Construction of a Molecular Beam Mass Spectrometer for *In-Situ* probing of a Diamond Chemical Vapour Deposition Environment

Edward Crichton, June 2007



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Abstract

Chemical vapour deposition via microwave plasma activation (MWCVD) is an established technique for the production of synthetic diamond. In this study we have used molecular beam mass spectrometry (MBMS), a powerful technique for *in-situ* monitoring of plasma and combustion systems, to probe the gas phase environment of diamond deposition.

Attempts were made to apply a previous MBMS system to analyse 'Ultrananocrystalline' diamond (UNCD) depositing plasmas. At typical UNCD deposition pressures (100 Torr) the experiment was found to be inadequate. The key failings were identified to be the poor conductivity of the sampling probe, the high background (without the luxury of beam modulation), and the fragility of the sampling orifice.

A new MBMS system has been constructed for the *in-situ* probing of a modern MWCVD diamond deposition system. This system aims to replicate conditions within an Element Six loaned reactor so to provide complementary spectroscopic measurements taken within.

Care was taken to recreate the substrate environment around the sampling orifice. This was done by manufacturing a molybdenum 'dummy' growth substrate with a replaceable sampling orifice. The high stagnation pressure meant the design focused on optimising pumping rather than exclusively minimising length. The final design featured a 3-stage system, incorporating a mechanical chopper in the second stage. This design should therefore implicitly increase the signal-to-background ratio at the expense of some of the absolute signal strength.

The detection limit is currently estimated to be of order 10^{-5} mole fraction. The signal-to-background ratio for closed-shell species is measured to be 0.8. This is in good agreement with our model estimate of 0.7 based on our empirically estimated pump speeds. A, simple computational, **chemkin**-based model suggests that, although reactive losses for closed-shell species will be negligible on the time scale of expansion, radical fractions could drop by as much as an order of magnitude at typical pressures.

Experimental trends for methane, acetylene and possibly methyl radical as a function of total pressure and carbon input have been recorded. These values are consistent with Y. A. Mankelevich's computational model of the CRDS reactor. Acetylene and methane were found to have no discernible trend in mole fraction with pressure. This observation is reproduced in equilibrium (senkin) calculations. The mole fraction of acetylene was found to increase near linearly by a factor of 4 with 0.9-4.4% methane input. Methane was found to reduce over the same range by a factor of 2. This trend conflicts with simplistic equilibrium arguments. Measurements of methyl radicals appear to lack consistency and so, on balance, appear to be the result of some form of background independent of the chopping procedure. I declare that the work in this dissertation was carried out in accordance with the Regulations of the University of Bristol. The work is original, except where indicated by special reference in the text, and no part of the dissertation has been submitted for any other academic award. Any views expressed in the dissertation are those of the author.

SIGNED: DATE:.....

The most merciful thing in the world, I think, is the inability of the human mind to correlate all its contents. We live on a placid island of ignorance in the midst of black seas of infinity, and it was not meant that we should voyage far. The sciences, each straining in its own direction, have hitherto harmed us little; but some day the piecing together of dissociated knowledge will open up such terrifying vistas of reality, and of our frightful position therein, that we shall either go mad from the revelation or flee from the deadly light into the peace and safety of a new dark age.

H. P. Lovecraft, in The Call of Cthulhu

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Chapter 1

Diamond

Aside from the traditional value of diamond as a precious stone, it has the promise of increasing industrial importance in the 21st century. Through the use of synthetic techniques, the potential exists for the production of controlled, low defect diamond for electrical, optical and mechanical use [1–3]. This introductory chapter will outline some common techniques used for diamond chemical vapour deposition (CVD). The plasmas featured within this chapter will be left as 'black boxes' for the production of the necessary deposition precursors. A fuller description of plasmas will be given in chapter 2.

1.1 Introduction

The start of any diamond publication is usually initiated with a long discussion of its extreme properties. Instead of a lengthy section on diamond's assets, here, the following table, (figure 1.1) reproduced from [2], should be sufficient for a casual interest in diamond as a material.

One of the two most familiar allotropes of carbon, diamond, owes many of its properties to its high number density and optimised σ -bonded framework. Figure 1.2 shows sketches of the structures of diamond and, for comparison, graphite. In 'standard' conditions, graphite is the thermodynamically stable form of carbon $(\Delta_f G_{\text{Diamond}}^{\ominus} = 2.857 \text{ kJmol}^{-1}, [4])$. At elevated pressures, however, such as deep within the Earth, the higher density phase (diamond) becomes more favourable, though large kinetic barriers to interconversion still exist [5]. If diamond is to be generated by high pressures at any practical rate, high temperatures and catalysis must be employed (see figure 1.3). Since the early 1980s an alternative route

1. Diamond

extreme mechanical hardness (ca. 90 GPa) and wear resistance highest bulk modulus $(1.2 \times 10^{12} \text{ N m}^{-2})$ lowest compressibility $(8.3 \times 10^{-13} \text{ m}^2 \text{ N}^{-1})$ highest room temperature thermal conductivity $(2 \times 10^3 \text{ W m}^{-1} \text{ K}^{-1})$ thermal expansion coefficient at room temperature very low $(1 \times 10^{-6} \text{ K})$ broad optical transparency from the deep ultraviolet to the far infrared highest sound propagation velocity (17.5 km s^{-1}) very good electrical insulator (room temperature resistivity is ca. $10^{13} \Omega \text{ cm}$) diamond can be doped, becoming a semiconductor with a wide bad gap of 5.4 eV very resistant to chemical corrosion biologically compatible some surfaces exhibit very low or 'negative' electron affinity

Figure 1.1: Some of the outstanding properties of diamond. Table, reproduced from [2].

of chemical vapour deposition (CVD) has been developed. Instead of relying on thermodynamics, it uses gas and gas-surface kinetics to trap metastable diamond. It eschews high density, moderate energy methods, such as catalytic high pressure high temperature (cat. HPHT) methods in favour of a higher energy (per particle), low density environment.



Figure 1.2: Sketched structures of a) graphite and b) diamond, the two most familiar allotropes of carbon.



Figure 1.3: A carbon phase diagram (adapted from [5]) showing the thermodynamically-favoured carbon phases as a function of pressure (P) and temperature (T). Shaded is the region of catalytically-mediated high pressure, high temperature synthesis of diamond from graphite (cat. HPHT).

1.2 Chemical Vapour Deposition

The label CVD applies to a vast range of deposition techniques, covering amongst others thermal, plasma, reactive, molecular beam and even simple condensation based methods. They all share one feature: activated gaseous precursors depositing a solid through interaction with a substrate surface.

Activation

The principle of diamond CVD is to take simple hydrocarbons, activate them, and, through control of the substrate parameters and gas phase chemistry, encourage the deposition of a solid, metastable state of carbon. There are three common methods of activation in the diamond literature, thermal, combustion and plasma decomposition. These labels describe the source for the necessary radicals and atomic species, obtained from similar input gases, which deposit diamond under near identical substrate conditions.

Gas Phase Environment

The favourable chemical environment for diamond growth is achieved, in practice, through reduced pressures and dilution of hydrocarbons with hydrogen (argon and oxygen are often also included as additives). A more substantial discussion of the chemical and physical roles of these gases will be provided in chapter 2. Empirically, the roles of C/O/H have been summarised in the Bachmann diagram [6] (see figure 1.4). It is an underlying principle that, at least to first order, diamond CVD is independent of the nature of the activation technique.



Figure 1.4: The original Bachmann C/H/O phase diagram, reproduced from [6]

The diagram is subdivided into three areas; non-diamond deposition, diamond deposition and no growth regions. Since its conception, it has allowed researchers to predict the likely outcome of a particular precursor gas mixture. For instance, no combination of water and carbon dioxide could be induced to deposit diamond, but any mixture of carbon monoxide and hydrogen is a potential CVD gas mix. A mixture of oxygen and acetylene will deposit amorphous carbon at low oxygen levels, but deposit nothing in leaner gas mixtures, except for a narrow window where the gas ratio is near unity. The diamond growth region is not an entirely featureless deposition region; instead it is continuous spectrum of improving 'quality' with reduced growth rate as a line is traced from the nondiamond to the no growth regions. This hints at a balance of increases in all carbon deposition rates with increased C input and loss of carbon as combusted products (CO and CO_2) from the chamber with O additions.

Substrate

As stated above, all CVD techniques aim for the same substrate environment. Growth temperatures are typically in the range 600 - 1000 °C [1]. Temperatures below this range lead to either no growth or amorphous carbon deposition, whereas those above lead to graphitic carbon deposition. The bulk of the diamond literature concentrates on just three substrate materials: silicon, due to the availability of highly precise surface media, molybdenum, due to its robustness in high power environments and HPHT diamond, for single crystal growth.

In the first two cases, diamond seeds must be adhered, via ultrasonic pretreatment, or ground in, through mechanical polishing prior to film growth. These seeds (probably also along with induced surface defects) act as nucleation sources [7] which grow, fuse together and then competitively increase in size to form a continuous film. Aside from an initial nucleation phase, film thickness increases linearly with deposition time. Once power is withdrawn from the system, depending on the substrate material, the film will either remain attached to the substrate (silicon or diamond) or de-laminate into a free-standing film (molybdenum).

The CVD Diamond Material

The resulting films exhibit a textured, normally aligned, 'columnar' structure (see figure 1.5). Due to the competitive nature of growth, films increase in coarseness, towards the growth face. Film surfaces have roughnesses typically in the range (400-1000 nm [8]) whereas the back face exhibit roughness of the same order as the substrate surface.

1. Diamond

For some applications, a high smoothness is required, a lower 'quality' is aimed for. This is achieved either by increasing the hydrocarbon fraction or, following Gruen *et al.* [9–12] replacing hydrogen with argon as a carrier gas. These films are generally referred to as nanocrystalline diamond (NCD) or nanodiamond. Gruen and co-workers set their work apart from the literature, with claims of superior film properties (see table 3 in [8]). They thus, coined the term ultrananocrystalline diamond (UNCD) to describe their films. The resultant films are much less coarse, reportably with grains sized 2-5 nm.



Figure 1.5: A comparison of microcrystalline diamond (MCD, *left*) and Nanocrystalline diamond (NCD, *right*). a) and b) are surface views, c) is a schematic view of the structure of diamond films and d) and e) are cross-sections of the film showing Si in light grey (bottom layer) and diamond dark grey (top layer).

1.2.1 Techniques in Diamond CVD

There are many alternative techniques for the vapour deposition of diamond thin films. The following section outlines just those that have had *in-situ* mass spectrometry applied to them (see section 3.4).

Hot Filament

Along with microwave plasma activation, hot filament techniques make up the vast majority of diamond CVD literature. This is largely due to the relatively low cost, simple reactor design and also, in terms of research, its amenity to *in-situ* probing. The general method, still applied today, was first described by Matsumoto *et al.* [13]. A metal filament, typically tantalum, is resistively heated to ~ 2200 K in a 1% methane in hydrogen mixture. Diamond quality is limited by contamination from the metal filament and the limited spatial extent of the activation region. Another slight disadvantage is the fragility of filaments which prevents the use of many oxidising species (such as oxygen). Growth rates of $1 - 10 \,\mu$ mhr⁻¹ are achievable from powers in the region of 150 W. These powers lead to minimal substrate heating, so unlike other techniques, a heater is often employed to achieve deposition temperatures. Figure 1.7a shows a possible reactor configuration.

Combustion Torch

A simple oxyacetylene torch can be encouraged to deposit diamond via the use of appropriate gas ratios (see figure 1.4) [14]. High growth rates at atmospheric pressures (~ $50 \,\mu mhr^{-1}$) can be achieved from gas mixtures typically 51 % / 49 %acetylene to oxygen. Some of the relevant experimental details are shown in Figure 1.7c.

Microwave Plasma Enhanced Deposition

The synthesis of diamond via microwave plasmas was first achieved by Kamo *et al.* [15]. Their experimental set-up is shown below (figure 1.6). A mixture of 1 - 3% methane in hydrogen was passed through a quartz flow tube reactor. A substrate holder was placed at the intersection of a tuneable (2.45 GHz) microwave waveguide. In their initial paper, single crystals of diamond were deposited on (800 - 1000 °C) substrates of silicon and molybdenum from gas



pressures of 10-60 Torr. Microwave plasmas are now commonly operating up to 200 Torr at powers 0.8-6 kW.

Figure 1.6: The MWCVD original system from [15].

Most MWCVD reactors are now based on the 'ASTeX' style design (figure 1.7b below). In these reactors the microwave radiation is coupled to the chamber via an antenna. The main advantage here is that the quartz window is remote from the plasma and therefore the chance of it being damage or silicon contamination is minimised. MWCVD boasts the highest controllability of diamond products, as the technique is the least sensitive to the addition of aggressive ingredients.



(a) A Hot Filament System



(b) The more common 'ASTeX' (c) A Combustion torch system style Microwave system

Figure 1.7: Sketches of three of the most common diamond depositing reactor types.

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Chapter 2

Reactive Plasmas

Reactive plasmas describe systems that interact through chemical means, either reactive etching or chemical deposition. Microwave plasma chemical vapour deposition (MWCVD) is included under this umbrella term, as it is set apart from physical deposition mechanisms such as sputtering or sub-implantation. This chapter briefly describes the plasma, discussing some of the ionic, chemical, and thermo-physical attributes of the constituent gases and how they affect plasma properties.

2.1 Plasmas In Principle

A plasma is defined as a region of ionised gas. They are most typically comprised of atomic or molecular cations and counterbalancing electrons. This strict definition does not refer to any co-existing, neutral gas phase. However, as will be explained later, the plasma and neutral background's properties, in this slightly 'special' case, are closely interrelated. Therefore reference to the 'plasma', within this thesis, will be used loosely to include the neutral population.

If the plasma is driven electromagnetically, then the lightest species (typically free electrons) will be most efficiently affected. Thus, they will obtain higher temperatures than heavier cations. As the neutral background gas cannot interact directly with the applied power they can only be heated through - sometimes negligible - secondary interactions. The temperature distributions can be so disparate that, whereas electron and ion energies are usually quoted in electron volts, neutral molecules are often in thermal equilibrium with their surroundings.

2.1.1 Initiation of the Discharge

There are many ways to generate a plasma, of these the simplest is probably sufficient gas heating. If a gas's thermal temperature approaches its ionisation potential (IP), such as a rocket's re-entry from orbit, then a spontaneous plasma begins to form ($\sim 9000 \,\mathrm{K}$ for 'pure' air at 1 atm [1]).

An electron current can also be used to initiate and maintain a discharge. If sufficient bias is placed across two electrodes, then field emitted electrons from the cathode are accelerated across the gap. If the electron kinetic energy becomes comparable to the gas's IP then the gas can undergo breakdown. As the gap becomes more conductive, so a direct, two component (anionic and cationic), current can flow in their respective directions.

In the case of the plasma reactor described in this thesis, there are no electrodes to supply current, or sufficient heating (prior to discharge) to cause a significant degree of ionisation. Instead we have to rely on the vanishingly small number of naturally occurring free electrons coupling to the applied microwave fields. Prior to the discharge, a standing wave is present in the chamber with the substrate and the magnetron acting as either end of a cavity. There is a local maximium located, *by design*, above the substrate with no other significant maxima within the low pressure system (see figure 2.1).

An isolated free electron in an oscillating electric field will be continuously accelerated and decelerated without any net gain in energy. If we now introduce a background of neutral particles, it is clear that these will act to resist an electron's motion. A more subtle secondary effect is also introduced; because much of electron's collisions will be irreversible (random in direction) they lead to a net build up of energy. So despite the resistance imposed by the background it is also key to heating of the electrons.

2.1.2 Maintaining the Discharge

It is useful to split electro-magnetically (EM) driven plasmas into two groups; ones where electrons are free to make many oscillations per collision, and ones which have no long term cycling of electrons due to background scatter. A more rigourous definition for a criterion is given in [2] which sets ~ 20 mbar (~ 15 Torr) as an appropriate divide in room temperature hydrogen gas. Below this divide, the electron temperature is related to E/ω and the plasma shape is determined by



Figure 2.1: Hagelaar *et al.*'s simulated electric field amplitude as a function of position within the reactor (adapted from [2]). The reactor here is a bell-jar type, so only qualitative comparisons can be made with the 'Astex type' reactor described in this study (see chapter 1).

the local field shape (of frequency ω and amplitude E). At higher pressures the reduced electric field E/n determines the electron temperature. Therefore many plasma characteristics are now also dependent on the local gas temperatures and number densities (n). As plasma heating will affect these parameters, the plasma can therefore exhibit significant hysteresis. An example given in [2] is the empirical observation that, at typical powers, microwave plasmas cannot be ignited above ~ 20 Torr. Below this pressure the leading tail of electrons energy distribution can still achieve enough energy to ionise neutrals. Once the plasma is stable the pressure can now be raised considerably as heating will have led to a significant drop in density.

Once the plasma is established it can interact with the supplied microwaves by absorbing and reflecting energy to varying extents. Due to the density of charged species, plasmas are conductive. Therefore external fields can only penetrate the discharge interior to an extent dependent on conductivity. The more conductive (dense) a plasma, the less microwave energy can penetrate. This reason, along with the increased efficiency of third body quenching of ions at the periphery, leads to reduced plasma volumes at higher pressures.

2.2 MWCVD Chemistry

2.2.1 Hydrogen

It may seem strange to start a discussion of the chemistry of diamond depositing plasmas with hydrogen rather than the diamond precursor species, but it is arguably as important an element as carbon in the CVD process. It is the most widely used 'diluent' gas, as it is able to form stable, chemically active (with carbon) plasmas for a wide range of pressures and powers. As such, it dominates the neutral chemistry and gas-phase properties of the reactor. The following plot (figure 2.2) shows the computed [3] equilibrium state of hydrogen gas as a function of temperature. Above ~ 2000 K, hydrogen atoms begin to make a significant contribution to the total hydrogen balance. By ~ 3000 K, the two components are of equal concentration (1 /3 of the molecular hydrogen input has dissociated). It is within this range that typical microwave CVD plasma temperatures [4–7] are quoted¹.

It is not a coincidence that this also matches a local maximum in heat capacity. Increasing the temperature in this region requires the most significant outlay in exciting the molecular hydrogen vibrational progression. Once hydrogen dissociation is significant, the heat capacity tends asymptotically to the atomic value (5/2R). The large degree of dissociation is now thought to be a vital aspect of diamond synthesis [10]. Atomic hydrogen drives the chemistry of both the gas-phase and gas-surface interactions.

In the gas phase, hydrogen atoms facilitate rapid interconversion between hydrocarbons (see figure 2.3). This rapid shuffling of species leads to a largely thermodynamic distribution of hydrocarbon species within the plasma [11]. Outside the plasma, homogeneous recombination of atomic species is not efficient, so super-equilibrium concentrations of hydrogen may reach the substrate [10].

 $^{^1\}mathrm{The}$ work of Goyette et~al. is an exception to this with values 800-1300 K [8,9] see Appendix A.


Figure 2.2: The equilibrium mole fraction of 100 Torr hydrogen gas and its associated constant pressure heat capacity (C_p) as a function of temperature.

 $C_2H_6 \stackrel{H}{\rightleftharpoons} C_2H_5 \stackrel{H}{\rightleftharpoons} C_2H_4 \stackrel{H}{\rightleftharpoons} C_2H_3 \stackrel{H}{\rightleftharpoons} C_2H_2 \stackrel{H}{\rightleftharpoons} C_2H \stackrel{H}{\rightleftharpoons} C_2$

 $\|_{\rm CH_3}$

$$\operatorname{CH}_4 \stackrel{\mathrm{H}}{\rightleftharpoons} \operatorname{CH}_3 \stackrel{\mathrm{H}}{\rightleftharpoons} \operatorname{CH}_2 \stackrel{\mathrm{H}}{\rightleftharpoons} \operatorname{CH} \stackrel{\mathrm{H}}{\rightleftharpoons} \operatorname{CH}$$

Figure 2.3: A primitive diamond gas-phase mechanism showing the H mediated chemistry.

Once at the diamond surface, H atoms can activate surface sites by abstracting surface terminating hydrogens. The resultant surface 'dangling bonds' are capable of reacting with incoming hydrocarbons, thereby depositing carbon. One further role attributed to hydrogen is the removal of adsorbates back into the gas phase; it is hydrogen atom's enhanced ability to etch unsaturated, non-diamond surface species, relative to saturated species, that leads to the kinetic trapping of diamond. These processes are summarised in 2.4.



Figure 2.4: A summary of the key processes in MWCVD diamond deposition.

2.2.2 Hydrocarbons

Figure 2.5 shows the predominant hydrocarbon present at high temperatures, and should therefore give an idea of the sort of chemical environment present in diamond CVD. For diamond to be deposited, we understandably require a 'participating' source of carbon. Carbon must be present in a volatile, dissociable state. Simple C_{1-2} hydrocarbons such as methane and acetylene provide these properties. With boiling points in the range 112-186 K, and a significant degree of dissociation at plasma temperatures, they are the most commonly used carbon sources. The exact selection of a simple hydrocarbon is not critical, for the reasons stated above. So the predominant favouritism for methane in the literature is largely economic.

In order to optimise the CVD process it would be useful to identify carbon species which are 'responsible' for diamond growth, rather than ones which predominantly lead to other carbon phases. These are generally species labelled as 'growth species'. It would be incorrect, however, to see diamond growth species as 'monomer' units of diamond akin to crystal precipitation. Their role is to act as a way of transporting carbon from the activating region to the diamond surface in a form which is still reactive enough to incorporate. For example, the increase in concentration of any hydrocarbon, radical or otherwise, is always associated with a decrease in diamond 'quality' (see the 'Bachmann diagram' in chapter 1, figure 1.4). It is the synergic activity of H with these species that leads to diamond growth.



Figure 2.5: The equilibrium profiles (calculated [3]) of the major carbon containing species from heating 100 Torr of 1% methane in hydrogen as a function of gas temperature. Areas where the total does not appear to sum to one, such as the switch over from acetylene to carbon, occur when minor species (not shown) have a significant fraction of the total carbon fraction (e.g. C_n at ~ 3500 K).

Many species have been proposed as the growth species including CH_4 , CH_3 , C_1 , C_2 , C_2H_2 and C_2H_1 . Methyl radical (CH_3) is currently favoured as the major contributer to diamond growth. It has accumulated a large amount of circumstantial evidence to support this postion. As well as being detected with concentrations exceeding all other radical species in nearly all diamond CVD environments [10], it also is supported by some compelling molecular beam studies [12–14].

In the previous decade, workers at the Argonne National Laboratories have suggested an alternative growth mechanism in hydrogen poor environments based on the carbon dimer radical. Initially prompted by the strength of dicarbon emission in their $Ar/H_2/CH_4$ plasma [15, 16], they have since consolidated their arguments through the computation of a low energy mechanism [17] which bears agreement with an apparent lowering of the diamond activation barrier. There have also been quantitive estimates of dicarbon concentration via absorption spectroscopy [8, 18].

This alternative mechanism is still controversial as, to date, no study has been completed on the concentrations of other species in this media. For instance methyl could still be present in significant concentrations thus rendering the need for an alternative mechanism obsolete [19].

2.2.3 Argon

Argon is also a common additive to the CVD process. Its role in plasma processes is unclear; some researchers place great importance of the role of metastables (Ar*) [20, 21], while others consign its role to that of a spectator contributing mostly thermal effects. At low to medium concentration [22], Ar is reported to enhance growth rate and to allow operators to decrease the $^{\rm H/C}$ ratio without compromising diamond 'quality'. This continues up to Ar fractions in the region 80-90% where the grain size and deposition rate decreases rapidly towards the nanocrystalline growth regime. There is also an associated shift in the visible output of the plasma from an H_{α} Balmer emission to a C₂ Swan band dominated spectrum. Gruen and co-workers have postulated that another mechanism is responsible for diamond formation in these lower hydrogen concentration plasmas [8,17,18,23,24].

Plasmas become increasingly unstable as the argon fraction is increased further, reaching a practical limit of about 97%. The origin of this instability can be explained by considering that third-body-induced ion recombination is much less efficient than for H_2 ; argon, being atomic, lacks the rotational and vibrational freedom through which to disperse an electron's binding energy. In the presence of hydrogen, another, more efficient, mechanism is able to remove argon ions. Argon ions can form an argon hydride cation with molecular hydrogen. This ion has the potential to irreversibly accept an electron producing neutral H and Ar fragments [20].

$$Ar^{+} + H_{2} \leftrightarrows ArH^{+} + H \tag{2.1}$$

$$\operatorname{ArH}^+ + e^- \to \operatorname{Ar} + \operatorname{H}$$
 (2.2)

This reaction scheme gives a plausible explaination for the relatively late, in terms of argon fraction, crossover of plasma characteristics [22].

As was stated before, argon metastable states play an important role in Gruen's description of high argon concentration plasmas. The first electronically excited state of argon is a triplet with an impressivily long radiative lifetime [25] of 55.9 s. If this metastable species could be formed from electron impacts, then this stored internal energy (11.8 eV) could drive non-thermal chemistry. Gruen [8,21] suggested that C_2 production is largely a result of Penning ionisation² followed by dissociative recombination:

$$Ar^* + C_2H_2 \to Ar + C_2H_2^+ + e^-$$
 (2.3)

$$C_2H_2^+ + e^- \to C_2 + 2H$$
 (2.4)

This mechanism was used to provide an explanation for his apparent observation of highly non-equilibrium populations of C_2 in argon-methane plasmas. Gruen had used the values of Goyette *et al.* [8,26] who estimated a plasma temperature of around 1200 K via broadband absorbance spectrometry (see appendix A). This relatively low value is not sufficient to produce their own simultaneously measured values of the C_2 'a' state through thermal chemistry.

Other groups have estimated argon plasma temperatures ~ 3000 K [27, 28]. These higher temperatures make a thermal population a much more probable explanation. Measurement of a higher temperature in argon plasmas is also to be expected from its reduced thermal conductivity ($\propto m^{-3/2}$) and lower (atomic) heat capacity.

 $^{^{2}}$ for a discussion of Penning ionisation, see the review of Siska [25].

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Chapter 3

Molecular Beam Mass Spectrometry

Since its development in the 1960-70's [1], Molecular Beam Mass Spectrometry (MBMS) has proven itself as a valuable probe of aggressive gas phase environments [2,3]. This chapter introduces the principles of MBMS, the practicalities of operation and finally a short history of its application to CVD diamond studies. As such, it briefly discusses the theory and implementation of quadrupole mass spectrometers (QMS) and molecular beams. Another key section tackles the issue of calibration imposed by mass-dependent efficiencies imposed by gas dynamics, chemical reactivity and the spectrometer itself.

3.1 Mass Spectrometry

3.1.1 In Principle

Mass spectrometry describes a wide range of inertial techniques employed in order to separate ions due to the ratio of their charge (q) to their mass (m). This is accomplished by the use of electric (\mathbf{E}) or magnetic (\mathbf{B}) fields (static or time varying) acting on the charged particle as described by the Lorentz Force Law:

$$F = q\boldsymbol{E} + q\boldsymbol{v} \times \boldsymbol{B} \tag{3.1}$$

It is apparent (from 3.1) that there are marked differences between the effects of the two field types. The electric field will act to accelerate a positive ion in the direction of the field vector regardless of its initial velocity. A magnetic field acts to push the particle in a direction (specifically the cross product) perpendicular to the field and velocity (\boldsymbol{v}) . A consequence of this is that it will only act on ions that have velocity components perpendicular to that of the field. Moving charges, therefore, tend to circle around the magnetic field vector without altering the speed (|v|) of the particle. These accelerations $(\propto 1/m)$ can be used to separate ions in velocity (*e.g.* time of flight, TOF) or position (*e.g.* Magnetic Sector). The quadrupole mass filter differs from the previous examples as it uses timedependent fields to resolve ions. Mass separation, is instead, derived from path stability as explained in the following section.

3.1.2 Quadrupole Mass Spectrometers

A thorough description of the theory of quadrupoles is given in [1]. The potential in a perfect quadrupole field ($\Phi(\mathbf{x},\mathbf{y})$), of electric field strength (E_0), is described by a 'saddle-point' function (see figure 3.1a):

$$\Phi = \frac{1}{2}E_0(x^2 - y^2) \tag{3.2}$$

In the real world, the quadrupole field can be approximated (close to the central axis) by the arrangement of four cylindrical rods as shown in figure 3.1b.



Figure 3.1: Quadrupoles: Perfect and 'Real', a) A perfect quadrupole field $\Phi(x, y)$, and b) a practically achievable quadrupole electrode array.

Close to the central axis in a real quadrupole, with electrodes placed at a

distance r_0 from the origin, equation 3.2 becomes:

$$\Phi = \frac{\Phi_0(x^2 - y^2)}{2r_0^2} \tag{3.3}$$

A static quadrupole field (as shown in figure 3.1b) would cause ions to oscillate harmonically in one plane (yz) but to diverge to the perpendicular electrodes. In operation, a quadrupole filter uses a combination of static (V') and periodic $(V\cos(\omega t))$ potentials. The periodic defocusing caused by V in isolation would cause all ion trajectories to become unstable with time (t). Inertia leaving the heaviest least affected acts to some extent as a low mass filter. The inclusion of a direct component serves to offer a periodic restoring force provided the paths are resonant with the oscillating field (at frequency ω).

$$\frac{\partial^2 x}{\partial t^2} + \left(\frac{e}{mr_0^2}\right) (V' - V\cos(\omega t))x = 0 \tag{3.4}$$

$$\frac{\partial^2 y}{\partial t^2} - \left(\frac{e}{mr_0^2}\right) \left(V' - V\cos(\omega t)\right)y = 0 \tag{3.5}$$

where e is the elementary charge and m is the mass of a singly charged ion.

In order to obtain general, machine independent, treatment, these equations (3.4 & 3.5) are typically re-cast in the form of the Mathieu equation using the following dimensionless quantities:

$$a = \frac{4eV'}{m\omega^2 r_0^2} \qquad q = \frac{2eV}{m\omega^2 r_0^2} \qquad \xi = \frac{\omega t}{2}$$
 (3.6)

These equations give rise to a complex range of solutions [1] some of which are periodic and stable. Those solutions that are useful for spectrometry are bounded in an area close to the origin (see fig 3.2). If appropriate voltages are selected, the filter can have a certain band pass as shown in figure 3.2. Normally, the quadrupole is operated with a fixed ratio a/q so that it crosses the stable region near the apex at (0.706, 0.23699) or $V'/V \sim 1.7$. In the diagram, m_1 and m_3 represent masses that are too heavy and too light respectively. In order to generate a mass scan, V' and V are scaled to shift the position of masses along the line. In this kind of operation the mass of ions transmitted is linearly proportional to the scaling of the voltages.

Note that in this ideal case, stability is not a function of the initial conditions,



Figure 3.2: A schematic stability diagram as a function of a and q. The dotted line shows a particular operating condition, selecting between three masses $(m_1 < m_2 < m_3)$.

either velocity or position of the ion. In reality, however, ions with a trajectory that takes them a significant fraction of r_0 away from the origin will be exposed to field imperfections from the non-hyperbolic electrodes.

3.1.3 In Practice

This section describes how the quadrupole is constructed from relatively simple components. This simplicity makes for cheap, compact, robust devices and means QMS has become the most important method for moderate resolution applications [1].

Ioniser

The MS ioniser, or ion source - often simply called source - is mounted at the front of the quadrupole (See figure 3.4). Its purpose is to generate a relatively collimated beam of ions, to the quadrupole, that is diagnostic of local gas phase species. A common technique for the ionisation of relatively robust, volatile species is the electron ioniser. In principle, a collimated, monochromatic (often \sim 70 eV), beam of electrons bombards a gas sample. With the ionisation thresholds of small molecules typically in the range 10-15 eV, single collisional events lead



Figure 3.3: A schematic diagram of a typical quadrupole MS probe, adapted from [4].

to ionisation with high efficiency.

In practice, the electron beam is generated via thermionic emission from a heated filament. These free electrons are then accelerated to ionisation energies through an electrode aperture, into a central chamber. Collisions generate cations which can then be extracted via a weaker, perpendicular field. A combination of the weak extraction field and the thermal spread of emitted electrons serves to smear energies to $\pm 0.5 \,\mathrm{eV}$ of the central value.



Figure 3.4: A schematic diagram of a simple ion source, adapted from [5]. As a single component it presents the user with the most options for optimising detection within the MS. The operator is usually allowed to specify the electron emission current, the 'cage' extraction voltage and the electron energy (all in *italics*).

Quadrupole and Filters

From the stability diagram (figure 3.2) it can be seen that there is a balance between throughput and resolution. Also this figure shows it is possible to envisage independently tuning the high and low mass resolution. Improved resolution is also obtainable by increasing the number of radio frequency (r.f) cycles to which the ion is exposed, i.e. 'sharpening' the boundary of the stability diagram. The advantage of the linear quadrupole over most MS techniques is that all of this tuning is achievable through electronics, not requiring any mechanical or geometric alterations.

As stated earlier, for good resolution it is advantageous for the ions to take a large number of rf periods to traverse the quadrupole. In short filters, high frequencies are used but in more moderate length quadrupoles it is sufficient to limit ion kinetic energies to $\sim 3 \,\mathrm{eV}$. These 'low' energies present problems, however, as ions spend longer entering and exiting the quadrupole. At the extremes of the quadrupole the fields fall off with distance. These fringing fields represent points on the operation line prior to the stability region. The larger the number of cycles spent in this region, the greater the loss of signal to the *x*-electrodes (low pass filter). Brubaker [6] solved this problem by the introduction of a delayed DC ramp or pre-filter. This short quadrupole operated in rf only mode is placed inline before the main filter. Thus, the path through the stability diagram initially starts with a increase in *q* followed by simultaneous increase in both parameters once approaching the main filter. This generates a path for the resonant ion that is permanently within the stability region. A post filter is often also implemented for the same reason.

Secondary Electron Multiplier

Channeltron Electron Multipliers (CEM) [7] are constructed from a lead silicate tube coated in a proprietary, high work function semiconductor. This coating, used to to minimise the thermal electron emission, is interrupted on the outside to produce a single internal path to ground. The general features are a collection horn, a narrow curving tube and an output electrode (see figure 3.5).

In order to detect positive ions the collector is held at a potential as much as -3 kV, whilst the output is held at 0 V. Accelerated ions produce 2-3 secondary electrons on impact with the collector. These secondary electrons are accelerated down the tube by the positive bias, striking the walls and liberating more electrons

forming a cascade. Typically $10^{-7}-10^{-8}$ electrons are produced from a single event. At gains higher than $10^{-4}-10^{-5}$ the output electron density is such that material can be desorbed and ionised, whereby it will be accelerated back to the collector. The tube is therefore curved to minimise this feedback. A curved CEM will allow gains $< 10^{-8}$ when operated in 'pulse counting' mode (as opposed to analogue mode).



Figure 3.5: A schematic diagram of a typical Channeltron Electron Multiplier operating in positive ion counting mode.

This pulse counting mode is used in applications where detection of small signals is required. The Channetron is operated at saturation so that each pulse event is identical. The signal is then measured as a count-rate rather than an analogue output current. The high gain means that a discrimination level can be set that rejects low level noise, leading to high signal-to-noise. However in pulse counting mode for rates in excess of $\sim 10^7 \, \text{s}^{-1}$, counting will be limited by the pulse width.

Channeltrons are often mounted slightly off-axis with a deflector plate to guide ions. This reduces the spurious signals from metastables and photons produced from the ioniser filament or an external source.

Slow damage through the impact of high energy ions on the collector, and the high electron densities at the output, induce physical/chemical processes which lower electron emission and therefore gain. Under UHV conditions, the total life-time output should be $\sim 30 \text{ C}$ [7]. Many environmental factors, such as operation at high pressures, large count accumulation, unnecessarily high gain and back streaming of pump oils set the actual lifetime.

3.2 Molecular Beams

A molecular beam is a 'train' of molecules with some degree of correlated motion, despite the absence of any overall hydrodynamic flow. Like a light ray, it can be collimated with apertures (skimmers), attenuated (scattered) as it traverses a sufficiently dense medium (*e.g.* a relatively high vacuum chamber background), or reflected off surfaces. Beam sources comprise of a deliberate 'leak' into a molecular flow regime system from continuum conditions. If this leak is sufficiently small (effusive) then the transition preserves the composition and internal energy of the extracted sample. If, however, the leak is large, then molecular collisions drive a supersonic, adiabatic acceleration or jet.

A recurrent theme in the discussion of compressible gas flows, of which a jet is an example, is the use of dimensionless quantities. The purpose of these are to enhance the generality of explanation, and free authors from the machine-specific properties of real devices. In order to facilitate this normalisation, a reference condition, known as stagnation, is chosen. This is located arbitrarily far away from the system under study, where properties are well defined and static. In the study of jets, this condition, usually denoted with a 0 subscript, is located far upstream of the leaking orifice. So, in further discussion, the dimensionless analogues of properties such as pressure (p/p_0) , temperature (T/τ_0) , flow velocity (v/v_0)) will be used widely. The dimensionless analogue of length is orifice diameters (x/d) where x is the physical length and d is the diameter of the orifice 'throat' (greatest constriction). Due to the non-isotropic nature of the jet, it is also sometimes useful to define some properties - such as flow velocity - parallel (axial) and perpendicular (radial) to the centre-line of the expansion. These are denoted with the subscripts \perp and \parallel , respectively.

In a jet, a proportion of the gas's internal energy is used to provide the flow work of the expansion, resulting in significant cooling. Non-effusive sources actively draw gas through the orifice and are therefore higher in intensity than their effusive counterparts. The expansion also rapidly reduces the collision probability, thus effectively halting chemistry within a few orifice diameters. In order to use this, and to minimise later pumping requirements the beam is often skimmed into another chamber forming a collimated beam. Thus a molecular beam is seen to be a viable method for transporting, relatively unperturbed, a sample of gas from the CVD (20-200 Torr) to MS (10^{-7} Torr) environments.

3.2.1 Describing the 'leak'

Depending on the quality of the vacuum into which the sample is expanding, there are two main paradigms to describe the evolution from isentropic¹ expansion to a molecular beam [9]. In both cases the system is assumed to achieve the stagnation sound speed (a_0) at the throat (greatest constriction) into the low pressure regime.

In the relatively high background pressures (p_b) of a mechanically pumped system, the background gases are non-negligible. The intense, sonic jet forces the background back, so that there exists a core of expansion to which information about the background cannot penetrate, known as the 'zone of silence'. This region terminates rapidly in a boundary 'shock'² where the forces exerted by the energetic, low density, supersonic expansion balance the inward pressure of the relatively denser background gas (see figure 3.6a). Note that inside the isentropic region, streamlines are straight, whilst outside, curved streamlines show gas being dragged round by the jet (see figure 3.6b). Another important potential shock is the Mach disk which crosses the centre line at a distance (x_m/d) downstream of the orifice:

$$\frac{x_m}{d} = 0.67 \sqrt{\frac{p_0}{p_b}}$$
 (3.7)

 p_0/p_b being the ratio of stagnation to background pressure.

This shock marks the termination of supersonic flow (see figure 3.6b: top); it is also a potential source of background invasion. Within the shock, irreversible, dissipative forces dominate, leading to a dramatic increase in entropy. These viscous regions are also a source of deleterious chemical change, as local temperature and density rise dramatically. Location of a skimmer upstream of this surface facilitates a further pressure reduction, the effect of which is to prevent the formation of a Mach disk shock at the beam centre [10]. It can introduce some additional shock structure, however (see section 3.3.2).

If, instead, a higher pump speed is used - such as that of a diffusion pump or turbomolecular pump - then the meaning of a shock structure becomes less clear. Miller [9] points out that if the pressure is reduced low enough, then the mean free path, and therefore shock thickness, will eventually exceed the dimensions of the apparatus. Instead of a terminating shock he suggests a smooth transition to

¹The key conserved quantity is the stagnation entropy (S_0) [8] (also see figure 3.6b :bottom)

 $^{^{2}}$ A region of discontinuity in pressure and density. Infinitely abrupt in perfect, continuous, fluids but in real, granular, media it is approximately equal to the mean free path.



Figure 3.6: Sketched, computed and experimental images of a free-jet: a) A sketch of the structure of a free-jet (from [10]), b) Computed Mach number (top), streamlines and deviation from stagnation entropy (both bottom) (also from [10]) and c) experimental refractive index gradients as visualised by Schlieren photography [11].

molecular flow. For estimation of flow properties, he suggests the implementation of a hypothetical 'quitting surface' (see figure 3.7). Upstream is the isentropic expansion and downstream is the molecular flow region. Many properties (such as $\boldsymbol{v}, T_{\parallel}$) are collisionally determined and are therefore 'locked-in' at such a surface.

Both of the above pressure regimes have been used for MBMS, with careful location of the skimmer in the former case. It is also clear that the technical requirements of the lower pressure system are less stringent. It is therefore of more practical expedience to opt for the latter system.



Figure 3.7: A sketch of the quitting surface as proposed in [9].

3.2.2 Calculating Beam Properties

Although there are a range of possible source geometries, the discussion here will be limited the centre line properties of a three-dimensional axisymmetric flow. It is important to note that much of the information in the following section is derived from the discussion on free-jets by Miller [9]. Some caution must be taken when interpolating results from free-jets to MBMS. There is a key geometric difference with these expansions. Miller discusses a converging nozzle with no diverging section, post throat. MBMS typically uses an entirely diverging nozzle. So, to maintain technical accuracy, even use of the term 'freejet' should be avoided. It is likely that the resultant expansion will be even less isotropic. Furthermore, some form of additional shock structure must also form to communicate between the supersonic flow boundary and the static nozzle wall. For successful sampling this non-isentropic, viscous, region must be attached to the nozzle wall and not communicating with the centre-line.

Two key dimensionless quantities dominate the properties of the expansion. The heat capacity ratio γ and the Mach number M. From basic thermodynamics, for a single component perfect gas, γ (c_p/c_v) must take values of 5/3 in atomic, 7/5in cold and 9/7 vibrationally hot, diatomic gases. Mach number (M) - which is itself is a function of distance downstream of the orifice - is defined at the simplest level as the ratio of the flow velocity to the sound speed. At a slightly deeper



Figure 3.8: A Sketch of left) a typical molecular beam nozzle and right) a more representative MBMS orifice.

level it represents a comparison of the directed, and random thermal motion of a gas flow [12]:

$$\frac{v^2/2}{u} = \frac{\gamma - 1}{2}M^2 \tag{3.8}$$

where u is the internal energy per unit mass.

For any isentropic process, many properties can be calculated from the following relations (equations 3.9 - 3.12 [12]). They can therefore be applied to the expansion prior to the shock termination or 'quitting'.

$$\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-1}$$
(3.9)

$$\frac{v}{v_0} = M \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{-\frac{1}{2}}$$
(3.10)

$$\frac{p}{p_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-\frac{\gamma}{\gamma - 1}}$$
(3.11)

$$\frac{\rho}{\rho_0} = \frac{n}{n_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-\frac{1}{\gamma - 1}}$$
(3.12)

Another useful property is the initial beam beam intensity (molecules per steradian) [9] which holds indefinitely in the absence of scattering:

$$I_0 = \frac{\kappa n_0 d_1^2}{4} \sqrt{\frac{2\gamma R T_0}{(\gamma+1)m}} \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}}$$
(3.13)

 κ is a peaking factor, dependent on γ , adjusting for non-effusive sampling.

3.3 Compositional Distortions and Calibrations

It is often noted in the literature that it is desirable to sample gas from the reaction mixture under effusive conditions. If the orifice is smaller than the local mean free path then there can be no communication of information between the orifice region and it surroundings. It must therefore be completely non-perturbing and exhibit no 'pull' effects. Furthermore, the sampling must be truly 'collisionless' as the last interaction suffered was the knock a molecule received in the direction of the effusing orifice. Species are emitted into the vacuum system in a spherical distribution. Partial pressures detected will therefore be indicative of the sampling region and will not be affected by any mass separation effects (see section 3.3.2). The only consideration is the $1/r^2$ fall-off of signal with distance.

This desirable state is impractical for many systems of interest. Minute sampling orifices will lead to necessarily small signals and are prone to rapid blockage³. Instead, for our system, a much larger orifice must be used. Now transitions through the orifice and towards molecular flow are mediated by a series of collisions of decreasing frequency. These non-effusive jets lead to beam enhancement as the admitted distribution becomes more collimated and subsequently mass discriminating [9]. Despite the expansion anisotropy, the spherical fall-off of signal, suggested above, is still a reasonable approximation for large distances (many x/d). This suggests a continued general preference for a compact design.

Those who wish to obtain a more detailed account on this subject, and of the inherent signal distortions in MBMS, are directed to the reviews of Knuth [3,13], and the work of Singh [14–16], which are the main sources for this section. For ease of explanation, distortions have been grouped into three subsections: beam formation, beam transit and mass spectrometric. Although this may seem like a daunting list of obstacles, the following sections will outline how, with minimal assumptions, they are mitigated for stable species and ameliorated for radicals.

A repeated feature for the first two sections is that typical MBMS experiments

³Especially in the context of a CVD system with growth rates $1 - 100 \,\mu mhr^{-1}$

display a high degree of angular resolution. This means that only features which propagate along the centre-line will reach the detector.

3.3.1 Beam Formation

The first feature which needs to be assessed is what is actually being sampled. During CVD most models suggest a high amount of surface mobility of radicals and atoms. Species are able to move around relatively freely until they reach a reaction site, diffuse away, or are quenched. The design of the new reactor sampling through the substrate - may at first suggest that we would be sampling from this boundary layer of thickness δ . Knuth [13] suggests $d/\delta > 1$ as a criterion for achieving 'bulk' sampling (See figure 3.9).

It is also known that MBMS can often display axial shifts in species concentration profiles relative to non-invasive techniques [3]. Species appear to be being sampled as much as 5 orifice diameters upstream from the sampling orifice. In other words, in these non-effusive conditions, the sampled gas is accelerating into the orifice. In this situation Knuth [3] states that, if the product of the Reynolds and Schimdt numbers (Re and Sc respectively) satisfy the following inequality at stagnation :

$$(ReSc)_0 = \frac{a_0 d}{D_0} \gg 1$$
 (3.14)

then the shift in the effective sampling position $(\delta x/d)$ is empirically given by:

$$\frac{\delta x}{d} = 0.19\sqrt{(ReSc)_0} \tag{3.15}$$

where a_0 , d and D_0 are the local sound speed, a characteristic length such as the throat diameter, and the diffusion coefficient at stagnation respectively. The above analysis predicts an axial shift of ~1.1 diameters or $110 \,\mu\text{m}$ for dilute argon in hydrogen gas at 1500 K and 100 Torr.

This effect is further quantified by Swihart *et al.*'s paper [17], simulating the upstream extraction process from a CVD diamond reactor. Figure 3.10, taken directly from that publication, shows the axial concentration profiles with and without sampling. It can be seen that species with a thick boundary layer, such as acetylene, display minimal apparent shift. However, those species with a thin boundary layer, such as H atoms with their strong trend for substrate recombination, are significantly displaced.



Figure 3.9: A diagram demonstrating bulk vs boundary sampling for a range of orifice diameters (d) including comparisons to the important characteristic lengths, δ , the boundary layer thickness, and λ_m , mean free path. Note only centre-line gas will actually reach the detector due its small solid angle.

Swihart *et al.* also point out that, whilst treatment is sufficient for systems dominated by bulk flow and species diffusion, chemical activity and thermal diffusion will also affect shifts. In addition to ReSc shifts, reactive flows should also show dependence on the ratio on the system's Damköhler number (Da) and the thermal diffusion ratio (k_T) :

$$Da = \frac{\dot{\omega}d^2}{c_X D_X} \qquad k_T = \frac{D_X^T}{\rho Y_X D_{km}} \tag{3.16}$$

where $\dot{\omega}$, c, D_X^T and Y_X are the species production rate, concentration, thermal diffusion coefficient and mass fraction respectively.

The dimensionless Damkölher number is a comparison of the flow and reaction rate. The authors hinted at correlations within their model results and these parameters but were unable to cement these into any generalised statements.

One may be tempted to suggest that gases travelling through an aperture of finite length ~ d, will cause contamination⁴ of the signal due to in-diffusion from the the channel walls. Knuth counters with an argument based around the characteristic times for diffusion to the centre-line (τ_D) and flow (τ_F):

⁴Here 'contamination' is a relative term as any wall loss or recombination would be occurring on a surface of identical composition and similar temperatures and pressures to that of the substrate.



Figure 3.10: Axial concentration profiles along the MS sampling axis (solid), and far from the orifice (dashed), simulated by Swihart *et al.* [17] within an atmospheric pressure radio frequency diamond deposition reactor.

$$\tau_D \sim \frac{(d/2)^2}{D} \qquad \tau_F \sim \frac{d}{a_0} \qquad \frac{\tau_F}{\tau_D} \sim \frac{4D}{a_0 d} = \frac{4}{(ReSc)_0}$$
(3.17)

An estimate for this ratio based again on argon in hydrogen⁵ with a local gas temperature of 1500 K yields a value of 0.1 at 150 Torr. So diffusion-driven contamination should not dominate.

All of this points to a 'bulk' plasma measurement. This is not, however, a statement that the concentrations at this point will be entirely substrate independent; concentrations at this point may well be highly dependent upon sink rates at the substrate. What this means is that species reaching the detector will be more characteristic of species in the high temperature gas-phase directly above the substrate, and *not* those of the more moderate $(800-900^{\circ}C)$ substrate surface region.

During the first few nozzle diameters of flow, the large perpendicular pressure gradients give rise to mass-dependent radial diffusion. This effect is the first serious distortion to the detected intensities as, like Mach-number focusing discussed later (see 3.3.2), it is an unavoidable consequence of the sampling. This effect

⁵This ratio has a slight dependence on composition due to differences in collision cross-section and heat capacity ($ReSc \propto \sigma \sqrt{\gamma}$).

must be quantified for any subsequent mole fraction determination. The final paragraphs of this section will outline how this can be empirically achieved via comparison to an effusive source.

Alternatively Knuth [13] has derived expression (3.18) for a binary mixture from the work of Sherman [18]. The ratio of number density ratios at point x/dalong the centre-line and stagnation, referred to as the 'enrichment factor' α_D is obtained from:

$$\alpha_D = \frac{n_H/n_L}{(n_H/n_L)_0} = 1 + \frac{\eta^{T_0}/\eta_0 T}{(ReSc)_0} \left(\frac{m_H - m_L}{m_0} \frac{\gamma}{\gamma - 1} - \alpha_0\right) F(\gamma, x/d)$$
(3.18)

where subscripts H, L refer to the high and low mass component and α_0 is the stagnation thermal diffusivity. $F(\gamma, x/d)$ tends toward a limit of 13, 16, 18 for γ values of 5/3, 7/5 and 9/7 respectively [18].

Another potential worry with MBMS is the extent to which chemical reactions occur during extraction. In the initial expansion phase, the sample of plasma is accelerated through an orifice. As it cools and expands, its composition will relax to maintain local equilibrium within the expansion (see figure 3.11). Gradually as collisions - the mechanism by which equilibrium is maintained - become less frequent, relaxation loses efficiency. Eventually a composition is said to be 'frozen' when it ceases to evolve at any appreciable rate. It is therefore hoped that whilst chemical change may well be rapid in the first few collisions, close to the sampling conditions, it is slow in regions of low pressure and temperature. This chemical change is important in high density expansions, such as at the output of an MHD accelerator (original application of figure 3.11) but may not be as important in this study; The authors noted that "[the characteristic flow time (τ_f)] decreases two orders of magnitude in a very short distance near the throat ... and hence gives justification to the 'sudden freezing at throat' criterion widely used in low density nozzles" [19].

A commonly [8,9,13,20] used method to assess the extent of relaxation, which avoids detailed numerical analysis, is that of the 'sudden freeze model'. It approximates that, for each chemical relaxation, the expansion is split into two regions by a hypothetical surface in space. Upstream of this surface, the equilibrium is maintained, whilst downstream the composition is unchanging up to the point of detection. The position of this surface can be approximated by finding the



Figure 3.11: A sketch of a plausable, if conservative (see note in text), model of kinetic freezing through adiabatic expansion subdivided into three regions: 1) A region of equilibrium composition (which may even be pre-throat, within the CVD chamber), 2) a region where reaction and flow rates are comparable and 3) a frozen composition region. (adapted from a diagram found in [19]).

location where the following differential relation holds [13]:

$$\frac{d\tau_{H,p}}{dt} = C \tag{3.19}$$

where $\tau_{H,p}$ is a characteristic, constant enthalpy, pressure, relaxation time, defined as the time for a deviation from equilibrium composition to reduce to 1/e of its initial value. *C* is a 'near unity' constant currently assessed to be ~1.6 [3]. The derivative for our purposes would be taken along the expansion centre-line.

In this work we have attempted to construct a model of the expansion using the program senkin [21] which is part of the chemical kinetics package Chemkin II [22]. It is a 'zero'-dimensional model for a reacting gas mixture. In practice a zero-dimensional region should be regarded as one with negligible volume which is still arbitrarily large on the scale of molecules⁶. These unit regions can then be 'sewn together' in a manner akin to numerical calculus to form a model system.

In order to model the chemical relaxation, along the beam centre-line, a row of **senkin** calculations can be 'stitched together', via a scripting language (see Appendix D), to form a one-dimensional model. Each unit's composition is calculated with a pressure and temperature obtained from equations (3.9,3.11) over a time related to the flow velocity (see appendices C and D). Its output is then supplied as the input composition into the next unit of the model. This 'plug' of gas is propagated until we are sure the 'quitting' surface is passed, and thus is of the frozen composition.

The implicit assumption that new material never enters the centre-line should hold, provided the expansion remains isentropic. As stated before (section 3.2.2), this should be the case in the absence of any shock structure. The use of a one dimensional model may also cause concern, but one should be satisfied that the experiment is only detecting the centre-line properties emitted from a point-like source (ours being $100 \,\mu$ m). Unlike equation 3.19, this model should allow us to assess relaxation processes in expansions containing multiple chemical reactions with relative ease. Its implications for species losses are discussed in section 4.3.4.

3.3.2 Beam transit

Unlike within the CVD chamber, molecules in the molecular beam will have significantly different radial and axial components to their velocity. The axial components are largely derived from the expansion acceleration, whereas the radial values will be more strongly related to the thermal velocity in the stagnation conditions. A useful quantity to describe this is the perpendicular speed ratio⁷ (S_{\perp}) . This is the ratio of the radial thermal to hydrodynamic velocities. A species perpendicular speed ratio will be mass dependant as, although the acceleration though the orifice will be largely uniform across mass, the thermal speed will not. Thus lighter species will escape the beam fastest leaving the composition 'top-heavy'. This effect is known as Mach-number focusing. A simultaneous, empirical calibration for this and radial diffusion is discussed later for this (equation 3.26).

⁶This 'sleight of hand' preserves the full edifice of thermodynamic and kinetic laws.

⁷Related closely to M encountered previously

Alternatively, in the special case where the detected angle and speed ratio are small $(S_{\perp}^2 \theta^2 \ll 1)$ and free molecular flow is achieved prior to the first skimmer, then the effect is independent of source conditions and system geometry [23]. In this case Sharma *et al.* derive the Mach number focusing enrichment factor α_M in a dilute two-part mixture as:

$$\alpha_M = \frac{n_m/n_M}{(n_m/n_M)_0} \approx \left(\frac{m_M + m_m}{2m_m}\right)^{0.6} \left(\frac{m_m}{m_M}\right)^{1.4} \left(\frac{d_{M,M}}{d_{M,m}}\right)^{0.8}$$
(3.20)

where the subscript M refers to the major component, m the minor component of the gas mixture, and d is the effective collision diameter. Within the paper they do warn that as their derivation was for monoatomic gases, errors may be significant for species with high rotational collision number.

Skimmer interference, another potential worry, is a general term referring to attenuation of the beam by molecules originating from some kind of skimmer interaction. To reduce the reflection of beam material back onto itself, a narrow skimmer with a sharp leading edge is desirable. But a wider angle skimmer would be preferred if reflections from the internal skimmer walls are to be reduced. Thus, there is a balance in order to minimise interference. It is assumed that skimmers purchased from a reliable vendor will meet this. As shown in figure 3.12 below, beam density is a key factor in skimmer interference.

At low densities collisions will be rare, as the reflected molecules are unlikely to meet another molecule as they travel through the beam. As the density increases, collisions start to occur close to the upstream side in a diffuse 'shock like' region. At greater density still, reflected material is prevented from entering into the beam by the formation of shock waves originating from the leading edge obliquely. This may at first seem to be the best scenario, as skimmer interference is mitigated upstream, but in this case interference occurs downstream of the orifice from reexpansions and reflected internal shocks. Some degree of reflected shocks may be an unavoidable consequence of the presence of the skimmers in the expansion but, they can be diminished via lowering the downstream pressure [10].

Background gas will also attenuate the beam. It is sometimes stated that the criterion for negligible scattering is if the background hard-sphere mean free path (λ_m) exceeds that of the beam path. This is not wholly satisfactory, as even a slight deflection will lead to loss from the beam. This stems from the fact that material scattered away from the centre-line will not be detected (see the start of section 3.3) and neither will material scattered towards the centre-line



Figure 3.12: Illustration of skimmer interference phenomena showing, from top to bottom, low, intermediate and high densities (adapted from Anderson [20]).

- as it will no longer be coaxial. If collisions only lead to the complete removal of species from the beam then a Beer-Lambert like relationship can be used to assess scattering losses:

$$I = I_0 e^{-n_b Q\ell} \tag{3.21}$$

where the beam intensity I is a function of the initial intensity (I_0) , background number density (n_b) , effective cross-section (Q) and length the beam traverses (ℓ) . It should be noted that Q is not the hard sphere cross-section but rather an 'effective' cross-section which Anderson [20] defines loosely as: [being dependent] on the interaction potential of the molecules, their masses, the relative velocities and the geometry of the system. In other words it is a machine-dependent function, that can only be obtained empirically for any 'real' device. Values are typically in the range 100-300 Å² [20] for room temperature sources. The cross-sections may be much less, however, at beam energies derived from a hot plasma source [9,13]. When this type of analysis is conducted, it is often found that the attenuating length appears to be reduced relative to the actual distance travelled. In effect, the beam edges are acting as a pump pushing background gas along the beam axis and therefore depleting it upstream (see the curved streamlines in figure 3.6b above).

Two methods for reducing background scattering are (i) shortening any experiment length in the high pressure regions and (ii) the ubiquitous desire for increased pumping rate.

3.3.3 Mass Spectrometric Considerations

If we neglect species fragmentation in the mass spectrometer, the signal obtained from a spectrometer is summarised below [15]:

$$I_{X^+} = i_e \sigma_X n_X \beta_{X^+} t_{X^+} \theta_{X^+} \ell_{cage} \tag{3.22}$$

where I_{X^+} , the measured count rate, is a function of the emission current i_e , σ_X is the electron energy dependent ionisation cross-section and n_X the number density of species X in the ioniser, β_{X^+} is the mass dependent extraction efficiency of ions from the ioniser, t_{X^+} is the mass dependent transmission efficiency of the quadrupole, θ_{X^+} is the mass dependent detection efficiency of the channeltron and ℓ_{cage} is the length of the ioniser cage.

Mass spectrometers are often operated $\sim 70 \,\text{eV}$ as this is roughly the energy of a maximum in ionisation cross-section of typical species. At this energy, the direct ionisation channel may not be the dominant channel for ion production.

During a relatively low energy $(\leq 25 \text{ eV})$ electron collision there are two main types of ionisation event. The electron can directly ionise a parent, generating a singly charged ion.

$$X + e^- \to X^+ + 2e^-$$
 (3.23)

Alternatively, molecules can undergo dissociative ionisation into fragments. Typically, one of these will be a singly-charged cation whilst the others are neutral (or occasionally negative) and thus remain undetected.

$$XY + e^- \to X^+ + Y + 2e^-$$
 (3.24)

In the context of mass spectrometry, ions produced by these processes are practically indistinguishable. At higher energies, spectra can be further complicated by the formation of multiply charged products (observed at $m_{x+/n}$ where n is the number of electronic charges). These processes lead to complex spectra, that require some form of deconvolution. This is usually completed by generating a model based on the published cracking patterns, and some chemical intuition about which species are likely to be present. Relative contributions from each cracking pattern can be estimated by using subtraction and least squares fitting [13] or, more robustly, using statistical approaches [24]. Unless the model is very good and based on sound data, weak signals may be lost in the error of cracking patterns. Also there is some risk of artefact production in *a priori* assumptions of the sample composition in complex mixtures.

Threshold potentials $(\Delta E_a^{XY \to X^+})$ for dissociation are typically > 2 eV above the direct ionisation threshold $(\Delta E_i^{X \to X^+})$ [15]. So, by selecting an electron energy (E_e) such that $\Delta E_i^{X \to X^+} \leq E_e \ll \Delta E_a^{XY \to X^+}$, signal should only be observed via direct ionisation. The combination of this method (threshold ionisation) and MBMS is a common tool in the plasma science literature [14, 25–33].

A major drawback with this method, however, is the small size of ionisation cross-sections near threshold, leading to signals that are necessarily weak. The gain is that deconvolution should now only be needed when the quadrupole resolution is not sufficient to separate two species whose respective thresholds are unfavourably positioned - such as looking for argon (m/z 39.96, $E_i = 15.8 \text{ eV}$) in a mixture with propyne (m/z 40.03, $E_i = 10.4 \text{ eV}$). Here, the required deconvolution step is just a subtraction scaled by, the generally better known, ionisation cross-sections.

One caveat to threshold ionisation is that fragmentation onset is internal energy dependent, and thus thresholds for hot molecules are shifted towards lower energies. This may not be important for simple molecules, but may be significant for larger molecules of interest (e.g. large hydrocarbons) with many degrees of freedom.

Many authors choose to ionise at a single fixed 'optimised' energy for each species which, providing there is confidence in an unambiguous assignment, is sufficient to calibrate and obtain quantitative data. Alternatively Singh [14] used



Figure 3.13: A sketch of detector count rate ($\propto \chi_X \sigma_X$) as a function of ioniser energy. Note the change of gradient as the appearance potential is reached. The slight curvature at the threshold is due to the thermal spread of ionising electrons and ion parents.

the gradients of linear fits in the immediate vicinity of the threshold. Typically, procedures follow this algebraic form $[14, 26]^8$:

$$\frac{I_{X^+}}{I_{R^+}} = \left(\frac{\chi_X}{\chi_R}\right) a_{X,R}^{\rm GD} a_{X^+,R^+}^{\rm MS} \frac{\sigma_X(E_e^X)}{\sigma_R(E_e^R)}$$
(3.25)

where R represents an internal standard, of known mole fraction (χ_R) , such as argon, $a_{X,R}^{\text{GD}}$ is a relative mass discrimination factor due to the gas dynamics of expansion and a_{X^+,R^+}^{MS} is a relative mass sensitivity factor for the mass spectrometer. Intensity and cross-section ratios can be replaced with more robust gradient ratios in the initial, linear region of energy profiles.

If the ionisation cross-section in unknown, such as with certain radicals, then

 $^{^{8}}$ the second reference lacks a gas dynamic term but at their pressures of interest (< 1 Torr) effusive sampling probably dominates.

it is viewed as legitimate [2] to used the profile of a 'similar' species shifted to match the threshold energy. If the sensitivity factors are unknown, they can be calculated via an effusive leak into the spectrometer [26]. Using a known chamber ratio of species, X, to internal standard, manipulation of equation 3.22 suggests:

$$a_{X,R}^{\text{GD}}(X) = \frac{\binom{n_X/n_R}{\text{reactor}}}{\binom{n_X/n_R}{\text{effusive}}} = \frac{\binom{I_X/I_R}{\text{reactor}}}{\binom{I_X/I_R}{\text{effusive}}}$$
(3.26)

$$a_{X^+,R^+}^{\mathrm{MS}}(X^+) = \frac{\beta_{X^+} t_{X^+} \theta_{X^+}}{\beta_{R^+} t_{R^+} \theta_{R^+}} = \frac{(I_X/I_R)_{\mathrm{effusive}}}{(\sigma_X/\sigma_R)(\chi_X/\chi_R)_{\mathrm{known}}}$$
(3.27)

If, instead of computing these coefficients for each signal, a overall trend is plotted for each as a function of mass, then values for species that have not directly been calibrated can be estimated. The factor $a_{X,R}^{\text{GD}}$ should be relatively insensitive to temperature, but must be calculated for each composition. a_{X^+,R^+}^{MS} should be independent of both composition and temperature. These relative mole fractions are made absolute by manipulating the definition of mole fraction:

$$1 = \sum_{X} \chi_X \tag{3.29}$$

Division through by the internal standard χ_R (already included in the summation) yields the conversion factor:

$$\frac{1}{\chi_R} = \sum_X \frac{\chi_X}{\chi_R} + 1 \tag{3.30}$$

Conversion to number density is more difficult, requiring knowledge of the local gas temperature and an assumption some form of equation of state (*e.g.* pV = nRT).

3.4 MBMS applied to diamond growth studies

Work on *in-situ* measurement of the diamond growth process via mass spectrometry began with the work of Harris *et al.* [34–36]. Their experiment [34] consisted of a narrow quartz sampling tube mounted within the substrate of a hot filament CVD reactor. The tube was maintained at a pressure 0.3 Torr with the reactor operating at 20 Torr. This was seen as a sufficient quench for neutrals. They used this apparatus to measure the concentrations of methane and acetylene as a function of filament - substrate separation. They also linked this to 1D flow reactor calculations and used this to suggest that only acetylene, ethene, methane and methyl radical where present in enough concentrations to make a significant contribution to growth.

Further work [35] included the detection of carbon monoxide as a function of oxygen additions. Oxygen was found to reduce the *depositing* hydrocarbon mole fraction. They also suggested that the hydroxyl radical could play a role in the etching of pyrolytic carbon, thus boosting film quality. In a later paper [36] they estimated the concentration of methyl via a 'self-scavenging' argument. It was claimed that wall losses in the probe were negligible for methyl; the only effective sink mechanism was the recombination. Thus, provided the concentrations of ethane and ethene were negligible in the sampling region, then their total concentrations would be half that of the initial methyl sampled. This estimate was further extended to provide an estimation of H atom mole fraction.

Ultimately, this kind of microprobe experiment was unable give any concrete information on radical species concentrations during CVD. A considerable advance was achieved at Sandia National Labs with the implementation of true MBMS sampling. Results were obtained in HF [26,37] and MW systems [38–41]. The Sandia experiment consisted of a reaction chamber of typically at 20 Torr of 93 % H₂ - 7 % Ar with small additions of a carbon precursor. A 300 μ m orifice in the centre of the substrate admitted reactor gas into a 10³ mTorr chamber. The resultant beam (see 3.2) was skimmed and then mechanically chopped before reaching a mass spectrometer chamber. One of the major demonstrations of the work was that thermal effects rather than those of ionic plasma chemistry often dominate.

Once the assumption of thermal chemistry was made, then the author was able to explain the strong correlations at a fixed temperature:

 $[CH_3] \propto [CH_4] \qquad [CH_3]^2 \propto [C_2H_2]$ (3.31)

which also hold in hot filaments reactors⁹, a similarity that would be highly co-incidental in any alternative ionic model. In terms of H atom production, they concluded thermal dissociation and electron bombardment were probably of

⁹prior to filament poisoning at high carbon inputs.
comparable rate.

The studies of Hsu were extended by McMaster *et al.* [40,41] to include using acetylene as an alternative carbon source. It was found that the chemistry was relatively insensitive to the input composition; the $^{C}/_{\rm H}$ ratio is the main parameter of interest for neutral composition, a conclusion which was echoed throughout the subsequent literature.

In 1995 the University of Bristol, School of Chemistry, began publishing its CVD MBMS studies with a series of publications on a hot filament reactor [42–46]. The system was sampled through a steel cone with a 100 μ m orifice into a collimation chamber pumped by a 240 L s⁻¹ turbomolecular pump. The resultant beam was modulated with a tuning fork type chopper and then skimmed into a MS chamber.

Species concentrations were studied with the inclusion of the deep dopants nitrogen (N₂, NH₃, CH₃NH₂, HCN), phosphorous (PH₃), the growth 'enhancer' chlorine (CH_{4-n}Cl_n, HCl, Cl) and for a wider range of carbon sources than previously studies by mass spectrometry. It was was found that, like above, detected composition from diamond conditions was independent of the type of hydrocarbon precursors used. It was the thermodynamic products which often determined the gas phase chemistry. One exception to this was the use of N₂ which was thought to be active in the removal of H atoms leading to an increase in growth rate with an associated reduction in growth quality.

The authors noted that optimum growth rates where observed on the high temperature (High [H]) side of the maxima in methane mole fraction. This would lend credence to the idea that a species in rapid equilibrium with methane was incorporating carbon into the growing surface. The authors also stressed the possible role of thermal diffusion effects in favouring lighter species in the hotter regions. This presumably would lead to a reduction in the growth rates and dopant incorporation at high filament temperatures; heavier precursors being more concentrated in the colder regions.

These HF studies were followed by a conversion (see section 4.1) of the experiment to analyse CVD in a MW plasma system [25,47–50]. The setup was similar to the above except now the sample was extracted though a 5 cm tapered pipe and passed unmodulated into the spectrometer. Leeds *et al.* [47,48] found similar observations of general input independence with the exception of dinitrogen addition. Gas temperatures of ~ 1500 K at process conditions were also estimated by the calibrating the MS signals dependence against temperature.

Petherbridge *et al.* extended the work to include oxygen by probing $^{CH_4/CO_2}$ balance. They observed a local maximium in the observed concentrations of methyl, hydrogen and methane corresponding to onset (as a function of C/O balance), and highest 'quality' of diamond growth (50% CH₄). They also contradicted a widely-held belief at the time that $OH/O/O_2$ were important etchant species, by their assertion that these were only present in undetectable amounts. Mass spectrometry data suggested oxygen was converted entirely to CO_2/CO . Thus, it could be thought that the role of O_2 was to reduce the 'active' hydrocarbon concentration down to a level manageable by H atom activity (c.f. the suggestions Harris *et al.* above). The experiment was then used to probe the chemistry of 'dopant'¹⁰ sulfur (CS₂, H₂S) additions to CVD mixtures [49, 50].

At a similar time to the Bristol MWCVD work, Kohse-Höinghaus *et al.* were applying MBMS to diamond deposition via a low pressure (40 Torr) oxyacetylene torch [53, 54]. The gas sample was expanded though a 150 μ m orifice in a 45 ° quartz cone into a collimation chamber evacuated with a *large* (3000 L s⁻¹) diffusion pump. The experiment was notable as it had the slight advantage of using a time of flight (TOF) reflectron mass spectrometer. This has improved mass resolution over quadrupoles, allowing the distinction between species of similar m/z such as Ar and propyne.

They observed a large collection of longer chained hydrocarbons that thus far had not been observed in diamond CVD. Examples are the acetylenic hydrocarbons $C_{2n}H_2$, the radicals, formyl and propargyl (an important aromatic and soot precursor [55]). These data where also simulated [54] within the **chemkin** chemical kinetics package [22] with strong agreement for stable species and qualitative agreement for radicals.

Further MBMS investigations of carbon dioxide/methane plasmas have been conducted by Aubry *et al.* [32, 56]. They also observed the acetylenic hydrocarbons and aromatic precursors(C_3H_n). Their pressures were low (10 Torr) for comparison with modern diamond CVD.

It is somewhat surprising that these species were absent in the Bristol studies of oxygen containing plasmas. It may be that sensitivity may have been limited in Bristol as, relative to the two previous studies, it was underpumped. The enhanced pumping in the former, and lower gas loading in the second, would

¹⁰Sulfur temporarily achieved n-type dopant status in [51] but lost this in [52].

have been advantageous to detection.

A recent paper by Park *et al.* [27] detailed the construction of a MBMS system sampling a RF-plasma torch. This article is of particular relevance to the current study as the pressure range, growth rate, substrate temperature, and to a lesser extent, the chemical composition are comparable. Using an $Ar/H_2/CH_4$ gas mixture their CVD system deposited amorphous carbon at a rate ~ 60 μ m hr⁻¹. Deposition conditions mirror modern diamond CVD with substrate temperatures and pressures in the range 850-1150 K and 20-33 kPa.

In order to dissipate the heat impinging on the substrate from the high input power (10-15 kW), a complex orifice assembly was constructed. The surface molybdenum plate was separated from the water-cooled copper back-plate via an inconel¹¹ spacer. The thermal conductivity of this 'gap' could be adjusted via a set of small gas channels containing a variable Ar/He mixture. The whole assembly was clamped together to form a mechanical seal.

The substrate was drilled with a $75 \,\mu$ m orifice which formed the apex of a 68° nozzle. The expansion chamber was pumped by a $1200 \,\mathrm{L} \,\mathrm{s}^{-1}$ turbomolecular pump and housed a 1 mm skimmer ~ 10 mm behind the substrate. The beam was modulated in the next chamber with a tuning fork, and passed through a 15 mm aperture to the MS chamber. These two chambers where pumped by $250 \,\mathrm{L} \,\mathrm{s}^{-1}$ turbomolecular pumps. All of this functionality is encapsulated within a substrate-to-source separation of 37 cm.



Figure 3.14: The sampling nozzle, as depicted in [27].

Another relevant MBMS study is that of a remote Ar/C_2H_2 cascading arc plasma [57–59]. An *impressive* list of species was detected; the naked carbon

¹¹A high temperature nickel alloy.

clusters C_{1-5} , singly hydrogenated species $C_{1-5}H$, and the acetylenic hydrocarbons $C_{1-5}H_2$ (and $C_{1-5}H_4$). A direct comparison between this work and diamond CVD is difficult due to the low pressures (~ 200 mTorr), low neutral gas temperatures and the dominance of ion induced reactivity [57]. It does, however, demonstrate the potential sensitivity of MBMS to species thus far unreported from MWCVD diamond.

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Chapter 4

Reactor Designs and Assessment

4.1 Original design



Figure 4.1: A schematic diagram of the MPCVD MBMS experiment as it was during 1998 to 2005.

The mass spectrometer design had changed little from the original designs of

Leeds et al. [1] (see figure 4.1). This design involved the coupling of a pre-existing MBMS system onto a hot filament [2] and ASTEX-style MPCVD system. The original MBMS system had a shallow angle skimmer mounted perpendicularly to the substrate assembly. By translating the hot filament, it was possible to profile the species densities as a function of distance from the filament. It was seen, for the reasons listed below, that the natural choice for sampling of the microwave system would similarly be perpendicular to the chamber axis. First, sampling through the growth substrate, another realisable sampling geometry, had already been reported elsewhere [3]. It was thought that perpendicular sampling would allow direct sampling from the plasma. This different emphasis would increase knowledge about the gas-phase processes responsible for the formation of growth and doping precursors. Second, as the MPCVD reactor was already in existence, design freedom was limited. It was not felt that the necessary water cooling, pumping and electrical service could be supplied to a substrate plate designed for sampling. A final reason was the lack of 'in house' expertise in designing microwave cavities. The translatable substrate gave an extra degree of tuning freedom which it was deemed risky to lose. This simple coupling of experiments led to some considerable experimental difficulties:

Unlike in the hot filament experiment, the reduction of cylindrical symmetry imposed by perpendicular sampling in the MPCVD reactor represents a major perturbation. Altering the chamber geometry distorts the cavity mode structure leading to, for example, parasitic secondary plasmas and a distorted plasma appearance. Distortion could sometimes be so great that the plasma position shifts away from the probe, thus nullifying the primary advantage of perpendicular sampling. In order that this be minimised, the skimmer was replaced by a $\sim 1 \text{ cm}$ -wide molybdenum cone welded to the end of a length ($\sim 5 \text{ cm}$) of 1 cmdiameter stainless steel tube (see figure 4.2 below). The tip of the refractory molybdenum cone is difficult to machine so it was drilled through with a focused 532 nm laser. This produced a channel of length $\sim 1 \text{ nm}$ without a great deal of control over the channel width.

Though this alteration was essential to achieve sampling from the plasma edge, it also significantly limited the sensitivity to reactive species. The conduction of this thin section of pipe smoothed out the sharp drop-off in pressure required to obtain clean MBMS sampling. Another complication of the system was the aggressive nature of the sampled environment. The region in the immediate



Figure 4.2: The sampling arrangement in the original system

vicinity of the plasma is filled with hot reactive species that, depending on their chemistry, can act to block the orifice or even etch it. This, coupled with intrinsic brittleness, and thermal cycling over many experimental runs led to a limited probe lifetime. In addition, the length of tube and the plasma position were partially correlated due to interference by the probe with the cavity. Thus, the only way to establish the correct probe length for a new gas mix was trial and error.

Prior to the start of the project, data acquisition had consisted of typing numbers into a hand-held calculator [1] as they appeared on the spectrometer monitor and then averaging 'chunks' of perhaps ten values, and then recording that average. This practice was unsatisfactory for several reasons:

The noisy signals produced by the spectrometer required large quantities of data to be acquired in order to see the true signal, which was impractical for manual acquisition. The long collection time for data meant it was difficult to perform experiments, take backgrounds, and perform a calibration on the same day. Long experiments could be particularly problematic as signals were known to drift over time [1]. The plasma system also had the added complication that etching or blocking of the orifice limited the time over which experimental



Figure 4.3: A photographic image of the probe tip (glowing red hot) 'immersed' in an argon/hydrogen/methane plasma as viewed through a side port window.

conditions could be held constant.

The most compelling reason for improving the data acquisition system, however, was its inefficiency. A huge amount of data was generated by the spectrometer but was ignored as it was only possible to record data displayed on one channel at a time. Electronic acquisition would therefore not only speed up experimentation, it would also provide information as a function of all the electron energies selected. Thus ioniser energy profiles could be used to reducing any ambiguity in m/z assignments.

The spectrometer had originally been supplied with software to acquire data over a serial cable (RS-232), so there was no reason it was necessary to persist with manual methods. The original software was however unstable and difficult to use. Coupled with the likelihood that it would be incompatible with modern operating systems, the decision was made to use the program Labview 6 to log data.

Considerable effort was expended on investigating the chemistry of Ar / H_2 / CH_4 plasmas for nanodiamond deposition. One of the main aims of the project was to monitor the evolution from microcrystalline to nanocrystalline diamond as a function of the Ar / H_2 balance (20-2 % H_2). Test experiments involved use of a mixing ratio of 89:10:1 (Ar : H_2 : CH_4), as these conditions did not lead to aggressive etching of the sampling orifice and could also be run for long periods without significant soot production.

Experiments were hampered by the instability of the Ar/H_2 only plasmas, without methane addition. Plasma backgrounds were often unobtainable. Instead, a cold gas mixture was chosen as a control. The cold gas now represented a significant gas loading on the spectrometer, which was now operating close to the high pressure interlock protecting the channeltron (set at 5×10^{-6} Torr see section 3.1.3).

It was found that the ion counts associated with certain species in the background gas were greater than their 'plasma-on' values. A similar feature was observed by Leeds [1]. In that work, a system of background subtractions was devised that could be used to 'multiply up' the signal:

$$I_{T_{corr}}(X) = \left(\left(\frac{I_{RT}(H_2) - I_{BG}(H_2)}{I(H_2) - I_{BG}(H_2)} \right) \times I(X) \right) - I_{BG}(X)$$
(4.1)

where I(X) and $I_{BG}(X)$ are, respectively, the count rates obtained for species X in the full plasma and the cold gas background of X without carbon source. $I_{RT}(H_2)$, $I_{BG}(H_2)$ and $I(H_2)$ are the cold gas signal of dihydrogen, its signal at base vacuum and the signal in the full plasma. $I_{T_{corr}}$ therefore represents the background subtracted intensity of a species X, scaled so that it is comparable with room temperature measurements (ready for direct calibration against bottle gases at known partial pressures).

The justification of this equation was the dependence of signal on temperature $(I \propto 1/\sqrt{T})$. Put simply, this is the interplay of CVD chamber number density (which scales as 1/T) and an increase in aperture conductance (which scales as \sqrt{T}). So, when the plasma is active, there is less material entering the MS system. When looking for species at low signal levels, the cold background may have risen so much that it obscured the true signal. No physical interpretation for these backgrounds was given. In 4.1, the dihydrogen signals are used to gauge the temperature dependance of the gas flow and 'correct' the plasma signal to its room temperature equivalent. Once done, the room temperature background subtraction can be made.

From the above argument, an increase in gas temperature from 300 to 2000 K only leads to a factor of ~ 3 decrease in signal. It may be suggested that dissociative ionisation is responsible for this background, as the electron source in the ioniser will generate a spread of energies. However, this is usually treated as negligible > $\pm 0.5 \text{ eV}$. The 'tail' attributable to dissociation would have to stretch typically to at least 2 eV below the appearance potential. Note that some non-

trivial background was still present, even when there was no deliberate carbon source in the feed gas.

The above analysis misses one key source of background, which will not be subtracted by this method; catalytic formation of species on the hot filament cathode within the ioniser can lead to spurious signal [4]. If the background of gas in the spectrometer is significant, then radicals can be produced, then ionised and detected. Backgrounds formed from the carbon containing process gas lingering in the system after leaving the molecular beam (10^{-6} Torr) would constitute significant signal. Backstreaming rotary pump oil may well have contributed also. Under these high MS pressures the subtraction above (equation 4.1) was multiplying up this background. These enhanced signals were then compared with conditions without background from deliberate addition of carbon. This erodes confidence in the assignment of 'radical' signals at high (~ 100 Torr) stagnation pressure.

There are two main ways of reducing this signal component. Firstly, greater pumping speed in the MS chamber would reduce the background pressure, making it less important. The second method is to chop the beam mechanically, and lock detection to this frequency. The second method is *essential* in poorly pumped systems [5] where the beam component could be well below half the total signal for typical species.

4.2 Updated design

The following section describes the thought process which led to the design of the updated version of the experiment. It must be acknowledged that the design is not the work solely of the author; considerable contributions came from Prof. M.N.R. Ashfold and Drs J. Brandon¹ (specifically see sections 4.2.1, 4.2.2) and J. Smith.

Restating the experimental aim; gas is extracted from a high pressure CVD chamber and conveyed to a mass spectrometer with sufficient sensitivity to obtain absolute stable species mole-fractions, *and* estimates for radicals. The system discussed here achieves this through maintaining a line of sight between the deposition substrate and the MS ioniser through a three-stage differentially-pumped vacuum system. This line of sight is modulated to provide the background sub-

¹Element Six Ltd, King's Ride Park, Ascot

traction necessary to obtain radical sensitivity. The following figure (4.2) sets out the basics of the experimental apparatus designed to perform to these specifications. Subsequent sections (4.2.1 - 4.2.4) will go into greater detail about its various components.



Figure 4.4: A sketch summarising experimental the MBMS system. The labels in italics correspond to the section headings below.

The main tool for design appraisal was a simple spreadsheet model constructed by the author based on equations contained in [5–7]. Those equations are collected in Appendix B. Given stagnation conditions, it allows the estimation of chamber pressures, background scattering losses, beam intensity and, with some assumptions, estimated beam-to-background ratio. Isentropic expansion parameters could also be calculated, most notably the 'quitting surface' location and the centreline Mach number (Appendix C).

4.2.1 CVD Chamber

The chamber design is based on that of a chamber previously loaned to the department from Element Six (E6). A description of the fabrication is given in [8], and only departures from this design will be described in detail here. From here on this previous Element Six reactor will be referred to as the CRDS² reactor to distinguish it from the MBMS reactor.

The chamber is a water-cooled-aluminium cylinder, the top of which connects to the microwave supply system. There is a quartz window placed approximately halfway up which separates the air-filled waveguide from the low pressure plasma chamber. Unlike the CRDS reactor, which has a thick aluminium base plate through which run a series of water cooling and pumping channels, the MBMS design had to incorporate a direct, unhindered, line of sight to the spectrometer ioniser. It was quickly decided that the E6 base contained too much functionality and needed simplification. As the power density above the substate could be of order $100 \,\mathrm{W} \,\mathrm{cm}^{-3}$, water cooling was essential. The decision was taken to pump through two opposing side $ports^3$ on the chamber wall. Though this pumping is not as radially symmetric as that of the CRDS reactor, it was hoped that any 'pull' effects will be minimal. The centre of the base was now free to be hollowed out into a diverging expansion nozzle. The larger the solid angle of this nozzle the better the sampling, for reasons analogous to the skimmer considerations encountered in section 3.3.2. This had to be balanced, however, with a concomitant reduction in cooling efficiency, as water channels would have to be further from the central axis.

In the CRDS reactor, the substrate consists of a polished molydenum disc. As the main aim of this project was to sample conditions in an environment faithful to deposition conditions, it was decided to manufacture a 'dummy' stub (see below section 4.2.2) with a central sampling channel. This stub would have to make a high quality seal with the chamber base, so a compressed 'o'-ring flange mount was machined into the base. The size of this was dictated by the necessary distance to keep the 'o'-ring sufficiently far from the high temperature region. A sketch of Dr J. Brandon's final reactor base design is given in figure 4.5.

 $^{^2\}mathrm{After}$ Cavity Ring-Down Spectroscopy, the primary research technique used on that reactor.

³Windows in the CRDS reactor.



Figure 4.5: A cross-sectional sketch of the aluminium reactor base design of Dr J. Brandon, Element Six Ltd. The diagram also shows where the sampling insert should be located and the relative positions of the diamond 'growth' surface and the first molecular beam skimmer.

4.2.2 Sampling Insert

As stated before, this insert is designed to mirror the substrate in the CRDS reactor. Of the many components making up this experiment, this perhaps, is the most individually critical in terms of the level of detail required for design. It must provide a high quality seal between the plasma process (20-150 Torr) and the first stage of expansion (1 - 0.1 mTorr). It must be resistant to chemical etching by plasma species and thermally robust ($T_{sub} \sim 900^{\circ}$). Possible materials for its fabrication included the diamond growth media silicon and molybdenum, or the more inert quartz, each of which have significant advantages. Silicon is readily fabricated with processes such as ion milling and lithographic techniques. This would allow for the production of a reproducible orifice channel, but silicon's brittleness would make machining the bulk material difficult.

Quartz is a common material use for sampling in MBMS due to its chemical inertness and the ease of manufacturing, reliable small scale orifices, via various glass working techniques. Chemical inertness is desirable when trying to measure concentrations in an unperturbed system, such as the free-flowing output of a burner. However, in CVD there is always the presence of a substrate, so inertness has no real advantage. Quartz's major drawback is that it is an electrical insulator and will therefore not reflect microwaves. Poor design could lead to significant microwave energy being dumped into the low pressure chamber below. This is not only a waste of power, it could also discharge, significantly disrupting sampled compositions. Molybdenum is a refractory metal, thus it is simultaneously robust to the CVD conditions and difficult to machine into any desirable nozzle profile. Thankfully, in this case there is a short cut; molybdenum electron microscope apertures are commercially available⁴ with a range of orifice sizes with a good aspect ratio (\sim unity). The housing of these can be machined via ordinary metal working techniques and the orifice sealed in place with a suitable braze.



Figure 4.6: A sketch of, Dr John Brandon's molybdenum sampling insert shown in cross-section.

Care was taken with the design to reduce the natural tendency for a strong radial heat profile (see figure 4.7). Provided the plasma ball is roughly homogeneous in temperature, then the normal stub will have largely axial heat flow to the water-cooled base. The thinning out of material in the sampling stub will cause heat to flow with some outward component generating a temperature profile. If this profile is significant, then the local gas temperature may increase, aiding the discharge in a hot spot. This may distort the sampling region composition, or even damage the delicate orifice. Also of consideration is that the 'o'-ring seal (fluorocarbon) cannot exceed 200 °C thus the insert and water-cooled base must make contact remote from the groove. With the use of thermal breaks to guide heat flow, it was possible for J. Brandon to develop a design which optimised the sampling and axial heat flow.

⁴Agar Scientific Ltd, 66A Cambridge Rd, Stansted



Figure 4.7: Sketches of heat flows to a water-cooled base representing *left*: a real growth stub, *right*: A plausible 'dummy' stub.

4.2.3 Stage One

The purpose of the first chamber is to provide the pressure differential which leads to the desired isentropic expansion. In principle, any non-trivial pressure reduction would suffice, for example via a high throughput roots blower, but for the reasons stated earlier (see section 3.2.1) it is desirable to achieve more substantial pressure reduction. Preferably the pressure should be low enough that the mean free path of gas molecules are the same order as the size of chamber (also section 3.2). As no satisfactory way could be envisaged to operate a pulsed nozzle from CVD conditions, the system will be subject to significant gas loading.

The first chamber is evacuated by a large $(3000 \text{ L s}^{-1}, \text{H}_2)$ cryo-cooled diffusion pump. In order to maximise pumping, the chamber cross-section was matched to the area of the pump inlet. The width was chosen so that it closely matched the diffusion pump flange. Allowing the expansion to travel the resultant box height would lead to significant background attenuation. A cone shaped mount for a skimmer was therefore placed to position the skimmer 15 mm back from the orifice. This should ensure a clean conversion to molecular flow prior to the skimmer⁵, thus avoiding further evolution of the gas downstream of the skimmer

 $^{{}^{5}}x_{q}$ is estimated to be between 1-2 x/d for all desirable pressure and temperatures irrespec-

(see 3.3.2).

The decision to maximise the pump rate, was not immediately obvious. Many authors seek almost exclusively to minimise path length, thus minimising the ' $1/r^2$ ' losses. Our system model(see appendix B) suggested that in our system, due to the heavier gas loading than many other systems scattering in stage one was the most important loss mechanism.



Figure 4.8: A schematic drawing of the 1st stage pumping box.

4.2.4 Stages Two and Three

The subsequent chambers are both pumped via 250 L s^{-1} turbomolecular pumps. Both are backed via an oil-free scroll pump, chosen to avoid the potential background generated by the backstreaming rotary pump oil. The purpose of stage two is to allow the mechanical chopping of the beam. Location of the chopper in this stage was not a trivial choice. On initial inspection of the problem one may be tempted to locate the chopper prior to the first skimmer. This is because a chopper located in its present position could cause some molecules from the 1st stage background to be chopped and detected. However, this type of background is minor since the amount of background in stage one coaxial to the centreline will be negligible when compared to that of the beam. Location of the chopper in the

tive of γ . A skimmer location of 150 x/d gives a comfortable margin from moderate conductance limitation.

first stage would lead to intense scattering, conductance reduction and pressure modulation in subsequent stages. This pressure variation would also modulate background signals at the frequency of the chopper. Regardless, it is difficult to envisage a design which would allow this without greatly increasing the distance to the first skimmer.

A three-stage design was chosen, as it was not felt practical for the required differential pumping to be achieved in only two stages. Three-stage systems seem to be typical for other MBMS systems [3, 9-12]. One of the key features of this section of the assembly is that the spectrometer is mounted perpendicularly to the centreline. As mentioned earlier (see section 3.1.3), there is the possibility that the direct line-of-sight from the plasma to the CEM detector could lead to significant background. The plasma may generate large quantities of UV radiation or metastable species states. Those emitted through the sampling orifice have the potential to generate ions in the vicinity of, or directly on the channeltron surface. The resultant un-mass-selected signal would appear with roughly the same frequency as the beam modulation, and could be problematic. There are two common methods in the literature to avoid line-of-sight background.

The use of a ion energy filter, such as the 'Bessel box' used by Agarwal [10], provides a course correction around an obstacle for ions, but not for neutral species. The background will, therefore, have its energy quenched remotely from the detector. The primary advantage for MBMS is that designs can be produced where distances between the ionsier and detector are relatively short, thus maximising signal.

The alternative method is to mount the spectrometer with its axis perpendicular to the beam centreline. This requires a specialist ion source which is able to rotate ion trajectories through 90 ° with minimal mass discrimination⁶. These 'cross-beam' sources were specifically designed for the purpose of sampling molecular beams. In general, cross beam designs require a greater orifice-to-source distance in order to avoid fouling of the various vacuum components.

For the purposes of this experiment, the functionally of an ion energy filter, aside from that which is stated above, is largely redundant. Ion densities in MWCVD plasmas are predicted to be low (total ion mole fraction $\sim 10^{-1}$ [13]). As previous diamond MBMS studies have failed to detect ions, our elevated plasma pressures make detection even less likely. So the desire to perform a survey of

⁶There is some evidence of discrimination between direct and dissociative ionisation ions [11].

ions as a function of energy is not an experimental priority. Instead, the more economic cross-beam method was implemented by the construction of an inner chamber with a side port. The beam line now points towards the face of the second turbomolecular pump to maximise its extraction.



Figure 4.9: The 2nd stage, with the 3rd stage embedded within it.

4.3 System Validation

This section collects together various tests of the apparatus prior to 'real' experiments on deposition plasmas. Some tests estimated signal strength and detection limits and thus suggest the likely species which will be observable. Others gauge systematic shifts and calibrations which will allow us to compare results with the literature. A test condition was chosen of 100 Torr, room temperature gas consisting of 500 sccm H_2 , 40 sccm Ar and 25 sccm CH_4 . Any deviations from these conditions will be discussed within the relevant sections.

4.3.1 Energy scale calibration

There is often a shift between the user-specified and output energies of electron ionisation sources. This mismatch is linear and typically of a few electron volts. This shift must be quantified if ionisation threshold and appearance potentials are to be used in species assignment. The simplest method of estimation is to measure species threshold and compare with reference data. The following chart (figure 4.10) shows fitted regression lines to the linear region of the group of Ar^+ versus energy curves. The non-linear regions close to the threshold have been omitted for clarity. From this figure, a shift of 2.0 eV can be estimated.



Figure 4.10: m/z 40 intensity as a function of ioniser energy. All curves extrapolate to an *x*-intercept of ~ 17.71 eV, implying a shift from the published literature of 1.95 eV ([14]). These data were taken whilst conducting an independent experiment altering pressure and gas phase composition, both with and against, the chopper.

This displacement does not tackle all sources of energy shift, just those due to the device electronics. Section 3.3.3, previously mentioned the effect of internal energy on large species' ionisation potentials.

4.3.2 Chopper position

Figure 4.11 shows the Ar⁺ signal as a function of the chopper delay from the test gas condition. The signal peaks around 7 - 11%, close to the centre of the chopper 'open' period, as measured by the optical infrared syncronisation circuit (OPTO-IR) 0 - 21%. The lack of signal saturation during the 'on'-phase is just a reflection of the similarity of the solid angle of the chopper slit and the second skimmer. A delay of 8% and gate width of 1% produces a signal-to-background ratio $\binom{n_B/n_3^7}{n_3^7}$ of 0.8.



Figure 4.11: Mean count rate (m/z 40, 20 eV) as a function of the chopper position variable in the Labview virtual instrument (see section 5.3.1). The horizontal error bar represents the selected gate width whereas the vertical bar is one standard deviation of ten measurements. The physical duty cycle recorded by the OPTO-IR circuit is 21%.

The shorter the gate width, the more chopper cycles will be required to obtain the spectrometer's 'dwell' time (see chapter 5). So, there is a balance between ab-

 $^{^{7}\}mathrm{Here}$ written as the ratio of beam number density (n_B) to the 3rd Stage number density (n_3)

solute signal strength and experiment time. The closeness of data points around the turning point suggests that there is little advantage of using a much narrower gate than 1 %.

4.3.3 Beam to background ratio n_B/n_3

It was stated that in the design stages a spreadsheet model was constructed to estimate system performance. This model is summarised in appendix B. A similar, but less detailed, pumping model was developed by the authors of [5] and it is useful to make comparison between their model and the one presented here. In order to achieve this, a brief description of their model is required.

Singh et al. [5]

The model of an MBMS system of m chambers, described in [5] is algebraically equivalent to the following equation, but here, uses different notation.:

$$\frac{n_B}{n_3} = \left(\frac{d_1}{2L}\right)^2 \prod_{i=1}^m \frac{F_i}{C_i} \tag{4.2}$$

This is based on their assertion that the number density in the beam (n_B) is related to the stagnation density (n_0) :

$$n_B(x) = n_0 \left(\frac{d_1}{2x}\right)^2 \tag{4.3}$$

Provided $d \ll L$, then the ratio of the instrument length (L) to the sampling orifice radius $(d_1/2)$ models the inverse square law decay of beam flux (see section 3.3.2). The product is an estimation of the ratio n_0/n_3 based on the effusive in-flow between chambers (C_i) and the pump out-flow (F_i) . This model was developed for assessing an MBMS system sampling a radio frequency inductively coupled plasma (ICP). ICP plasmas typically operate at pressures below 1 Torr. Consequently, effusive sampling criteria are usually met, gas loading is low and therefore background scattering is of no concern. Another consequence is that molecular beam enhancement is negligible as its presence makes little difference to the ioniser background pressure (see comment in [5] that '[this assumption] introduces less than 10 % error').

The model presented here

However, the effusive model is not such a good representation in our system, since beam enhancement will significantly increase flow through the system. In this model, the same method was used to calculate the background pressure but, to obtain the beam density, Miller's [6] equations (2.19a-c) were used as a starting point:

$$I_0' = \frac{\kappa n_0 d_1^2}{4} \sqrt{\frac{2\gamma R T_0}{(\gamma+1)m}} \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}}$$
(4.4)

 I'_0 , the angular dependant intensity (molecules s⁻¹ sr⁻¹), is then converted to a simple intensity for beam entering the ioniser I_B (molecules s⁻¹) by obtaining the solid angle, in steradians (sr), of the beam. As there are 4π sr in a sphere then the solid angle projected by the smallest constriction (diameter d' at distance L'from the expansion throat) is, provided $L' \gg d'$, simply:

Solid Angle
$$\approx 4\pi \frac{\text{area of smallest constriction}}{\text{surface of sphere radius } L'} = \frac{\pi}{4} \left(\frac{d'}{L'}\right)^2$$
(4.5)

In our system, with high stagnation pressures affecting pump loading, it is prudent to include background scattering in I_B . Section 3.3.2 described the use of a Beer-Lambert like relationship, such that the non-scattered fraction for mchambers would be:

$$\frac{I_i}{I_0} = \prod_{i=1}^m e^{-n_i \ell_i Q}$$
(4.6)

The final stage is to convert the incident intensity into a beam number density in the ioniser, to enable comparison with the background gas number density n_3 (see figure 4.3.3). Division by the parallel flow velocity $v_{\parallel,\infty}$ (see appendix C) yields the number of beam molecules within the length of the ioniser (molecules m⁻¹) at any given moment. For number density, this instead, must be associated with an unit volume. In the following equation (4.7), this is obtained by using the area of the inlet. Equally, the ioniser's cross-sectional area could have been used, but this is not well known. These values are of the same order of magnitude, so the particular choice will not affect the model's utility. The purposes of these models are to optimise performance relative to a given system parameter, not to optimise performance 'absolutely'.



Figure 4.12: Conversion of absolute beam intensity at the detector to an effective number density is achieved by dividing out the parallel flow velocity $v_{\parallel,\infty}$ and the characteristic area, in this case the opening of the ioniser $\pi d_d^2/4$. This is then ratioed to the number density of background gas in the ioniser, n_3 .

$$\frac{n_B}{n_3} = \frac{4I_B}{v_{\parallel,\infty}\pi d_d^2 n_3} \tag{4.7}$$

Model Comparison

In order to compare the models, both were fed the same parameters and the same stagnation conditions. Instead of using the manufacturer's specified pump speeds, which will suffer conductance losses, the effective rates should be calculated from empirical chamber pressure ratios. This has the effect of fitting n_0/n_3 to the apparatus. For pure hydrogen, a comparison of manufacturer (Edwards) specified and experimental pump rates are displayed below:

Stage	Model	Speed / Ls^{-1}	
		Absolute	Real
1 st Stage	250M cryo-diffstak	3000	220
2 nd Stage	EXT 255 turbomolecular	180	156
3 rd Stage	EXT 255 turbomolecular	180	152

The use of the 'real' pump rates in the spreadsheet model (see appendix B) yields the following results for room temperature hydrogen:

CVD Pressure	MS Pressure	Beam to background ration $\binom{n_B}{n_3}$	
Torr	10^8 Torr	Singh $et al$	This model
150	11	11	0.58
125	9	11	0.61
100	7	11	0.66
75	5	11	0.71
50	4	11	0.77

Figure 4.13: A comparison of n_B/n_3 estimated via the model in [5] and the model proposed here

There are two main differences between the models. First Singh *et al* are much more optimistic about the absolute value of n_B/n_3 , and second, their model is not a function of stagnation pressure. In Singh's model, a comparison is made between beam and background densities assuming they occupy the same volume - the ioniser. In their system, this was probably valid due to their large $(1 \text{ cm}) 2^{\text{nd}} \rightarrow 3^{\text{rd}}$ stage aperture. In this system, the beam width and therefore the volume occupied by the beam is fixed by the chopper slit-width of 3 mm. The explicit inclusion of the solid angle avoids this within the model presented here. The experimental value of 0.79 given in section 4.3.2 is much closer to our prediction (see the highlighted line in figure 4.13), though this similarity is somewhat fortuitous.

Singh's model is purely about the system geometry and so it shouldn't be expected to depend on applied pressure. The downward trend with pressure in our estimated ratio is due to background scatter, which was of little concern in [5].

4.3.4 Chemical loss

As mentioned earlier an attempt was made to obtain a qualitative feel for the extent to which the MBMS perturbs the gas composition (see section 3.3.2). The model, described in appendix D, was used to this end. In order to use the SENKIN program, it must be supplied with a kinetic model, chem.inp, and library of species thermodynamics Therm.dat. These two files were obtained from the GRI-mech model [15]. These kinetic data are often fitted to experiments at high temperature and moderate pressures. Therefore, the model probably reflects chemistry better early in the expansion.

The procedure for calculations were as follows. A mixture of gas was equilibrated (1s) at a fixed $\operatorname{pressure}(P)$ and $\operatorname{temperature}(T)$, representive of some plasma condition. The purpose of this was to obtain a composition related to the thermal portion of the plasma. A scripting file was written to compute the composition evolution for each P/T along the centre line. The value of the adiabatic index, γ , was fixed at the low temperature value of the bulk diluting gas (e.g. dihydrogen 7/5). The error (~ 7% at 2000 K) in γ is slight, and reduces as the flow evolves and the temperature falls. Simulations run with a thermally evolving value for γ were not qualitatively different from those that were fixed, possibly due to the rapid cooling of the expansion. In any case, this error was not seen as large compared to other assumptions. The chemical evolution of the heat capacity should be slight, provided the reactive portion of the beam is small. The GRI-mech 3.0 mechanism contains the following species: C, CH₂, CH₂*, CH₃, CH₄, C₂H₂, C₂H₃, C₂H₄, C₂H₅, C₂H₆, Ar, C₃H₇, C₃H₈, CH, H₂, H.

In order to choose an appropriate step-size $(\Delta x/d)$, the chemical loss of H atom was studied for a range of different step-sizes (see figure 4.14). A step-size of 0.05 orifice diameters was chosen for subsequent simulation, as the results seem to have converged by this value. The distance corresponds to a step of 2-1 ns or a total simulation time of 50 ns.

To model typical CVD extraction, an equilibrated gas mix of 1% CH_4 in H_2 at 2000 K and 150 Torr (19998 Pa) was 'propagated' through the model. Figure 4.15a shows the effect of the expansion on the composition with the static and large $[CH_4]$ and $[H_2]$ omitted. It is first apparent that most species show negligable change in mole fraction. Therefore, these results provide confidence in the absolute mole fractions of closed shell molecules.

Two species, however, show a marked drop in mole fraction, methyl and hydrogen atoms. What is surprising is the lack of evidence for the self-scavenging methyl losses suggested by Harris *et al.* (see section 3.4):

$$2CH_3 \rightarrow C_2H_4 + H_2 \text{ or } C_2H_6 \tag{4.8}$$

These 'dimer' species appear unaltered by the methyl despite being of comparable initial concentration. The other likely loss mechanisms, recombination to produce methane, are probably responsible for methyl loss:

$$CH_3 + H \rightarrow CH_4$$
 (4.9)



Figure 4.14: The loss of H atom as a function of distance for various step-sizes. The results appear to have converged by step-size < 0.05 x/d.

$$CH_3 + H_2 \to CH_4 + H \tag{4.10}$$

A calibration for this loss of methyl radical will be difficult as it will depend on the chemical and physical conditions. This suggests that radical species are not absolute and could contain errors as high as an order of magnitude at these pressures. Therefore they should perhaps be treated as a (still scientifically valuable) lower bound at high pressures.



(a) H (o), CH₃ (\blacksquare), C₂H₆ (+), C₂H₄ (\triangle), C₂H₅ (\blacktriangle), C₂H₂ (\diamond) and C₃H₈(×) mole fractions as a function of expansion progression.



(b) Pressure (solid) and temperature (dashed) as a function of expansion progression

Figure 4.15: The effect on species concentration a) of the expansion conditions displayed in b). For comparison, Miller's hypothetical 'quitting' surface [6] would be located at $1.5 \, \text{s/d}$ under these conditions.

4.3.5 Detection limit

A method of determining the absolute detection limit suggested in [9] was employed. This method takes a fixed pressure of gas in the CVD chamber. The signal (count rate) for each detectable isotope (or isotopomer) are measured and plotted against their relative abundance. This line can be extrapolated back to the lowest detectable signal, giving an absolute limit on detected relative abudance. In reality, signals are background limited, and so the smallest detectable deviation from the background should be extrapolated to. As background varies between masses (and ioniser energy), transmission efficiencies are functions of mass, and reactive losses in expansion depend on species, so too will this detection limit. Thus, strictly, this detection limit should be quoted for each species separately.

Krypton was used as a reference gas, as its large number of isotopes (see figure 4.17))would lend itself to a better estimation of the detection limit. A minor addition of krypton (3 sccm) was added to the test gas, and the various Kr signals were measured at 20 eV, and the linear portion fitted. The resultant gradients are plotted against mole fraction in figure 4.17. From this plot, the a detection limit of between 10^{-5} and 10^{-4} mole fraction can be estimated.

Species	m/z	Relative abundance
	(amu)	(%)
⁷⁸ Kr	77.9	0.35
$^{80}\mathrm{Kr}$	79.9	2.28
$^{82}\mathrm{Kr}$	81.9	11.58
$^{83}\mathrm{Kr}$	82.9	11.49
$^{84}\mathrm{Kr}$	83.9	57.00
$^{86}\mathrm{Kr}$	85.9	17.30

Figure 4.16: Krypton isotopes: Their masses and relative abundances


Figure 4.17: Krypton mole fraction against intensity, estimating a detection limit between 10^{-5} and 10^{-4} mole fraction. The simultaneously-measured ⁴⁰Ar signal has also been added (after scaling by relative cross-section obtained from [16]).

4.3.6 Compositional sensitivity

In section 3.3.3 it was suggested that changes in composition could distort signals due to mass separation effects. Thus, without a point-by-point calibration, even obtaining relative trends may be problematic. It is, therefore, important to check whether the expansion dynamics change significantly over the variable ranges used in this study. To gauge the affect of changing the total pressure and the carbon input fraction - the two variables probed in chapter 6 - a small, fixed, flow rate of nitrogen was added to the typical process gas. At 0.3% (2 sccm) this was not thought sufficient, in itself, to perturb flow properties significantly. Signals can be acquired in phase with the chopper (open) or out of phase (closed) (see section 5.3.1). Absolute signal (without background) should be obtained by subtracting closed from open signals.

Nitrogen signals (see figure 4.18) show the expected linear trends with CVD chamber pressure. Therefore, over this experimental range a species' ioniser partial pressure is proportional to its partial pressure in the CVD chamber. Increasing methane concentrations appears to have little effect (there is the possibility of a slight downward trend in nitrogen signal with increasing methane additions but this is of a similar scale to the error bar. Thus, it is safe to assume that these small additions of methane are not significantly affecting gas dynamics.



Figure 4.18: The affect of nitrogen signal (at 2 sccm) from cold process gas (500 sccm H₂, 40 sccm Ar and 25 sccm CH₄ at 100 Torr, unless otherwise stated) as a function of a) pressure and b) methane input. Plotted are points are acquire whilst the chopper is open (•) and closed (•) the chopper. Absolute signal after subtraction (×) is also plotted. 91

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Chapter 5

Experimental Method

5.1 Microwave Plasma Reactor



Figure 5.1: The CVD reactor whilst in operation. The top window looks into the air cooled (green hose) waveguide, whereas the bottom looks into the CVD chamber. The PTFE pipes (brass fittings) supply cooling water, stainless steel pipes supply process gas and the opposing left-right pipes are pump ports.

5.1.1 Components

Microwave radiation at 2.45 GHz is generated by a 1.5 kW ASTeX magnetron (HS-1000). This power is transported via a waveguide through a thermal load (CS-1000) and a directional coupler (DCS-1000), also fabricated by ASTeX. The load protects the magnetron from excessive reflected power, whilst the coupler allows measurement of this reflected power via a RF-diode. A custom tapered transition¹, Flann (S/N N146028), alters the waveguide from 9A to 10 - the bore of the three stub tuner and antenna feed through. The tuner facilitates fine tuning of cavity resonance and the antenna couples the microwave energy to the chamber.

The Element Six plasma reactor (see figure 5.1) is a water-cooled cylinder with an internal diameter of 120 mm and a height of 175 mm. It is split horizontally into two sections by an 'o'-ring sealed quartz window. The top half is an air-filled cylindrical waveguide, whereas, below is the vacuum CVD chamber. Operational pressure within the CVD chamber is monitored via a 1000 Torr (Chell MK861) capacitance manometer, whilst the base pressure is monitored with a Pirani gauge (Edwards PRM10). Process gas is supplied to two opposing ¹/4" inlets from a multiple mass flow controller assembly controlled by a control box (MKS 247C). The CVD chamber is pumped by a (Edwards E2M2) rotary pump connected to two ports perpendicular to the gas inlets. This exhaust is throttled by a feedback controlled (MKS 252A) butterfly valve (MKS 253A-1-40-1).

The reactor floor is not one solid piece, rather, it is fabricated from three components (see chapter 4). First there is a water-cooled aluminium base-plate with a hollowed-out central portion. Onto this an 'o'-ring-sealed molybdenum substrate was bolted with a set of flush, counter sunk, stainless steel screws. Silver conductive paint was then used to seal the expansion orifice (SEM aperture, Agar Scientific A0409M or similar) on the experiment centreline. This can be ensured to reasonable accuracy via threading a sufficiently thin wire (such as 75 μ m wire for an 100 μ m aperture) through both, prior to applying the adhesive. Unheated, the paint and therefore the aperture, could simply be removed via ultrasonic cleaning in acetone. After plasma treatment, this was not sufficient and the orifice had to be mechanically removed with a knife blade. The observation that the colloidal paint's resistance to solvents changed suggests a significant degree of sintering upon plasma heating.

¹necessary for the re-use of a pre-acquired magnetron

The first stage of differential pumping is evacuated via 3000 L s^{-1} (H₂) cryocooled diffusion pump (Edwards 250M cryo-diffstak). This, in turn, is backed by a rotary pump (Edward E2M80). The chamber pressure is monitored by a low pressure Pirani gauge ($0.1 \rightarrow 1 \times 10^{-5}$ Torr, KJL 902006).

The second and third stages are pumped by two 180 L s^{-1} (H₂) turbomolecular pumps (Edwards EXT 255) these are backed by an oil-free scroll pump (ULVAC DIS-250). Both are monitored by a Penning ionisation gauge (Edwards CP25-K). An image of the entire system is shown if figure 5.2

5.1.2 Operation

Power-on sequence

From base vacuum, the usual 'resting' state of the reactor, the following procedure can be used:

- 1. If MBMS is required then the liquid nitrogen dewar on the diffusion pump should be filled, after which the MS-isolating gate-valve can be opened.
- 2. Turn on the chamber cooling systems. The nearest tap to the experiment has to be fully opened and the two flow meters on the outflow manifold should be registering flow. The air blower should also be switched on to protect the quartz window from overheating.
- 3. Gas lines are manually opened via the blue taps on the gas manifold. Flow rates of process gases can be selected on the mass flow meter controller.
- 4. Select 20 Torr on exhaust throttle controller and set to 'auto'.

The pressure should be left briefly to settle at this new value.

5. Turn on the microwave power supply, which automatically starts the magnetron cooling fan.

Wait for an audible click of the internal relay switches.

6. Start the microwave supply by pressing the green HVOFF button. The output should now read $\sim 50 \,\mathrm{W}$ (If the OVLD light activates then the supply has failed. Press the red HVON button, pause briefly and then retry).

- 7. Start gently ramping up the microwave power via the 'power set' potentiometer, tuning out reflect power, if it exceeds ~ 100 W, by adjusting the 3 stub tuner incorporated into the wave guide.
- 8. A plasma should have struck in the region of 700 1000 W . If the plasma fails extinguish microwaves (HVON) and check CVD chamber pressure and gas composition (flow rates). Retry from 6.
- 9. Pressure can be raised up to ~ 150 Torr provided it is balanced with increases in power (some further tuning may be required to minimise reflected power.)

Power-off sequence

- 1. Press the HVON button and wind down the power potentiometer to 0 W.
- 2. Switch the exhaust throttle value to 'open' and turn off flow controllers. Wait ~ 20 mins to be sure of an adequate cooling off period.
- 3. Turn off the microwave power supply, the cooling fan and the chamber water cooling tap.
- 4. Isolate the experiment from the high pressure gas lines via the blue taps on the gas manifold.

The experiment is now ready to be left idling.

5.2 Mass Spectrometer



Figure 5.2: The entire system, with the diffusion pump and the 1st stage pumping box at the front left, the reactor near the centre and the various control boxes to the right. The mass spectrometer (not shown) is mounted out of the back 90° to the box section.

5.2.1 Components

The residual gas analyser consists of 3 components. The quadrupole spectrometer is a Hiden Analytical positive ion counter (HAL RC PIC 101) housed within the vacuum system on a 4.5" conflat feedthrough flange. Attached to the reverse face of the flange is the RF Head which drives the instrument and amplifies the CEM output pulses into standard TTL² pulses. A dedicated controller computer and signal processor referred to by Hiden Analytical as a mass spectrometer interface unit (MSIU) collects signals. The final tier is an external PC, connected via ethernet, running Hiden's proprietary operating program, Massoft.exe.

²transistor-transistor logic

5.2.2 Operation

For a detailed explanation of the MS operation the reader is directed to the two key Hiden Analytical manuals; HA-085-014, HA-085-097 "*RC PIC analyser operator's manual*", and "*Massoft version 5 manual set*", respectively. Discussion here will only consider modes and parameters used regularly.

The 'Global' parameters

For the scan modes discussed below, the following globals are useful:

Energy The electron energy employed in the ioniser $(6 \rightarrow 150 \,\mathrm{eV})$.

Cage The voltage used to extract ions from the ioniser $(0 \rightarrow 10 \text{ V})$.

Emission The current of electrons emitted from the filament $(20 \rightarrow 1000 \,\mu\text{A})$.

SEM The voltage across the detector (secondary electron multiplier) $(0 \rightarrow 3000 \text{ V})$.

Discrim The discriminator which rejects low level noise $(\pm 100\%)$.

Dwell The period of time the count rate is estimated over $(1 \rightarrow 6\,000\,\mathrm{ms})$.

The selected MS global values are summarised below in figure 5.3.

=

Global	Typical Value				
Energy	> 20	eV			
Cage	3	V			
Emission	180	μA			
SEM	2100	V			
Discrim	-10	%			
Dwell	count	rate	dependant		

Figure 5.3: The typical MS global values used throughout this project

Parameter optimisation

The 'Energy' depends crucially on the species in that it must be significantly above the threshold (at least $+1 \,\mathrm{eV}$). As was explained in section 3.3.3 the maximum electron energy setting often depends on the chemical environment under study due to interference from dissociative ionisation.

Another consideration is for species present in high concentration where the maximum high energies may lead to high count rate. Signals much greater than (10^6 s^{-1}) may saturate the detector due to pulse width resolution and the 40 MHz system clock (see section 3.1.3). Furthermore as the operational lifetime of the detector its set by the total number of detected ions, count rates are best kept under 10^6 s^{-1} . The values used here (see figure 5.9) were selected after empirical assessment of ionisation profiles (see section 6).

A profile of the effect of cage voltage is shown in figure 5.4. The maximum signal is obtained in the region of 3-5 eV. The voltage was therefore left at the manufacture's specified voltage of 3 eV.

Figure 5.5 plots the signal as a function of SEM voltage. The optimum voltage is at the onset of the saturated 'plateau' region of the profile. At this position the signal strength is balanced with the device lifetime (the higher the voltage the higher the kinetic energy of ions entering the detector).

The discriminator (Discrim) should be set as low as possible without collecting thermal noise. This was done by isolating the spectrometer and selecting unlikely species masses (*e.g.* m/z 5-11). The discriminator can be set by finding the point which practically eliminates signal.

The selected dwell times (see figure 5.9) depend on signal strength. Prolonged exposure to high count rates are undesirable as they limit the detector lifetime. Therefore, for concentrated species (acetylene, argon and hydrogen) dwell times of only a few hundred milliseconds should suffice. Weak, noisier, signals may require longer to obtain reliable data.

The scan modes

Within this experiment the operation of the mass spectrometer is usually limited to three 'gallery' modes.

- Multiple Ion Detection MID mode allows the monitoring of a list of species where the scan parameters can be optimised from ion to ion.
- Mass Scan This mode plots the familiar mass spectra (a histogram of signal vs mass) from a fixed set of global parameters. Care should be taken when interpreting the relative signal strengths due to differences in species ioni-sation cross-sections.



Figure 5.4: Argon signal vs cage voltage; a voltage corresponding to the maximum signal is prefered, here 3-5 V.



Figure 5.5: Argon signal vs multiplier (SEM) voltage. A voltage set just after the onset of the 'saturated' region is prefered, here $> 2\,000\,\mathrm{kV}$.

Map Records species intensity against one of the user-specified global parameters. This mode is helpful in tuning parameters but is also useful to record appearance potentials (*i.e.* signal 'mapped' with *energy*).

5.3 Data Acquisition System



Figure 5.6: The internal components of the chopping system. From top to bottom are the rotating wheel, the mounting plate and second skimmer. The nipple shown protruding out towards the top right is the mounting flange for the mass spectrometer. The gold component mounted in the aluminium block either side of the chopper is half of the OPTO-IR circuit.

5.3.1 Components

As discussed earlier (chapter 4) a tooth-wheeled chopper is mounted across the beam axis. This chopper incorporates an OPTO-IR circuit which supplies a TTL level (the 'OPTO_OUT' BNC cable) at the chopping frequency and the same duty cycle, though perhaps not the same phase or anaytical form³.

³he TTL OPTO-IR circuit can only exist in either state 0V or +5 V, whereas, in reality the chopper blade will sweep through the beam blurring edges.

It had been intended to acquire raw signals (subject only to amplification in the R.F. head) from the MSIU (aux i/o: 'PULSE_OUT' pin) and use a counter/timer card to compare signals between chopper open and closed. This would allow the user to obtain data in 'real' time. The primary advantage is that one is truly comparing data collecting with close proximity in time to each other, reducing any drift errors. Also it is practically useful to spot any experimental problems or tune parameters. Unfortunately, due to the somewhat esoteric nature of the MSIU's data handling and firmware this was unrealisable in the project's lifetime. Instead, the MSIU is gated via delayed (relative to the chopper OPTO-IR edge) TTL high gate supplied from a counter timer card (NI6022). Each experiment is therefore conducted twice, with delays corresponding to signal 'on' and signal 'off'. This resultant data must be subtracted in a spreadsheet package to obtain 'real' signal.

This card is operated via a Labview 8 program (Gate_Hiden_Box.vi) This program uses a counter (CTR1) to measure the rising edge separation of the chopper (Period). The prefered delay and gate width for acquisition relative to the chopper signal (%) is user specified and the same counter is used to generate the acquisition gate. This is supplied via a BNC cable to the gating circuit (aux i/o: 'HIGH_GATE_IN' pin). In the absence of this cable, the MSIU will run un-gated. In this current incarnation of the program, it must be restarted every time a new chopper frequency is used.

5.3.2 Operation

To set the TTL gate, use the following proceedure:

1. Turn on the chopper controller, select 'joystick' control and the desired frequency.

Note that the frequency specified will not be the actual chopping frequency, rather it is the motor stepping frequency.

- 2. Check that 'on' is selected on the joystick. This will start the chopper motor.
- 3. Open and run Gate_Hiden_Box.vi. Wait for the program to acquire the chopper frequency (Ready light). Check the 'chopper frequency' is reasonable given the above approximate chart (figure 5.7).

motor frequency	chopping frequency		
Hz	Hz		
50	2.5		
100	5		
200	10		
500	25		
1k	50		

Figure 5.7: Stepper motor frequency vs chopping frequency.

- 4. Select a gate 'delay' and 'width'. If a continuous train of gates is required select 'Disable gate selection'.
- 5. Click on the 'update gates' button.

The gate will now be generated for each rising edge of the chopper. To select a different gate parameters:

6. Deselect the 'Disable gate selection' and change the parameters, and follow from 4.



Figure 5.8: The front panel of Gate_Hiden_Box.vi showing the measured chopper frequency, the user specified width, delay and a graphical indication of the current settings.

5.4 MBMS experimental procedure

The ideal procedure would be to measure each species' ionisation threshold for each experimental condition. Thus, one could minimise any ambiguity in mass spectra contributions. In reality, low signal levels near threshold require large time scales to resolve. During experiments, the continuous deposition of diamond on the orifice will reduce signal levels. This limits the length of time an experiment can be held 'constant' for a legitimate foreground/background subtraction. The experiment was therefore limited to measuring signals at a fixed energy to enhance experiment speed, leading to greater confidence in this subtraction.

It is hoped that if thresholds are taken once during typical of a group of experimental conditions - for instance at the centre of a sequence of measurements - then the increase in assignment ambiguity is small. The choice of fixed energy is unimportant provided that the ionisation cross-section is well known. The chosen energy should also be experimentally determined to be in the linear region between ionisation and any appearance potentials⁴. A good source of cross-section data for simple hydrocarbons is the NIST website [1] computed using the Binary-Encounter-Bethe (BEB) model (reviewed in [2]) experimental values for noble gas atoms have also be determined by Wetzel *et al.* [3].

The experimental method to measure species trends, reported in chapter 6, were conducted as follows:

- 1. Establish a plasma with the MS-isolating gate valve open (see section 5.1).
- 2. Activate the gating system (see section 5.3) with a gate width of 8% and delays of 6% and 50% for on and off signal respectively.
- 3. Setup MID mode (see section 5.2) with the parameters given in figure 5.9).
- 4. Collect data for each experimental condition both with (I_X^{on}) and against (I_X^{off}) the chopper.
- 5. Subtract on off, $I_X = I_X^{\text{on}} I_X^{\text{off}}$

 $^{{}^{4}}$ It is prudent to use empirical appearance potentials not to rely on literature values which may be incomplete

Species	m/z	Dwell Time	Energy
	amu	ms	eV
Н	1	1000	16
H_2	2	100	18
CH_3	15	1000	15
CH_4	16	200	18
C_2H_2	26	200	16
Ar	40	100	19

Figure 5.9: The selected dwell times along with the optimised energies for the species under test.

6. Ratio species signal with respect to argon and then multiply by the relative cross-section (figure 5.10) to obtain a normalised signal (*c.f.* equation 3.25).

$$\frac{I_X \sigma_{Ar}(E_{Ar})}{I_{Ar} \sigma_X(E_X)}$$

Species	Energy	$\sigma(E)$	source
	eV	$Å^2$	
Н	16	0.108	[1]
H_2	18	0.157	[1]
CH_3	15	0.356	[1]
CH_4	18	0.701	[1]
C_2H_2	16	1.444	[1]
Ar	19	0.44	[3]

Figure 5.10: Species cross-sections at their optimised energies. The first five are theoretical data (see [2]) whereas the final value is obtained empirically.

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Chapter 6

Results and Discussion

6.1 Diamond

The first question to be addressed is whether the conditions from which the apparatus samples are related to the actual conditions in the CVD of diamond. During the preliminary MBMS experiments, conditions were maintained at an input of 25/40/500 sccm of CH₄/Ar/H₂, 100 Torr and 1.5 kW. Figure 6.1 demonstrates the depositing nature of this environment around the sampling orifice. Deposition of carbonacous material has reduced the diameter of the hole from its initial value of 100 µm down to ~ 80 µm. This material has the general appearance of nano-crystalline or 'ballas' diamond.

An established [1–3] technique for the characterisation of diamond and diamond like films is laser Raman spectroscopy (LRS). Figure 6.2 is a LRS spectrum centred on the characteristic 1332 cm^{-1} diamond resonance. It shows a clear, sharp, peak at this location indicated the presence of diamond. The broad features around 1350 and 1580 cm^{-1} are the carbon 'D' and 'G' peaks (see the previous references). The presence of the 'D' peak and the absence of any sharp 'G' features demonstrate a lack of any crystalline, large scale, graphitic phases. A peak, commonly observed in nano-crystalline diamond, assigned to 'transpolyacetylene' [4] is also present at ~ 1180 cm^{-1} . These non-diamond sp^2 features can therefore be attributed to grain boundary material. The overall appearance of the spectrum strongly suggests, like the electron-micrograph, that this material is nano-crystalline diamond. This is to be expected as the substrate stub has never been observed to exceed 500 °C, the lower limit on our optical pyrometer.



Figure 6.1: *Top*, the electron microscope aperture prior to diamond growth and *bottom* after several hours' experimentation time.



Figure 6.2: A LRS spectrum obtained with an excitation wavelength of 325 nm demonstrating the reactor produces nanocrystalline diamond from the edge of the MBMS sampling region.

6.2 Plasma Species Measurements

This section looks at some mass thresholds recorded sampling from the full plasma (see 6.1) and gauges the likelihood that they represent signals of interest. The discussion starts with easier species $(Ar/CH_4/C_2H_2)$ and moves onto those that proved more difficult $(H_2/H/CH_3)$.

6.2.1 m/z = 40

Fitting the m/z = 40 energy profile with a single linear function yields an IP of 15.7 eV (after calibration with the -2.0 eV, see 4.3.1) which is close compared to the established value [5] of 15.8 eV for argon (see figure 6.3).



Figure 6.3: Two energy profiles of m/z = 40 channel extracting from a 100 Torr plasma accumulated with (\blacksquare) and against the chopper (\Box), the on-off difference (+).

6.2.2 m/z = 16

Fitting the m/z = 16 energy profile with a single linear function yields an IP of 13.4 eV which is high compared to the established value [5] of 12.6 eV for methane (see figure 6.4).

6.2.3 m/z = 26

Fitting here leads to an IP of 11.8 eV in agreement with the NIST value of 11.4 eV of acetylene (see figure 6.5).

6.2.4 m/z = 2

Molecular hydrogen, the majority gas phase component, was also problematic. Figure 6.6 shows signal as a function of ioniser energy. If the curve is fitted with a single linear component an IP of 15.2 eV is obtained matching closely with NIST's evaluated value of 15.4 eV. It can also be seen that the 'true' signal $(I_{\rm H_2}^{\rm on} - I_{\rm H_2}^{\rm off})$ is weak. Unreliable readings for the hydrogen signal will make any subsequent calibrations which rely on assertions about mole fraction (see equation



Figure 6.4: Two energy profiles of m/z = 16 channel extracting from a 100 Torr plasma accumulated with (\blacksquare) and against the chopper (\Box), the on-off difference (+).



Figure 6.5: The energy profile of m/z = 26 channel extracting from a 100 Torr plasma accumulated with (\blacksquare) and against the chopper (\square), the difference is also plotted (+).

3.29) suspect.

It is not clear what the origin of this insensitivity is. Certainly most pumps, including the turbo-molecular pumps employed on stages 2 and 3, are less efficient at evacuating hydrogen. This would lead to a higher static concentration of hydrogen in the ioniser. Using the manufacturer-stated pumping speeds (F) allows us to estimate the relative effectiveness as a ratio $(F_{\rm H_2}/F_{\rm N_2})$ of 0.8. This ratio appears too close to unity to produce such a large background signal.



Figure 6.6: The energy profile of m/z = 2 channel extracting from a 100 Torr plasma accumulated with (\blacksquare) and against the chopper (\Box), the difference is also plotted (+).

Another possible explanation is that gas dynamics (particularly Mach number focusing discussed in section 3.3.2) are strongly discriminating against hydrogen. If this is the case, then the next section's discussion (6.2.5) of H is impacted upon. If we find molecular hydrogen difficult to observe due to mass separation effects, the H-atom signal should be worse.

A further possibility is that the seals between stages, particularly at the first orifice, are too porous to fully hold back hydrogen. Of particular worry is that the colloidal silver paint is not forming an effective gas seal. This would go someway to explaining the order of magnitude difference between the manufacture's specified pump rate (3000 L s^{-1}) and the empirically determined value (220 L s^{-1}) , see section 4.3.3). This discrepancy would otherwise have to be explained in terms of a severe conductance limitation (a situation that the design was explicitly attempting to avoid, see section 4.2.3).

6.2.5 m/z = 1

For reasons given in previous sections (especially in chapter 2) it would be of great utility to be able to measure the concentration of atomic hydrogen. Figure 6.7 displays the m/z = 1 signal as a function of energy from 14 to 19 eV. The data can be fitted with two linear fits, yielding ionisation potentials (high and low energy) of 13.0 and 15.4 eV after correction.

The lower of these two ionisation energies is close to but just outside the lower limit of expected values for hydrogen atom's IP (13.6 eV [5]) assuming uncertainties in estimates of potentials of about ± 0.5 eV. The second potential, estimated at around 15.4 eV, is too low for the expected value for dissociative ionisation of molecular hydrogen (17.3 eV [5]). But it is closer to the appearance potential from dissociative ionisation of water (a known contaminant of the system) with recorded values of 16.0 eV and above.

It is a valid question to ask whether fitting with two linear components is warranted. Due to the closeness of the two potentials and the high count rates passed the second of these thresholds, it is difficult to demonstrate that there is a clear linear region after the first threshold. The first threshold may, indeed, be an artefact of attempting to fit two linear components with only a coincidental similarity to the hydrogen ionisation energy.

The second ionisation potential is very close to the direct ionisation of molecular hydrogen (15.4 eV [5]). One may be tempted to suggest that the instrument lacks the mass resolution at the edge of its tuning range. To try to answer this, a histogram was obtained showing the signal as a function of fractional mass increases (see figure 6.8). The scan was taken at 16.6 eV (14.6 eV after correction). From this, it appears there is clear resolution of the peaks, with signal dropping to zero between masses. However, the mass one peak is unusual as it does not peak at at the expected mass, rather its maximum is around $0.7 \rightarrow 0.8$ amu.



Figure 6.7: The energy profile of m/z = 1 channel extracting from a 100 Torr plasma. 6.7a a linear graph focusing around the predicted threshold and 6.7b) a logarithmic graph of the entire scan. The two plots are data accumulated with (\blacksquare) and against the chopper (\Box) , the difference is also plotted (+).



Figure 6.8: The full histogram of count rate as a function of mass $(0.4 \rightarrow 3 \text{ amu})$ showing clear separation between m/z 1 and 2. The gaps in the data represent 0 count rate.

6.2.6 m/z = 15

As stated earlier (section 2.2.2), one of the key radicals of interest in diamond CVD is the methyl radical. Measurements near threshold were initially encouraging as there appeared to be a resolvable difference between open and closed chopper values. The linear fit gives 9.7 eV which is in close agreement with NIST's preferred value of 9.8 eV (see figure 6.9a). The signal was found to be very variable (*cf.* figures 6.9a & 6.9b). Species with low count rates are particularly affected by absolute signal strength; if this is low, then it is harder to resolve fractional on/off ratios. Absolute signal is largely a consequence of equipment geometry. So alignment and the orifice size (or the extent to which deposition has reduced it) will strongly affect signals.

Another concern is the origin of this background. We would expect the beamto-background ratio to be much more favourable for radicals than closed shell molecules. Even in the 'best case', below (figure 6.9a), we obtain the same value



Figure 6.9: Two energy profiles of m/z = 15 channel extracting from a 100 Torr plasma accumulated with (\blacksquare) and against the chopper (\Box), the difference is also plotted (+)

as that of argon (~ 0.8, see section 4.3.2). The origin of the background is uncertain.

Figure 6.10 shows that the 'methyl' signal is unlikely to be due to fragmenta-

tion of methane, as even when methane is present in large quantities, contribution to the m/z 15 signal is negligible below 15 eV.



Figure 6.10: Energy profiles with linear fits (dashed) for m/z 16 (\Box) 15 (\triangle) and for comparison 14 (\circ) showing the onset of fragmentation from 100 Torr of cold methane. The linear fits suggest, after correction, appearance potentials of m/z 15, 14.1 eV and m/z 14, 15.5 eV. These are in agreement with the reference values tabulated in [5] of around 14.2 eV and 15.1 eV respectively.

6.3 The Background

The background in the mass spectrometer proved problematic when attempting to measure radicals with low count rates. If this background could be eliminated, then there could be a significant enhancement in sensitivity even in the absence of any increases in absolute signal strength. Figure 6.11 plots the background at a relatively high energy of 18 eV throughout the mass range. A high energy is most informative as all species will be ionised, but as hydrocarbons typically have IPs $10 \rightarrow 12 \text{ eV}$, their relative strengths are strongly enhanced. The spectrum shows what appears to be some long-chained hydrocarbon fragmenting into a series of peaks separated by roughly 15 amu.

This background spectrum does not contain any evidence of contamination from diffusion pump oil. If this were the case then it would be expected [6] to see counts at mass 77, corresponding to a C_6H_5 moiety liberated from the pump fluid (Santovac 5, i.e. a pentaphenyl ether [6]).

The origin of the hydrocarbon background is therefore unknown. The other components include contribution from air O_2 , N_2 , and CO_2 . The largest peak in the background, H_2O , due to water desorbing from the MS surfaces, which would be difficult to remove without baking out the equipment.



Figure 6.11: The MS background at 20 eV (18 eV after correction) taken whilst isolated from the CVD system. The general, undulating, trend suggests some form of long chained hydrocarbon with several 'air' components superimposed.

6.4 Carbon Input Trend

The following data, figure 6.12, was obtained by taking the differences between signals with and against the chopper at a fixed energy for each species. Plasma power and pressure were fixed (1.5 kW & 100 Torr) and the methane flow rate was adjusted (0.9-4.4%).

The signal from H atoms was not observed to have any experimentally consistent value and thus it is doubtful whether a true 'observation' has been made. In this plot (6.12), acetylene is the dominant hydrocarbon and appears to scale fairly linearly with methane input. Methane concentrations are initially comparable in concentration but as more carbon is added, its contribution to the total carbon mole-fraction is reduced.

The signal attributed to methyl appears to increase for small additions and then appears to saturate, or even fall back. It should be noted that the error bar (standard error σ/\sqrt{n}) for these methyl measurements is sometimes larger than the absolute value (20 & 25 sccm). Therefore, inferences about the exact shape of the curve, and its reliability are questionable. If this signal were genuinely attributable to methyl then its behaviour is surprising. One would expect methyl to be in a partial equilibrium with methane due to the hydrogen-mediated chemistry discussed in section 2.2.2. Methyl should therefore track that of methane, as observed by Hsu [7] at lower pressures (see figure 6.13). Further differences include that Hsu observed a general upward trend in methane as more carbon was added. Our gas chemistry may be quite different to that of a 20 Torr reactor, as increases in pressure and power suggest an increase in the neutral gas temperature [8]. This will shift any partial equilibria linking CH₄ and C₂H₂ towards acetylene and higher entropy.



Figure 6.12: Trends (logarithmic (6.12a) and linear 6.12b) in counts of m/z 15 (×), 16 (•) and 26 (\blacktriangle) obtained at 15, 18, 19 eV (13, 16, 17 after correction) respectively for increase in methane additions to the plasma (0.9-4.4%). The signal has been normalised by division by m/z = 40 (at 19 eV) and then divided by the ratio of electron impact ionisation cross-sections ($I_X \sigma_{Ar}/I_{Ar} \sigma_X$).


Figure 6.13: Hsu's MBMS data obtained showing species mole fractions as a function of input methane [7].

6.5 Process Pressure Trend

Figure 6.14, was obtained in the same way as previously (section 6.4) except that, this time, pressure was varied from 70 to 150 Torr. The applied power was fixed, but at lower pressures reflected power could not always be tuned out ($\sim 15 \text{ W}$). Considering the absolute value of input power (1.5 kW) this is considered unimportant.

The graph 6.14 shows no apparent trend with pressure. This is perhaps surprising as one may assume that temperature might increase with more efficient energy transfer from electrons to neutrals [8]. This effect will, to some extent, be counteracted by increases in the number of neutrals over which the fixed power has be to spread.

Methyl radical signals also differ by as much as an order of magnitude from the previous data set. Closer inspection of the data reveals that whilst the absolute signals for all other species measured have dropped, the methyl signal remained constant. A drop in absolute signal can be rationalised as occurring from deposition on the sampling orifice (these data sets were collected in that order). The fact that the methyl signal did not also drop suggests that it may have originated from some unknown background.



Figure 6.14: Trends (logarithmic) in counts of m/z 15 (×), 16 (•) and 26 (\blacktriangle) obtained at 15, 18, 19 eV (13, 16, 17 after correction), respectively, for increasing pressure. The signal has been normalised by division by m/z = 40 (at 19 eV) and then divided by the ratio of electron impact ionisation cross-sections $(I_X \sigma_{Ar}/I_{Ar} \sigma_X)$.

6.6 Assessment of the MS data

It is difficult to check the consistency of these MS given the lack of published data in comparable, particularly in terms of pressure, systems. As a rough first approximation, equilibrium calculations have been used to good effect in modelling diamond synthesis at low pressures [9]. The senkin [10] chemical kinetics package can be used to calculate these values if the simulation time is of the order of a few seconds. These data have been plotted in figure 6.15 below:

A temperature of 1750 K was used for the simulations and represents the best fit out of the series 1500, 1750 and 2000 K. The precise value of the temperature manifests itself largely in the relative positions of methane and acetylene but not the trends. In terms of trends - the MS data have not been directly calibrated - the fit is reasonable for pressure showing no obvious change in species concentration over the range. Increases in carbon input are not modelled so well. Although



Figure 6.15: Logarithmic comparisons of the a) pressure and b) carbon input trends with equilibrium composition ($T_{\text{gas}} = 1750 \text{ K}$). The senkin output (lines) is the ratio of methane (solid grey, MS (\bullet)), acetylene (solid black, MS (\blacktriangle)) and methyl (dashed black, MS (\times)) to that of argon whereas the MS data (points) is the same as above ($I_X \sigma_{Ar}/I_{Ar} \sigma_X$). Both are plotted on the same axis without scaling.

there is good agreement with the measurements of acetylene, methane appears to have a conflicting trend. This may be a sign that the equilibrium approximation is poor for methane. Alternatively, it is possible that this trend will be eliminated with subsequent calibration.

In order to go beyond this equilibrium approximation it is useful to compare data with a more explicit simulation of a diamond CVD reactor. Assuming the pressure independence extends as far as 150 Torr, then these data can be compared with those produced by the ongoing computer modelling project of the CRDS reactor. These data were obtained under identical conditions (except at slightly elevated pressures) by Dr. Yuri Mankelevich [11] and are reproduced in figure 6.16.

Species	Model	Mass Spectrometry
	χ_X/χ_{Ar}	$I_X \sigma_{Ar} / I_{Ar} \sigma_X$
C_2H_2	2.91×10^{-1}	1.57×10^{-1}
CH_4	1.24×10^{-2}	1.39×10^{-2}
CH_3	6.13×10^{-4}	1.28×10^{-3}

Figure 6.16: A comparison between 2D model data [11] and the MS experiment data (at 130 Torr). The model estimate corresponds to typical CRDS reactor conditions $(25/40/500 \text{ sccm CH}_4/\text{Ar}/\text{H}_2, 150 \text{ Torr} \text{ and } 1.5 \text{ kW})$ at a distance of 0.5 mm above the substrate (where locally $T_{\text{gas}}=1320 \text{ K}$).

The agreement for methane and acetylene is remarkable (within a factor of 2) given the lack of direct calibration and the lack of characterisation of sampling the environment. This may therefore prove to be rather fortuitous. The model location of 0.5 mm, a feature of the 1 mm model resolution, is many times further into the plasma than the (very) rough estimate of the sampling shift (see section 3.3.1). This will probably not affect acetylene concentrations as the boundary will be thick on this scale. Methane, which one would expect to be largely excluded from the plasma interior, will likely have a thin boundary and thus should display a significant shift. MS would therefore be expected to underestimate methane concentrations (c.f. a factor of 4 in the computational results of Swihart *et al.* [12] from a 1 atm $Ar/H_2/CH_4$ thermal plasma).

6.7 Conclusions

A new MBMS system has been constructed to closely match the CRDS system with the aim of obtaining complementary measurements. The new design explicitly attempts to incorporate sampling from conditions directly associated with diamond growth. A removable molybdenum insert was designed to match typical substrate conditions. The temperature of the current substrate was empirically observed to not exceed 500 °C. This led to the production of nano-cystalline diamond at low deposition rates at the diamond orifice. This sampling insert was the prototype design, and therefore it seems reasonable to expect that improvements can be made in order to increase temperatures closer to those relevant for growth of micro-crystalline diamond. Regardless it is not clear that the substrate temperature, although greatly affecting morphology and growth rates of films, manifests itself to a large extent in gas phase processes.

Due to the greatly increased gas loading during typical operating, as compared to the previous MBMS experiment conditions (factor of ~ 5), the design focused on gas management to a greater extent than many within the literature. Our design seeks to improve signal-to-background ratio (n_B/n_3) at the expense of some of the absolute signal strength.

Estimates of the detection limit suggest that for argon it is in the region $10^{-5} - 10^{-4}$ mole fraction. The system has a $n_B/n_3 \sim 0.8$ for closed-shell species, which was estimated to be 0.7 with our simple spreadsheet model.

Empirically, system performance is currently somewhat disappointing with certain important species un-estimable. For instance, without reliable readings for molecular hydrogen, direct calibration could not proceed as planned. It would appear that either hydrogen is significantly more difficult to pump than the manufacturer's specifications state or the system sealing is inadequate. Hydrocarbon backgrounds (which were hoped to be eliminated due to the use of a scroll pump and diffusion pump cold trap) and low absolute signal strength also complicate measurements.

Our measurements of acetylene and methane, pressure and carbon input trends, were on the whole, reproduced by simple equilibrium arguments. However, methane's trend with increased carbon was not. That said, measurements agree to within a factor of 2 with absolute values calculated for the CRDS reactor by Mankelevich despite the lack of direct calibration.

This consistency awaits further tests to check that the trends are also reproduced by the model. Assuming the gas phase model is accurate, it predicts that H, H₂, Ar, CH₃, CH₄, C₂H₂, C₂H₄ and possibly C₃H₂ and C₄H₂ (given the 10^{-5} detection limit) should be detectable. Empirically, there is, as yet, no evidence of the latter three species, though the final two concentrations are near the limit of detection (both $<1\times10^{-4}$).

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Chapter 7

Future Work

The new experiment is not currently performing up to expectations. Absolute signal is relatively low making estimate of on/off differences difficult for species of low concentration ($\chi_X < 10^{-3}$). Unexpected hydrocarbon backgrounds exacerbate this problem. This chapter looks at the major problems and provides possible solutions and improvements that are possible with only minor modifications.

7.1 System Optimisation

7.1.1 Geometric Factors and signal strength

Absolute signal strength is primarily a geometric issue. The first thoughts about increasing signal strength will always initially be to increase the size of the sampling orifice. As a first approximation, signal strength should increase as the square of the aperture diameter (see equations 3.13, 4.2). This may, however, have a deleterious effect on background scattering during transit and diffusion pump operation.

Another component of increasing the absolute signal is to increase the solid angle of the sampled beam. This has an obvious limit at the angle subtended at the detector inlet (8 mm). Selection of skimmers was limited by the supplied MS chopper wheel; there was no value in increasing the angle that was subtended by the skimmers past that subtended by the chopper slit. A replacement chopper and final orifice have been recently obtained which will, in theory, maximise absolute signal strength. As the slots in the new wheel are twice the width (6 mm as opposed to three) at the beam centre line one would expect a factor of 4 increase in signal.

The final method of increasing signal, reducing the distance between the sampling and detection - is not trivial and would require new mass spectrometer housing. It is difficult to see where any significant length reduction could be made given the same design constraints.

7.1.2 Alignments

System alignment is a difficult process which involves bringing the system up to air, and then moving the various components (usually relative to a HeNe laser fixed at the experiment centre-line). The mounts that fix the skimmers are simply annular clamps with no fine adjustment. These don't give the operator much precision as to the placement of skimmers. Once the alignment appears to be optimised then the systems are re-sealed and evacuated.

If system alignment is a factor in our low species counts, then a more systematic, adjustable mount, would be of considerable advantage. Ideally this mount could be operated without need to break the vacuum, so fine tuning of the system could be complete with respect to the MS signal. A mobile mount replacing the cone section between stage 1 and 2, would meet this criterion, though would require some engineering to retro-fit these components. If this mount included 'z'translation along the beam centre-line, it would allow investigation any unforeseen skimmer interference effects resulting indirectly from pump under-performance. A good example of inclusion of this within a MS design is describe by Park *et al.* [1].

7.2 Calibration

The system has not yet been calibrated. As the dynamic effects of the expansion are, to a large part, geometric, then calibration will need to be conducted once the system has been optimised. A suggested procedure was outlined at the end of section 3.3.3.

Another feature related to calibration is that the sampling region has not been fully characterised. In section 3.3.1 a rough estimate of the axial shift of species concentration measurements of $110 \,\mu$ m was given. In reality, this will depend on the properties of each species individually. If these effects are to be quantified in terms of modelling, then a higher simulation resolution will be required locally around the sampling orifice (see the recipe given in Swihart *et al.* [2], discussed in section 3.3.1) than is currently implemented in the CRDS reactor model.

7.3 Cold Trapping

A good method for removal of hydrocarbon background from a MS is condensation [3]. A 77 K liquid nitrogen-cooled cold-finger would provide an economic method of removal of background without resorting to larger pumps. Location of the trap in the second stage would appear to be the most logical. Placement in the first stage could lead to severe conductance issues (see the analogous discussion of chopper location, section 4.2.4). Whereas location in the final stage limited to placement after the MS due to the current design - would be somewhat 'after the fact'; it would lead to a reduction in background but only of the species which are long lived in the MS system.

It is possible to envisage a copper cold finger, entering the system via the QF 25 fitting currently supporting a Penning gauge (see figure 4.9). This could support a copper annulus symmetrically placed about the centre-line. This would remove the general condensible background gas and go some way (depending on design skill) to trap off-axis beam material and reducing reflection-scatter losses, whilst the beam centre-line remains un-affected by the trap's presence.

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Appendix A

Summary available of Spectro(scopic/metric) Data

A.1Temperatures

Conditions Technique		Values	Ref.
H_2/CH_4 (microcystalline	diamond production)		
	$BAS^{a}(C_{2}(a))$	$1200 \pm 100 \mathrm{K}$	[1]
18 Torr, 1200 W	$CARS^{b}(H_{2})$	2200-2150 K	[2]
	LIF c (?)	550-2600 K	[2]
$H_2/Ar/CH_4$ (microcystal	line diamond product	ion)	
800 W, 60/37/3	LIF $(C_2(a))$	$2100 \pm 200 \mathrm{K}(50 \to 100 \mathrm{Torr})$	[3]
79/18/3	CARS $(C_2(a))$	$2100 \rightarrow 2550 \pm 200 \mathrm{K}(500 \rightarrow 800 \mathrm{W})$	[4]
		$2100 \rightarrow 2550 \pm 200 \mathrm{K}(15 \rightarrow 54 \mathrm{Torr})$	
$Ar/H_2/CH_4$ (nanocrystal	line diamond product	ion)	
90 Torr, 2100 W	$\operatorname{CRDS}^d(\operatorname{C}_2(\mathbf{a}))$	$3010 \pm 340 \mathrm{K}$	[5]
$800 \mathrm{W}, 95/4/1^e$	BAS $(C_2(a) \& C_2)$	$3000 - 4000 \mathrm{K}$	[6]
$CH_4(0.5)$	$OES^{f}(C_{2}(a))$	$\sim 3500\mathrm{K}$	[7]
	(CH?)	$\sim 3500\mathrm{K}$	
	(H balmer?)	$\sim 4100 \mathrm{K}$	
100 Torr, 800 W, 97/2/1	BAS $(C_2(a))$	$1150 - 1250 \mathrm{K}$	[8]
	OES $(C_2(a))$	$800 - 1250 \mathrm{K}$	

 a Broadband Absorption Spectroscopy

^bCoherent Anti-Stokes Raman

 c Laser Induced Fluorescence

^dCavity Ring-Down Spectroscopy ^eThese were adjusted to maintain plasma stability ^fOptical Emission Spectroscopy

A.2Composition

Species	Value	Technique	Conditions	Ref.
H_2/CH_4	(microcystalline diamond production)			
CH ₃	$1 \times 10^{14} \rightarrow 5 \times 10^{14} \mathrm{cm}^{-3} \ (1 \rightarrow 5 \% \mathrm{CH}_4)$	BAS	30 Torr, 0.8 kW, -	[9]
	$4 \times 10^{-4} [3 \times 10^{13} \mathrm{cm}^{-3}]^a \rightarrow 1 \times 10^{-3} [7 \times 10^{13} \mathrm{cm}^{-3}] (1 \rightarrow 10 \%)$	TDLAS^{b}	19 Torr, 0.6 kW, -	[10]
	$(1 \times 10^{-4}) [9 \times 10^{12} \mathrm{cm}^{-3}] (0.2 \to 1.2 \mathrm{kW})$	$MBMS^{c}$	$20 \mathrm{Torr}, - , 98/2$	[11]
CH_4	$8 \times 10^{-3} [7 \times 10^{14} \mathrm{cm}^{-3}] \to 2 \times 10^{-2} [2 \times 10^{15} \mathrm{cm}^{-3}] \ (1 \to 10 \%)$	TDLAS	19 Torr, 0.6 kW, -	[10]
	$6 \times 10^{-3} [6 \times 10^{14} \mathrm{cm}^{-3}] \rightarrow 1 \times 10^{-3} [9 \times 10^{13} \mathrm{cm}^{-3}] (0.2 \rightarrow$	MBMS	$20 \mathrm{Torr}, - , 98/2$	[11]
	$1.2\mathrm{kW})$			
	$3 \times 10^{-3} [4 \times 10^{14} \mathrm{cm}^{-3}] \rightarrow 5 \times 10^{-3} [7 \times 10^{14} \mathrm{cm}^{-3}] (0.5 \rightarrow 4 \%)$	FTIR^d	30 Torr, 0.3 kW, -	[12]
$C_2(a)$	$5 \times 10^{11} \rightarrow 2.5 \times 10^{12} \mathrm{cm}^{-3} \ (25 \rightarrow 35 \%) \ \mathrm{CH}_4^{e}$	BAS	55 Torr, 0.8 kW, -	[13]
C_2H_2	$1 \times 10^{-3} [9 \times 10^{13} \mathrm{cm}^{-3}] \to 7 \times 10^{-2} [2 \times 10^{15} \mathrm{cm}^{-3}] (1 \to 10 \%)$	TDLAS	19 Torr, 0.6 kW, -	[10]
	$1 \times 10^{-3} [1 \times 10^{14} \mathrm{cm}^{-3}] \rightarrow 1.5 \times 10^{-2} [2 \times 10^{15} \mathrm{cm}^{-3}] (0.5 \rightarrow 4 \%)$	FTIR	30 Torr, 0.3 kW, -	[12]
	$2 \times 10^{-4} [2 \times 10^{13} \mathrm{cm}^{-3}] \rightarrow 1 \times 10^{-3} [9 \times 10^{13} \mathrm{cm}^{-3}] (0.2 \rightarrow$	MBMS	20 Torr, - , 98/2	[11]
	$1.2\mathrm{kW})$			
C_2H_4	$< 1 \times 10^{-3} [< 1 \times 10^{14} \mathrm{cm}^{-3}] (0.5 \rightarrow 4 \%)$	FTIR	30 Torr, 0.3 kW, -	[12]
C_2H_4	$< 1 \times 10^{-4} [< 9 \times 10^{12} \mathrm{cm}^{-3}] \ (0.2 \to 1.2 \mathrm{kW})$	MBMS	20 Torr, - , 98/2	[11]
C_2H_6	$1 \times 10^{-4} [9 \times 10^{12} \mathrm{cm}^{-3}] \rightarrow 2 \times 10^{-4} [1.7 \times 10^{12} \mathrm{cm}^{-3}] (1 \rightarrow 10 \%)$	TDLAS	19 Torr, 0.6 kW, -	[10]

 a only mole fraction avaliable, [density] assumes $T=2100\,{\rm K}$ and ideality $^b{\rm Tunable}$ Diode Laser Absorption Spectroscopy

^cMolecular Beam Mass Spectrometry

^dFourier Transform Infra-Red

^eValues were extrapolated to suggest $< 1 \times 10^{11} \,\mathrm{cm}^{-3}$ in 'normal' methane flow rates

Species	Value	Technique	Conditions	Ref.
$H_2/Ar/CH_4$ (microcystalline diamond production)				
CH ₃	$1.67 \times 10^{-4} [1.5 \times 10^{13} \mathrm{cm}^{-3}]$	MBMS	20 Torr, 0.8 kW, 270/29/1	[14]
CH_4	$1.30 \times 10^{-3} [1.2 \times 10^{14} \mathrm{cm}^{-3}]$	MBMS	$20 \operatorname{Torr}, 0.8 \mathrm{kW}, 270/29/1$	[14]
$C_2(a)$	$5 \times 10^9 \rightarrow 8 \times 10^{10} \mathrm{cm}^{-3} \ (40 \rightarrow 75 \mathrm{Torr})$	LIF	- , $2.1 \mathrm{kW}, 40/25/2$	[3]
	$5 \times 10^9 \rightarrow 7 \times 10^{10} \mathrm{cm}^{-3} \ (0.7 \rightarrow 0.8 \mathrm{W})$	LIF	$65 \mathrm{Torr}, - , 40/25/2$	[3]
	$1.5 \times 10^{10} \rightarrow 7.5 \times 10^{10} \mathrm{cm}^{-3} \ (2 \rightarrow 5 \% \mathrm{Ar})$	LIF	$65 \mathrm{Torr}, 2.1 \mathrm{kW},$ -	[3]
C_2H_2	$9.47 \times 10^{-4} [8.7 \times 10^{13} \mathrm{cm}^{-3}]$	MBMS	$20 \operatorname{Torr}, 0.8 \mathrm{kW}, 270/29/1$	[14]
Н	$1.21 \times 10^{-4} [1.1 \times 10^{14} \mathrm{cm}^{-3}]$	MBMS	$20 \operatorname{Torr}, 0.8 \mathrm{kW}, 270/29/1$	[14]
$Ar/H_2/$	CH_4 ('ultra'nanocrystalline diamond production)			
C_2	$1 \times 10^{13} \mathrm{cm}^{-3}$	BAS	$152 \mathrm{Torr}, 0.8 \mathrm{kW}, 92/7/1$	[6]
$C_2(a)$	$2 \times 10^{12} \rightarrow 4 \times 10^{14} \mathrm{cm}^{-3} \ (85 \rightarrow 95 \% \mathrm{Ar})$	CRDS	$90 \mathrm{Torr}, 2.1 \mathrm{kW}, 95/4/1$	[5]
	$1 \times 10^{13} \mathrm{cm}^{-3}$	BAS	$152 \mathrm{Torr}, 0.8 \mathrm{kW}, 92/7/1$	[6]
	$3 \times 10^{10} \rightarrow 7 \times 10^{11} \mathrm{cm}^{-3} \ (50 \rightarrow 150 \mathrm{Torr})$	BAS	- , $0.8 \mathrm{kW}, 97/2/1$	[8]
	$3.5 \times 10^{10} \rightarrow 4 \times 10^{11} \mathrm{cm}^{-3} (0.5 \rightarrow 1.5 \mathrm{kW})$	BAS	$100 \mathrm{Torr}, - , 97/2/1$	[8]
	$3 \times 10^{11} \rightarrow 6 \times 10^{10} \mathrm{cm}^{-3} \ (0 \rightarrow 20 \% \mathrm{H}_2)$	BAS	100 Torr, 0.8 kW, -	[8]
	$2 \times 10^{14} \mathrm{cm}^{-3}$	BAS	$152 \mathrm{Torr}, 0.8 \mathrm{kW}, 92/7/1$	[6]

Undefined and miscellaneous model parameters

Ι	Intensity (mol^{-1})
p	Pressure (Pa)
ρ	Density (kgm^{-3})
T T	Temperature (K)
d	Orifice Diameter (m)
F_i	Pump speed out of chamber i (Ls ⁻¹)
γ	adiabatic index
d	Diameter, typically of orifice
$L \ \& \ \ell$	length
R	Molar gas constant (8.3145 J mol ^{-1} K ^{-1})
m, M	Molar mass (kg mol^{-1}), Molecular mass
	(kg)
$\sigma \& Q$	Cross-section; hard sphere and effective.
κ	'peaking' factor, a function of γ , see [15]
n_i	number density
A, A', B, B',	Correlation parameters, see $[15]$
$C_1, C_2, C_3 \& C_4$	
Ω	Collision integral, see [16], chapter 11.
f_d	A correction term 'of order unity', see
	[16], chapter 11.
subscript	meaning
~	Terminal value
$\frac{1}{2}$	Stagnation value
	Property Measured parallel to the conter
	line
a	'Quiting' value
ч В	Beam value (with the exception of $D_{(n)}$)
<i>i</i> (integer)	Value in <i>i</i> th chamber
(IIII)	value III (UII UIIAIIIDEI

Appendix B

Simple Pumping Model

The model consist of a system of pumped boxes, separated by infinitely thin walls followed by a small detector. All transported molecules are assumed to enter the background prior to the next orifice. The implicit assumption is therefore that molecular beam enhancement has negligible effect on chamber pressure. It is clear that as pump rates will be reduced by conductance and the beam flow will lead to increased gas loading, therefore, this represents a 'best case' for the pumping. It is also clear that the transport between chambers here will be significantly different from skimmers used in the real experiment, though these effects are likely to be more subtle (see 3.3.2).



Figure B.1: A spreadsheet pump model to test pumping configuration. The bold parameters $(T_0, P_0, m, \gamma, \sigma, d_i, l_i F_i \text{ and } v_{\parallel,\infty})$ are fed to the model.

Parameter (dimensions)	Relation	Source
Pressure	$p_i = p_{i-1} \frac{C_i}{F_i}$	
(I a, IOII) Conductance $(L s^{-1})$	$C_i = \frac{\pi d_i^2}{4} \sqrt{\frac{RT_{i-1}}{2\pi m}}$	
(m)	$\lambda_i = \frac{RT_i}{\sqrt{2}\sigma m}$	
Nozzle Intensity	$I_0 = \frac{\kappa n_0 d_1^2}{4} \sqrt{\frac{2\gamma R T_0}{(\gamma+1)m}} \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}}$	[15]
(molecules $s^{-1} sr^{-1}$) Scattered fraction	$\frac{I_i}{I_{i-1}} = e^{-n_i \ell_i Q}$	[17]
(\dots) Detected Solid angle ^{<i>a</i>}	$\Theta = \frac{\pi}{4} \left(\frac{d'}{L'}\right)^2$	inspection
(sr) Intensity at detector	$I_B = I_0 \Theta \prod_{i=1} \frac{I_i}{I_{i-1}}$	inspection
(molecules s ⁻¹) Beam-to-background ratio	$\frac{n_B}{n_3} = \frac{4I_B}{v_{\parallel,\infty}\pi d_d^2 n_3}$	dimensionality
() Beam-to-background ratio	$\frac{n_B}{n_3} = \left(\frac{d_i}{2L}\right)^2 \prod_{i=1} \frac{F_i}{C_i}$	[18]
()	v 1	

^{*a*}for small angles where d' is the greatest obstruction at a distance L'.

Appendix C

Simple Expansion Model

This model consists of two chambers separated by an infinitely-thin wall containing a orifice. Gas in the first chamber is in a stagnation state at an assumed temperature and pressure, whilst the second chamber has negligible pressure. Upstream from the orifice the apparent axial shift is calculated, and downstream isentropic flow properties are calculated as a function of distance. The largest departure from reality in the model is probably the internal profile of the nozzle.



Figure C.1: A spreadsheet nozzle model to obtain beam parameters. Bold parameters $(T_0, P_0, m, \gamma, \sigma, d)$ are fed to the model.

(...)

Parameters (dimensions)	Relation	Source
Stagnation mean speed $(m \ s^{-1})$	$\bar{c}_0 = \sqrt{\frac{8RT_0}{\pi m}}$	
Stagnation sound speed $(m \ s^{-1})$	$a_0 = \sqrt{\frac{\gamma R T_0}{m}}$	
Stagnation mean free path	$\lambda_m = \frac{RT_0}{\sqrt{2}\sigma m}$	
Stagnation binary diffusion coefficient $(m^2 - 1)$	$D_{AB} = \frac{3}{16} \frac{(4\pi kT/M_{AB})^{1/2}}{n\pi d_{AB}^2 \Omega_D} f_d$	[16]
(m ⁻ s ⁻) Reynold Schmidt product	$ReSc = \frac{a_0d}{D_0}$	[19]
() Axial shift	$\frac{\delta x}{d} = 0.19\sqrt{ReSc}$	[19]
() Flow-to-diffusion ratio	$\frac{\tau_F}{\tau_D} = \frac{4}{ReSc}$	[19]
() Mach number ($0 < x/d < 1$) ()	$M = 1 + A (x/d)^{2} + B (x/d)^{3}$	[15]
Mach number $(0.5 < x/d < 3)$	$M = (x/d)^{(\gamma-1)} \left[C_1 + \frac{C_2}{(x/d)} \right]$	[15]
(\dots)	$+\frac{C_3}{\left(\frac{x}{d}\right)^2} + \frac{C_4}{\left(\frac{x}{d}\right)^3} \right]$	
Relative temperature (\dots)	$\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-1}$	[15]
Relative flow velocity	$\frac{v}{a_0} = M\left(1 + \frac{\gamma - 1}{2}M^2\right)^{-\frac{1}{2}}$	[15]
(···) Relative pressure	$\frac{p}{p_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-\frac{\gamma}{\gamma - 1}}$	[15]
(···) Relative density	$\frac{\rho}{\rho_0} = \frac{n}{n_0} = \left(1 + \frac{\gamma - 1}{2}M^2\right)^{-\frac{1}{\gamma - 1}}$	[15]

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Property (dimensions)	Relation	Source
Terminal speed ratio (\dots)	$S_{\parallel,\infty} = A' [\sqrt{2}n_0 d\sigma]^{B'}$	[15]
Terminal Mach number	$M_{\parallel,\infty} = \sqrt{\frac{2}{\gamma}} S_{\parallel,\infty}$	[15]
() 'Quitting' surface (m)	$x = x_q$ when $M = M_{\parallel,\infty}$	[15]

Appendix D

Simple Chemical Relaxation Model

In this model a plug of gas of negligible volume is subjected to pressures / temperatures dictated by the previous model, at a series of consecutive locations along the centre-line. The gas plug remains at each location for a time related to the flow velocity, also from the previous model. This gas plug need only be propagated as far as the quitting surface as intermolecular chemistry must have been arrested by this point. In the previous model, the flow properties assumed a thermally perfect gas. In this case, the gas is chemically reacting so the heat capacity will evolve with time. For this model to function, any reacting portion of the flow must therefore be small. Step sizes should also be small so that the loss of adiabacity from fixing P/T at each step is small. This model necessarily ignores / evades any heterogeneous chemistry on the orifice walls. This assumption is sound provided equation 3.3.1 holds.

Property	Relation	Source
(dimensions)		
Time Step (s) Mole fraction array	$\Delta t(x) = \frac{\Delta x}{v(x)}$ $X_0 = \{\chi_1, \ \chi_2, \ \chi_3 \dots \}$	



Figure D.1: An illustration of the model for a perl [20] script running native senkin chemical kinetics code [21] to estimate chemical relaxations. The bold parameter (Δx) and arrays of parameters $(v(x), T(x), p(x), X_0)$ are fed in to the model.

Appendix E Calculated thermodynamic data

The following scheme was used to produce a list of species which may be of use to researchers modelling carbon/hydrogen pyrolysis or plasma systems:

1. The MOLPRO computational package was use to calculate the CCSD(T)/ccpVTZ and cc-pVQZ electronic energies (E_{VnZ}) of each species. From these and the following equation (E.1), values can be extrapolated to estimate the infinite basis limit $E_{V\infty Z}$. This represents the best possible value from this level of theory with this family of basis sets:

$$E_{V\infty Z} = \frac{64(E_{VQZ} - E_{HF/VQZ}) - 27(E_{VTZ} - E_{HF/VTZ})}{37} + E_{HF/VQZ} \quad (E.1)$$

 E_{HF} represents the electronic energy of the same system at the Hartree Fock level of theory.

- 2. These data then have to be corrected for their zero point and thermal energy up to standard temperature $(T_r = 298K)$. Reasonable accuracy is obtainable for geometries and statistical constants at less demanding levels of theory. Therefore, the thermochemical facility of GAUSSIAN98 was used to calculate thermal corrections (H(T)) for the temperature range of interest (298-4000 K) using B3LYP/6-31G* methods.
- 3. Once the *ab-initio* energies have been thermally corrected, they need to be converted from heats of formation from ions and electrons (the typical output of *ab-initio* packages) into the more familar heat of formation from standard states at the same temperature (in this case dihydrogen and graphite at 298 K). This process is usually referred to as 'anchoring' (see fig. E.1 below) as it uses reference compound(s) to fix the heat of formation to real world values. The choice of reference is important as it must contain the same number and type of atoms. Furthermore, the final accuracy will be limited by the quality of experimental data that is available for the reference and the similarity of bonding. As the greatest error introduced in

ab-initio methods is the estimation of bond strengths it is best to choose references with similar bonding so that any such errors are reduced by cancellation. For instance a natural choice for an ethynyl radical reference would be acetylene (thus the major error being CCSD(T)'s estimate of C-H bond strength). However, with C₂ there would be a trade-off between the C-C bonding being over-represented in acetylene combined with the missing C-H bonds (eventually yielding $\Delta_{\rm f} H_{\rm C_2}^{\oplus}(298) = 196.7$ kcal mol⁻¹), and the precision of spectroscopic carbon atom measurements being used as a reference that lacks any bonding (yielding 198.8 kcal mole⁻¹). It is often difficult to assess which is the optimum anchoring route but, provided a certain amount of chemical intuition is used, errors are small compared to that of the *ab-initio* itself.



Figure E.1: A schematic diagram of a generic anchoring method. The method relies on having a good quality reference(s) with identical constituents and preferably similar bonding characteristics. First, a heat of reaction is calculated from *ab initio* methods. The anchored species' heat of formation is obtained by summing this plus the reference(s) heats of formation.

$$\Delta_{\rm f} H_{\rm Anchored}^{\Theta} = \Delta_{\rm r} H_{ab\text{-}initio}^{\Theta} + \Delta_{\rm f} H_{\rm Reference}^{\Theta} \tag{E.2}$$

- 4. The next step is to assess the available experimental data for the particular species given the *abinitio* estimate. Where there is a conflict in the available data, the calculated value can be used as a guide to which is most representative. Where no reliable data are available, or the error bar is large, the computational value can be used.
- 5. Once a list of 298 K heats of formation have been established, they can be tabulated as a function of temperature, by adding the heat content function [H(T)-H(298)] obtained from the GAUSSIAN98 thermal corrections. GAUSSIAN98 also yields Enropies (S(T)) and constant volume heat capacities $(C_v(T))$, and as these are not functions of absolute energy, they can be reported directly as 'finished' values.
- 6. These data were then fitted to the following dimensionless NASA-style polynomials (E.3, E.4 & E.5) using Dr C. Western's **least32** fitting program. First the constant pressure heat capacity was fitted at high (1000-4000 K) and low (298-1000 K)) temperatures generating 10 parameters. These parameters were fixed and the final a_6 and a_7 high and low where generated by fitting the enthalpy and entropy, respectively. So for each species, a list of 14 parameters were obtained.

$$\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$
(E.3)

$$\frac{H^0}{RT} = a_1 + \frac{a_2T}{2} + \frac{a_3T^2}{3} + \frac{a_4T^3}{4} + \frac{a_5T^4}{5} + \frac{a_6}{T}$$
(E.4)

$$\frac{S^0}{R} = a_1 \ln(T) + a_2 x + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} + a_7$$
(E.5)

E.0.1 Results

Species	$\Delta_{\rm f} H^{\ominus}$	Source	Species	$\Delta_{\rm f} H^{\ominus}$	Source	Species	$\Delta_{\rm f} H^{\ominus}$	Source
	kcal mol^{-1}			kcal mol^{-1}			kcal mol^{-1}	
Н	52.1	NIST [22]	C_2H	135.9	Burcat	C_3H_8	Uncha	nged
H_2	0	def^n	C_2H_2	54.2	NIST	$l-C_4$	258.4	ab- $initio$
С	171.2	NIST	C_2H_3	71.9	Tsang	C_4H	200.7	ab- $initio$
CH	141.9	NIST	C_2H_4	12.5	NIST	C_4H_2	116.6	ab- $initio$
$CH_2(X)$	92.3	NIST	C_2H_5	Unchar	$nged^a$	n-C ₄ H ₃	130.2	ab- $initio$
$CH_2(a)$	101.3	$NIST + T_e{}^b$	C_2H_6	Uncha	nged	$D_{3h}C_6$	298.6	ab- $initio$
CH_3	35.1	Tsang $[24]$	C_3	196.4	ab-initio	C_6H	257.8	$ab\mathchar`-initio$
CH_4	-17.9	NIST	$c-C_3H$	171.1	ab-initio	C_6H_2	173.4	ab- $initio$
$C_2(X)$	198.5	Burcat [25]	$c-C_3H_2$	118.7	ab-initio	C_8H	309.5	ab- $initio$
$C_2(a)$	200.6	$NIST + T_e$	C_3H_7	Uncha	nged	C_8H_2	217.6	ab- $initio$

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 a GRI-mech 3.0 [23] b Reported ground state plus spectroscopic (NIST) separation.

The full evaluated data as prepared a chemkin thermodynamic data (*.dat). The first line contains species name, followed by a reference (here as a date day/month/year), species composition by element, state (S/L/G), three temperatures defining data the ranges and finally the line number. The subsequent 3 lines list all fourteen coefficients starting with the high temperature set in the order $a_1 \rightarrow a_7$.

```
н
                  200104H 1
                                            G 0300.00
                                                         4000.00 1000.00
                                                                                1
2.50062925E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
                                                                                2
2.54838451E+04-4.58081882E-01 2.50062925E+00 0.0000000E+00 0.0000000E+00
                                                                                З
0.0000000E+00 0.0000000E+00 2.54834641E+04-4.58524814E-01
                                                                                4
H2
                  200104H 2
                                            G 0300.00
                                                         4000.00 1000.00
                                                                                1
3.27612402E+00 8.67653741E-05 2.93894363E-07-1.06208616E-10 1.08894345E-14
                                                                                2
-9.26639546E+02-2.91357587E+00 3.46881012E+00 2.56211518E-04-6.96094229E-07
                                                                                3
7.12658094E-10-1.73192903E-13-1.04022441E+03-4.14418605E+00
                                                                                4
С
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                                                         4000.00 1000.00
                                           G 0300.00
                                                                                1
2.50062925E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
                                                                                2
8.54237897E+04 3.66453611E+00 2.50062925E+00 0.0000000E+00 0.0000000E+00
                                                                                З
0.0000000E+00 0.0000000E+00 8.54234087E+04 3.66413648E+00
                                                                                4
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                                                         4000.00 1000.00
                                            G 0300.00
                                                                                1
2.68418341E+00 1.65062629E-03-6.48320597E-07 1.21399275E-10-8.84055787E-15
                                                                                2
7.06656055E+04 5.73574259E+00 3.52840040E+00-1.37736289E-05-7.90744611E-07
                                                                                3
2.09892410E-09-1.02317032E-12 7.04093073E+04 1.23374262E+00
                                                                                4
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CH2
                                           G 0300.00
                                                        4000.00 1000.00
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4.56111948E+04 6.75833057E+00 3.49627977E+00 2.66458330E-03-2.21225658E-06
                                                                                3
1.84370094E \hbox{--}09 \hbox{--}5.67499423E \hbox{--}13 \hspace{0.1in} 4.53441500E \hbox{+-}04 \hspace{0.1in} 2.87831987E \hbox{+-}00
                                                                                4
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                                          G 0300.00 4000.00 1000.00
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1.67583531E+04 7.48668073E+00 3.86237078E+00 2.59745506E-03 2.26275953E-06
                                                                                3
-2.51220646E-09 7.97595915E-13 1.63876099E+04 6.44627557E-01
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CH4
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                                            G 0300.00
                                                        4000.00 1000.00
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5.09815985E{-}01 \hspace{0.1cm} 1.19955882E{-}02{-}4.98467439E{-}06 \hspace{0.1cm} 9.84593516E{-}10{-}7.52768832E{-}14
                                                                                2
-9.61309514E+03 1.62343178E+01 4.70421710E+00-9.93512528E-03 3.75130040E-05
                                                                                3
-3.54531693E - 08 \ 1.15920131E - 11 - 1.02331584E + 04 - 2.82964067E + 00
                                                                                4
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                                                         4000.00
                                                                  1000.00
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                                                                                2
9.89391951E+04 5.13794321E+00 3.87553250E+00-3.11894754E-03 8.27404225E-06
                                                                                З
-7.08362472E-09 2.11266835E-12 9.88527792E+04 1.45865009E+00
                                                                                4
C2 A
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                                 G 0300.00 4000.00 1000.00
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1.00069773E+05 7.42662168E+00 3.76424925E+00-1.93528953E-03 4.32258596E-06
                                                                                3
-2.71593170E-09 5.18053045E-13 9.98907439E+04 2.89162613E+00
                                                                                4
                  200104C 2H 1
                                            G 0300.00
                                                         4000.00 1000.00
C2H
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4.04192744E+00 3.04660735E-03-1.17344851E-06 2.17205026E-10-1.57189471E-14
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6.71281926E+04 1.93159321E+00 3.86505102E+00 6.60819587E-03-1.15851468E-05
                                                                                3
1.12236181E-08-3.99557632E-12 6.70386797E+04 2.12323246E+00
                                                                                4
                  200104C 2H 2
                                        G 0300.00
                                                        4000.00 1000.00
C2H2
                                                                                1
4.43055758E+00 5.29609598E-03-2.02773496E-06 3.74014484E-10-2.70149153E-14
                                                                                2
2.57107958E+04-2.55048704E+00 9.11515196E-01 2.39947510E-02-3.85727625E-05
                                                                                3
3.16630666E-08-9.95214777E-12 2.62247345E+04 1.33833483E+01
                                                                                4
C2H3
                  200104C 2H 3
                                           G 0300.00
                                                         4000.00 1000.00
                                                                                1
3.42266796E+00 9.27100680E-03-3.88322981E-06 7.72666006E-10-5.94538502E-14
                                                                                2
3.45056181E+04 5.68266022E+00 1.48458302E+00 1.48970740E-02-9.14339234E-06
                                                                                3
1.86497058E-09 4.10720427E-13 3.50160012E+04 1.55918194E+01
                                                                                4
                  200104C 2H 4
C2H4
                                           G 0300.00
                                                        4000.00 1000.00
                                                                                1
2.40448028E+00 1.32545408E-02-5.58645497E-06 1.11738364E-09-8.63505682E-14
                                                                                2
4.85100542E+03 8.46779614E+00 1.78038092E+00 8.82502649E-03 1.27311393E-05
                                                                                3
-2.03919367E-08 8.14449265E-12 5.31381835E+03 1.31604478E+01
                                                                                4
                  200104C 3
                                            G 0300.00
                                                         4000.00 1000.00
C3
                                                                                1
4.95737785E+00 2.84448726E-03-1.32198883E-06 2.83808071E-10-2.31099231E-14
                                                                                2
9.71947482E+04-1.91698071E+00 5.05450583E+00 2.37693014E-04 5.43626266E-06
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