1. - Introduction

The experimental apparatus used in this work was originally built for photofragment spectrometry [1] but later extensively modified for beam-surface scattering on Cl_2 + GaAs paper [2].

A supersonic gas pulse is produced by piezoelectric gas valve, skimmed and the chopped by a rotating (200 Hz) slotted disc, before passing through a further collimating element to produce a gas pulse of ~35µs and an angular divergence of 2 degrees. The pulsed supersonic beam surface, chopper and skimmer are housed in a rotatable differentially pumped (source) chamber.

The main scattering chamber is extensively cryo-pumped to obtain low operating pressures. The beam-surface angle is variable and the chosen beam/surface geometry can also be rotated with respect to the detector to enable measurement of the angular scattering pattern. The sample is GaAs mounted on a removable molybdenum sample holder which can be heated (by a resistive element) from -70 to 600°C. The sample may also be withdrawn from the beam-detector path so that TOF measurements may be made of the beam itself.

Gas molecules hit the surface after a flight of 67 mm and are scattered towards the detector 500 mm away. The detection system, housed in triply differentially pumped UHV (Ultra High Vacuum) chambers, consists of a liquid nitrogen cooled large volume ioniser followed by a quadrupole mass spectrometer and a fast pulse counting channel electron multiplier (channeltron).

Two dedicated processors based controllers are used in the system: one, TOF timing unit, controls the speed of the chopper disc and the firing of the pulse beam in synchronisation, whilst the second is used to store data acquired from the channeltron ion detector.

At the start of this project a personal computer (Apple Macintosh IIci) was interfaced to the two controllers to establish the running parameters for an experiment, and to download accumulated data from an experimental run. The Macintosh was also used for post-experimental data processing, display, analysis and storage. The custom built TOF unit became increasingly unreliable and it was decided to replace it with a PC-based system and at the same time replace the original PASCAL control program with one based on the industry standard LabView system running on a fast PC running under windows. TOFSys software now interfaces both controllers and provide all the same acquisition and data processing options of the PASCAL based system.

In addition, it is possible to fire an excimer laser synchronously with the gas pulse, either to dissociate molecules in the pulse or to photo dissociate molecules / photo ablate molecules on the surface. The apparatus also has facilities for counter propagation of a dye-laser beam just above the surface to allow REMPI (Resonance Enhanced Multi Photon Ionisation) / LIF (Laser Induced Fluorescence) probing of desorbing/ scattered species.

Determination of both sample cleanliness and initial surface state may be performed by a RHEED [3] (Reflection High Energy Electron Diffraction) system installed in the main scattering chamber.

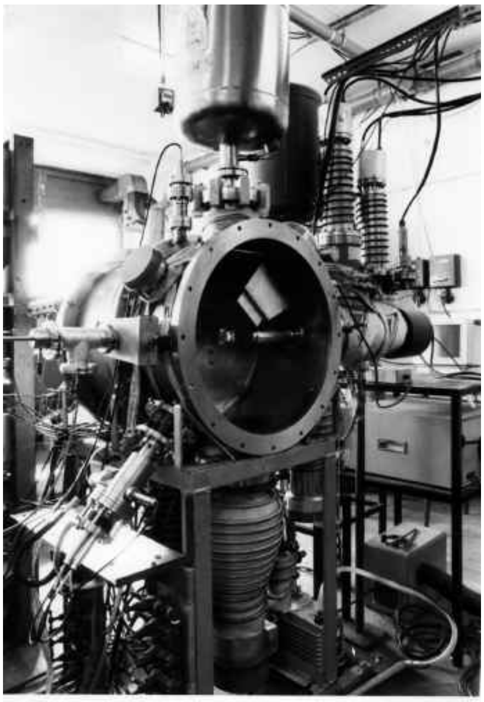


Figure 2.1 A view of the apparatus

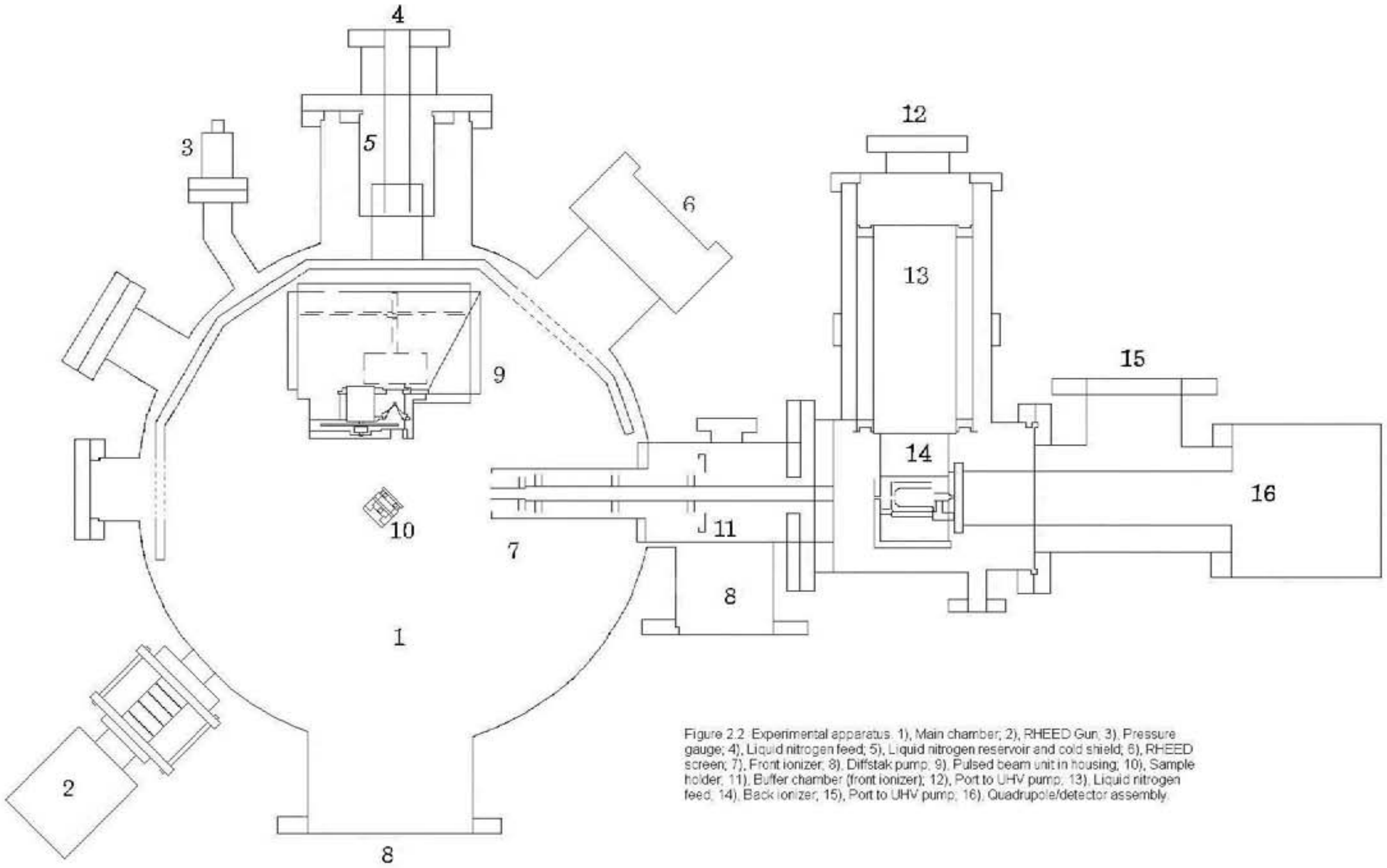


Figure 2.2 Experimental apparatus. 1), Main chamber; 2), RHEED Gun; 3), Pressure gauge; 4), Liquid nitrogen feed; 5), Liquid nitrogen reservoir and cold shield; 6), RHEED screen; 7), Front ionizer; 8), Diffstak pump; 9), Pulsed beam unit in housing; 10), Sample holder; 11), Buffer chamber (front ionizer); 12), Port to UHV pump; 13), Liquid nitrogen feed; 14), Back ionizer; 15), Port to UHV pump; 16), Quadrupole/detector assembly.

Main Chamber

The main chamber houses the sample of GaAs, where the reaction between the sample and the molecular beam takes place. It also contains the front ioniser of the detector and the RHEED apparatus. It is a cylindrical in shape, approximately 52 cm in diameter and 25 cm deep and is made of steel with aluminium flanges. The pumping is provided by an Edwards 160-700-ISO Diffstak oil diffusion pump, which is backed up by an Edwards EDM12 rotatory pump. The pump is isolated from the main chamber by a quarter swing butterfly valve. Halogens are highly corrosive to the rotatory pump oil (and should not be emitted in to the laboratory), so there is a foreline liquid nitrogen cold trap which can be removed to a fume cupboard at the end of the experiment. The diffusion pump is baffled to prevent oil spraying up onto the surface and uses Santovac 5 oil which has a very low vapour pressure. Pressure in main chamber is measured by a Balzers cold cathode gauge.

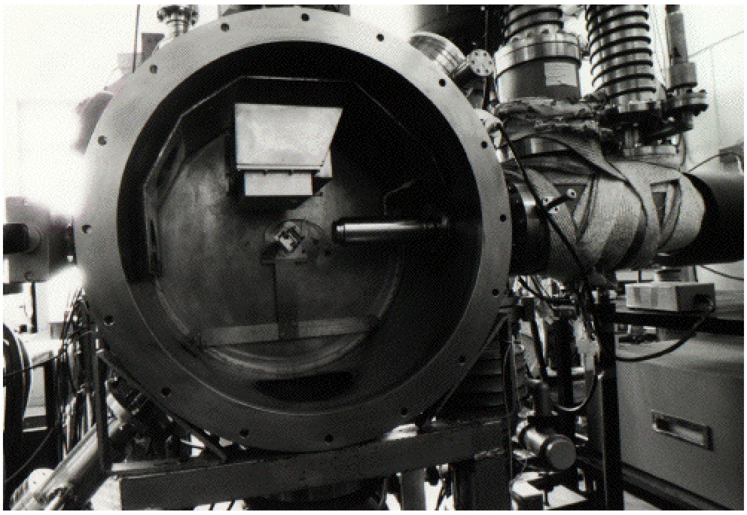


Figure 2.2 The main chamber. We can see the ioniser, the sample holder and the beam source unit.

In cross beam reactive scattering, the pressure needs to be low enough to eliminate multiple collisions of the reactive species with each other or with background gases and maintain the single collision criterion for the experiments. The requirement is thus to increase the mean free path length of a particle to that of several times the length of the reaction chamber, so that it will either be trapped on the chamber walls (if cool enough) or be pumped away before it collides with another particle. This is achieved when the pressure is tipically about 10^{-7} mbar. For surface reactions, the requirement is to prevent contamination of the surface, so the vacuum has to be lower, around 10^{-11} mbar. Prevention of surface contamination means a reduction in collisions of background gases with the sample, which are more probable than collisions between gas particles, due to the relatively large surface area of the sample. To reduce the final pressure a large surface area liquid nitrogen filled cryotrap is used. The cryotrap is specially appropriate as the main contaminate for gallium arsenide are surface oxides and the main source of these is water, which is easily removed by the cryotrap. The cryotrap is filled continuously during the working week.

Figure 2.3 A very good view of the three elements: ioniser, the surface and the beam source unit.

Source chamber

The source chamber is behind the main chamber, and the two chambers are separated by a rotating aluminium plate. The rotating plate is mounted on a tube which surrounds the tube of the sample holder. It also houses the source beam. The pulse beam assembly and plate can rotate freely, allowing the beam hit the surface at a range of angles. When the beam and sample are locked at a particular angle, it is the beam source that is rotated to measure the angular distribution of the products. An absolute angle optical encoder is used to measure the angle of the pulse beam relative to the detector axis to an accuracy of 0.3°.

The chamber is of the same size as the main chamber and an unbaffled diffusion pump (Edwards EO6) pumps it with Santovac 5 oil. The diffusion pump is backed by the Edwards EDM12 rotatory pump and cryotrap and can be isolated from the chamber with a quarter swing butterfly valve.

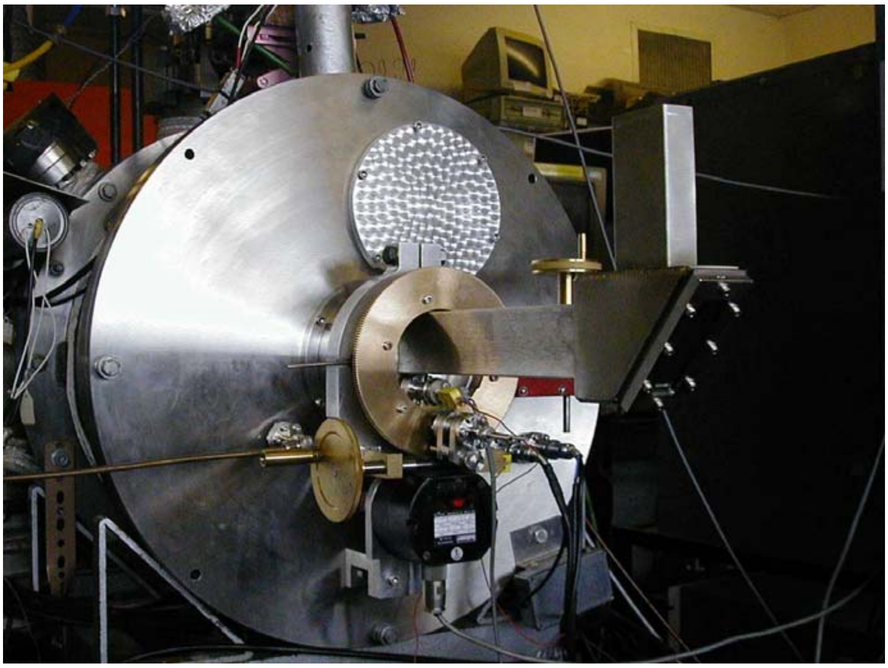


Figure 2.4 The source chamber. We see the system to rotate the sample holder and beam source unit.

The quadrupole/detector chamber

The detector chamber also houses a micromass 12-12 quadrupole mass filter, and a Galileo 4870 channeltron. The chamber is pumped using a radial electric field pump and liquid nitrogen. The typical base pressure is approx. 10^{-10} mbar.

Separating the buffer and ioniser chambers is a slide valve which can be used to select one of the three options:
1.- A complete blank to isolate the UHV of the ioniser
2.- A 0.01” hole for direct beam observation/measurements
3.- A 0.125” hole for scattered beam observation/measurements

The ioniser chamber

The ioniser chamber, situated inside the quadrupole chamber, contains a modified Brink type ioniser. Pumping is achieved by a radial electric field pump and a liquid nitrogen cryo-cooled interior. The typical base pressure is approximately 10^{-10} mbar. There are two ionisers, back and front and are described later.

Sample Holder

The GaAs sample is mounted so that the surface is in the centre of the main chamber, at the point where the gas beam and the detector axis converge. The sample holder is a self-contained unit which slots into a support fork with pin connectors for the temperature probe and heating element.
The whole unit is attached a steel tube that runs down the central axis of the apparatus, from the main to the source chamber and out the machine. This tube can rotate and allows the angle of incidence of the beam hitting the surface to be changed.

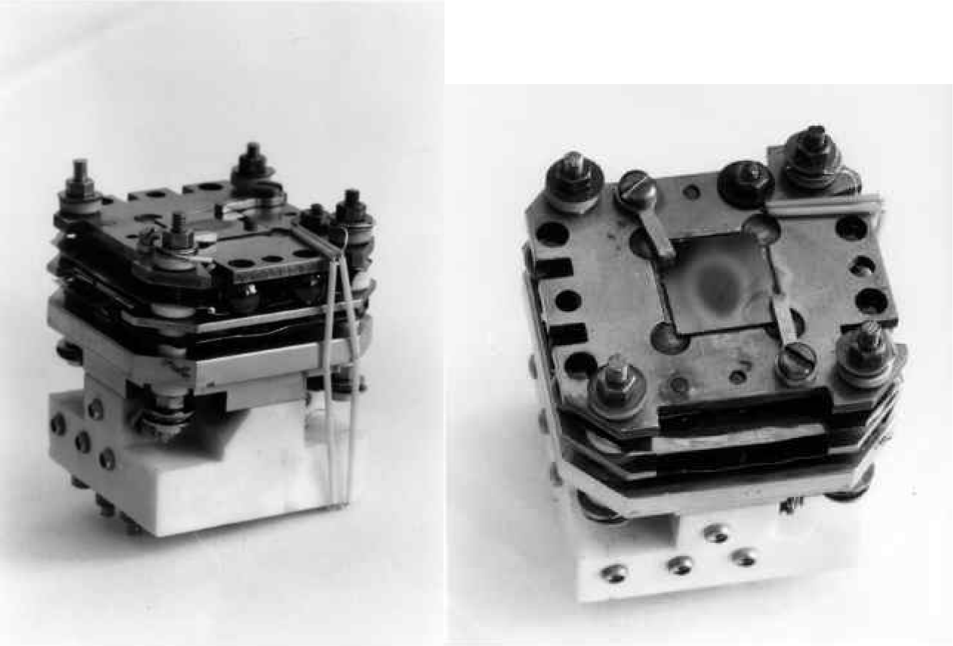
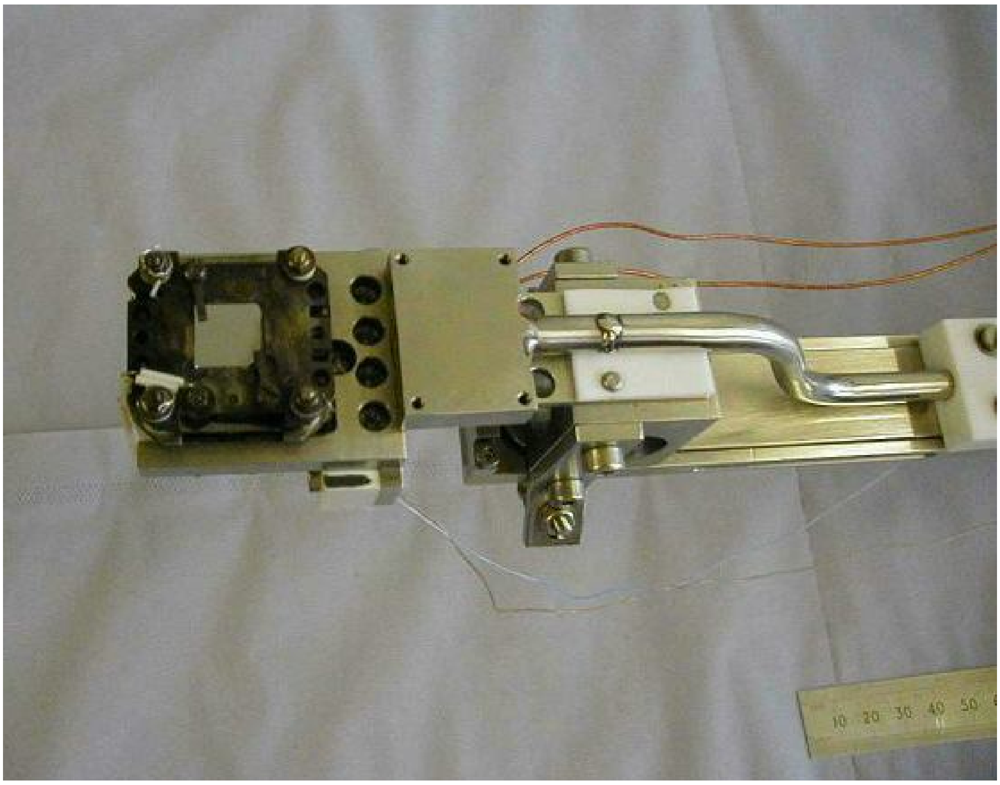


Figure 2.5 The sample holder.

The detector can also see the surface at different angles as the surface beam angle can be locked and the whole unit rotated relative to the detector axis. The angle of the surface is measured with a relative angle optical encoder, which has an accuracy of 0.3° and measures the angle between the surface and the beam, with 0° the beam at the surface normal. The sample can be drawn back towards the source chamber, so that the detector can view the beam directly.

The sample holder is a machinable glass ceramic block (MAKOR^{TM}) with a molybdenum plate (30 x 30 x 3 mm) attached above the block. Immediately below the plate is a heater element made up of 25 mm of 0.2 mm Pt/Rh wire, zig zagging back and forth beneath the sample. The heater element is electrically insulated by ceramic tubing and between it and the MAKOR block are a number of tantallum heat shields separated by ceramic spacers and synthetic sapphire balls. The molybdenum top plate has a recess in which the sample sits, slightly protruding and secured with clips. To improve the thermal contact between the sample and the molybdenum plate, the recess is "wetted" with indium, which is molten at most experimental temperatures. The temperature probe is secured as close to the surface as possible to give as accurate a measurement of surface temperature as possible. The wiring for the probe and heater are attached to the pin connector sockets within the MAKOR block. A stainless steel block situated behind the sample holder can be cooled with liquid nitrogen. By attaching copper braid between the block and the sample heater top face we can cool the sample to approximately -70°C.

Before mounting, a fresh sample of GaAs is first cleaned by refluxing in 1,1,1-trichloroethane and then acetone.



Picture 2.6 Sample holder and the fork where is attached

Vacuum system

The diffusion pump achieves a pressure around 10^{-9} torr, then a large surface area liquid nitrogen filled cryotrap is used to obtain a base pressure of approximately 2×10^{-10} mbar.

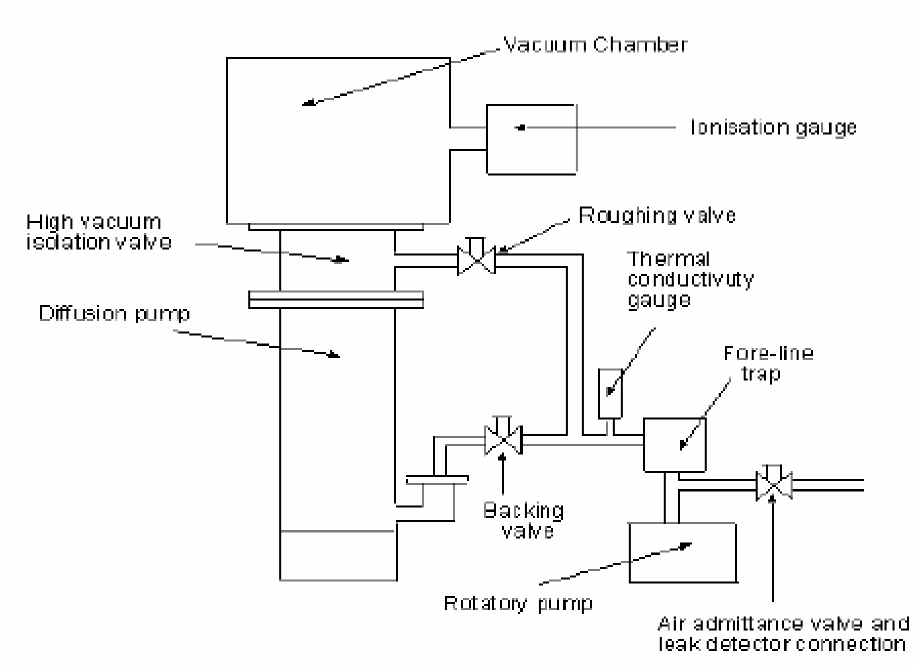


Figure 2.7 Typical diffusion pump system

A rotatory pump, in this case a rotatory pump, is connected to the diffusion pump to maintain the required backing pressure for correct operation of the diffusion pump, and to enable the chamber to be pumped out from atmospheric pressure to the starting pressure of the diffusion pump. To start the system, the isolation and roughing valves are closed and the backing valve is opened. The rotatory pump is started and evacuates the diffusion pump body to less than 10 mbar when its heaters can be switched on.

A useful indicator of contamination time for a sample is the time taken for a monolayer of a gas to form on its surface. This monolayer time can be estimated in the following manner:

The impingement rate of molecules against a surface is given by:

$$\gamma = \frac{P}{\sqrt{2\pi mkT}} \quad \text{cm}^{-2}\text{s}^{-1} \qquad (2.1)$$

$$\gamma = 3.535 \text{ x } 10^{22} \frac{P}{\sqrt{M_r T}} \text{ cm}^{-2}\text{s}^{-1} \quad (2.2)$$

An approximation for the monolayer formation time τ can be obtained by considering the number of binding sites N on the surface (assuming 1 molecules binds to one site and a sticking probability of 1):

$$\tau = \frac{\text{No. of sites per cm}^2}{\text{Impingement rate per cm}^2} = \frac{\text{N}}{\gamma} \quad (2.3)$$

$$\tau = \frac{\text{N}\sqrt{\text{M}_\text{r}\text{T}}}{3.535 \text{ x } 10^{22}\,\text{P}} \text{ s} \quad (2.4)$$

The effective surface area (A) of a binding site is given by A = 1/N

$m = M_r m_u$ $m_u = 1.6606 \text{ x } 10^{-27}$ kg

M_r = relative molecular mass P = background pressure/ Torr

T = temperature/ K k = Boltzmann constant

N = number of surface sites/ cm^2 (for GaAs, N = $6.25 \text{ x } 10^{14}$)

A = $1/(6.25 \text{ x } 10^{14}) = 1.6 \text{ x } 10^{-15}$ cm^2

E.g. For a base pressure of 10^{-6} Torr, temperature 300K, a clean sample could be covered by contaminant gas molecules (mass 50) in less than 2.5 seconds.
At 10^{-10} mBar the monolayer time arises to around 6 hours.

Gas handling apparatus

The gas line used in these experiments is built primarily with glass and Teflon valves to prevent the corrosive gases damaging the apparatus and the production of contaminants. Figure 2.8. Where glass is inappropriate, stainless steel and brass are used, which initially react with the halogen and become passivated. Care is taken when changing the halogen, to allow time for the complete exchange of the halogenated surfaces. The gas mixtures are stored in 1 litre bulbs which allow for the quick exchange between the different mixtures. When making a new gas sample, the apparatus is pumped out by an Edwards EDM 2 rotatory pump with a liquid nitrogen cold trap to remove the corrosive gases. The apparatus is then flushed three times with helium to remove any contamination.

Preparation of gas mixtures

Before any new gas mixture is made up, the gas line and the flask/associated pipe work are first evacuated. Then three flushing cycles: refilling with helium, evacuating, etc., are repeated to remove any traces of residual air when a gas mixture is being made, one half of the buffer is introduced first, and then the halogen is added, followed by the remainder of the buffer. This is to allow good mixing of the two components. The glass flask is then sealed, the gas lines evacuated, and then the final mixture in the flask is opened to the pulse beam unit.

Product detection

Etching products are detected using a quadrupole mass spectrometer with electron bombardment ionisation and a channeltron ion counter, positioned so that the central axis intersects with the beam at the sample surface. The spectrometer has two ionisers on the same axis, the front ioniser close to the surface at 82 mm, and the back ioniser 500 mm from the surface. The back ioniser allows for a greater flight time, so provides high TOF resolutions.

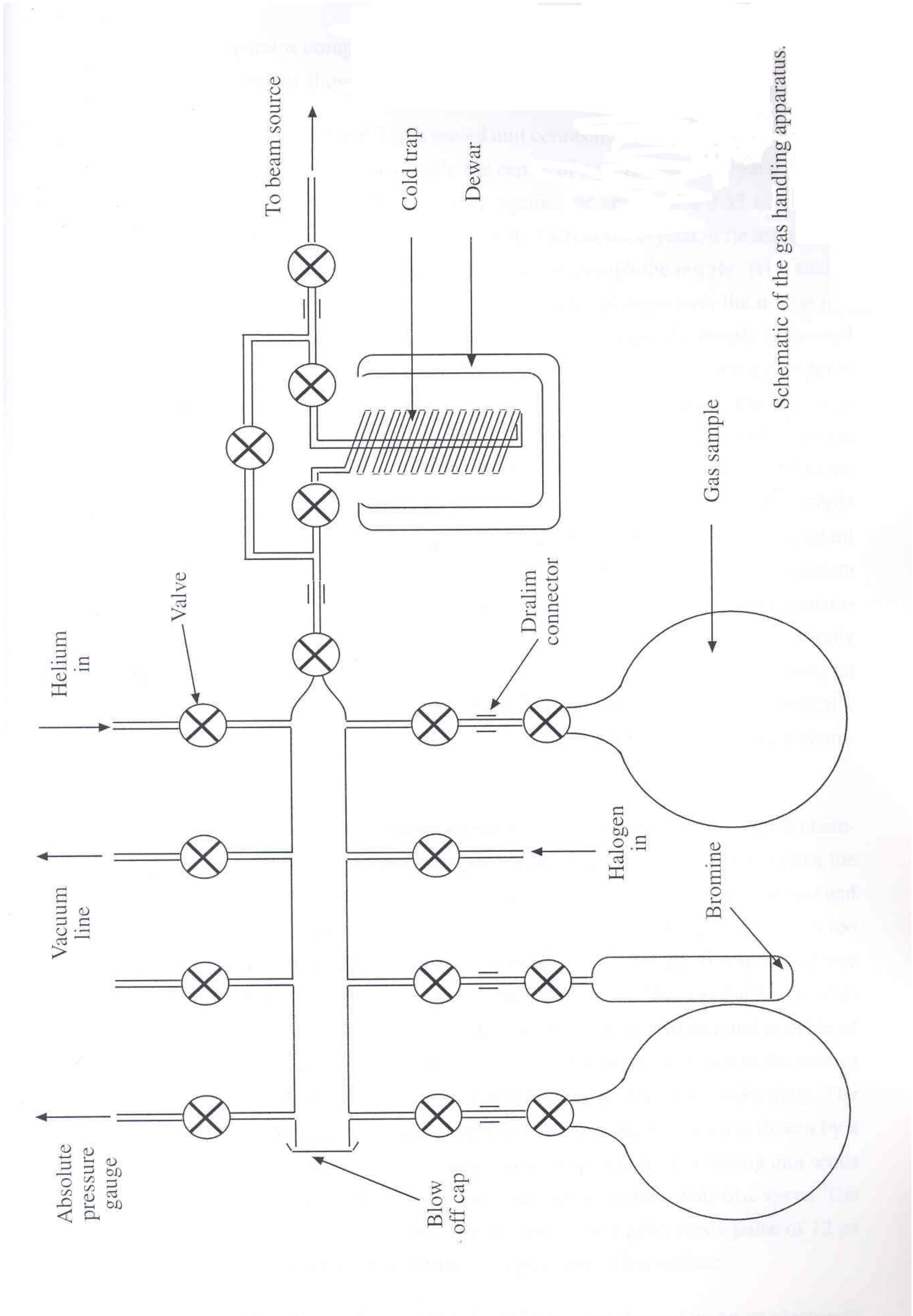


Figure 2.8 The gas-handling apparatus

Ionisers

The apparatus has two collinear space charge ionisers in the detection system. The front ioniser is situated only 67 mm from the scattering centre and provides a higher sensitivity detection for angular measurements and temperature profiles of reactive species. The second ioniser is situated 500 mm from the scattering centre and provides high-resolution TOF Spectra for fast running species and narrow TOF distributions. When the front ioniser is in operation the back ioniser is switched off and a series of ion lenses guide the ions along the detection axis, through the back ioniser and into the quadrupole mass spectrometer. When the back ioniser is in use the front ioniser and guiding electron lenses are switched off.

Front Ioniser

The front ioniser is positioned within the main chamber with only the ioniser entrance exposed to the main chamber. The ioniser is cooled by a liquid nitrogen filled jacket and pumped by a 4” 100 MK2 Diffstak oil diffusion pump, which is filled with Santovac 5 oil and backed by the same EDM12 rotatory pump as the other chambers. The 4” oil diffusion pump is in the buffer space between the front ioniser and the back ioniser. The liquid nitrogen is filled from the main chamber cryotrap via a 1/4 “ steel tube, so needs to be filled continuously as it takes a long time to cool.

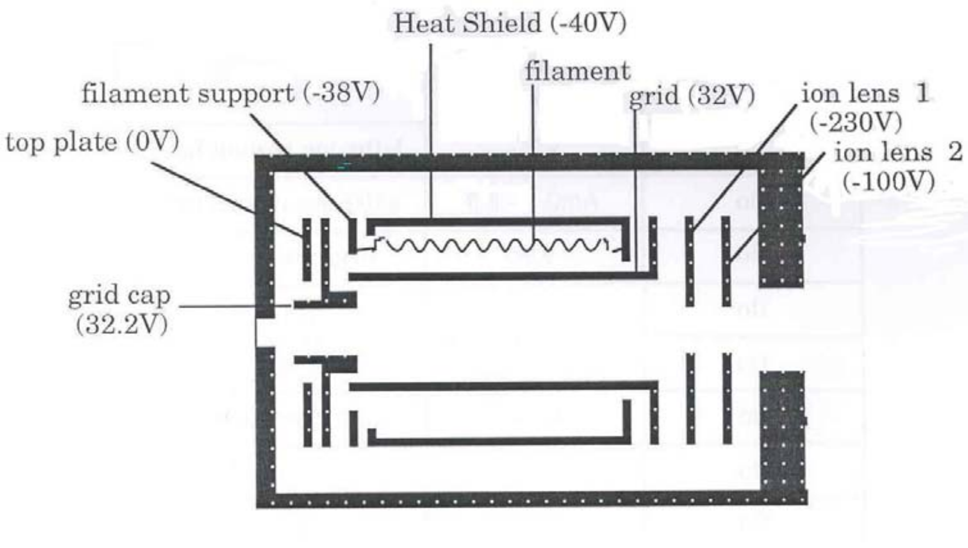


Figure 2.9 Schematic of the front ioniser

The front ioniser is a modified Brink type electron bombardment space charge ioniser [4,5], where electrons are emitted from a hot filament and are accelerated back and forth through a positively charged grid surrounding the central axis. The electros thus have many opportunities to collide and ionise the product molecules.

The front ioniser is passing through the back ioniser and is connected to the quadrupole/detector assembly.

Back ioniser

The back ioniser is positioned beyond the buffer space and behind a slide valve. The slide valve has a 3 mm hole for reactive scattering measurements and a 0.4 mm hole for beam measurements. The back ioniser is similar to the front ioniser, but doesn’t have the grid cap. The ion lenses are used to extract and focus the ions, produced from either ioniser, into the quadrupole mass filter. The back ioniser is pumped with an Edwards radial electric field pump and a liquid nitrogen filled cryotrap. The cryotrap is filled, even when the back ioniser is not in use, so as to align the back ioniser entrance and exit holes with the main axis.

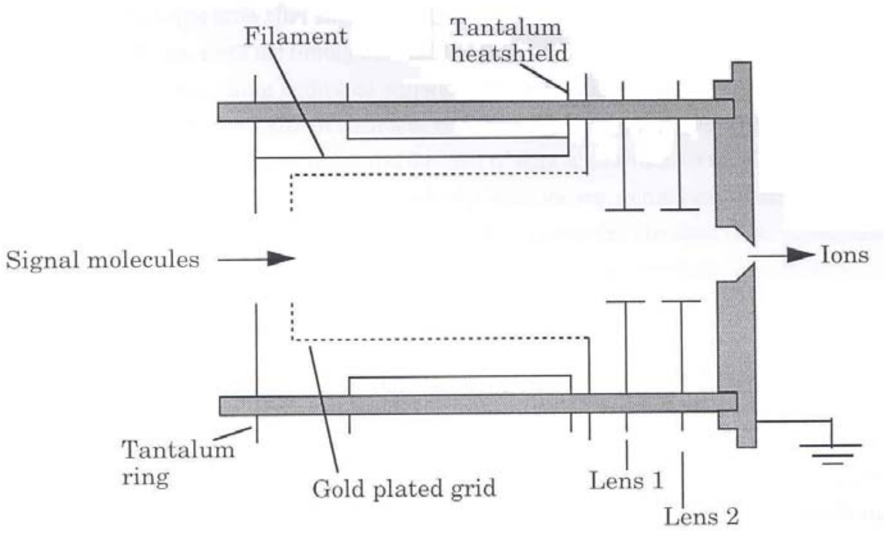


Figure 2.10 Back Ioniser.

RHEED apparatus

The reflected high energy electron diffraction (RHEED) apparatus is in the main chamber. A collimated, monoenergetic electron beam is directed at a grazing (~1°) angle to the sample surface and the transmitted electrons produce a diffraction pattern on a fluorescent screen, which is approximately in line with the electron beam.

There are typically three different RHEED patterns observed in these experiments:

(i) A series of intense, short and well defined streaks which are positioned perpendicular to the surface being observed. This indicates a clean, flat, well ordered crystal surface.

(ii) An ordered pattern of longer, dispersed and spotty streaks. This shows a clean but rough surface as the beam is unable to penetrate the surface due to its unevenness to produce a transmission diffraction pattern.

(iii) A broad glow with no distinct pattern. This indicates the presence of surface oxides.

The presence of surface oxides on GaAs(100) reduces the product signals, but does not affect the chemistry to any great effect. Thus, the removal of surface oxides by high temperature etching can be monitored using the total count of a TOF measurement. Comparing the total count to that of an experiment where the surface was known to be clean gives an indication of how clean the surface is.

Pulsed beam apparatus

The pulsed supersonic molecular beam source in the apparatus consists of four components: a pulsed piezoelectric valve, a skimmer, a chopping wheel, and a final exit collimating disc. Figure 2.11. The piezo valve produces gas pulses of ~150 µs pulse duration which after passing through a supersonic skimmer, are the narrowed by chopping with a slotted high speed rotating disc.

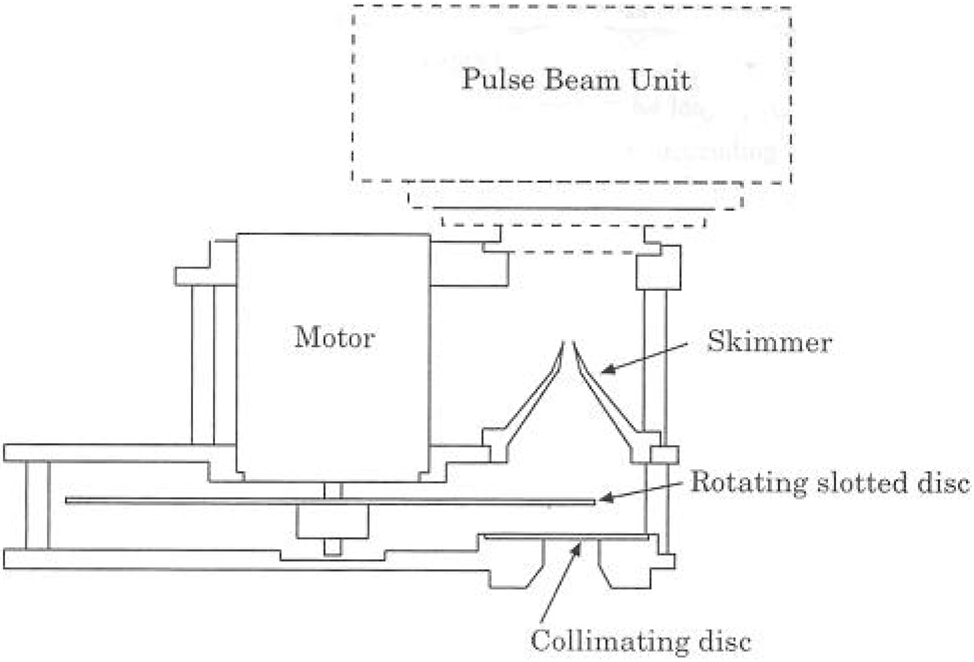


Figure 2.11 Cross-section of pulse beam cradle

The gas pulse hits the rotating disc, which allows only a fraction of the original pulse to travel through, the remainder being deflected off to one side. The slots are made narrow enough (1-2 mm typically) to produce gas slices of 30-40 μs from a disc rotating at 200 Hz. The synchronisation of the pulse beam triggering relative to the disc position is controlled by the TOF electronics.

The basic element of the molecular beam source is a pulsed piezoelectric valve. The piezo valve, Figure 2.12, is a sealed unit connected to the external gas supply via a flexible steel tube. A plunger is attached to the centre of a piezo electric crystal and the other end has a 1 mm Viton seal which pushes up against the centre of a 0.35 mm monel nozzle, sealing it. DC pulses cause the piezoelectric disc to flex slightly with each impulse. This flexing action causes a driver rod to lift slightly, unsealing and then resealing a nozzle which in turn allows a small volume of gas to be emitted.

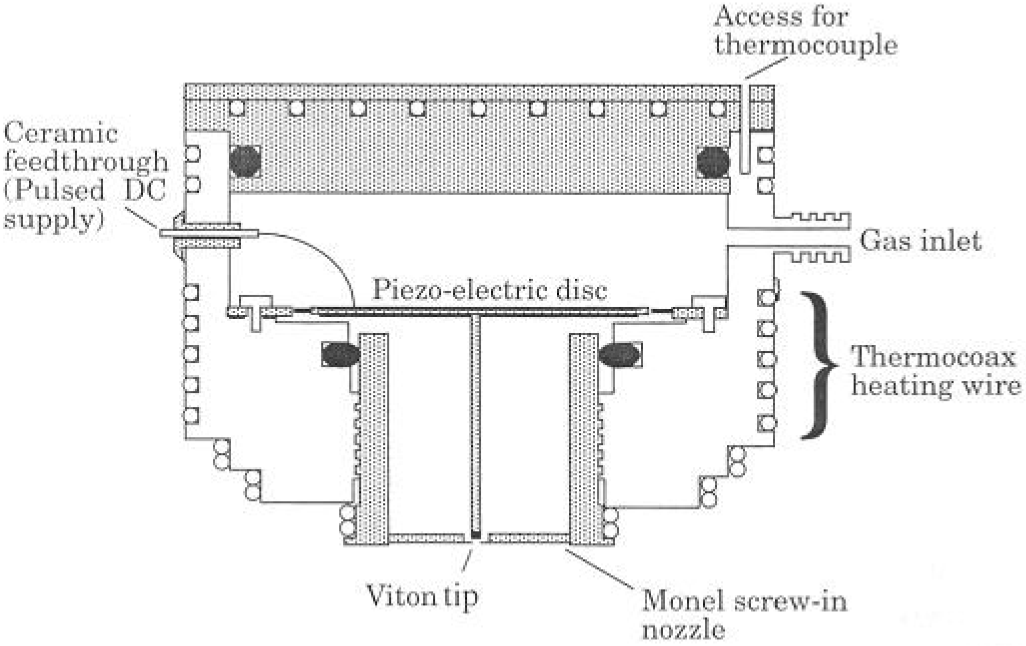


Figure 2.12 Pulsed piezoelectric valve

Since pure bromine gas is frequently used, the piezoelectric element and electrical connections are coated with a halogen resistant paint to prevent corrosion. The end of the plunger which seals the nozzle hole is covered with a Viton tip which is superglued on.

Once the nozzle of the pulse beam unit is opened, the released gas undergoes supersonic isentropic expansion into the source chamber, where it passes through a skimmer into the space occupied by the chopper disc before the collimating disc. The skimmer is a double cone design with a 1.27 mm entrance diameter and it set 14 mm away from the nozzle. The ~150 µs gas pulse created by the piezo valve is too long to provide the required time resolution and the profiles of the start and the finish of the pulse are not sharp enough. To create a shorter, sharper gas pulse, the ~150 µs pulse has a small slice chopped out by a rotating slotted disc. The disc is 76.2 mm in diameter and is made of 0.5 mm thick aluminium. There are four slots 2 mm wide and 9 mm deep (towards the centre) at 90° spacing and four 0.25 x 9 mm slots spaced between the other four wider slots. The disc is rotated at 200 Hz by a synchronous two-phase hysteresis motor which is driven by a purpose built power supply. The timing unit sends a digitally generated sine wave to this unit as a reference signal to control the disc speed. The wide slot generates a pulse of 34 µs duration and the narrow slot generates a pulse of 12 μs duration. The gas pulse travels 68 mm from the chopping disc to the surface.

Synchronization of chopper wheel/pulse beam/TOF

One of the tasks of the timing electronics is to synchronise the triggering of the piezo valve with respect to the absolute position of the disc. This is to ensure that the peak of a gas pulse impinges directly on the centre of a slot (along the beam axis). Then, the synchronisation of the piezo valve and the chopper disc is achieved using an electronic interface (which also controls the signal detection). An infra-red optical sensor mounted diametrically opposite the beam position, shown in the Figure 2.13, monitors the position of the disc and initiates the pulse sequence which is shown in the figure 2.14

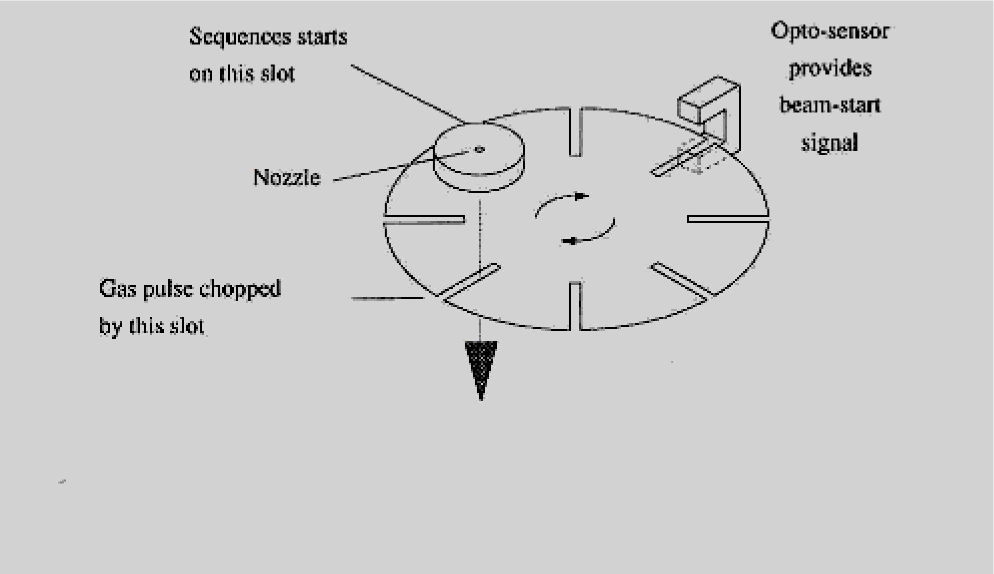


Figure 2.13 Schematic of the chopper disc and opto-sensor

The interface identifies which slot size is present by comparing the signal width from the optical sensor and comparing it to a reference value halfway between the wide and narrow pulse lengths. The interface ignores either the pulse shorter or longer than the reference value, depending on which one is required. T_p is the slot repeat period and T_d is the piezo valve pulse delay, so T_p - T_d is the time required for the gas pulse to reach the disc at the same time as next slot. The time of flight (TOF) data collection is started at some time, T_t, after the pulse beam leaves the disc. This is set empirically to start the TOF spectrum a short while before molecules reach the detector. Since the start pulse occurs on the falling edge of the opto-sensor signal, the actual start (centre of slot) is $T_w/2$ earlier, where T_w is the slot width (34 or 12 μs).

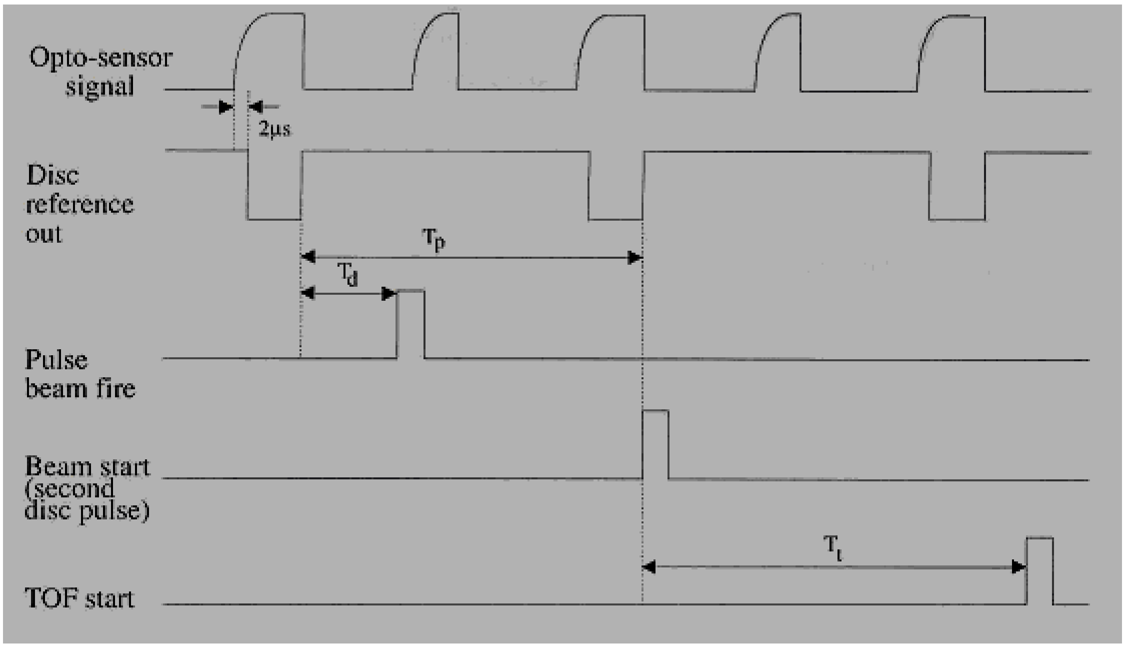


Figure 2.14 Timing sequence for the pulse beam apparatus. The disc reference pulse, created by the opto-sensor triggers the delay for the piezo valve to fire (T_d). The delay allows the gas pulse to reach the disc when a slot passes by and chops it. T_t is the time of flight delay to allow the products to reach the detector before the software starts storing the signal.

References

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