peakheight ##.####^^^^  Parameter
#####  "
mask6$ = "Std Dev = ##.####^^^^ "
ENO$ = "Enter name of "
```

```
bl1$ = "E-Exit C-Calibrate G-Graphics help  "
bl2$ = "I-Intensity "
bl3$ = "Y-keys move "

bottomline$ = bl1$ + bl3$

menuword$ = "window"
menuwordflag = 1
DIM  Value(maxarraysize)
DIM  pixel(maxarraysize)
DIM  Time(maxarraysize)
DIM  mass(maxarraysize)
DIM Histogram(302)      ' based on number of pixels on vertical
display
DIM  Massofint(maxintmass)
DIM  Filenamelist$(maxautosize)
DIM  Parmlist(maxautosize)

' changeable default values go here
drive$ = "c"
basedir$ = "qb45"
outfilext$ = ".txt"
infilext$ = ".dat"
idirname$ = "tekdat"
odirname$ = "compdat"
displaycolor = 14
mmddyy$ = ""
dateflag$ = "N"
100 'main program starts here
  SCREEN 0, 0, 0, 0
   x1 = mainmenu(mascalflag)
  IF x1 = 1 THEN SHELL       'DOS command
  IF x1 = 2 THEN GOSUB 2000    'Load data file
  IF x1 = 3 THEN GOSUB 3000    'Graphics
  IF x1 = 4 AND mascalflag = 1 THEN GOSUB 6400    'automatic
      extraction
  IF x1 = 6 THEN GOSUB 5000    'Setup program
  IF x1 = 8 AND mascalflag = 1 THEN GOSUB 8000    'Save mass axis
```

```
      to  file
   IF x1 = 9 AND mascalflag = 1 THEN GOSUB 8200    'Report noise in
      system
   IF x1 = 7 THEN 999           'exit program
   IF x1 = 10 THEN ssaass = mainhelp
  GOTO 100
999 END

2000 'load data file from main menu only
  CLS
    GOSUB 2900 'print directory listing of input files
   p1$ = drive$ + ":\" + basedir$ + "\" + idirname$ + "\"
   IF dateflag$ <> "Y" THEN
      PRINT ENO$ + infilext$ + " file to load data from : "
      INPUT filename$
       infilename$ = p1$ + filename$ + infilext$
   ELSE  'dateflag$ is a "Y"
      PRINT "Enter index of " + mmddyy$ + "  " + infilext$ + " file to
       work with : "
      INPUT fileindex$
      IF LEN(fileindex$) > 2 THEN fileindex$ = LEFT$(fileindex$, 2)
       infilename$ = p1$ + mmddyy$ + fileindex$ + infilext$
  END IF
   PRINT infilename$
   GOSUB 2800 '  read in the data from the filename given
   GOSUB 2750 '  shift all values
   GOSUB 2700 '  generate pixel numbers
  RETURN

2700 ' generate pixel numbers
   FOR i = 1 TO record
      pixel(i) = psv + (zoom * scrnh - INT(zoom * scrnh * Value(i) /
      delval))
  NEXT i
  RETURN

2750 'shift all values to positive numbers
   FOR i = 1 TO record
```

```
        Value(i) = Value(i) - minval
    NEXT i
    RETURN

2800 ' read data into arrays
     record = 0
      maxval = -99999
      minval = 99999
     OPEN infilename$ FOR INPUT AS #1
     DO WHILE (NOT EOF(1) AND record < maxrecord)
         INPUT #1, inTime$, inVal$
        record = record + 1
         Time(record) = VAL(inTime$)
         Value(record) = VAL(inVal$)
        IF Value(record) > maxval THEN maxval = Value(record)
        IF Value(record) < minval THEN minval = Value(record)
    LOOP
      delval = maxval - minval
    CLOSE #1
    RETURN

2900 msg1$ = drive$ + ":\" + basedir$ + "\"
       cmd$ = "dir /w /p " + msg1$ + idirname$
      SHELL cmd$
     RETURN

3000 'graphics routines go here
     SCREEN 9, 0, 0, 0
3005        'jump to here after moving the window
     CLS
       massindex = cursor + scrstrt
      GOSUB 3900    ' draw spectrum
      GOSUB 3910    ' draw bottom line
3010 'jump to here after moving the cursor
      GOSUB 3800    ' draw line
       GOSUB 3700    ' print information
3050 ' menu selections go here
     z$ = INKEY$
```

```
IF z$ = "" THEN GOTO 3050
 IF z$ = "V" OR z$ = "v" THEN GOSUB 3600   'view different file
IF z$ = "E" OR z$ = "e" THEN GOTO 3099    'exit graphics
 IF z$ = "C" OR z$ = "c" THEN GOSUB 7000   'calibrate spectrum
 IF z$ = "Y" OR z$ = "y" THEN GOSUB 3200   'select window/cursor
    movement
IF z$ = "Z" OR z$ = "z" THEN GOSUB 3890   'zoom factor
IF z$ = "G" OR z$ = "g" THEN
     zzxxyy = helpgraphics(masscalflag)
  GOTO 3000
END IF
 IF (z$ = "I" OR z$ = "i") AND mascalflag = 1 THEN GOSUB 3300   'get
    peak height for this peak
IF z$ = "." OR RIGHT$(z$, 1) = "M" THEN
     IF menuwordflag = 1 THEN scrstrt = scrstrt + 1
    IF menuwordflag = -1 THEN cursor = cursor + 1
END IF
IF z$ = ">" OR RIGHT$(z$, 1) = "t" THEN
     IF menuwordflag = 1 THEN scrstrt = scrstrt + 25
    IF menuwordflag = -1 THEN cursor = cursor + 25
END IF
IF z$ = "<" OR RIGHT$(z$, 1) = "s" THEN
     IF menuwordflag = 1 THEN scrstrt = scrstrt - 25
    IF menuwordflag = -1 THEN cursor = cursor - 25
END IF
IF z$ = "," OR RIGHT$(z$, 1) = "K" THEN
     IF menuwordflag = 1 THEN scrstrt = scrstrt - 1
    IF menuwordflag = -1 THEN cursor = cursor - 1
END IF
IF z$ = "/" OR RIGHT$(z$, 1) = "H" THEN
     IF menuwordflag = 1 THEN scrstrt = scrstrt + 250
    IF menuwordflag = -1 THEN cursor = cursor + 100
END IF
IF z$ = "?" OR RIGHT$(z$, 1) = "P" THEN
     IF menuwordflag = 1 THEN scrstrt = scrstrt - 250
    IF menuwordflag = -1 THEN cursor = cursor - 100
END IF
```

```
    IF cursor > 640 THEN cursor = 640
    IF cursor < 0 THEN cursor = 0
     IF scrstrt > record - 640 THEN scrstrt = record - 640
     IF scrstrt < 1 THEN scrstrt = 1
     IF menuwordflag THEN 3005
    IF NOT menuwordflag THEN 3010
3099 RETURN

3200 'change cursor word
       menuwordflag = -menuwordflag
      IF menuwordflag THEN menuword$ = "cursor"
      IF NOT menuwordflag THEN menuword$ = "window"
   RETURN

3300 'peak height for peak under cursor
     peakval = peakheight(mass(massindex))
  RETURN

3600 'view different file
      INPUT "enter new .txt file name ", filename$
      infilename$ = p1$ + filename$ + infilext$
     GOSUB 2800  'see main menu goto's for documentation
    GOSUB 2750
    GOSUB 2700
   RETURN

3700 'print screen information
   LOCATE 1, 1
    PRINT USING mask1$; Time(massindex); massindex
   LOCATE 2, 1
    PRINT USING mask3$; Value(massindex); pixel(massindex)
    bl4$ = bl3$
    IF mascalflag = 1 THEN
      LOCATE 1, 40
       PRINT USING mask2$; mass(massindex)
      LOCATE 2, 40
       PRINT USING mask4$; peakval
       bl4$ = bl2$ + bl3$
```

```
   END IF
   LOCATE 1, 65
    PRINT filename$
   LOCATE 23, 1
    bottomline1$ = bl1$ + bl4$ + menuword$
    PRINT bottomline1$
  RETURN

3800 'draw line
     LINE (cursor, scrnh - pixel(massindex))-(cursor, 300),
      displaycolor - 3
  RETURN

3810 'erase line
     LINE (cursor, pixel(cursor))-(300, pixel(cursor)), 0
  RETURN

3890 'get new zoom value
   LOCATE 22, 1
   PRINT "                                                  "
   LOCATE 22, 1
    INPUT "Enter new zoom value ", zoom
   LOCATE 22, 1
   PRINT "                                                  "
   LOCATE 22, 1
    INPUT "Enter new shift value ", psv
    GOSUB 2700 'generate new pixels
  RETURN

3900 'this is where the spectrum is printed to the screen
     scrend = scrstrt + 640
    FOR gi = scrstrt TO scrend
          PSET (gi - scrstrt, scrnh - pixel(gi)), displaycolor
   NEXT gi
   RETURN

3910 'draw bottom line
     LINE (0, 300)-(640, 300), displaycolor - 2
```

```
   RETURN

5000  'program setup goes here
   CLS
    zzdf = setup
   RETURN

6000 'select peaks of interest here
   CLS
     PRINT "Select peaks of interest,  0 exits"
    j = 0
   PRINT
     Massofint(0) = 1          ' to normalize if no normalization is chosen
    flagspi = 1
   DO WHILE flagspi > 0
      j = j + 1
        INPUT "enter mass of interest ", Massofint(j)
        flagspi = Massofint(j)
       IF j > maxintmass THEN PRINT " maximum number of peaks
       exceeded "
  LOOP
    numintpeak = j - 1    ' number of interesting peaks
     PRINT "You selected the following mass peaks as interesting "
    FOR jj = 1 TO numintpeak
       PRINT Massofint(jj);
    NEXT jj
   PRINT
   PRINT "C = Continue  R = Redo E = Exit"
6050 y$ = INKEY$
   IF y$ = "C" OR y$ = "c" THEN 6100
   IF y$ = "R" OR y$ = "r" THEN 6000
   IF y$ = "E" OR y$ = "e" THEN 6199
   GOTO 6050
6100 PRINT "enter normalizing mass or 0 for no normalization"
    INPUT normalizer
    normalflag = -1
    IF normalizer = 0 THEN normalflag = 0
    IF normalizer = 0 THEN normalindex = 0
```

```
    FOR jj = 1 TO j - 1
        IF normalizer = Massofint(jj) THEN
           normalflag = Massofint(jj)
          normalindex = jj
     END IF
    NEXT jj
    IF normalflag = -1 THEN PRINT "You must choose a valid peak to
       normalize  with"
    IF normalflag = -1 THEN 6100
    IF normalflag = 0 THEN
       PRINT "You have chosen not to normalize"
   ELSE
       PRINT "You have chosen to normalize to mass ", normalflag
   END IF
   PRINT
    PRINT "C = Continue  R = Redo from start  E = Exit "
6150 y$ = INKEY$
   IF y$ = "C" OR y$ = "c" THEN 6199
   IF y$ = "R" OR y$ = "r" THEN 6000
   IF y$ = "E" OR y$ = "e" THEN 6199
   GOTO 6150
6199 RETURN

6400 'Automatic data analysis routine
   CLS
    GOSUB 6000 'enter mass peaks of interest
   IF y$ = "e" OR y$ = "E" THEN 6499
6405 PRINT
    PRINT ENO$ + outfilext$ + " file to save dataset to : "
    INPUT Datafilname$
    p1$ = drive$ + ":\" + basedir$ + "\" + odirname$ + "\"
     Dfilename$ = p1$ + Datafilname$ + outfilext$
   PRINT
    PRINT "Enter common characters in data set names (7 max) "
   INPUT common$
    clength = LEN(common$)
    nclen = 8 - clength
    PRINT USING "Enter # postfix characters, a comma, and a
```

```
      parameter for that data set"; nclen
     PRINT "Enter a comma by itself to exit this loop"
    PRINT
    ix = 0
    parmflag$ = "a"
    DO WHILE parmflag$ <> ""              'get names of files to use
      ix = ix + 1
        INPUT Filenamelist$(ix), Parmlist(ix)
       IF Filenamelist$(ix) = "" THEN parmflag$ = ""
        Filenamelist$(ix) = common$ + Filenamelist$(ix)
   LOOP
    ix = ix - 1
    PRINT "Using directory " + idirname$
    kx = 0
    FOR jx = 1 TO ix                      'print list of files to be used
      kx = kx + 1
        fx1$ = Filenamelist$(jx)
        px1 = Parmlist(jx)
       PRINT USING fileout1$; fx1$; px1;
      IF kx = 3 THEN
        PRINT
        kx = 0
      END IF
    NEXT jx
    PRINT
    PRINT "C = Continue R = Redo  N = redo Name list  E = Exit "

6420 xz$ = INKEY$
    IF xz$ = "C" OR xz$ = "c" THEN
        PRINT "processing ", common$
        GOTO 6450 'continue
    END IF
    IF xz$ = "E" OR xz$ = "e" THEN GOTO 6499 'exit
    IF xz$ = "R" OR xz$ = "r" THEN GOTO 6400 'redo from start
    IF xz$ = "N" OR xz$ = "n" THEN GOTO 6405 'redo name list
    GOTO 6420

6450 'loop the loop, walk the walk, talk the talk
```

```
   OPEN Dfilename$ FOR APPEND AS #9
    p1$ = drive$ + ":\" + basedir$ + "\" + idirname$ + "\"
   FOR jx = 1 TO ix
          infilename$ = p1$ + Filenamelist$(jx) + infilext$
        GOSUB 2800  'read in the file
         GOSUB 2700  'shift numbers to positive values
          'histogram is not needed for data acquisition
        IF normalindex = 0 THEN
           normval = 1
      ELSE
            normval = peakheight(Massofint(normalindex))
      END IF
       FOR i = 1 TO numintpeak
            peakval = peakheight(Massofint(i)) / normval
            PRINT USING mask5$; Massofint(i); peakval; Parmlist(jx)
           PRINT #9, Filenamelist$(jx) + ".dat    ";
           PRINT #9, USING "####.#          "; Parmlist(jx);
           PRINT #9, USING "###.# "; Massofint(i);
          PRINT #9, USING "  ##.#####^^^^ "; peakval
      NEXT i
   NEXT jx
   CLOSE #9
   BEEP
   BEEP

6499 RETURN

7000  'Mass  calibration  routine
     IF time1 = -1 THEN
         time1 = massindex
        PRINT "Enter the mass for this point                    "
       INPUT mass1
      RETURN
    END IF
     IF massindex > time1 THEN
         time2 = massindex
        PRINT "Enter the mass for this point                    "
       INPUT mass2
```

```
    ELSEIF massindex = time1 AND time2 = -1 THEN
      PRINT "Enter the mass for this point                    "
      INPUT mass1
     RETURN
    ELSEIF massindex = time1 THEN
      PRINT "Enter the mass for this point                    "
      INPUT mass1
    ELSE  'massindex < time 1
      mass2 = mass1
       time2 = time1
       time1 = massindex
      PRINT "Enter the mass for this point                    "
      INPUT mass1
   END IF
   IF mass1 = mass2 THEN
      time1 = -1
      time2 = -1
      mascalflag = 0
    RETURN
   END IF
     dt = Time(time2) - Time(time1)
   IF dt = 0 THEN
      INPUT "Dt = 0", lksdjf$
    RETURN
   END IF
    alpha = (SQR(mass2) - SQR(mass1)) / (dt)
   IF alpha = 0 THEN
      INPUT "alpha = 0", lksdjf$
    RETURN
   END IF
     time0 = (SQR(mass2) - alpha * Time(time2)) / (-alpha)
   FOR ii = 0 TO record
        mass(ii) = (alpha * (Time(ii) - time0)) ^ 2
   NEXT ii
    maxmass = mass(record)
    mascalflag = 1
7299 RETURN
```

```
8000 'save mass axis to .txt file in form  record#, mass, signal
   CLS
   PRINT
    PRINT infilename$
   PRINT
    INPUT "enter name of .mas file to save mass data to ",
      mfilename$
    mfilename$ = drive$ + ":\" + basedir$ + "\" + mfilename$ + ".mas"
   OPEN mfilename$ FOR OUTPUT AS #7
     PRINT "Enter P for partial mass file or any other key for full
      mass file. "
8010 mdfv$ = INKEY$
    IF mdfv$ = "" THEN 8010
    IF mdfv$ = "P" OR mdfv$ = "p" THEN
      PRINT
        PRINT "Minimum mass in this data set : ", mass(1)
        PRINT "Maximum mass in this data set : ", mass(record)
        INPUT "Enter start of mass range to be saved ", stamassv
       IF stamassv < mass(1) THEN stamassv = mass(1)
       INPUT "Enter end of mass range to be saved ", endmassv
        IF endmassv > mass(record) THEN endmassv = mass(record)
      PRINT
       PRINT #7, "  i       mass(i)       Value(i) "
      FOR i = 1 TO record
          IF mass(i) >= stamassv AND mass(i) <= endmassv THEN PRINT
             #7, USING "#####    ####.######    ##.######^^^^"; i;
             mass(i);  Value(i)
     NEXT i
   ELSE
      FOR i = 1 TO record
            PRINT #7, USING "#####    ####.######    ##.######^^^^";
             i;  mass(i);  Value(i)
     NEXT i
   END IF
   CLOSE #7
     PRINT "file saved hit enter to continue "
   RETURN
```

```
8200 'find noise in system
     INPUT "Find noise on mass range, or peak (R/P) ? : ", rp$
    IF rp$ = "r" OR rp$ = "R" THEN
      PRINT
       INPUT "enter mass1 : ", mass1
       INPUT "enter mass2 : ", mass2
      IF mass1 > mass2 THEN
         tmpm = mass1
         mass1 = mass2
         mass2 = tmpm
      END IF
        average = sumrange(mass1, mass2)
        sigma = stdev(mass1, mass2, average)
       PRINT "sigma = ", sigma, "average ", average
       INPUT lskdjf$
   END IF
    IF rp$ = "p" OR rp$ = "P" THEN
      PRINT
        INPUT "Enter peak of interest : ", peakin
       peakout = peakheight(peakin)
        sigma = stdev(startavg, endavg, baseline)
       PRINT "start = ", startavg, "end = ", endavg
       rp1$ = "max ##.####^^^^  base ##.####^^^^  height ##.####^^^^
             sigma ##.####^^^^ "
       PRINT USING rp1$; pmax; baseline; peakout; sigma
       INPUT lskdjf$
    END IF
   RETURN

FUNCTION baslinavg (peak)  'find baseline
SHARED startavg, endavg, maxmass
   SHARED errorflag1
   IF errorflag1 = 1 THEN PRINT "entered baslinavg"

SELECT CASE peak
  CASE .9 TO 1.1                    ' range 1.1 to 1.5
       startmod = -.1
      endmod = -.2
```

```
    CASE 1.9 TO 2.1                    ' range 3 to 5
        startmod = -1
       endmod = -3
    CASE 11.9 TO 16.1                   ' range 11 to 11.5
        startmod = peak - 11.5
       endmod = peak - 11
    CASE 16.9 TO 20.1
        startmod = peak - 21
       endmod = peak - 24
    CASE 24.9 TO 27.1
        startmod = peak - 21
       endmod = peak - 24
    CASE 27.9 TO 32.1
        startmod = peak - 32.5
       endmod = peak - 34
    CASE 34.9 TO 40.2                  'HCl peaks and argon
        startmod = peak - 32.5
       endmod = peak - 34
    CASE 40.9 TO 45.1
        startmod = peak - 45.5
       endmod = peak - 46.5
    CASE 45.9 TO 48.1                  'CHxCl product peaks
        startmod = peak - 45.5
       endmod = peak - 46.5
    CASE 48.9 TO 52.1                   'CH3Cl precursor peaks
        startmod = peak - 62.5
       endmod = peak - 67.5
    CASE 77.9 TO 88.5                   'Krypton isotopes
        startmod = peak - 62.5
       endmod = peak - 67.5
    CASE 116.5 TO 125.5                  'CHCl3 isotopes
        startmod = peak - 110
       endmod = peak - 114
    CASE ELSE                          ' range x-.7 to x-.3
        startmod = .7
       endmod = .3
  END SELECT
startpk = peak - startmod
```

```
endpk = peak - endmod
IF endpk > maxmass THEN PRINT "Error: MaxMass < endpk in function
      baslinavg"
IF startpk > maxmass THEN PRINT "Error: MaxMass < startpk in
      function  baslinavg"
sum1 = sumrange(startpk, endpk)
baslinavg = sum1

   IF errorflag1 = 1 THEN PRINT "left baslinavg"

END FUNCTION

FUNCTION helpgraphics (msf)
  SCREEN 0, 0, 0, 0
  CLS
  PRINT "C O M M A N D  L I S T "
  PRINT
  PRINT " GRAPHICS COMMANDS "
  PRINT
   PRINT "C = calibrate mass axis "
   PRINT "E = exit "
   IF msf = 1 THEN PRINT "I = find peak height "
   PRINT "V = view new .dat file  "
   PRINT "Y = select cusor/screen movement mode "
   PRINT "Z = zoom in or out "
  PRINT
   PRINT " right arrow moves cursor/screen 1 channel to the right "
   PRINT " left arrow moves cursor/screen 1 channel to the left "
   PRINT " crtl-right arrow moves cursor/screen 25 channels to the
      right  "
   PRINT " crtl-left arrow moves cursor/screen 25 channels to the
      left  "
   PRINT " up arrow moves cursor/screen 250 channels to the right "
   PRINT " down arrow moves cursor/screen 250 channels to the left
      "
  PRINT
   INPUT "hit enter to continue ", lskdjf$
END FUNCTION
```

```
FUNCTION mainhelp
  CLS
  PRINT " M A I N  M E N U  H E L P "
  PRINT
  PRINT
    PRINT "A = automatic data extraction"
  PRINT "D = DOS command "
  PRINT "E = Exit "
   PRINT "G = Graphics subroutines "
   PRINT "L = Load a data file "
   PRINT "M = Produce a Mass axis data file "
    PRINT "S = Statistics subroutines "
   PRINT "T = Set program parameters "
  PRINT
    INPUT "enter your selection ", ch$
  SELECT CASE ch$
  CASE "A", "a"
    GOTO ade
  CASE "S", "s"
     GOTO stat
  CASE "M", "m"
    GOTO massa
  CASE ELSE
       PRINT "this should be self explanitory"
  END SELECT
    INPUT "hit enter to continue", lskdjf$
endmass: GOTO endfunc

massa: 'produce a mass axis file
  CLS
    PRINT "This option will produce an ascii file containing the
calibrated"
    PRINT "mass axis for the data set in question. This will be a two
column"
    PRINT "comma delineated file. Data will be in the format  Mass,
Signal"
  GOTO endmass
```

```
stat: ' statistics information
  CLS
   PRINT "When you enter the Statistics routine, you are asked to
      choose"
   PRINT "either a peak or a range to work with. If you choose a
      range,"
   PRINT "you will be asked to supply the range and will get
      statistics"
   PRINT "for that range. If you choose a peak, you will be asked for a"
   PRINT "peak, and will be given statistics for the range used to
      find"
   PRINT "the baseline for that peak."
  GOTO endmass

ade: 'automatic data extraction help
  CLS
   PRINT "Automatic data extraction is possible only if you have a
      list "
   PRINT "of the datafiles you wish to extract from and a parameter
      for "
   PRINT "each of those datafiles. The date feature is built into this "
   PRINT "function for ease of typing. The date feature allows you to "
   PRINT "enter a date (or any group of characters) that is present in"
   PRINT "all of the filenames of the group. You may then enter only
      the"
   PRINT "last few characters of the filename and the program will
      access"
   PRINT "the file you desire by building the filename for you."
   PRINT "Enter a , on the line by itself to exit this loop."
  GOTO endmass
endfunc:  PRINT "Have A Nice Day!"
END FUNCTION

FUNCTION mainmenu (mcf)
10000 CLS
   SHARED infilename$
   SHARED dateflag$
  SHARED mmddyy$
```

```
  PRINT "M A I N   M E N U"
  PRINT
   IF dateflag$ = "Y" THEN PRINT "Date is set to " + mmddyy$
   IF mcf = 1 THEN PRINT "A = automatic data extraction"
  PRINT "D = Dos command "
   PRINT "E = Exit program "
  PRINT "G = Graphics "
   PRINT "L = Load data file ", infilename$
   IF mcf = 1 THEN PRINT "M = Produce mass axis data file"
   IF mcf = 1 THEN PRINT "S = Standard deviation on mass range "
   PRINT "T = Set program parameters  "
  PRINT "H = Help "

   flag = 0
10022  x$ = INKEY$
   IF x$ = "" THEN 10022
   IF x$ = "D" OR x$ = "d" THEN flag = 1
   IF x$ = "L" OR x$ = "l" THEN flag = 2
   IF x$ = "G" OR x$ = "g" THEN flag = 3
   IF x$ = "A" OR x$ = "a" THEN flag = 4
   IF x$ = "T" OR x$ = "t" THEN flag = 6
   IF x$ = "E" OR x$ = "e" THEN flag = 7
   IF x$ = "M" OR x$ = "m" THEN flag = 8
   IF x$ = "S" OR x$ = "s" THEN flag = 9
   IF x$ = "H" OR x$ = "h" THEN flag = 10
    mainmenu = flag
    IF flag = 0 THEN 10000
END FUNCTION

FUNCTION peakheight (peak)
    SHARED Value(), mass(), record, record1
   SHARED pmax, baseline
    SHARED errorflag1
    IF errorflag1 = 1 THEN PRINT "entered peakheight"
    baseline = baslinavg(peak)
   pmax = 9999
   ps = peak - .3
   pe = peak + .3
```

```
   WHILE (mass(record1) > ps)  'correct for finding baseline after
peak
      record1 = record1 - 100
  WEND

   PRINT                      'record1 is index of last mass used in baseline

   FOR i = record1 TO record
     IF mass(i) < pe AND mass(i) > ps AND Value(i) < pmax THEN pmax =
Value(i)
     IF mass(i) > pe THEN i = record
  NEXT i
    peakheight = baseline - pmax
    IF errorflag1 = 1 THEN PRINT "left peakheight"
END FUNCTION

FUNCTION setup
    SHARED mmddyy$, dateflag$
    SHARED idirname$, odirname$
    SHARED displaycolor
    SHARED drive$, basedir$
     SHARED infilext$, outfilext$
   SHARED maxrecord
20000 CLS
   PRINT
   PRINT "Setup Menu "
   PRINT
    PRINT "1 = change display color                    ", displaycolor
     PRINT "2 = change directory name for data input   ", idirname$
     PRINT "3 = change directory name for data output ", odirname$
     PRINT "4 = change date of data to work with       ", mmddyy$
     PRINT "5 = change input file extension            ", infilext$
     PRINT "6 = change output file extension           ", outfilext$
    PRINT "7 = change base directory                   ", basedir$
    PRINT "8 = change drive letter                    ", drive$
     PRINT "R = change number of records to input      ", maxrecord
    PRINT "S = Save setup"
```

```
    PRINT "L = Load saved setup"
    PRINT "E = exit"
20005 zzxy$ = INKEY$
    IF zzxy$ = "" THEN GOTO 20005
    IF zzxy$ = "1" THEN GOSUB 20100
    IF zzxy$ = "2" THEN GOSUB 20200
    IF zzxy$ = "3" THEN GOSUB 20300
    IF zzxy$ = "4" THEN GOSUB 20400
    IF zzxy$ = "5" THEN GOSUB 20050
    IF zzxy$ = "6" THEN GOSUB 20060
    IF zzxy$ = "7" THEN GOSUB 20070
    IF zzxy$ = "8" THEN GOSUB 20080
    IF zzxy$ = "S" OR zzxy$ = "s" THEN GOSUB 20500
    IF zzxy$ = "L" OR zzxy$ = "l" THEN GOSUB 20600
    IF zzxy$ = "E" OR zzxy$ = "e" THEN GOTO 20025
    IF zzxy$ = "R" OR zzxy$ = "r" THEN GOSUB 20150
    PRINT zzxy$
    GOTO 20000
20025 GOTO 20999
  RETURN

20050 INPUT "Enter new input file extension (3 characters only) ",
        infx$
    IF LEN(infx$) <> 3 THEN GOTO 20050
     infilext$ = "." + infx$
  RETURN
20060 INPUT "Enter new output file extension (3 characters only) ",
        outfx$
    IF LEN(outfx$) <> 3 THEN GOTO 20060
     outfilext$ = "." + outfx$
  RETURN
20070 INPUT "Enter input new base directory name ", bd$
    basedir$ = bd$
  RETURN
20080 INPUT "Enter new drive letter ", dl$
    drive$ = dl$
  RETURN
20100 INPUT "Enter new value for display color (2 - 14) ", xd
```

```
    IF xd < 2 THEN xd = 2
    IF xd > 14 THEN xd = 14
     displaycolor = xd
   RETURN
20150 INPUT "Enter maximum number of records to read from data
        files ", maxrecord
   RETURN
20200 INPUT "Enter new directory name to input data files from ",
        idirname$
   RETURN
20300 INPUT "Enter new directory name to output data file to ",
        odirname$
   RETURN
20400 INPUT "Enter date of data to work with (mmddyy) ",
        Inmmddyy$
    IF LEN(inmmddyy$) <> 6 THEN GOTO 20400
    mmddyy$ = inmmddyy$
    dateflag$ = "Y"
    PRINT dateflag$
   RETURN
20500 'save setup
     filename$ = drive$ + ":\" + basedir$ + "\mspset.sav"
    OPEN filename$ FOR OUTPUT AS #4
     WRITE #1, drive$
     WRITE #1, basedir$
     WRITE #1, idirname$
     WRITE #1, odirname$
      WRITE #1, outfilext$
      WRITE #1, infilext$
     WRITE #1, dateflag$
     WRITE #1, mmddyy$
      WRITE #1, displaycolor
    CLOSE #4
   RETURN
20600 'load setup
     filename$ = drive$ + ":\" + basedir$ + "\mspset.sav"
    OPEN filename$ FOR INPUT AS #4
     INPUT #1, drive$
```

```
    INPUT #1, basedir$
    INPUT #1, idirname$
    INPUT #1, odirname$
    INPUT #1, outfilext$
    INPUT #1, infilext$
    INPUT #1, dateflag$
    INPUT #1, mmddyy$
    INPUT #1, displaycolor
   CLOSE #4
  RETURN
20999 END FUNCTION

FUNCTION stdev (mass1, mass2, average)
    SHARED Value(), mass(), record
      pt1$ = "##### ##.######^^^^ ##.######^^^^ ##.######^^^^ "
    sigm = 0
    FOR i = 0 TO record
       IF mass1 < mass(i) THEN startrec = i
       IF mass2 < mass(i) THEN endrec = i
       IF mass1 >= mass(i) AND mass2 >= mass(i) THEN i = record
    NEXT i
    FOR i = startrec TO endrec
       sig = average - Value(i)          'deviations
       sigm = sigm + sig * sig           'sum of squares of deviations
       PRINT USING pt1$; i; Value(i); sig; sigm
    NEXT i
      PRINT endrec - startrec, "records ", startrec, endrec
      stdev = SQR(sigm / (endrec - startrec))
END FUNCTION

FUNCTION sumrange (begin, ending)     ' returns average value over
      range
SHARED mass(), Value(), record, record1, record0
   SHARED errorflag1
   IF errorflag1 = 1 THEN PRINT "entered sumrange"
  IF begin > ending THEN
     temp = ending
     ending = begin
```

```
      begin = temp
   END IF
FOR i = 1 TO record
    IF (mass(i) < begin) THEN record0 = i    'save start of range
    IF (mass(i) >= begin) THEN i = record    'exit loop
NEXT i
tot = 0
    IF errorflag1 = 1 THEN PRINT "record0 = ", record0, "mass (r0) =",
       mass(record0)
    IF errorflag1 = 1 THEN PRINT "ending = ", ending, " begin = ", begin
FOR j = record0 TO record
    IF (mass(j) < ending) THEN tot = tot + Value(j)
   record1 = j                              'save last value of j used
    IF (mass(j) >= ending) THEN j = record  'exit loop
NEXT j
IF errorflag1 = 1 THEN PRINT "tot = ", tot, "divisor = ", record1 -
      record0
sumrange = tot / (record1 - record0)
IF errorflag1 = 1 THEN PRINT "left sumrange"
END FUNCTION
```

A-8 COMPSORT

```
DECLARE FUNCTION dirnam! ()
DECLARE FUNCTION menu! ()

10        'initialization  block
      CLS

        maxarrsize = 1500
        maxmatsize = 50

        DIM Tmparr(maxarrsize)
        DIM Sigarr(maxarrsize)
       DIM Masarr%(maxarrsize)

     CONST FALSE = 0, TRUE = NOT FALSE
        hmass = 200     'highest mass expected in spectrum plus some
      DIM fa%(hmass)

       flag1$ = "no"
       flag2$ = "no"
       flag3$ = "yes"
        ife$ = "txt"
       wd$ = "compdat"
      md$ = "qb45"

20      nameflag = 1
      dum1 = menu              'run main menu routine
       dum2 = dirnam            'make directory name

        cmd$ = "dir " + dir$ + "*." + ife$ + " /w /p"
        SHELL cmd$               'print files in selected directory
         outstring$ = "Enter name of ." + ife$ + " file to work with from
      above list : "
       PRINT outstring$
       INPUT indate$            'get file name to work with
      IF LEN(indate$) <> 8 THEN
```

```
        PRINT "filename must contain 8 characters for this program "
        PRINT "Please rename the file before continuing "
        PRINT "Type     Help Rename   for information "
        PRINT "Type     exit          when ready to resume"
        cmd$ = "cd " + dir$
        SHELL
        nameflag = 0
      END IF
      IF nameflag = 0 THEN 20
       indate$ = indate$ + "." + ife$    ' make full file name
       postfix$ = RIGHT$(indate$, 4)     ' "." + ife$
       sfname$ = LEFT$(indate$, 8)       ' original indate$
       fFname$ = LEFT$(sfname$, 6)       ' date part of indate$
       doFname$ = RIGHT$(sfname$, 2)     ' identifiers
       revname$ = doFname$ + fFname$     ' reversed identifiers and
      date
       inFname$ = dir$ + indate$         ' complete path name : input file
       srtFname$ = dir$ + revname$ + ".srt"        'name of sort file
       rawFname$ = dir$ + revname$ + ".raw"        'name of raw data
      file
       finFname$ = dir$ + "wo" + fFname$ + postfix$
       doneFname$ = dir$ + revname$ + postfix$

        abd$ = "temp #####.# mass ####  average  ##.####^^^^ sigma
      ##.####^^^^"
       abc$ = "Sigarr(iz)  ##.####^^^^ dev  ##.####^^^^ devtot
      ##.####^^^^"
        aa$ = "####.###  ####  ##.####^^^^"
      test = 1
100     GOSUB 2000 'get data from inFname$ into arrays
      GOSUB 9500 ' sort data

    ' GOSUB 1000 'print data on screen
      IF flag2$ = "yes" THEN GOSUB 1100   ' make raw data file
      IF flag1$ = "yes" THEN              ' make statistics file
       OPEN srtFname$ FOR OUTPUT AS #9
         n = 1: devitot = 0: average = Sigarr(0)
          storetemp = Tmparr(0)        'store first temperature
```

```
          storemass% = Masarr%(0)      'store first mass
          storeindex = 0               'point to first element of array
        FOR j = 1 TO ii
            IF storetemp = Tmparr(j) AND storemass% = Masarr%(j)
THEN
              average = average + Sigarr(j)   'keep total
            n = n + 1                         'keep number of entries
          ELSE
             average = average / n            'find average
             FOR iz = storeindex TO j - 1     'sum deviations
                deva = average - Sigarr(iz)
                devitot = devitot + deva * deva
           NEXT iz
           IF (n - 1) < 2 THEN n = 2
              sigma = SQR(devitot / (n - 1)) 'find sigma
             PRINT #9, USING aa$; Tmparr(j - 1); Masarr%(j - 1);
                 sigma
            storeindex = j
             devitot = 0: n = 1: average = Sigarr(j)
              storetemp = Tmparr(j): storemass% = Masarr%(j)
          END IF
        NEXT j
          ' calculate last value
         average = average / n             'find average
          FOR iz = storeindex TO j - 1     'sum deviations
             deva = average - Sigarr(iz)
             devitot = devitot + deva * deva
        NEXT iz
         IF (n - 1) < 2 THEN n = 2
           sigma = SQR(devitot / (n - 1)) 'find sigma
           PRINT #9, USING aa$; Tmparr(j - 1); Masarr%(j - 1); sigma
        CLOSE #9
      END IF

       IF flag3$ = "no" THEN END   ' no need to make spreadsheet file

    'average data
       numtmp = 0
```

```
    FOR i = 1 TO ii - 1
       numtmp = numtmp + 1
        Sig = Sigarr(i)
       j = 1
        DO WHILE (Tmparr(i + 1) = Tmparr(i) AND Masarr%(i + 1) =
            Masarr%(i))
          Sig = Sig + Sigarr(i + 1)
         j = j + 1
           Sigarr(i) = -9999
         i = i + 1
      LOOP
         Sigarr(i) = Sig / j
    NEXT i
      PRINT "finished averaging data "
    '  GOSUB 1000 'print data on acreen

    ' condense arrays
     j = 1
     FOR i = 1 TO ii
         IF Sigarr(i) <> -9999 THEN
             Sigarr(j) = Sigarr(i)
           Masarr%(j) = Masarr%(i)
            Tmparr(j) = Tmparr(i)
           j = j + 1
       END IF
    NEXT i
      ii = j - 1
'   PRINT "arrays condensed "

'   GOSUB 1000 'print data on screen

    ' generate header line for spreadsheet
   outline$ = "    x-axis   "

    GOSUB 6000 ' generate first line of output

OPEN finFname$ FOR OUTPUT AS #3
 'PRINT outline$
```

```
 PRINT #3, outline$

 FOR i = 1 TO ii          ' assume more than 1 mass in data set
     tmpstr$ = STR$(Tmparr(i))
    flag = 0
    fp$ = ""
    ep$ = ""
    FOR a = 1 TO LEN(tmpstr$)
        IF MID$(tmpstr$, a, 1) = "." THEN flag = 1
        IF flag = 0 THEN fp$ = fp$ + MID$(tmpstr$, a, 1)
        IF flag = 1 THEN ep$ = ep$ + MID$(tmpstr$, a, 1)
   NEXT a
    IF flag = 0 THEN ep$ = "."
    flen = LEN(fp$)
    elen = LEN(ep$)
     tmstr$ = STRING$(9 - flen, " ") + fp$ + ep$ + STRING$(5 - elen, "
           ")
      outline$ = tmstr$
     DO WHILE (Tmparr(i + 1) = Tmparr(i))
         sigstr$ = STR$(Sigarr(i))
         outli$ = sigstr$ + STRING$(14 - LEN(sigstr$), " ")
         outline$ = outline$ + outli$
       i = i + 1
   LOOP
      outline$ = outline$ + STR$(Sigarr(i))
     PRINT #3, outline$
NEXT i
CLOSE #3
GOSUB 9100
OPEN finFname$ FOR INPUT AS #4
 i = 0
DO WHILE NOT EOF(4)
    LINE INPUT #4, inline$
   i = i + 1
LOOP
CLOSE #4
OPEN finFname$ FOR INPUT AS #5
OPEN doneFname$ FOR OUTPUT AS #6
```

```
     PRINT #6, inline$
    FOR j = 1 TO i
       LINE INPUT #5, inline2$
       IF j <> i THEN PRINT #6, inline2$
    NEXT j
    CLOSE #5
    CLOSE #6
     cmd$ = "erase " + finFname$
    SHELL cmd$
    'CMD$ = "erase " + outFname$
   'SHELL CMD$
     PRINT "Compsort finished: Files are in C:\QB45\COMPDAT "
   BEEP
999  END


1000    ' print out data arrays
      k = 1
      FOR j = 0 TO ii
            PRINT j, Tmparr(j), Masarr%(j), Sigarr(j)
         IF (k * 20 = j) THEN
            INPUT "hit any key to continue "; xx$
          k = k + 1
        END IF
      NEXT j
     RETURN

1100    ' print sorted data to .raw file
     OPEN rawFname$ FOR APPEND AS #8
1110   k = 1
       INPUT "enter mass to print out ", omass%
      FOR j = 0 TO ii
         IF omass% = Masarr%(j) THEN PRINT #8, j, Tmparr(j),
              Masarr%(j),  Sigarr(j)
     NEXT j
      INPUT "Another mass? (Y/N) ", dd$
     IF dd$ = "y" OR dd$ = "Y" THEN 1110
     CLOSE #8
```

```
    RETURN

2000 ' input data into arrays
     OPEN inFname$ FOR INPUT AS #2
      numlins = 0
      ii = 0

      DO WHILE NOT EOF(2)      ' store the data in arrays

         LINE INPUT #2, inlinex$
         ii = ii + 1
         numlins = numlins + 1
         fin$ = MID$(inlinex$, 1, 12)              'data set name
          Tmp = VAL(MID$(inlinex$, 16, 4))         'temperature for this
              point
         Mas% = VAL(MID$(inlinex$, 31, 3))         'mass for this point
         Sig = VAL(MID$(inlinex$, 39, 12))         'area under the curve
              from qmasp
         Tmparr(ii) = Tmp
        Masarr%(ii) = Mas%
         Sigarr(ii) = Sig
         IF (ii + 1 > maxarrsize) THEN
           PRINT "ii = ", ii
          GOSUB 9999
        END IF
      LOOP
      CLOSE #2
       PRINT "data input complete "
      RETURN

6000  FOR i = 1 TO ii
       x% = Masarr%(i)
      SELECT CASE x%
         CASE 1
            IF fa%(x%) = 0 THEN outline$ = outline$ + "        H    "
         CASE 2
            IF fa%(x%) = 0 THEN outline$ = outline$ + "        H2    "
         CASE 12
```

```
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        C    "
CASE 13
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        CH    "
CASE 14
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        CH2    "
CASE 15
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        CH3    "
CASE 16
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        CH4    "
CASE 17
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        OH    "
CASE 18
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        H2O    "
CASE 20
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        Ne20    "
CASE 22
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        Ne22    "
CASE 26
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        C2H2    "
CASE 28
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        N2    "
CASE 32
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        O2    "
CASE 35
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        Cl    "
CASE 36
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        HCl    "
CASE 37
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        Cl    "
CASE 38
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        HCl    "
CASE 40
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        Ar    "
CASE 47
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        CCl    "
CASE 48
    IF fa%(x%) = 0 THEN outline$ = outline$ + "        CHCl    "
CASE 49
```

```
            IF fa%(x%) = 0 THEN outline$ = outline$ + "      CCl+    "
          CASE 50
            IF fa%(x%) = 0 THEN outline$ = outline$ + "      CHCl+   "
          CASE 51
            IF fa%(x%) = 0 THEN outline$ = outline$ + "     CH2Cl    "
          CASE 52
            IF fa%(x%) = 0 THEN outline$ = outline$ + "     CH3Cl    "
          CASE 83
            IF fa%(x%) = 0 THEN outline$ = outline$ + "   CHCl2aa    "
          CASE 85
            IF fa%(x%) = 0 THEN outline$ = outline$ + "   CHCl2ab    "
          CASE 87
            IF fa%(x%) = 0 THEN outline$ = outline$ + "   CHCl2bb    "
         CASE ELSE
           IF fa%(x%) = 0 THEN
              outl$ = STR$(Masarr%(i))
              outli$ = STRING$(10 - LEN(outl$), " ") + outl$ + "    "
               outline$ = outline$ + outli$
           END IF
        END SELECT
         fa%(x%) = 1
    NEXT i
   RETURN

'9000 ' sort data in dos
     '  CMD$ = "sort /+31 < " + inFname$ + " > sorttmp1.001"
   ' SHELL CMD$
     '  PRINT "first sort completed"
     '  CMD$ = "sort /+30 < sorttmp1.001 > sorttmp2.002"
   ' SHELL CMD$
     '  PRINT "second sort completed"
     '  CMD$ = "sort /+16 <  sorttmp2.002 > " + outFname$
   ' SHELL CMD$
      '  PRINT "initial sorting completed"
   ' RETURN

9100     'final sorting
```

```
      cmd$ = "sort /+12< " + finFname$ + " > sorttmp1.000"
    SHELL cmd$
      cmd$ = "sort /+11< sorttmp1.000 > sorttmp2.000"
    SHELL cmd$
      cmd$ = "sort /+9< sorttmp2.000 > sorttmp1.000"
    SHELL cmd$
      cmd$ = "sort /+8< sorttmp1.000 > sorttmp2.000"
    SHELL cmd$
      cmd$ = "sort /+7< sorttmp2.000 > sorttmp1.000"
    SHELL cmd$
      cmd$ = "sort /+6< sorttmp1.000 > " + finFname$
    SHELL cmd$
      cmd$ = "erase sorttmp2.000"
    SHELL cmd$
      cmd$ = "erase sorttmp1.000"
    SHELL cmd$
      PRINT "final sorting completed"
   RETURN
9500    'sort routine
      limit = ii - 1
    k = 0
   DO
      flag = FALSE
      k = k + 1
      IF k = 80 THEN k = 0
      IF k = 0 THEN PRINT ".";
       FOR i = 1 TO limit
          IF Tmparr(i) = Tmparr(i + 1) AND Masarr%(i) > Masarr%(i + 1)
    THEN
            SWAP Tmparr(i), Tmparr(i + 1)
           SWAP Masarr%(i), Masarr%(i + 1)
            SWAP Sigarr(i), Sigarr(i + 1)
           flag = i
       END IF
         IF Tmparr(i) > Tmparr(i + 1) THEN
            SWAP Tmparr(i), Tmparr(i + 1)
           SWAP Masarr%(i), Masarr%(i + 1)
            SWAP Sigarr(i), Sigarr(i + 1)
```

```
            flag = i
          END IF
        NEXT i
          limit = flag
      LOOP WHILE flag
      PRINT
     RETURN


9999     PRINT "size of array too small, change maxarrsize in
             compsort.bas"
         PRINT "and recompile compsort.bas or shorten data file"
     END

FUNCTION dirnam

      SHARED wd$, md$, filename$
     SHARED dir$
       dir$ = "c:\" + md$ + "\" + wd$ + "\"
      dirnam = 0

END FUNCTION

FUNCTION menu

       SHARED flag1$, flag2$, flag3$
     SHARED ife$, wd$, md$
10000   CLS
     PRINT
     PRINT "C O M P S O R T  D A T A  M E N U"
     PRINT
     PRINT
      flag = 0
       PRINT "1  = make stat file from data", TAB(50);
      PRINT flag1$
       PRINT "2  = make list of raw data for a mass", TAB(50);
      PRINT flag2$
       PRINT "3  = make spreadsheet output file ", TAB(50);
```

```
      PRINT flag3$
       PRINT "4  = change input file extension ", TAB(50);
      PRINT ife$
       PRINT "5  = change working directory ", TAB(50);
      PRINT wd$
       PRINT "6  = change main directory ", TAB(50);
      PRINT md$
       PRINT "9  = begin processing data now "
10100   ink$ = INKEY$
      IF ink$ = "" THEN GOTO 10100
     SELECT CASE ink$
     CASE "1"
        dflag = 0
        IF flag1$ = "no" THEN
           flag1$ = "yes"
          dflag = 1
       END IF
        IF dflag = 0 THEN flag1$ = "no"
     CASE "2"
        dflag = 0
        IF flag2$ = "no" THEN
           flag2$ = "yes"
          dflag = 1
       END IF
        IF dflag = 0 THEN flag2$ = "no"
     CASE "3"
        dflag = 0
        IF flag3$ = "no" THEN
           flag3$ = "yes"
          dflag = 1
       END IF
        IF dflag = 0 THEN flag3$ = "no"
     CASE "4"
          INPUT "Enter new input file extension ", ife$
     CASE "5"
          INPUT "Enter new working directory ", wd$
     CASE "6"
         INPUT "Enter new main directory ", md$
```

```
        CASE "9"
           GOTO 10200
        END SELECT
        GOTO 10000
10200   menu = flag

END FUNCTION
```



A-9 Program Usage

The system of programs used relies on the directory structure shown below.

C:	Root directory
C:\QB45	Working directory (where programs are run)
C:\QB45\TEKDAT	Tektronix data directory (TDS524A data files)
C:\QB45\TEKBAK	Tektronix data storage (TDS524A .WFM files)
C:\QB45\COMPDAT	Compilation file directory (output of COMPSORT)
C:\QB45\BASBAK	Backup of basic files (including versions of QMASP)
C:\QB45\MASDATA	Data files for QMASP mass spectra
C:\QB45\OPTDATA	Data files for QMASP optical spectra

The programs used expect to find the files they require in these directories. The program GETWFM, (not listed) for example expects to take files from the C:\QB45\TEKBAK directory and move them to the C:\QB45\TEKDAT directory where it will then expand them into .DAT files for use by the MASPEC program. All programs

can and should be run from the directory C:\QB45. Please remember that the .DAT files take lots of space, and the .WFM files do not.

Using a specific program

GETWFM

Type "GETWFM mmddyy" where mmddyy is the date code used on the data of interest. GETWFM will then search the TEKBAK directory for the .WFM files that contain that date, transfer them to the TEKDAT directory, convert them to .DAT files using the CNVRTWFM program supplied by Tektronix, and then erase the .wfm files copied to TEKDAT to save space.

MOVEWFM

Type "MOVEWFM". This program copies .WFM files from the A: drive to the TEKDAT directory, converts them to the .DAT format using the CNVRTWFM program from Tektronix, copies the .WFM files to the TEKBAK directory for storage, and then erases the .WFM files in the TEKDAT directory.

MASPEC

Start the program by typing "MASPEC". Once started, you will see the main menu, from which you may make choices of what to do next. The initial main menu will not allow choices that make no sense. For instance you cannot get statistical data unless a file is loaded in memory. You may load a file by chosing L for load. You may also load a file by chosing G for graphics followed by V for view. Rudimentary help is available by chosing H for help. Program parameters may be changed by chosing T for set. You may also leave the MASPEC program in memory and run a dos command series by chosing D for DOS. When done with the DOS shell, simply type exit to return to MASPEC. Finaly, when you first start up MASPEC you may chose E to exit the program.

Once a file is loaded, the file name will be displayed on the screen, and once a mass axis calibration has been completed, more options become available. You may then produce a mass axis data file for a mass range by chosing M or you may chose S to get statistical data on a mass range. The most important feature, however, is the A option. This is the automatic data extraction portion, and will be described later.

The graphics mode has several options which are not displayed on the screen due to lack of screen space. Once a file is loaded, the file name is displayed in the upper right corner. You may choose G for graphics help to see a detailed list of movement keys, but the arrow keys will move the cursor for you. The mode of movement may be switched between cursor and screen movement by pressing Y. If the movement mode is set to screen (the default) then the arrow keys move the screen and the cursor stays still and vice versa if the movement mode is set to cursor. The mass axis is calibrated by choosing two known mass points from the spectra displayed. Choose the lowest point first. You may then chose an upper mass point. The calibration is automatic after you chose the second point. Once the mass axis is calibrated, you may choose I for intensity. This will give you the intensity of the point you have currently selected with the cursor line. You may also chose Z for zoom. Using zoom requires you enter two values. The first is for the zoom factor, the second is for a shift factor. The zoom values and the current view remain even if you view a different file, so spectra comparisons are simplified.

The automatic data extraction mode requires that you have a

calibrated data file in memory. This mode is entered by pressing A when in the main menu. Once started, detailed instructions are printed on the screen each step of the process. First, you will enter a list of masses you are interested in. A mass of zero will exit this routine. You will be asked if you are satisfied with your choices. A mistake is easily corrected by reentering the list at this point. After you have continued, you will be asked for the name of the file in which you wish to store the data obtained. The format used previously has been mmddyyDA for a data file or mddyyAR for the argon normilization file. You will then be asked to enter the date code used for the data you are interested in. This is usually simply the date in the mmddyy format. Next, a loop is started in which you enter the postfix of a file followed by the parameter that was changed when this file was obtained. Repeat this process till all files in a data set have been entered. Entering a comma by itself exits that loop. You will be asked if you would like to normalize to a mass. Unless there exists a valid normalizing peak in the list of masses you entered earlier, chose not to normalize. Once satisfied with the list of masses and the list of postfixes and parameters, continue. The processing may take more than an hour if you have

entered a large data set. The output will be in the COMPDAT directory, and ready to work upon with COMPSORT.

COMPSORT

Enter "COMPSORT" to start this program. From the main menu, choose as many of the options as you like. Options 1, 2 and 9 create statistics files, raw data files, and spreadsheet outputs in that order. Any combination of these may be chosen. If you choose to make a raw data file, you will be asked for a mass range to report. The program will take the filename you select to work with and rearrange it as follows: mmddyyDA will become DAmmddyy. The extension will reflect the type of file. .TXT is for a spreadsheet file, .RAW is for raw data files, and .STS is for a statistics file. The .STS and .TXT files have titles built in for spreadsheets. The .STS file must be rearanged in a spreadsheet to produce error bars for the graphs.

A-10 Vita

James Michael Chenault was born in Boston, Massachusetts, on June 22, 1957. His family moved to central Missouri in the early 1960's, settling in Prairie Home, Missouri in 1963. James graduated from Prairie Home High School in 1975 and joined the U. S. Army that September. After completing military service in September of 1979, James used the G. I. Bill to study electronics technology at Central Missouri State University (CMSU), Warrensburg, Missouri, where he married Debbie Annette Keutzer on August 8, 1982. He completed his undergraduate degree in May, 1985 and worked as a technician until August of 1992, when he returned to CMSU study chemistry and to complete a minor in mathematics and computer science. After being enlisted by the McCap program, a local chapter of the Rodney McNair Foundation, he was accepted to graduate school at the University of Tennessee at Knoxville. There, he completed his masters degree in Chemistry from which this thesis was developed.