Development and Applications of Tandem Time-of-Flight Mass Spectrometry

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Declaration

This thesis was composed by myself and is based on work carried out in the Chemistry Department of the University of Edinburgh.

Signed:

Date: 08 MAY 2002
To my family and Alex
"...Ô temps, suspend ton vol! et vous, heures propices, suspendez votre cours!
Laissez nous savourer les rapides délices .
Des plus beaux de nos jours!..."

Alphonse de Lamartine

"...O time, suspend your flight! And you, propitious hours, suspend your course!
Let us taste the swift delights of the fairest of our days!..."
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Abstract

A novel tandem time-of-flight (TOF) mass spectrometer has been developed for studying the photo-induced dissociation of large molecules and elemental clusters. It consists of a linear first stage TOF analyser for primary mass separation and precursor ion selection, and a second orthogonal reflecting field TOF analyser for product ion analysis. The instrument is equipped with a large volume throughput molecular beam source chamber allowing the production of jet-cooled molecules and molecular clusters, as well as elemental clusters, using either a pulsed laser vaporisation source (LVS) or a pulsed arc cluster ion source (PACTS). A second differentially pumped chamber can be used with effusive sources, or for infrared laser desorption of large molecules, followed by laser ionisation. These primary ions can then be irradiated with a second, high energy laser to induce photodissociation. Detailed information about the fragmentation mechanisms can be deduced from the product ion mass spectra. A theoretical overview of the technique of tandem time-of-flight mass spectrometry is presented, together with a detailed description of the experimental procedures and equipment used.

In order to assist with the design and optimisation of the instrument a “virtual” mass spectrometer was drawn to scale using the SIMION software program, in order to simulate ion trajectories for differing voltages, geometry and dimensions of the ion optics. An ion gate was designed and manufactured to provide primary mass selection following the first time-of-flight mass analyser. The device consisted of four layers of interleaved wires; primary ions could be selectively transmitted by application of a fast rising high voltage pulse to the middle set of wires. The mass gate was measured to have a mass resolving power \( m/\Delta m = 30 \).

The tandem TOF mass spectrometer was used to investigate the photo-induced dissociation of the molecular ions of simple organic molecules, such as aniline and anisole. The molecular ions were generated by laser photoionisation at 266nm, and photodisassociated using the same laser wavelength. For aniline, it is shown that at low laser intensity (corresponding to one photon excitation) fragmentation occurs predominantly via loss of HNC or a hydrogen atom, whilst at higher intensities, a
number of fragment ions are formed, following two-photon excitation of the molecule ion. These results are in general agreement with the photo-dissociation pathways proposed by others. For further comparison, collision-induced dissociation spectra for the molecular ion of aniline were also recorded using a commercial mass spectrometer, equipped with an atmospheric pressure electrospray ionisation interface. For anisole, it is shown that at low laser intensity (corresponding to one photon excitation) the predominant product ions observed are \([\text{C}_6\text{H}_5\text{O}]^+\), \([\text{C}_6\text{H}_6]^+\) and \([\text{C}_5\text{H}_5]^+\).

In parallel with this work, a pulsed arc cluster ion source (PACIS) was constructed with the eventual goal of investigating the photodissociation behaviour of mass selected transition metal cluster cations. Preliminary cluster mass spectra were obtained for lead and platinum. However, the abundance of the cluster ions was too low to permit any tandem time-of-flight experiments to be carried out. Improvements to the source design, that would enhance the clustering process, are proposed.

Finally, in the light of the experimental results obtained during the course of this work, the potential applications and limitations of the tandem TOF/TOF mass spectrometer are discussed.
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Chapter 1

Introduction

Over the past decade time-of-flight mass spectrometry has grown from a relatively marginal technique to become a ubiquitous feature in the instruments present in most modern mass spectrometry laboratories. In his review of the technique in 1990, Price [1] already listed its many possible uses and anticipated its rise in popularity. The fundamental principles of TOF-MS are extremely simple: mass analysis of ions, with differing kinetic energy, is achieved by measuring their time-of-arrival through a flight tube, under vacuum, to a detector. The practical implementation of the technique, however, necessitates good time control, down to the nanosecond level, which can only be achieved with advanced electronics. The basic components of a TOF-MS consist of an ion source, a flight tube and a detector. Historically, the earliest and most widespread mode of ionisation was electron impact [2,3]. Over the years several other ion sources have been introduced, e.g. chemical ionisation (CI) [4,5], fast atom bombardment (FAB) [6] and plasma desorption (PD) [7]. These have, to a certain extent, been superseded by more effective and selective ionisation techniques such as matrix-assisted laser desorption ionisation (MALDI), electrospray ionisation (ESI) and atmospheric pressure ionisation (API). However, not all of these are easily interfaced with TOF-MS. In the early days, experimental control and data acquisition were achieved using CAMAC.
based electronic modules (pulse delay generators, transient digitisers, analogue to
digital converters, etc.). Nowadays stand-alone delay generators and high voltage
pulse generators are widely available, and ion signals from the detector can be
processed using powerful digital oscilloscopes and the data transmitted via interface
cards to personal computers equipped with high speed processors and dedicated data
acquisition software. Other software programs such as SIMION [8] are now widely
available to allow calculation and visualisation of ion trajectories. Instrument design
and configuration can therefore be tested in a "virtual" mass spectrometer.

Historically, the main problem that held up the development of TOF-MS was poor
mass resolution. This was addressed by Wiley and McLaren [9] who, in a seminal
paper published in 1955, proposed the use of a dual stage acceleration to focus the
ions. No less important was the later invention of the reflectron, or ion mirror, by the
Russian, Mamykin [10], which provided a further enhancement in mass resolution
with its energy focusing properties. Enabled by these technological breakthroughs,
the development of TOF-MS has literally exploded throughout the 1990s. Further
drive and impetus were brought about by the emerging applications in the field of
pharmaceutical research. The technique of matrix-assisted laser desorption/ionisation
(MALDI), first described by Karas and Hillenkamp [11] in 1988, was developed for
the analysis of large biomolecules. Within a very few years, MALDI time-of-flight
mass spectrometers were present in every research laboratory that dealt with drug
discovery, as a standard tool for the characterisation of proteins and peptides.

Progress in laser technology was achieved in parallel to developments in TOF-MS
instrumentation. Pulsed lasers are ideally coupled to time-of-flight analysers [12].
They deliver a short and intense pulse of energy to the molecule, such that ionisation
occurs as well defined temporal and spatial events, improving the mass resolution
considerably compared with that obtained with more traditional ion sources. The
relatively large initial kinetic energy distribution can be corrected for by using a
reflectron. Large molecules can be ionised intact [13] by adjusting the laser power
density to produce the molecule ion, and mass analysed in the TOF-MS, which has
unlimited mass range. Laser ionisation also offers other benefits: molecules that
contain a chromophore that strongly absorbs at the incident laser wavelength can be
selectively ionised from a mixture of analytes. Finally, multiphoton ionisation enables the ionisation potential of most molecules to be reached by the absorption of more than one photon of UV or visible radiation [14-17]. This process can also be resonantly enhanced, increasing the overall ionisation efficiency, via absorption to an intermediate excited electronic state of the molecule.

The properties of lasers make them suitable not only for sample photoionisation, but also for the desorption of molecules directly from a substrate. Solid samples irradiated by a short intense pulse of laser radiation are brought immediately into the gas phase. At relatively low laser power density, mostly neutrals are produced [18], but by increasing the laser fluence, the degree of molecule ions can be substantially increased. Above the ionisation energy, fragmentation is likely to occur. Grotemeyer recognised that, by separating the desorption and ionisation steps, some flexibility could be gained in optimising each step separately [19]. In the first step, laser desorption is used to bring molecules into the gas phase, followed almost immediately by irradiation with a second laser that delivers the required energy to induce ionisation. This technique, developed in parallel by several groups [17,20-22], is known as two-step laser mass spectrometry (L2MS). Another avenue in laser MS research led to the development of MALDI/TOF-MS, where a single laser is used for desorption and ionisation, which is enhanced by the addition of a matrix to the sample [11]. The matrix contains a chromophore that absorbs strongly at the incident laser wavelength and transfers energy to the molecule; ionisation can often occur via cation attachment. In L2MS however, the molecule can be analysed directly from its host matrix, without the need for any sample preparation. Since molecules are desorbed directly from the solid into the gas-phase, this alternative approach was found to be particularly suitable for the analysis of involatile and thermally labile molecules. Applications have included the study of pigments and azo-dyes adsorbed onto fabrics [21], the analysis of polyaromatic hydrocarbons (PAHs) in environmental samples [23], the analysis of additives in polymer materials [24], even looking for clues in the search for life on Mars by detection of PAHs in meteorite samples [25]. The flexibility afforded by the two-step laser approach enables the production of simple mass spectra that are easy to interpret. In some cases, however,
particularly for samples present in complex matrices, or when isobaric species cannot be separated, ambiguity arises in peak assignments, that is difficult to overcome [26]. In those cases, tandem mass spectrometry is desirable. The initial motivation for this work was principally to develop L2MS into a tandem technique that would enable, for example, the unambiguous characterisation of azo-dyes and PAHs in complex matrices.

Tandem time-of-flight mass spectrometry was used in the 1980s, for fundamental studies on the bonding properties of metal clusters [27,28]. Clusters lie halfway between the atomic and the bulk realm, ranging in size from a few atoms up to several tens of thousands. Cluster research was initially focused on the production and characterisation of metal clusters using a laser vaporisation source. Laser ablation of a solid metal target at high enough laser intensity produced a plasma. This intense plasma was cooled by a pulse of inert gas to induce clustering. Upon expansion of the inert gas into a supersonic molecular beam, the metal clusters were carried through to the ionisation chamber. Subsequent ionisation and time-of-flight mass analysis revealed the cluster size and abundance, while tandem time-of-flight mass spectrometry permitted the selection of a particular cluster size for photo-fragmentation and mass analysis in a second TOF-MS, providing structural information. More recent cluster sources, such as the pulsed-arc cluster ion source (PACIS), have been used to produce metal cluster ion beams [29]. Such a cluster source was built during the course of this project, and the intention was to test it in the tandem time-of-flight mass spectrometer.

TOF-MS has been a valuable technique not only for cluster studies, but also for the study of fundamental properties of organic molecules. Schlag and co-workers have used the technique to probe the photo-fragmentation dynamics of aromatic molecules. In particular, their experimental work on benzene led to the discovery of the "ladder switching" mechanism [30]. TOF-MS was an ideal technique for these studies since it could provide an instant snapshot of the photo-fragmentation event. Boesi et al. have used various instrumental configurations in order to obtain tandem time-of-flight mass spectra [31]. In effect, it was necessary to set up a tandem
experiment in order to mass select each benzene fragment, and to interrogate the further photo-fragmentation behaviour of each product ion under laser irradiation.

Traditionally, tandem mass spectrometry has been performed in magnetic sector and quadrupole instruments, using collision-induced dissociation (CID) [32-34]. This approach was particularly well suited to the study of molecules that could be easily ionised using continuous ion sources. Ion traps [35-37] have also been used to perform tandem experiments. Here, the ions can be mass selected and subjected to some means of dissociation, either CID or photo-induced dissociation (PID) whilst being held in the trap, before being ejected for analysis, e.g. in a time-of-flight mass spectrometer [38,39]. In principle, this can be repeated ad infinitum, leading to MS\(^n\). Tandem TOF/TOF mass spectrometry has not received such widespread interest, for several reasons. Firstly, it is relatively difficult to implement experimentally, due to the rather stringent constraints of time and spatial control of ions. Secondly, there is a major difficulty in the mass dispersion of product ions in the second time-of-flight region. Indeed, following the dissociation event, precursor and product ions all possess the same velocity (but different kinetic energies), so that post acceleration is required. Despite these problems, several experimental set-ups have been designed and tested.

One easily implemented method involves firing a dissociation laser across the ion path at the back of the reflectron, where the ions are almost stationary, thereby increasing the interaction time with the laser beam [9,40-42]. The product ions are accelerated and separated in the second half of the reflectron. This method effectively divides a reflectron TOF-MS into two linear time-of-flight regions, with limited mass resolution. Another method is to fire the dissociation laser at the space-time focus immediately following the ion extraction region. This approach has been used to deduce the fragmentation pathways of molecule ions, from studies of metastable decay of the ions so produced [43-45]. A double reflectron in a Z-shape configuration has also been used, together with laser induced dissociation [46]. Cotter and co-workers have used a similar configuration, with a collision cell at the intermediate stage, and a modified reflectron in the second stage to allow mass analysis [47]. An instrument consisting of two separate mass analysers placed
orthogonally has been used, with laser irradiation at the intersection of the two drift regions to induce dissociation [48-51]. A similar configuration, with a target placed at the end of the first stage, has been used for surface induced dissociation [52]. The present instrument also has orthogonal geometry, with the added flexibility of a wide range of ion sources making it a versatile tandem instrument.

It is interesting to note that the first commercial tandem TOF/TOF instruments have just appeared in the market place, validating the original concept behind the project, which commenced in 1996. At the beginning of this thesis, some theoretical background to L2MS is given, followed by a description of the experimental set-up used, which form Chapters 2 and 3, respectively. The choice of instrument configuration was greatly helped by ion trajectory simulations using the SIMION program [8]. An introduction to this software package together with a description of the simulations performed in the "virtual" mass spectrometer that was drawn to scale in the SIMION workbench, is given in Chapter 4. An essential feature of tandem mass spectrometry is the mass selection of a precursor ion. In this work, an ion-gating device was designed and manufactured. The design and characterisation of this device is described in Chapter 5. The development of the tandem TOF/TOF-MS, from early design options to final assembly, is recounted in chapter 6. Available in the laboratory were three stainless steel vacuum chambers, one of which housed a laser vapourisation source that had been used for elemental cluster generation [53,54]. The other two modular chambers were used to house the laser desorption/ laser ionisation source and the ion optics necessary for controlling the ion beam for subsequent fragmentation and mass analysis. This tandem TOF/TOF-MS was used initially to investigate the photo-dissociation of simple organic molecules such as aniline and anisole, before attempts were made to perform L2MS experiments in tandem. The results obtained for these experiments are presented in Chapter 7. In parallel with the development of the tandem TOF/TOF-MS, a pulsed-arc cluster ion source (PACIS) was built following the design of Siekman et al. [29]. It was housed in a separate cluster source chamber. The preliminary results obtained using the PACIS are presented in Chapter 8, together with a discussion of the problems encountered during these experiments. Finally, in Chapter 9, some suggestions are
made for possible improvements to the tandem TOF/TOF instrument, which could lead to future work.
Chapter 1. Introduction

References

Chapter 1. Introduction


Chapter 1. Introduction


Chapter 2

Laser Time-of-Flight Mass Spectrometry: Background Theory

2.1 Introduction

The main emphasis of this project is placed on instrumental development of the time-of-flight technique, hence it is given a thorough theoretical treatment in this chapter. The choices made in the design of the tandem TOF/TOF mass spectrometer were based on the theory explained here. The ions sources that couple to TOF-MS, ie Laser Desorption/ Laser Ionisation (LD/LI) for the analysis of large organic molecules (especially involatile and thermally labile), Laser Vaporisation (LVS) and Pulsed Arc Cluster Ion (PACIS) for the generation of elemental metal clusters, are experimental tools that enable some areas of research to flourish. Particular attention was paid to LD/LI and PACIS sources in this project, so the underlying principles of laser desorption and ionisation are also described here, along with a brief review of metal cluster formation.
2.2 Time-of-Flight Mass Spectrometry: Basic Principles

Time-of-flight mass spectrometry relies on the principle that when ions are accelerated in an electrostatic field, then left to drift in a field-free region, they separate in time according to their masses. The three main components of a time-of-flight mass spectrometer are therefore the ion source, the drift region and the detector, as shown in Figure 2.1. The mathematical treatment that follows was drawn from several sources [1-3] and all parameters were illustrated in the schematic diagrams of Figure 2.1 to Figure 2.5.
Figure 2.1: Schematic diagram showing the main parts of the single field time-of-flight mass spectrometer.
Chapter 2. Laser Mass Spectrometry: Background Theory

The total time-of-flight of an ion is equal to the time spent in the source plus the time spent in the drift region:

\[ t = t_s + t_D \]  \hspace{1cm} (2.1)

**Calculation of** \( t_D \)

\( t_D \) can be derived from the expression for the energy acquired by an ion in the electrostatic field:

\[ K_e = s_0 q E_s \]  \hspace{1cm} (2.2)

Upon leaving the source, the ions have acquired a kinetic energy equal to:

\[ K_e = \frac{1}{2} m v_D^2 \]  \hspace{1cm} (2.3)

These two values of \( K_e \) are equivalent, hence:

\[ s_0 q E_s = \frac{mv_D^2}{2} \]  \hspace{1cm} (2.4)

where: \( m \) = mass of the ion
\( q \) = charge of the ion
\( s_0 \) = distance of acceleration in the source
\( E_s \) = electrostatic field
\( v_D \) = velocity of the ion in the drift region

The velocity \( v_D \), and hence the time-of-flight \( t_D \) of an ion in the drift region, can thus be derived from Equation 2.4:

\[ v_D = \sqrt{\frac{2s_0 q E_s}{m}} \]  \hspace{1cm} (2.5)
Chapter 2. Laser Mass Spectrometry: Background Theory

\[ t_D = D \sqrt{\frac{m}{2s_0qE_s}} \]  \hspace{1cm} (2.6)

**Calculation of \( t_s \)**

The time \( t_s \) spent in the source can be derived from the following equations:

The electrostatic force upon an ion is:

\[ F = qE_s \]  \hspace{1cm} (2.7)

The force upon the ion can also be expressed as:

\[ F = ma \]  \hspace{1cm} (2.8)

where \( a \) is the acceleration. Hence, \( a = \frac{qE_s}{m} \). The differential equation \((dv = a \ dt)\) is integrated over the source region to give (assuming zero initial velocity):

\[ t_s = \frac{mv_D}{qE_s} \]  \hspace{1cm} (2.9)

By substituting \( v_D \) in the equation above, \( t_s \) is therefore:

\[ t_s = \sqrt{\frac{2ms_0}{qE_s}} \]  \hspace{1cm} (2.10)

**Total time-of-flight**

Substituting \( t_s \) and \( t_D \) from Equations 2.10 and 2.6 into equation 2.1 gives \( t \):

\[ t = t_s + t_D = \sqrt{\frac{2ms_0}{qE_s}} + D \sqrt{\frac{m}{2s_0qE_s}} \]  \hspace{1cm} (2.11)
It can be seen that the time-of-flight is proportional to $\sqrt{m/q}$. In a mass spectrum, the mass axis is usually given in (m/z) units, where $m$ is the atomic mass and $z$ is the number of electronic charges. For a positive ion:

$$z = \frac{q}{e}$$  \hspace{1cm} (2.12)

where $e$ is the elementary charge, $e = 1.602 \times 10^{-19}$ C. Thus, a mass spectrum can be derived by calibration with two known masses and determining the values for $a$ and $b$ in the equation:

$$\frac{m}{z} = at^2 + b$$  \hspace{1cm} (2.13)

Although time-of-flight mass spectrometry offers some advantages over other techniques, principally the recording of a complete mass spectrum for each ionisation event, it has taken some years to establish the technique. One of the main obstacles in its development has been poor mass resolution. Several factors affecting the mass resolution are discussed in the next section.

### 2.3 Factors Affecting Mass Resolution

#### 2.3.1 Temporal Distribution

Due to the ionisation event having a finite duration $\Delta t_0$, a temporal distribution is produced in the formation of isobaric ions (see Figure 2.2a). Excluding other factors, the mass resolution of the time-of-flight mass spectrometer is given by:

$$\frac{m}{\Delta m} = \frac{t}{2\Delta t_0}$$  \hspace{1cm} (2.14)

The temporal distribution can be minimised in two ways. Firstly, by reducing the ionisation time, $\Delta t_0$. In laser mass spectrometry, short pulses, typically down to a few
nanoseconds, are used for the ionisation event. This in effect approaches the digitisation rate of the signal from the detector, so that the temporal distribution is no longer a limiting factor on the mass resolution. The second approach is by increasing the total time-of-flight, which can be achieved by using low extraction voltages and/or long drift lengths. However, this would affect the sensitivity adversely, and high extraction voltages are helpful to reduce the kinetic energy distribution. In this case, a compromise has to be reached to obtain the best resolution without affecting sensitivity.

2.3.2 Spatial Distribution

In an ideal time-of-flight mass spectrometer, all ions will be created in a single narrow source plane perpendicular to the electric field. If this were the case, and no other broadening mechanisms were acting on the ion packet, each ion of the same mass-to-charge ratio would gain an equivalent amount of kinetic energy from the extraction field and arrive at the detector at the same time. When laser ionisation is used, the ionisation source plane is defined by the outer limits of the ionising laser beam. It is possible to focus the laser more tightly, thus reducing the beam size, and consequently the spatial distribution. However, a highly focused laser beam introduces space charge effects, which can cause a large kinetic energy distribution.
Figure 2.2: Schematic diagrams showing the effects of initial source conditions on the mass resolution: a) temporal distribution, b) spatial distribution, c) kinetic energy distribution and d) opposite initial velocity resulting in a "turn around" time.
Wiley-McLaren Space-Time Focusing

Due to the ionisation source having a finite size, $\Delta s_0$, ions of the same m/z formed at different points in the source are accelerated to different kinetic energies (see Figure 2.2b). However, ions formed at the rear of the source enter the drift region later, but with a larger velocity than the ones formed at the front of the source. There is a point in time, called the space-time focus, when the faster ions overtake the slower ones. In a single field extraction, this occurs at a distance $2s_0$ from the source. It is, however, impractical to place the detector at such a short distance from the source because there is insufficient mass dispersion. Greater flexibility over the position of the space focus can be achieved by using two-field extraction optics, where the demand for a high extraction field can be met in a second acceleration region. This was first proposed in 1955 by Wiley and McLaren [3]. A schematic diagram of the double field linear time-of-flight mass spectrometer is shown in Figure 2.3. The time of flight, $t_d$, of an ion in the second draw-out acceleration region of field $E_d$ and distance $d$, can be calculated using the principles and equations given in Section 2.2:

$$t_d = \frac{m(v_d - v_D)}{qE_d}$$  \hspace{1cm} (2.15)

where $v_d$ is the velocity of an ion at the start of the draw-out region and $v_D$ is the velocity in the drift region:

$$v_d = \sqrt{\frac{2s_0 qE_s}{m}} \quad \text{and} \quad v_D = \sqrt{\frac{2q(s_0 E_s + dE_d)}{m}}$$  \hspace{1cm} (2.16)

The total time-of-flight in a double-field mass spectrometer thus becomes:

$$t = t_s + t_d + t_D = \frac{mv_d}{qE_s} + \frac{m(v_D - v_d)}{qE_d} + \frac{D}{v_D}$$  \hspace{1cm} (2.17)
The condition for space-time focusing is that \((\frac{dt}{ds_0}) = 0\). Applying this condition to Equation 2.17, and defining:

\[
k_0 = \frac{(s_0E_s + dE_d)}{s_0E_s}
\]  

(2.18)

the position of the focusing point is given by:

\[
D = 2s_0 \sqrt{k_0} \left( 1 - \left( \frac{1}{\frac{d}{k_0 + \sqrt{k_0 s_0}}} \right) \right)
\]  

(2.19)

Since \(s_0\), \(d\) and \(D\) are fixed, the mass resolution depends on the ratio \((E_d/E_s)\). In practice, the best resolution is obtained by adjustment of the voltages on the repeller and draw-out electrodes that determine the ratio \((E_d/E_s)\). It should be noted that in the case of single field acceleration, where \(d = 0\) and \(k_0 = 1\), Equation 2.19 becomes \(D = 2s_0\) as shown previously.

### 2.3.3 Space-Charge Effects

As discussed earlier, focussing of the laser beam in the source will assist in the reduction of the effects of spatial resolution. However, this can result in very high ionising laser power densities, which leads to the production of a large number of ions in a reduced volume. This causes each ion to influence the others via electrostatic interactions. The effect of these repulsive forces is to move the ions to different regions of the ion source, where they will be extracted with varying amounts of kinetic energy. This phenomenon is akin to, and can be corrected in the same way as, the initial kinetic energy distribution.
Figure 2.3: Schematic diagram showing the double field linear time-of-flight mass spectrometer.
2.3.4 Kinetic Energy Distribution

A final and crucial factor affecting resolution is the initial kinetic energy of the ions, which arises due to a number of reasons. Firstly, the ions generated or sampled in the gas phase are subject to a Boltzmann distribution of initial velocity $v_0$. Secondly, the space-charge effects described previously produce an additional velocity component when tightly focused, high intensity, lasers are used for ionisation. Finally, the molecules desorbed from a surface also gain a velocity component in a range of directions, which, after ionisation, contributes to a kinetic energy distribution of the ions. To illustrate the effect of this distribution, Figure 2.2c shows two ions with the same initial starting position, but with a different initial kinetic energy vector in the direction of the detector. This will obviously result in different arrival times at the detector. A more extreme case is of two ions of the same mass-to-charge ratio, formed at identical points in space and time but possessing velocities in opposite directions in the time-of-flight axis, $+v_1 = -v_2$, as shown in Figure 2.2d. The ion moving in the opposite direction to the detector must be decelerated to zero before being accelerated back towards its initial position, where it will follow the same trajectory as the other ion. The separation in time of the detection of these two ions is the so-called “turn-around time”. The magnitude of this turn-around time is influenced by the initial velocity distribution of the ions and the electric field strengths in the ion-source. This effect can be minimised in a number of ways.

It is possible to reduce the turn-around time by minimising the ratio of the initial kinetic energy of the ions to the extraction potential. This can be achieved by increasing the value of the accelerating potential. However, this is only feasible to a certain degree since a longer flight tube would be required in order to maintain the same time-of-flight. It is also possible to attenuate the effect of energy resolution by reducing the initial spread in velocities of the precursor molecules. This can be achieved by seeding the sample in a pulsed supersonic molecular beam propagating parallel to the spectrometer axis, thus cooling the degrees of freedom by a series of two-body collisions. The narrow velocity distribution afforded by such a molecular beam can substantially reduce the temporal broadening of the ion packet.
In addition to space-time focusing, Wiley and McLaren described a way of energy focusing in their double field ion source called “time-lag focusing” [3]. Here, a time delay between the ionisation pulse and the application of a pulsed extraction field is introduced, such that the ions spread out in the field-free source. If the extraction field is switched on at the correct time, then most of the initial kinetic energy spread can be corrected for. This is because ions initially moving away from the detector are extracted at a higher potential, thereby attaining higher kinetic energies. In effect, the kinetic energy distribution is transformed into a greater spatial distribution, which can be corrected by applying the appropriate ratio of voltages to the double extraction optics. However, optimal energy focusing is obtained when \( (dt/ds_o) < 0 \), which is in conflict with the condition for time-space focusing. In practice, a compromise must be reached between the two effects, whichever is more prominent in a particular case. Another drawback of the time-lag focusing method is that it is mass dependent, so that optimal energy resolution will only be achieved for a small region of the mass spectrum, given a particular set of voltages on the extraction optics.

One of the major breakthroughs in terms of energy resolution was the invention of the reflectron by Mamyrin et al. [4]. This “ion mirror” provides a very efficient way of focusing ions of the same m/z but of different energy, simply due to the fact that ions with a greater kinetic energy spend more time in the reflectron than ions with lower kinetic energy. The space-time focus described earlier, which provides compensation for the spatial distribution, can be mirrored onto the detector using the reflectron, as shown in Figure 2.4. The added benefit is that the longer flight time allows a greater separation of ions of different masses, while achieving a high mass resolution. Reflectrons can be designed with a single stage reflecting field, or, as originally described by Mamyrin et al., they can be dual stage devices, with a steep retarding field followed by a less inclined reflecting field. The mathematical treatment for calculating the time-of-flight in the reflectron is similar to that previously described for the extraction optics in a linear time-of-flight mass spectrometer, since the deceleration and acceleration stages in the reflectron follow the same principles.
Figure 2.4: Schematic diagram showing a reflectron time-of-flight mass spectrometer.
In the following equations the reflectron mass spectrometer consists of all the stages immediately after the space-time focus, i.e. a drift region of length $L_1$ up to the deceleration fields, then a re-acceleration followed by a second drift region of length $L_2$ up to the detector. The parameters used in the equations are shown in Figure 2.4 and are also summarised below:

\[
\begin{align*}
  t & = \text{Time-of-flight} \\
  m & = \text{atomic mass} \\
  q & = \text{charge} \\
  K_e & = \text{kinetic energy acquired in the extraction optics} \\
  L_1 & = \text{length of the first drift region} \\
  L_2 & = \text{length of the second drift region} \\
  r_0 & = \text{penetration depth in the reflecting field} \\
  r_1 & = \text{length of the retardation region} \\
  r_2 & = \text{length of the reflection region} \\
  t_{L_1} & = \text{time of flight in } L_1 \\
  t_{L_2} & = \text{time of flight in } L_2
\end{align*}
\]

$R_1$ denotes the first, retardation part of the reflectron, while $R_2$ denotes the second, reflection region.

\[
\begin{align*}
  t_{R_1}, t_{R_2} & = \text{time-of-flight} \\
  v_{R_1}, v_{R_2} & = \text{velocity} \\
  E_{R_1}, E_{R_2} & = \text{electrostatic field}
\end{align*}
\]

In a single stage reflectron, with a penetration depth $r_0$, the time-of-flight $t$ is given by:

\[
t = \sqrt{\frac{m}{2K_e}} \left( L_1 + L_2 + 4r_0 \right)
\]  \hspace{1cm} (2.20)
The condition for energy focusing in this case is that $L_1 + L_2 = 4r_0$. This is reminiscent of the time-space focus condition ($D = 2s_0$) in the single field linear mass spectrometer. Here, the ions go back and forth, hence the factor 4.

In a dual stage reflectron, the time-of-flight $t$ is equal to:

$$t = t_{L1} + t_{R1} + t_{R2} + t_{L2}$$

$$t = L_1 \sqrt{\frac{m}{2K_e}} + 2 \frac{m(v_{R1} - v_{R2})}{qE_{R1}} + 2 \sqrt{\frac{2mr_0}{qE_{R2}}} + \frac{L_2}{v_{R1}}$$  \hspace{1cm} (2.21)

where: $$v_{R1} = \sqrt{\frac{2q(r_0E_{R2} + r_1E_{R1})}{m}} \quad \text{and} \quad v_{R2} = \sqrt{\frac{2qr_0E_{R2}}{m}}$$

The energy focusing condition in the dual stage reflectron is as follows:

$$L_i = 2r_0 \sqrt{k'_0} \left(1 - \frac{1}{k'_0 + \frac{r_1}{r_0}}\right)$$  \hspace{1cm} (2.22)

where: $$k'_0 = \frac{r_1E_{R1} + r_0E_{R2}}{r_0E_{R2}}$$

Since $r_0$, $r_1$ and $L_i$ are fixed, the mass resolution depends on the ratio ($E_{R1}/E_{R2}$). In practice, the best resolution is obtained by adjustment of the voltages on the retarding and reflecting electrodes of the reflectron that determine the ratio ($E_{R1}/E_{R2}$).

These improvements in mass resolution, combined with ever more sophisticated electronics for timing, detection and data acquisition, have led to time-of-flight mass spectrometry becoming widely accepted as a powerful technique in measurement science.
2.4 Orthogonal Acceleration TOFMS

The concept of orthogonal acceleration for time-of-flight mass spectrometry was first introduced by Guilhaus [5] and has since been coined oaTOF-MS and implemented in research and commercial instruments. Orthogonal acceleration of ions was used before, particularly with supersonic molecular beam sources, but was not described as an innovative concept. In those cases, the ion optics usually contained a set of deflection plates in order to steer the ions at 90° and thus correct for the initial velocity of the ions in the molecular beam direction. The originality of Guilhaus’s idea was to dispense with deflection plates, so that the ion trajectory retains an angle due to the velocity component in the initial (axial) direction of flight. The configuration of the instrument must allow for this angle, as shown in Figure 2.5.

The principles governing the trajectory of an ion in the orthogonal ion optics are similar to those of an ion traversing a set of deflection plates, as discussed in Chapter 5, in which the use of mass selection using ion gating devices is described.
Figure 2.5: Schematic diagram showing the principle of orthogonal acceleration.
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It can be seen from Figure 2.5 that the angle of drift $\alpha$ from the orthogonal direction due to the axial velocity component is determined by the ratio of the velocity components in the axial and orthogonal directions:

$$\tan(\alpha) = \frac{v_1}{v_2}$$ (2.23)

where $v_1$ and $v_2$ are the velocities in the axial and orthogonal directions, respectively. Since the velocity is derived from the acceleration voltages, $\alpha$ is also determined by:

$$\tan(\alpha) = \frac{V_1}{\sqrt{V_2}}$$ (2.24)

where $V_1$ and $V_2$ represent the acceleration voltages applied to the axial and orthogonal ion optics, respectively.

There is a crucial requirement for oaTOF-MS to be a viable technique, which is that the ions in the axial direction must have the same initial kinetic energy if they are to follow the same trajectory with drift angle $\alpha$. In molecular beams formed by supersonic expansion, this condition is not satisfied. All ions arrive at the orthogonal extraction optics with the same velocity, as opposed to the same kinetic energy, so that their trajectory is mass dependent in the orthogonal direction. The light ions leave the extraction optics with a relatively small drift angle $\alpha$, while the heavier ions with more momentum follow a trajectory with a larger drift angle. The traditional way to compensate for this has been to use deflection plates but the penalty is often poor mass resolution [6-8]. In oaTOF-MS, it is essential that the ions are given the same kinetic energy prior to orthogonal acceleration. To achieve this, a method described recently [9] involves collisional focusing in an RF-only multipole device, where the average ion energy is reduced to near that of the collision gas. The ions are then accelerated to a constant kinetic energy.
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2.5 Laser Desorption/ Laser Ionisation (LD/LI)

2.5.1 Introduction

Laser sources are uniquely suited to the time-of-flight MS technique [10], essentially due to their pulsed nature. Two broad areas of interest emerged, involving multi-photon ionisation (MPI) and desorption processes, respectively. The latter involved irradiation of a solid sample with a short, intense, laser pulse in order to bring it into the gas phase in an ionised state, for analysis in the time-of-flight mass spectrometer. Analytical interest grew following the successful desorption of intact large biomolecules. This resulted in the development of Matrix Assisted Laser Desorption/Ionisation (MALDI) mass spectrometry which now enjoys enormous popularity in the field of proteomics [11]. Other areas of interest included the study of interactions between molecules and surfaces [12]. Multi-photon ionisation played an important part in the spectroscopy of molecules and molecule ions [13,14]. While desorption and MPI techniques enjoyed growth in the fields of microprobe spectrometry (now known as MALDI/TOF-MS) and laser spectroscopy, respectively, the coupling of the two techniques came later. Cotter foresaw the potential of using desorption to bring molecules into the gas phase, subsequently post-ionised by a second laser [15]. The advantage of such an approach is that the two steps (L2MS) can be optimised independently. Applications of L2MS include the in situ analysis of involatile or thermally labile molecules directly from their host matrices [16], as well as structural elucidation by induced fragmentation [17]. Some fundamental aspects of laser desorption and laser ionisation are given in the following sections, bearing in mind that the applications of the tandem TOF/TOF mass spectrometer would be initially aimed at L2MS.

2.5.2 Laser Desorption

The use of pulsed laser radiation can lead to the desorption of intact large molecules and ions into the gas phase. The principal advantage of laser desorption is the ability to vaporise thermally labile species without decomposition. Posthumus et al. [18] were the first to demonstrate the use of pulsed CO₂ laser radiation for the
successful vaporisation of involatile and thermally labile large organic molecules, such as oligopeptides.

Various types of models and theories of laser desorption have been proposed due to the many different experimental conditions that have been used, which may lead to different types of mechanisms. Factors such as laser wavelength and power, type of substrate and sample thickness, all greatly affect the desorption process. The energy from the laser radiation can be imparted to the analyte in several ways, either directly or indirectly. Heating of the substrate with an infra-red laser leads to transfer of energy to the molecule, which undergoes either decomposition or thermal desorption. A matrix can be added to assist the process of energy transfer. Here, a UV laser is used to resonantly excite the matrix. This has led to the development of Matrix Assisted Laser Desorption/Ionisation (MALDI) mass spectrometry as a technique in its own right. When the laser wavelength coincides with a suitable transition in the solid material, direct resonant desorption is induced. Desorption phenomena depend largely on the heating rate of the substrate/sample, but other mechanisms have also been rationalised and are discussed in the following section.

2.5.3 Desorption Mechanisms

Thermal desorption

In 1987 Zare and Levine [19] introduced a general theory which suggested that laser-induced thermal desorption was a non-equilibrium process. The available energy breaks the bond between the substrate and the adsorbate rapidly but does not randomise throughout the adsorbate on the time scale of the desorption event. This was due to the frequency-mismatch of the weak substrate-adsorbate van der Waals bonds with the much stronger adsorbate covalent bonds. During rapid laser heating, energy can flow between surface phonon modes of the substrate and the weak physisorption bonds between substrate and adsorbate, but a "bottleneck" occurs in the energy flow from these weak bonds to the strong, higher frequency chemical bonds in the adsorbate. In this model, desorbed species are expected to leave the substrate internally "cold" due to very little/no energy transfer to the bulk. Voumard et al. [20] have measured the rotational and vibrational temperatures of IR-desorbed
aniline molecules and found that these were significantly lower than the surface temperature at the time of desorption. This led to the conclusion that a "bottleneck" mechanism was in operation, due to the internally "cool" desorbed molecules.

More recently, evidence has been reported supporting a thermal equilibrium model in preference to the "bottleneck" model. In this interpretation of the desorption process, it is thought that it is possible to heat the substrate so fast that the adsorbate-substrate surface bond can be broken (desorption) before cleavage of the internal bonds of the adsorbate (decomposition) occurs. Typically, in the case of metal substrates, absorbed optical energy is converted into thermal energy within picoseconds and surface temperatures in excess of 1500 K can be reached on the time scale of the laser pulse duration [21]. This kinetic model requires the adsorbate-substrate system to be in complete equilibrium, where decomposition and desorption are competing channels for energy disposal. Maechling et al. [22] have shown that desorption of aniline-d7 from a sapphire surface occurs with the aniline molecules being in full equilibrium with the sapphire surface. This has been confirmed by Hundschuh et al. [23] who have recently measured the surface temperature and from this concluded that desorption of aniline could in fact be described by thermal equilibrium kinetics.

**Resonant Desorption**

This type of desorption involves the input of photons in resonance with a vibrational mode (IR excitation) or electronic state (UV excitation) of the surface or adsorbate under examination. The photoactive internal molecular vibrational mode usually has a much higher vibrational frequency than the modes directly associated with the molecule-surface bonds. A theory of laser-stimulated desorption of molecules via electronic excitation of adsorbates was proposed by Lin et al. [24]. They describe how the incident vibrational excitation energy can be transferred among the adsorbate molecules by vibrational-vibrational energy transfer and that, if in the initial photoexcitation step the molecule can be pumped to a high enough vibrational level, desorption can occur.
**Shock Wave Desorption**

In the shock wave model, rapid thermal expansion is thought to cause desorption of molecules by momentum transfer [25]. It is a mechanism applicable to extremely high heating rates of samples with a large penetration depth. This model was first proposed by Lindner and Seydel [26], who irradiated a quartz substrate coated with a saccharide with 266 nm light incident on the quartz side of the sample. Laser power densities of around $10^{11}$ W cm$^{-2}$ were employed, which caused heating rates of around $10^{11}$ K s$^{-1}$. This heating produced a shock wave which traversed from the rear of the solid surface and led to the desorption of intact molecules via vibrational disturbance of the binding potentials. This technique offered extremely soft ionisation conditions, i.e. very little fragmentation was observed, due to the high heating rate which meant there was not enough time for the molecules to absorb sufficient internal energy.

A mechanism similar to the shock wave model is that of mechanical desorption [27]. In this process, laser-induced inhomogeneous heating of thick samples produces thermal expansion, resulting in mechanical stress and disintegration of the sample with the ejection of molecules into the vapour phase.

### 2.5.4 Laser Desorption of Molecules in L2MS

In L2MS, desorption and ionisation steps are separate, so it is essential to desorb predominantly neutrals. The ratio of ions to neutrals produced during a laser desorption pulse is determined by the rapid jump in surface temperature. This ratio can be calculated to a first approximation by the Langmuir-Saha equation [28]:

$$\frac{n^+}{n^0} = \exp\left(\frac{W - I}{kT}\right)$$  \hspace{1cm} (2.25)

where $n^+$ is the number of ions, $n^0$ is the number of neutrals, $W$ is the work function of the substrate, $I$ is the ionisation energy of the sample molecules and $T$ is the surface temperature. This equation describes a gas phase equilibrium process between ions and neutrals, but has also been applied with some success to non-equilibrium systems. The surface temperature is dependent upon laser power density,
and so consequently, the ratio of ions to neutrals is also affected. Cotter [29] demonstrated that at laser power densities of $10^8 \text{ Wcm}^{-2}$, similar to those used in L2MS experiments, the ratio of ions to neutrals is as low as $10^{-5}$. At elevated power densities of around $10^9 \text{ Wcm}^{-2}$, this ratio has been reported to be as high as 0.01-0.1.

The common problem that many groups working in this field have experienced is the difficulty in obtaining a stable desorption signal. This has led to much experimentation on methods of presenting samples for analysis. Lubman’s group [30] and Grotemeyer’s group [31] initially both used relatively thick samples deposited from solution followed by evaporation. Lubman’s group then tried to use samples dispersed in a glycerol matrix to improve shot to shot stability. Zare’s group [32] have mostly used very thin layers deposited onto highly absorbing substrates such as glass, MACOR and quartz. Levy’s group [33] have used samples pressed into pellets doped with dye which absorbs very strongly at the desorption laser wavelength, before settling on thin films of approximately 10 µm thickness. More recently, Zenobi’s group [34] have attempted the quantitative analysis of PAHs by dissolving the sample in a mixture of THF and high molecular weight PVC, which, upon drying, forms a very thin membrane. All of the sample can be successfully desorbed with a single laser shot, so that a reproducible signal is obtained by moving the target. However, no definitive method of sample preparation has been reported that delivers a strong and stable signal over a long period of time.
2.5.5 Laser Ionisation

Ionisation Schemes

A number of laser photoionisation schemes can be employed and are summarised graphically in Figure 2.6. Ionisation can only occur when the energy of the incident photon(s) exceeds the ionisation energy (IE) of the atom/molecule. The IE of the type of organic, polyatomic molecules commonly studied by two-step laser mass spectrometry lies in the range 6-11 eV. The most direct ionisation scheme is single-photon ionisation (SPI) where one high-energy photon is sufficient to overcome the ionisation potential. Although this ionisation scheme is the simplest in principle, it is the most challenging experimentally. The energy of the photons, corresponding to a wavelength range 206-113 nm, is strongly absorbed by oxygen and water in the atmosphere, so that this radiation must be generated and propagated either under vacuum or in an inert gas atmosphere. Despite these constraints, the set-up and use of vacuum ultraviolet (VUV) laser sources have been successfully implemented [35].
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Figure 2.6: Laser ionisation schemes
A more practical consideration is the absorption of more than one photon to reach the ionisation energy of the molecule, a process known as Multi-Photon Ionisation (MPI). There are many types of commercially available laser sources for this type of ionisation scheme, e.g. Nd:YAG lasers whose fourth harmonic operates at 266 nm, or optically pumped dye lasers that can be tuned over a range of wavelengths in the UV and visible spectrum. These lasers can be operated in air, hence avoiding some of the practical difficulties associated with VUV laser sources. A multi-photon process can be characterised by the number of photons that are needed to reach the ionisation energy, referred to as the order of the MPI process. Furthermore, the multi-photon ionisation process can be boosted by choosing a laser wavelength that corresponds to the excitation of the molecule into an intermediate eigen state, followed by further photon absorption beyond the IE, in which case the technique is referred to as Resonantly Enhanced Multi-Photon Ionisation (REMPI). Alternatively, in non-resonant MPI, the ionisation occurs via absorption of a photon into internal energies where no stable state of the system can be found. A so-called "virtual state" is created, whose lifetime is determined by the uncertainty principle and is of the order of only a few femtoseconds. Considering the processes competing against ionisation at the intermediate state, described in the following section, the probability for the system to absorb a further photon is very low. On the other hand, in REMPI, the ionisation efficiency is much greater due to the longer lifetime of the real intermediate state. In Figure 2.6, several REMPI processes are illustrated. When ionisation occurs via absorption of one photon into an intermediate state, followed by further absorption of one photon into the ionisation continuum, the process is described as [1+1]. When a second laser is used for ionisation (a two colour two photon ionisation), the process is labelled [1+1']. Three photons processes are also possible, where two photons are absorbed to reach the intermediate state, followed by further absorption of one photon to ionise the system, a [2+1] REMPI process.

The most commonly used REMPI methodology is a two-photon resonant process [1+1]. In this case, one photon excites a molecule from the ground state to a singlet excited state, $S_1 \leftarrow S_0$. A second photon then ionises the molecule, provided that the
second photon has sufficient energy. For organic molecules with IEs between 6 and 11 eV, two photons with wavelengths in the UV range are required. The fourth harmonic of a Nd:YAG laser at 266 nm fulfils this requirement and was used in this work. Although this wavelength does not coincide precisely with specific molecular resonances, the ionisation process can still be considered resonant to some extent due to the high density of vibronic states available in the molecules studied. In practice, the requirement for a molecule to have a particular vibronic transition at the ionising laser wavelength can be relaxed to the necessity for the molecule to contain a UV chromophore at or around this wavelength. A chromophore is a functional group of the molecule, present in many molecules, giving rise to an absorption band at approximately the same wavelength. An aromatic group based on the benzene molecule is an example. Benzene has three major bands in the UV region of the spectrum [36], one of which is centred at 260 nm, resulting from transitions involving the π-electrons of the aromatic system. If the correct wavelength (within a few nm) is chosen, this molecule can, in principle, be efficiently ionised via a two-photon REMPI process.

Competing processes in REMPI

In REMPI, successive absorption of photons leads to excitation, ionisation, and eventually fragmentation at sufficiently high laser power. In all three events, there is a kinetic competition between further excitation in order to proceed to the next event, and one of several decay channels for the various excited state populations. In all cases, this competition seeks to minimise the molecule ion abundance. In general, excitation proceeds via the first excited singlet state of the molecule, $S_1$, which is usually the most accessible, and generally has the simplest spectroscopic features. At this intermediate state, various photophysical and photochemical processes may occur. These are illustrated schematically in Figure 2.7 and consist in the following: a) The excited molecule may absorb a second photon, resulting in its excitation above the IE. This is the desired outcome for maximum ionisation; b) The excited state may decompose to form a neutral fragment, which may then absorb a further photon to produce a fragment ion; c) The excited state may undergo inter-system crossing (ISC) to a triplet electronic state, which, in general, cannot be ionised by a
photon of the same energy; d) The excited intermediate state may decay via fluorescence on a timescale competing effectively against further photon absorption; e) Intramolecular rearrangement may occur, which can lead to products which may or may not be distinguishable from the molecule ion. Processes b) to d) all compete against the production of the molecule ion. It has been reported that the ionisation efficiency seems to drop off very rapidly for bigger molecules, typically of relative molecular mass above 2000 [37]. There are several possible reasons for this, one of which is efficient relaxation at the first excited intermediate state. In general, for most molecules studied by two-step laser mass spectrometry, vibronic states of the S₁ system do not dissociate and display relatively slow non-radiative relaxation processes. Thus, the predominant process following excitation to S₁ is further absorption by this state, leading to excitation into the ionisation continuum.
Figure 2.7: Competing processes at the intermediate state
The multi-photon process can be rationalised through the use of absorption rate equations according to time-dependent perturbation theory [13]. Considering a \((n + m)\) absorption process, the general stimulated emission or absorption rate constant is:

\[
\alpha = \sigma_i I^n
\]

Equation 2.26

and the ionising absorption rate is:

\[
\beta = \sigma_m I^m
\]

Equation 2.27

where \(\sigma_i\) is an \(i\)-photon absorption cross section and \(I\) is the light intensity or photon flux. In Figure 2.8, a \([1+1]\) photon absorption process is illustrated with the nomenclature used in the following equations. The rate equations for the depopulation of the neutral ground state \(A\), the population of the intermediate state \(B\), and the yield of ions \(C\) are:

\[
\frac{dA}{dt} = -\alpha A + (\alpha + k_r)B
\]

Equation 2.28.a

\[
\frac{dB}{dt} = \alpha A - (\alpha + k_r + k_{nr} + \beta)B
\]

Equation 2.28.b

\[
\frac{dC}{dt} = \beta B
\]

Equation 2.28.c

where \(k_r\) and \(k_{nr}\) are the rate constants of the intermediate state \(B\) for spontaneous emission and nonradiative decay processes, respectively. A general solution for these equations has been published [38]. Ion yields are derived from the calculation of cross sections. The rotational envelope of the absorption band being usually spread over several \(\text{cm}^{-1}\), compared with a laser bandwidth of typically 1 \(\text{cm}^{-1}\), reduces the number of molecules that can contribute to the ion yield. The rotational envelope can be narrowed down by the use of a supersonic molecular beam, inducing substantially higher ion yields. Saturation occurs at laser intensity \(I_{sat}\), when the processes \(\alpha\) and \(\beta\) are saturated. Using much higher laser intensities than \(I_{sat}\) will not increase the molecule ion yield, but lead to other multi-photon processes, e.g. fragmentation.
Figure 2.8: Schematic diagram showing absorption and emission rates during laser irradiation.
The generation of molecule ions by REMPI can be impaired by fragmentation in several ways. These were rationalised by Gedanken et al. in a classification scheme [39]. Firstly, if there exists a fast dissociation channel of the molecule at the intermediate state, such that this relaxation process is the kinetically favoured one, then only fragment ions will be observed in the mass spectrum. This is usually the case for inorganic and metallo-organic molecules. The other case when extensive fragmentation occurs is at high laser intensities, when sufficient energy is imparted to the molecule ion for it to dissociate. The most favourable fragmentation channel, however, depends on the probability of further photon absorption by the molecule ion, compared with the probability of other dissociative processes, which in turn depend on the rate constants at each energy level, the transition moments between these levels, as well as the laser intensity and pulse duration. This often leads to a mass spectrum with a complex structure. However, three borderline cases can be distinguished and are illustrated in Figure 2.9.
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a) Ladder switching Model

Molecule → Molecule ion → Fragment ions

Molecule

b) Molecule ion Model

c) Autoionisation Model

Molecule → Molecule ion → Fragment ions

Molecule

Figure 2.9: Fragmentation models
Firstly, if the dissociation probability is greater than the absorption probability on every ionic level involved, then further photon absorption will occur within the ladder of states of the fragment ion, until the dissociation threshold is reached and the process switches to another fragment, and so on, throughout the duration of the laser pulse. This is known as the “ladder switching model” which was first proposed by Boesl and Schlag [40]. It is predominant for aromatic molecules and other molecules with low lying excited states and occurs at relatively low laser intensity, with pulse length in the nanosecond range. In the second case, once the molecule has been ionised, the probability for further photon absorption by the molecule ion is greater than the probability for dissociation. It is known as the “molecule ion model”. This is the case with picosecond lasers of relatively high intensity, where the molecule ion is highly excited but dissociation is not fast enough to occur in the time range available. Thus further photons are absorbed on the molecule ion ladder, until eventually a range of fragments are formed. At even higher laser intensity, when the probability for photon absorption is much greater than the probability for either electron loss or dissociation, excitation occurs on the neutral ladder of the molecule, which enters a highly “super-excited” state. This is then followed by spontaneous production of fragment ions and is referred to as the “auto-ionisation model”.

Despite the efforts made to rationalise the fragmentation channels during an ionisation event, it is a challenging experiment to unravel the phenomena at play by ordinary mass spectrometry. The ability to separate the ionisation and the dissociation events in a tandem TOF/TOF-MS instrument, and to follow step by step the various pathways, seems a desirable proposition. This was recognised by Boesl and Schlag during the elaboration of the ladder-switching model for benzene, for which experiment they designed a TOF/TOF-MS instrument, further described in chapter 6.
References


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Chapter 3

Experimental

3.1 Introduction

The construction of the tandem time-of-flight mass spectrometer follows a long history of instrument development in the area of laser desorption/ionisation mass spectrometry at Edinburgh.

The area of interest was initially the study of metal clusters produced using laser vaporisation, for which an instrument was purpose-built [1]. It consisted of a molecular beam chamber, an ionisation chamber and a linear time-of-flight mass analyser placed at right angles to the molecular beam.

The research emphasis then turned to laser desorption/ionisation of large organic molecules. These were desorbed from a metal substrate and entrained in the molecular beam, which carried them through to the ionisation chamber. Substantial instrumental development followed. A new mass spectrometer was built, which incorporated a reflecting field time-of-flight mass analyser placed collinear with the molecular beam. It emerged that greater sensitivity could be obtained by dispensing with the molecular beam, so laser desorption was then carried out directly in the ionisation chamber. The technique, coined two-step laser mass spectrometry (L2MS), has since been used in many analytical and fundamental studies.
Another direction of the work at Edinburgh was the development of laser mass microscopy, where the objective was to perform spatially resolved analysis. Yet another new instrument was developed that allowed accurate positioning of a tightly focused laser beam for the desorption stage.

A further development of L2MS was the extension to enable tandem mass spectrometric analysis. Instead of building a completely new instrument, the original molecular beam mass spectrometer mentioned above was used as the starting point. The benefit of doing such a conversion was that previous work on metal clusters could be revived and new avenues of research opened with tandem time-of-flight mass spectrometry.

This chapter describes the experimental set-up used for tandem mass spectrometric analysis. Details of the vacuum system, lasers, ion optics, ion signal detection, experimental control and data acquisition are given in the following sections.

### 3.2 Vacuum System

The system consisted of three chambers and two drift regions, which were differentially pumped to a high vacuum. All elements were constructed from 304 stainless steel except where stated otherwise. A schematic diagram of the system is shown in Figure 3.1 and a photograph of the actual system is shown in Figure 3.2.
Figure 3.1: Schematic diagram of the TOF/TOF mass spectrometer.

Figure 3.2: Photograph of the TOF/TOF mass spectrometer.
The molecular beam chamber (MB) consisted of a cube with external dimensions 63.5 x 37 x 37 cm, a total internal volume of 76 l. Two rectangular aluminium flanges, 40 x 20 cm, were mounted at each side to allow easy access to the inside of the chamber. Circular holes (32 mm dia.) were machined in these flanges to allow passage of laser beams. They were fitted with either NaCl or quartz windows (50 mm dia.) depending on the laser wavelength required. The windows were held on with PTFE clamps and sealed onto the flange with Viton O-rings. Another two holes (10.5 cm dia.), fitted with transparent PET windows (13.5 cm dia.), were machined in the flanges for visual control of the experiment. A circular aluminium flange (36 cm dia.) was mounted on the left hand side, to which an electrical feedthrough and a gas inlet were attached.

The chamber was evacuated by an oil diffusion pumped (CVC, Model PBA1000) equipped with a half-chevron water-cooled baffle. The pump had an enlarged casing (inlet flange 18" O.D.), designed for extremely fast pumping speed: approximately 2600 l/s at the baffle inlet. In order to handle large gas throughput, the diffusion pump was backed by a mechanical booster/rotary pump combination (Edwards EH250/ E2M40) capable of a pumping speed of 66 l/s at a typical foreline pressure of 0.3 mbar for air. The pressure was monitored by a Pirani (Edwards, PRE10K) and a Penning (Edwards, CP25K) pressure gauge that were positioned at the top of the MB chamber and connected to medium vacuum (Edwards, Pirani 502) and high vacuum (Edwards, Penning 505) controllers, respectively.

A pneumatic gate valve (Vacuum Research Company) separated the diffusion pump and the MB chamber. A second pneumatic gate valve (Airco Temescal, 5230) was placed in the foreline. It was thus possible to bring the chamber to atmosphere by isolating the diffusion pump momentarily without having to switch it off and let it cool down. The chamber could be pumped down quickly to medium vacuum through a roughing line connected to the booster/rotary pump, before opening the pneumatic gate valves to the diffusion pump. A speedivalve (Edwards) and a tee-piece were used to shut off the roughing line and to let the booster/rotary pump back the diffusion pump via the foreline. Finally, a skimmer, built in-house, was fixed to the
right hand internal side of the chamber, through which the molecular beam entered
the second chamber.

The laser desorption/ionisation chamber (L2) consisted of a cube (dimension 28.5
cm) with an internal volume of 19 l. It was separated from the MB chamber and the
linear TOFMS by two gate valves (VAT, Series 08) with pneumatic actuators. The
front, back and top sides of the chamber were fitted with circular flanges (28 cm
dia.). The top flange had a hole (32 mm dia.) in the middle to accommodate a NaCl
window (Specac, 50 mm dia.) through which the infrared desorption laser was
directed. The front flange was similarly fitted with a fused silica window (Comar, 50
mm dia.) to allow passage of the ionisation laser beam. It was also fitted with four
high voltage feedthroughs for the ion optics. On the back flange was mounted a
movable sample probe, which is described in Section 3.4. The chamber was
evacuated by an oil diffusion pump (Edwards, E09), fitted with a water-cooled
baffle, capable of a pumping speed of 2500 l s$^{-1}$. It was backed by a two-stage rotary
pump (Edwards, E2M18). The pressure in the chamber was measured with a Pirani
(Balzers, TPR010) and a cold cathode (Balzers, IKR020) pressure gauge connected
to a controller (Balzers, PKG100). The base pressure in the chamber was typically
2\times10^{-6}$ mbar.

The linear drift region (TOF 1), the interaction chamber (IC) and the reflectron
mass analyser (ReTOF 2) were all evacuated together. The TOF 1 region was
constructed from standard ISO 160 components: an ISO 160 tee-piece followed by
an ISO 160 four-way cross, followed by a second ISO 160 tee-piece. This modular
approach allowed some flexibility over the configuration of the instrument. For
instance, the electronic mass gate, which was mounted on a side flange of the ISO
160 four-way cross, could be placed at three different positions. The (IC) chamber
was of similar dimensions to the (L2) chamber, a cube (dimension 28.5 cm), with
two circular flanges (28 cm dia.) on both sides. These were fitted with fused silica
windows (Specac, 50 mm dia.) at the centre to allow in the photodissociation laser
beam. On the rear side of the chamber was a similar size circular flange to which was
fitted a gate valve with pneumatic actuator (VAT, Series 08), This separated the
vacuum chamber from the (TOF 1) detector. This was a dual micro-channel plate
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detector (R.M. Jordan, C-701 18mm) mounted on a 6" conflat flange. On top of this chamber was mounted the reflectron mass analyser (R.M. Jordan, D-850 AREF). Together with the (TOF1) and (IC) chamber, the total volume evacuated was 70 l. This was achieved using an oil diffusion pump (Edwards, Diffstack 160) situated below the (IC) chamber. The diffusion pump was equipped with a liquid N\textsubscript{2} cooled baffle, and backed by a rotary pump (Edwards, E2M18) with a pumping speed of 250 l s\textsuperscript{-1}. A turbo molecular pump (Edwards, EXT250) was also mounted on an ISO 100 conflat side flange halfway along the reflectron analyser. This was backed by a second rotary pump (Edwards, E2M18). A gate valve with pneumatic actuator (VAT, Series 11) separated the diffusion pump from the vacuum chamber. It was usually closed during standby, and open when carrying out experiments to provide more efficient pumping of sample residues. A Pirani and a cold cathode pressure gauge (Balzers, TPR010, IKR020) were mounted on a KF40 flange at the lower side of the (IC) chamber. Additionally, a second cold cathode gauge (Balzers, IKR050) was mounted on a DN 40 conflat flange opposite the turbo molecular pump, and a Pirani gauge (Balzers, TPR010) was placed on the foreline of the diffusion pump. The pressures were all monitored by the single vacuum gauge controller (Balzers, PKG100). The base pressure was typically 5x10\textsuperscript{-7} mbar.

3.3 Laser Systems

A total of three lasers were required to perform the tandem TOF L2MS experiments. Firstly, an infrared laser was needed for desorption of involatile organic molecules. Subsequent ionisation required the use of a laser radiation in the UV, and when photodissociation was induced, a third laser, also in the UV, was needed. Sample desorption was achieved using the CO\textsubscript{2} laser described below. Various makes and models of Nd:YAG lasers were used for photoionisation and photodissociation, depending on the availability of the systems in the laboratory at the time of the experiments. A brief description of these laser systems is given below.
3.3.1 Altec 861 CO₂ Laser

The laser system used for desorption experiments was a transverse excitation atmospheric (TEA) CO₂ laser. It was capable of generating 100 ns pulses of 10.6 µm radiation at a maximum repetition rate of 30 Hz. Using a gas mixture of 12% CO₂, 4% CO and a balance of He, the laser was capable of producing an output of 400 mJ/pulse. During the experiments described here, the laser was operated at 10 Hz with typical output pulse energies of about 100 mJ or less, as measured by a Gentec power meter (Model ED 100, 10 mV/mJ) attached to an oscilloscope.

The CO₂ laser was triggered externally with a TTL pulse of 5 V amplitude and 50 µs width. The laser beam was directed into the desorption chamber by two gold plated mirrors, and focused onto the sample target using a 30 cm focal length NaCl lens mounted on the top of the (L2) chamber. Adjustment of the beam energy was achieved by closing or opening an iris positioned in the path of the beam. Using this arrangement, typical power densities of 6-10 x 10⁶ Wcm⁻² were obtained for desorption spot sizes of 1 - 2 mm dia.

3.3.2 Quantel Brilliant Q-switched Nd:YAG Laser

The Quantel Brilliant laser could be used either for photoionisation of desorbed species in the L2MS experiments or for photodissociation of selected ions in the tandem TOF experiments. The Brilliant is a compact Nd:YAG laser consisting of a power supply and cooling group cabinet, connected by an umbilical to a modular optical head. It can generate the fundamental Nd:YAG wavelength at 1064 nm or the harmonics (532 nm, 355nm, 266 nm) at a repetition rate of either 10 Hz or 20 Hz. Harmonic generation is achieved using KDP (Potassium Dihydrogen Phosphate) crystals contained in sealed-off cells to ensure long term energy stability. Each crystal is mounted in a separate module, which can be easily plugged into the optical head with no alignment required. The 2nd and 3rd harmonic generators are phase-matched by precise mechanical positioning, while the 4th harmonic generator is temperature phase-matched. The appropriate harmonic wavelength is isolated using a set of dichroic mirrors contained in each respective module. The Brilliant laser has
output specifications of 360 mJ, 180 mJ, 65 mJ and 40 mJ per pulse for the fundamental, 2nd, 3rd and 4th harmonic wavelengths, respectively.

Only the 4th harmonic of the laser was used in the experiments carried out in the present work. The laser was run at a repetition rate of 10 Hz, in both internal and external mode. To control the laser externally, two TTL pulses (5 V amplitude, 50 µs width) were required to trigger the flashlamp and the Q-switch. The output beam was guided into the apparatus using 45° quartz prisms.

### 3.3.2 Continuum Surelite II Nd:YAG Laser

The Continuum Surelite II laser is very similar to the Quantel Brilliant, and was used for the same purpose, particularly during a long spell when the Brilliant was away for repairs at the manufacturer. The Surelite II also consists of a compact power supply and cooling group connected to the optical head by an umbilical. The laser head houses the optical components necessary to generate the Nd:YAG fundamental wavelength at 1064 nm and the harmonics at 532 nm, 355 nm, and 266 nm. A separate module contains the wavelength separation optics, consisting of sets of dichroic mirrors, was used to isolate each harmonic wavelength as required. The output specifications at 10 Hz are 650 mJ, 300 mJ, 100/150 mJ and 70 mJ for the fundamental, 2nd, 3rd and 4th harmonic wavelengths, respectively.

This laser was used in a similar fashion to the Brilliant and controlled externally by two TTL pulses (5 V amplitude, 50 µs width). The output beam was guided into the apparatus using 45° quartz prisms.

### 3.3.3 Quantel YG 581-C Nd:YAG Laser

This earlier model of Quantel laser was used occasionally for photoionisation when the other lasers were not available. It is also a Q-switched Nd:YAG laser, which can generate the Nd:YAG fundamental wavelength at 1064 nm or the harmonics at 532 nm, 355 nm, and 266 nm. It is equipped with a 9.52 mm (3/8") diameter amplifier pumped by four flashlamps in a close coupled configuration. The harmonic generators consist of KDP crystals. Each wavelength is isolated by a set of dichroic mirrors on rotatable mounts.
Measured maximum output pulse energies were 440 mJ and 200 mJ for the 2nd and 3rd harmonics, respectively. The 4th harmonic generator was situated outside the laser head and was not temperature controlled. This resulted in some instability of the output energy at 266 nm. A x4 telescope was used to narrow the beam size down from 16 mm to 4 mm, to increase the power density. A UG5 filter was used to isolate the residual 2nd radiation from the 4th harmonic output. A repetition rate of 10 Hz was used throughout, and the laser was operated only in internal mode as the external triggering was not functioning.

3.3.5 JK HyperYAG HY750 Laser

The final system available in the laboratory for use as a photionisatooon laser was the JK HY750, another pulsed Q-switched Nd:YAG laser. This laser could generate the Nd:YAG fundamental wavelength at 1064 nm or its harmonics 532 nm, 355 nm, and 266 nm. The laser can produce an optimised output pulse energy of 800 mJ, 320 mJ, 170 mJ and 70 mJ at the fundamental, 2nd, 3rd and 4th harmonic wavelengths respectively. The harmonics are generated using CDA and KDP crystals, and separated using Pellin Broca prisms.

Two TTL pulses (5 V amplitude, 50 μs width) are required to control the laser externally, with an optimised delay of 185 μs between firing the flashlamps and the Q-switch. A succession of dichroic mirrors or 45° quartz prisms was used to direct the laser beam into the apparatus.

3.4 L2MS Source

The L2MS source was similar to the one used by Dale [2]. The desorption laser (Alltec 861 CO₂) was steered into the (L2) chamber through a NaCl window mounted on the top flange of the chamber. The laser beam was directed at the mid-point between the repeller and draw-out electrodes, where the sample probe was situated. To allow rapid change over of sample, without having to vent the chamber to atmosphere and evacuate again to a high vacuum, the sample probe was introduced through a load lock mounted on one of the side flanges, as shown in
Figure 3.3. The load lock consisted of an NW 40 cross followed by a manual gate valve (VAT, Series 12), which was attached to a sliding base-plate, clamped to the side flange. The base-plate can be moved manually in the X and Y directions to enable precise positioning of the sample probe between the ion extraction optics. The sample probe consisted of a stainless steel bar (4 x 5 x 90 mm) with three stubs pointing upwards (4 x 4 x 22 mm) spaced approximately 16 mm apart. The sample of interest was deposited from solution directly onto one of the 0.16 cm$^2$ stubs and allowed to evaporate. It was found that the stubs perturbed the electrostatic field between the repeller and draw-out electrodes. To remedy this, the sample probe was floated at a potential between that of the repeller and the draw-out electrode. The sample probe was isolated by a nylon insulator wedged into the cylindrical tube that slid in and out of the load lock. A screw mechanism allowed the tube to be moved in small increments whilst mounted on the chamber, so that fresh parts of the sample could be exposed to the desorbing laser.
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Figure 3.3: Schematic diagram of the sample load lock
The ionisation laser beam (e.g. 266 nm harmonic of Nd:YAG laser) was steered into the (L2) chamber through a 50 mm quartz window mounted on the flange opposite the one holding the load lock. The beam was aligned so that it travelled between the ion extraction optics and across the plume of desorbed species, a few millimetres above the sample stub.

### 3.5 Time-of-Flight Ion Optics

The tandem mass spectrometer consisted of a linear analyser followed by an orthogonal reflectron time-of-flight mass analyser. Most of the ion optics used in the tandem instrument were, therefore, similar to those used in either individual analyser. Some additional elements were designed and built to select, retard and steer the ions into the second time-of-flight analyser.

The extraction optics in the linear instrument were of a Wiley-McLaren type [3], consisting of a repeller, a draw-out and a flight electrode. They were built in-house following a successful design tested by Costello [4]. A schematic diagram of the optics is shown in Figure 3.4. The electrodes were made out of gold-coated square aluminium plates (dimension 80 mm, 1.5 mm thic). The repeller plate had a 8 mm dia. hole in its centre to admit a molecular beam into the ion source region. The draw-out and flight electrodes had a 30 mm dia. hole in their centre, onto which was laid a fine nickel mesh (Buckbee Mears, 90% transmission) to keep a homogeneous electrostatic field between the plates. Silver conducting paint (Radio Spares) was used to fix the mesh onto the aluminium plates. The plates were held in position by four alumina tubes (5.3 mm O.D., 2.8 mm I.D.) that were slip-fitted at each corner. The distance between the plates was set using Delrin spacers (10 mm O.D., 6 mm I.D.) of the desired length. A 2 mm dia. threaded stainless steel rod was slid along the inside of the alumina tubes, and used to fix the optics onto square frames at both ends. The frames were attached to a stainless steel base plate which rested on a dual rail system, allowing precise positioning of the optics. The whole assembly could be translated along the axis of the spectrometer and clamped into position at the desired location. To steer the ions, a set of horizontal and vertical deflection plates was
mounted onto the main frame. [Gold plated, L-section plates. They were mounted onto a small frame, in similar fashion to the accelerating plates, by alumina tubes, Delrin spacers and a threaded rod. This small frame had the same dimensions as the accelerating plates and could thus be easily mounted onto the main frame and placed at the correct distance with the aid of Delrin spacers. It could also be easily replaced by another, similar, frame that held an einzel lens.
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Figure 3.4: Extraction optics used in the L2MS source. (Dimensions in mm).
Some way along in the first drift region was mounted a mass gating device to enable mass selection of a precursor ion. This was the subject of much development work, which is described in Chapter 5. A detailed description of the mass gate that was developed is given there.

The ion optics located in the interaction chamber, at the intersection between the two time-of-flight regions (TOF1 and ReTOF2), also consisted of extraction optics of a Wiley-McLaren type. The idea was to retard the ions coming from the TOF1 region so that they would slowly enter the area between the repeller and the draw-out electrode of the interaction region. The photodissociation laser and the repeller electrode would then be triggered, almost simultaneously, in order to induce dissociation to the chosen ions. Immediately after, the fragment ions would be pulse-accelerated into the ReTOF2. The "re-acceleration" optics were constructed using the same basic elements as for the extraction optics situated in the (L2) chamber, although the distances between the plates were slightly different, as indicated in Figure 3.5. The extraction optics assembly was fixed onto a stainless steel base plate under the repeller electrode, and the base plate clamped onto a dual rail in the same way as was done in the (L2) chamber.
Figure 3.5: Re-acceleration optics situated in the interaction region of the tandem mass spectrometer. (Dimensions in mm).
In addition to the extraction optics, a set of retardation optics was fitted in the interaction chamber. These consisted of two aluminium plates with a 30 mm dia. hole in the centre, covered by nickel mesh. The aim was to have one plate held to ground potential, that would mark the end of the TOF1 drift region. The second plate would be set at the potential of the draw-out electrode, which would also be the floating potential of the repeller electrode. During tests, it was found that the optics performed best with the two electrodes at ground potential. Modelling of the interaction optics provided an insight into this phenomenon, as discussed in Chapter 4. The retardation plates were constructed using the same basic elements as for the extraction optics situated in the (L2) chamber. Separated 15 mm apart, they were mounted onto a frame, which was fixed onto a stainless steel base plate resting on the dual rail system. A perspective of the complete set of optics, obtained with SIMION, is shown in Figure 3.6.
Figure 3.6: Ion optics used in the interaction chamber, showing the configuration of the electrodes. The trajectory of an ion moving through the optics calculated using SIMION is also shown.
The reflectron mass analyser was purchased from RM Jordan, Grass Valley, CA, USA (Model D-850AREF); an engineering diagram of the analyser is shown in Figure 3.7. The dual reflectron optics consist of a series of rings over a total distance of 110 mm. The front ring is covered with a grid made of fine nickel mesh (Buckbee Mears, 90% transmission) and is connected to ground. Between the first and the second ring, also covered with a grid and connected to voltage R1, is the first, retarding stage of the reflectron. The back plate was set at voltage R2, and is separated from R1 by 20 guard rings interconnected by resistors. This produces a homogeneous field in the second, reflecting part of the reflectron. Typical voltages for R1, R2 and all the others ion optics are listed in Table 3.1.
Figure 3.7: Diagram of the reflectron time of flight mass analyser (R.Mm Jordan, Model D-850AREF).
Table 3.1: Typical voltages applied to the ion optics.
Some additional optics were used occasionally, notably in the cluster experiments. In order to enhance sensitivity, two einzel lenses were fitted in the linear TOF1 analyser. Since the ion beam was well aligned along the axis leading to the MCP detector, the deflection plates situated in the (L2) chamber were redundant and could be replaced by the first einzel lens. This lens consisted of three cylindrical elements (35 mm O.D., 30 mm I.D.) of length 14 mm, separated by 3.5 mm. The lens was assembled in the same way as for the deflection plates onto a small frame that fitted onto the extraction optics assembly. A second einzel lens was built in much the same way, except that its frame was attached to a base plate so that the lens was free standing on the dual rail system. This einzel lens was situated in the (IC) chamber. A simulation of the effect of these einzel lenses is given Chapter 4. Finally, an ion buncher was developed. It was hoped that this would reduce the ion packet width at the laser photodissociation point, thus enhancing the yield into the ReTOF2 spectrometer. The buncher was built by simply adding a plate to the retardation optics. This could be easily done, given the modular nature of the construction of the optics, by adding Delrin spacers of the required length.
3.6 Ion Signal Detection

Detection of ions was achieved using dual micro-channel plates (MCP). These were made by Galileo Corp., Sturbridge, MA, USA, and purchased from R.M. Jordan, Grass Valley, CA, USA, who built the whole detector assembly mounted on a 6" Conflat flange.

Micro-channel plates consist of an array of small glass tubes, typically 10 \mu m in diameter and 1 mm in length, stacked together. The dual, chevron type MCP has two plates back to back, with the micro-tubes at an angle to suppress ionic feedback at high gain. The MCP for the linear TOF1 analyser was a Model C-701, with 18 mm dia. plates, and the one for the ReTOF2 analyser was a Model C-726, with 40 mm dia. plates, and thus a larger active area. Both models had a gain of $10^3$ at the maximum voltage of 1000V across each plate, and a gain of $10^2$ at the typical operating voltage of 700 V.

In order to detect positive ions the MCP's were operated in grounded anode mode. The front plates were set at a high negative voltage, typically -3800 V. A dividing circuit between the power supply and the MCP's ensured that the voltage across each plate was evenly distributed and did not exceed the maximum voltage of 1000 V.

3.7 Experimental Control

The operation of the desorption/ionisation lasers, mass gate and pulsed extraction optics required a precise timing sequence of suitable trigger pulses. Several pulse delay generators were available to supply the appropriate trigger signals.

A system of CAMAC (Computer Automated Measurement and Control) modules [5], controlled by in-house software, had been developed previously for experimental control and data acquisition. The computer programs were written by Butler [6] using the C high level programming language and were run on a DELL System 325 computer. Some of these CAMAC modules were used for experimental control. One such module was a CAMAC-based 8 channel pulsed delay generator (Kinetic
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Systems, Model 3655), which was capable of producing 200 ns FWHM TTL pulses with microsecond accuracy. These pulses were boosted via a custom-built line driver, housed in a NIM bin, to produce signal outputs of amplitude 5 V or 15 V, with a width of 10 µs or 50 µs, which were the required levels for external triggering of most of the equipment. Timing settings were entered via the computer keyboard and could be saved in configuration files, so that an experimental set-up could be recalled when desired. However, microsecond accuracy was not sufficient for some of the applications, notably the timing of the photodissociation laser and the pulsed extraction of ions into the second time of flight region. This CAMAC based system could be used in conjunction with the more recent and accurate stand-alone pulse delay generators described below.

Two commercial digital pulse delay generators were also used (Stanford Research Systems, Model DG535; EG&G, Model 9650A). Although these differ slightly in their operation, they can both be triggered either internally or externally (e.g. from the CAMAC system) and produce timing signals accurate to 1 nanosecond with a great degree of flexibility. The Stanford PDG has four delay outputs: A, B, C, D, switching from 0 to 5 V TTL. These can be combined to produce pulse outputs AB, CD, -AB, -CD, which are not independent. In comparison the EG&G PDG has four independent delay outputs, which were more flexible, with output levels selectable between 5 V TTL or 15 V, and a pulse widths adjustable with a screwdriver from 30 ns to 1 ms.

A typical experimental control set-up is shown schematically in Figure 3.8, and the corresponding timing sequences for the required trigger pulses in Figure 3.9.
Figure 3.8: Schematic diagram of a typical experimental control set up for experiments on the photodissociation of aniline
Figure 3.9: Timing sequence of trigger pulses for experiments on the photodissociation of aniline.
3.9 Data Acquisition

A four-channel, 500MHz, digital storage oscilloscope (LeCroy, Model 9344) was used both to monitor the timing sequences and to record the signals coming from the MCP detectors. The effect of changing the experimental parameters on the signal at the detector could be visualised in real time on the oscilloscope. This offered tremendous convenience for optimisation of the experimental conditions.

Spectra of interest were recorded onto 3.5" floppy disks in a binary format. To allow this data to be processed into ASCII format an application called wavetrans.exe was used to convert the data into a useable *.txt file. Although LeCroy supplied the option of saving a spectrum in the standard ASCII format, this method was memory intensive and, therefore, not suited to the storage of large numbers of data files. The ASCII data was imported into a technical graphics and data analysis software package (Microcal Software Inc., Origin 5.0) to generate time-of-flight mass spectra.
References


Chapter 4

SIMION: A Computer Program for Ion Trajectory Simulations

4.1 Introduction

As opposed to light optics, which can be readily tested on a bench using a visible wavelength, ion optics can only be evaluated by end to end measurements, since the ion path is invisible and enclosed in stainless steel vacuum chambers. Modelling of electrostatic fields has been attempted with rubber-sheets. These are stretched between electrodes where electrode height represents electrostatic potential. They can give good insight into the behaviour of ions in electrostatic fields. For example, the motion of an ion accelerated between two grids can be represented as a ball rolling down a slope. However, although rubber-sheet models help provide visual insight, they are not accurate representations because the forces on the ball are proportional to the sine of the slope rather than the tangent of the slope needed in electrostatic field gradients. Moreover, they are rather difficult to build. SIMION 3D Version 6 [1,2] is a computer program designed to simulate ion optics and to visualise the trajectories of ions flying through them under the influence of
electrostatic or magnetic fields. Much like a virtual rubber-sheet model, it is designed to promote intuition and understanding. In this work, only electrostatic fields were used, so the description is limited to those. It is, however, straightforward to apply the features of SIMION to magnetic optics problems.

SIMION uses 2D symmetrical and 3D asymmetrical potential arrays to model the ion optics. The electrodes are marked as electrode points in the array, and the program calculates the potential at all other non-electrode points. One or more potential arrays, each representing a particular set of optics, are then projected and positioned into an ion workbench volume, which can be sized up to 8 km³ (more than enough to accommodate an entire instrument!). There the optics can be viewed from different angles in 2D and 3D. SIMION then calculates the trajectory of the ions, depending on the parameters entered by the user, such as the ion’s initial starting position, initial kinetic energy, mass, charge, etc. A variety of ion optic problems can thus be simulated, particularly in time-of-flight instruments. The author of SIMION has used the program to design a modular ion beam deflector [3], and a univoltage ion gun for secondary ion mass spectrometry (SIMS) [4]. Other simulations include extraction optics [5,6], deceleration lenses [7] and a transit detector [8]. In this Chapter a brief description of the use of SIMION for calculating ion trajectories is given by explaining the theory behind the simulations and by providing a few practical examples.

4.2 Computational Methods

4.2.1 Calculation of Voltages in the Potential Array

The ion optics are marked in the potential array as electrode points. The voltages of these electrodes are entered and adjusted manually. The objective of SIMION is to estimate the voltages of the points within the array that are non-electrode points, so that the electrostatic fields can be defined everywhere.

Electrostatic fields can be modelled as boundary problem solutions of an elliptical differential equation called the Laplace equation:
\[ \nabla^2 V = \nabla \cdot E = \frac{dE_x}{dx} + \frac{dE_y}{dy} + \frac{dE_z}{dz} = 0 \]  

SIMION solves this equation using a finite difference technique called over-relaxation. Relaxation techniques are iterative, and the solution is reached after successive approximations. Here, the method uses nearest points to obtain new estimates for each point. As shown below, the four nearest points are used for 2D arrays:

\[
\begin{align*}
V_4 & \\
V_1 & V_0 & V_2 \\
V_3 &
\end{align*}
\]

Similarly, the six nearest points are used for 3D arrays. The potential of the centre point is calculated from the average value of its neighbours using the following equations:

2D arrays: 
\[ P_{0\text{new}} = \frac{P_1 + P_2 + P_3 + P_4}{4} \]  

3D arrays: 
\[ P_{0\text{new}} = \frac{P_1 + P_2 + P_3 + P_4 + P_5 + P_6}{6} \]

Once the potential at each point has been calculated using these equations, the potential array is scanned again and the value for each point is re-calculated. After a number of iterations, the value changes less and less, until the difference between successive values reaches the pre-defined convergence limit and the process is stopped. The potential array is fully relaxed or refined to the desired level of approximation.

In order to reduce the number of iterations and speed up the computation, SIMION introduces a dynamically self-adjusting over-relaxation factor. Each voltage adjustment is increased by this factor, which is normally 0.9, added to the simple
relaxation of 1. However, the ideal over-relaxation factor, the one that gives the fastest solution convergence, differs from one array to the next. SIMION adjusts the over-relaxation factor dynamically, using the maximum single point absolute voltage change to drive the factor, and a history factor to limit the dynamic rate of change.

SIMION uses a skipped point technique to further speed up the refining process. The approach is to initially refine a smaller array by skipping points, estimate the values of intermediate points (double the array density), then refine again. The time taken to refine the potential array becomes proportional to the number of points \( n \) in the array, as opposed to \( n^2 \) for the normal finite difference technique. Skipping of electrode points is compensated for by scanning the array and by flagging these special points at each level of refining. They are subsequently taken into account in the refining process.

Another very useful feature of SIMION is the fast voltage adjustment method. It enables the user to "fast adjust" the potential on each electrode during simulations, without having to refine the potential array every time. The method uses the additive property of the Laplace equation, which allows separate solutions for each boundary to be combined in a simple scaling/additive process. In this case, a potential array is created for each electrode (boundary) during the refining process. This array represents the specific solution for the effect of that electrode with a selected voltage, and is saved in a reference file. SIMION includes an additional potential array, the base array. The fast adjustment method works by using each reference electrode potential array file and a scaling factor to change the non-electrode point voltages in the base potential array.

4.2.2 Trajectory Calculations

In the refined potential array, the electrostatic forces can be determined for an ion located at any position. SIMION calculates these forces in terms of volts per grid unit, depending on the ion's current position and velocity. Calculations are made using linear interpolation with some corrections for electrode boundaries. The ion's current acceleration is derived directly from the force. These parameters are then used to calculate the ion's position and velocity at the next time step. SIMION uses a
standard fourth order Runge-Kutta method for this. It performs a numerical
integration of the ion’s trajectory in three dimensions. In order to minimise the
number of integration steps while maintaining accuracy, SIMION uses a self-
adjusting time step method. Large time steps are adequate in regions of the potential
array where voltage gradients are linear, but a small time step is necessary in other
areas of high gradient change. Several algorithms are present to allow for such events
as hitting an electrode or grid boundaries, velocity reversals and high field curvature.

4.2.3 Limitations

SIMION’s use of the Laplace equation constrains all electrostatic and magnetic
potential fields to conform to a zero charge volume density assumption. This means
that no space charge effects are taken into account in the estimation of the potential
fields. In order to compensate for this, SIMION supports three estimates of charge
repulsion: beam, coulombic and factor repulsion. This feature was not tested in the
present work but could be of interest to study the effect of space charge effects.

The accuracy of the simulations depends on the validity of the potential fields
estimated for each potential array. This in turns is dependent on the density of the
array; that is whether a coarse or a fine grid is used. The finer the grid the better the
simulation, but the more demanding it is on computer power. Therefore, it is
beneficial to make use of the symmetry options of the program, described in the
following Section, in order to maintain accurate simulations while keeping the
computer memory consumption low.

4.3 Some Practical Simulations

In order to illustrate the features and capabilities of SIMION, some simple ion
optics commonly used in time-of-flight mass spectrometry have been modelled.
Acceleration optics, steering optics and focusing lenses are taken as examples in the
following topics.
4.3.1 The Potential Array

The geometry of the ion optics is entered into a potential array using the *new* or *modify* function of SIMION. Each point in the array has a potential (e.g. voltage) and a type (e.g. electrode or non-electrode). Electrode points create the boundary conditions for the array and mark the shape of the ion optics. Potential arrays can be quite large. For example, a 3D array with a section of 100 points consists of one million points. Since each point uses 10 bytes of computer active memory (RAM), this simple array would need 10 megabytes of RAM. Large ion optics of complex geometry would soon become too cumbersome for simulation. Fortunately, SIMION uses the symmetry of the optics to reduce the potential array size.

An Einzel lens, used to focus an ion beam, has an axis of symmetry through the centre of its three cylindrical elements. It can be created in a 2D cylindrical array, which reduces considerably the number of points needed. As shown in Figure 4.1(a), the array of size (91x, 20y, 1z) contains blackened areas marking the half cross section of the Einzel lens. SIMION takes the symmetry into account when refining arrays and projecting them into the workbench volume. Figure 4.1(b) shows the Einzel lens projected as a surface of revolution about the X-axis to give an isometric 3D image.

Planar and mirror symmetries are also supported in SIMION. For example, Figure 4.2 shows a set of deflection plates entered in a 2D potential array with mirror symmetry about the X-axis. The size of the array is (81, 161, 1) but could be considerably less. Extra points in the X and Y direction were taken in this case to study the field penetration for these particular ion optics. For refining purposes, it is assumed that the array is only one layer of an infinite number of layers along the Z-axis. When projected into the workbench volume as an instance (see Section 4.3.2 below), the same number of points are taken along the Z-axis as for the Y-axis. Thus, in Figure 4.2, the deflection plates appear more elongated than real optics in the Z direction. However, this is not critical for trajectory simulations, since the ion beam travels along the X-axis and is deflected in the XY plane.
More complex ion optics have to be entered in a 3D potential array, despite the penalty in computer memory. The electrode points are obtained by highlighting points in two different planes, e.g. XY and YZ, and the intersection of the selected points are blackened as electrode points. This can be quite tricky to do, but fortunately it is possible to see the results of your actions in a 3D isometric view. Figure 4.3 shows a 2D and a 3D representation of the modify function of the ion optics used in the interaction chamber of the tandem time-of-flight mass spectrometer. Despite the relative complexity of the ion optics, they have a mirror symmetry about the Y-axis, which reduces the potential array size by half.

Once the potential array has been defined, it is refined in the manner described in Section 4.2.1.
Figure 4.1: SIMION diagrams showing: a) the modify function used to enter the geometry of the Einzel lens with cylindrical symmetry, b) a 3D isometric view of the Einzel lens.
Figure 4.2: SIMION diagram showing: a) the modify function used to enter the geometry of the deflection plates with planar and mirror symmetry, b) a 3D isometric view of the deflection plates.
Figure 4.3: SIMION diagram showing: a) the ion optics entered in the modify function in 3D with a mirror symmetry about the Y-axis, b) the same ion optics as seen in the workbench view.
4.3.2 The Ion Optics Workbench

In order to visualise the simulations, SIMION incorporates the concept of an ion optics workbench. The workbench is an imaginary volume that can be sized up to 8 km$^3$. Potential arrays are projected into the workbench as 3D images or instances. Figure 4.4 shows the acceleration optics used in the time-of-flight mass spectrometer. They can be viewed in the plane or in a 3D isometric view. An orientation sphere allows viewing from different angles. Another powerful feature is the potential energy view, shown in Figure 4.4(c). This allows a potential energy surface of a 2D plane to be seen within a 3D viewing volume by transforming 2D field gradients into surface slopes. In the example shown in Figure 4.4(c), it easy to understand the electrostatic forces placed upon an ion in the acceleration optics. This model is similar to the rubber sheet models in that it provides physical insight into the behaviour of the ion optics.

Multiple instances (potential arrays containing ion optics) can be positioned into the workbench volume in a layout that reproduces a real instrument. For the instances that were created with the fast adjustment method, voltages can be changed easily. Such an arrangement of ion optics set at particular voltages can be saved in an ion optics bench (.IOB) file. For example, Figure 4.7 shows a simulation that includes acceleration optics, an Einzel lens and a detector.
Figure 4.4: SIMION diagram showing three different views of the acceleration optics in the ion optics workbench: a) in the XY plane, b) a 3D representation, c) a potential energy view that gives an idea of the field gradients.
4.3.3 The Simulation

Once the ion optics have been drawn and positioned in the workbench, the real fun of watching ion fly begins. There is a comprehensive choice of parameters for definition of the ions, as shown in the menu displayed in Figure 4.5. A single ion or multiple ions may be flown, one after the other or in groups. Their trajectory may be followed on the screen as dots or as continuous lines. The mass and the charge of the ions are entered, and can be incremented to look at the effect of these parameters on the trajectories. The starting position of the ions is entered as co-ordinates X, Y, Z, with the option of incremental changes \( \Delta x, \Delta y, \Delta z \). The ions may be flown at an angle and with some initial kinetic energy. Their progress may be monitored with the help of time markers, which can be set at a particular time interval, e.g. every microsecond. Finally, data of interest, e.g. times-of-flight, may be recorded and stored in a file.
Figure 4.5: SIMION menu showing the define function, which enables selection of the parameters of the ions flying through the ion optics.
4.3.3.1 Determination of the Space-Time Focus

In this simulation, Wiley-McLaren acceleration optics [9] are modelled. The draw-out and flight electrodes were drawn as grids in the potential array. The dimensions were the same as for the optics described in Chapter 2 for the (L2) chamber. Nine ions of equal mass were flown in the XY plane, with a range of different starting positions obtained by incrementing by two grid points in the X and Y directions. The effect of these initial conditions was monitored in the ion trajectories with time markers placed every two microseconds. According to the theory of dual field acceleration, there should be a point in time when all the ions are in the same YZ plane. It can be seen from Figure 4.6 at what time and position the space-time focus occurs.

Figure 4.6: SIMION diagram showing the trajectory of ions starting at different positions. The simulation shows the space-time focus typical of double field acceleration optics.
4.3.3.2  **Focusing Effect of an Einzel lens**

This simulation provides visual insight into the focusing effect of an Einzel lens. The Einzel lens consists of a set of three aligned cylinders as shown in Figure 4.1(b). The simulation was performed using multiple instances to show a typical linear time-of-flight instrument with acceleration optics and a detector. The acceleration optics described in the previous Section and a simple beam stop were used. The Einzel lens was placed in the middle of the drift region. Nine ions of equal mass but with an incremental starting position along the Y-axis were flown. It can be seen from Figure 4.7 that without the Einzel lens the ions retain their spatial distribution, whereas applying a voltage on the middle element of the lens focuses the ions onto the detector.
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Figure 4.7: SIMION simulation in the “potential energy” view: a) No voltage is applied to the Einzel lens, b) Ions are focused onto the detector by applying a voltage on the Einzel lens.
4.3.3.3 Determination of the Time-of-Flight of an Ion

In this simulation, the linear TOF1 mass spectrometer described in Chapter 2 was modelled. The acceleration optics described in the above Section were used. A beam stop was placed at a distance of 1.794 m from the point of photoionisation situated between the repeller and draw-out electrodes. The *record* function was used to determine the time-of-flight of an ion of $m/z = 93$. As can be seen from Figure 4.8, the value was 30.079 μs, which corresponds to the experimental data obtained in the linear TOF1 mass spectrometer for the aniline molecular ion, $m/z = 93$.

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**TOF1 of Aniline (distance to detector: 1794 mm)**

(Repeller:+2100 V; Draw-out:+1600 V)

Figure 4.8: SIMION diagram showing that the time-of-flight of an ion of interest can be recorded.
4.3.3.4 Potential Contours

Another useful feature of SIMION is the potential contour function. This enables the presentation of lines of equal potential in the workbench view. This works in a similar manner to a topographical map, showing hilltops for regions of high potential and valleys for low voltage zones. In Figure 4.9, the potential contours are drawn every 100 Volts for the acceleration optics. It can be seen that the spacing between the lines is quite large between the repeller and the draw-out electrodes, but very tight lines are present between the draw-out and the flight electrodes. This indicates the difference in field gradient in the two regions, which is also graphically displayed in the potential energy view shown in Figure 4.4(c).

4.3.4 Other Features

SIMION offers some programming capability, which enables the user to control and change some of the flight parameters during the simulation. For instance, a program was used in chapter 6 to change the voltage setting on the repeller electrode in the interaction chamber. This feature enabled the simulation of the pulse acceleration of ions into the second, orthogonal, time-of-flight mass analyser.

Complex three-dimensional ion optics can be drawn in SIMION from building blocks saved in geometry files. This feature becomes useful when ion optics with intricate shapes are simulated.
Figure 4.9: SIMION diagram showing the potential contours in the acceleration optics: contours are plotted every 100 Volts.
References


Chapter 5

Mass Selection Using an Electronic Ion Gating Device (Mass Gate)

5.1 Introduction

In order to perform tandem mass spectrometry experiments, one must first be able to select ions of interest in a mass spectrometer. The selected ions, or precursor ions, can then be interacted with a gas, a surface or a laser, and the resulting ions (product ions) analysed in a second mass spectrometer. Selection is easily achieved with scanning instruments, such as sector or quadrupole, and numerous collision-induced dissociation studies have been carried out on instruments of this type [1]. In tandem time-of-flight mass spectrometry, it is necessary to add an ion gating device in order to perform collision-induced dissociation (CID) [2,3] or surface induced dissociation (SID) [4]. Without a mass gate, all ions would be subjected to fragmentation and the resulting mass spectrum would be a convolution of multiple, overlapped product spectra. When using PID [5], mass selection can also be achieved by firing the
pulsed laser at the appropriate time to interact with the precursor ion. However, if both time-of-flight drift regions are in a collinear arrangement, there can be an overlap of product ions with other ions in the normal spectrum [6]. Some means of rejecting undesirable ions would, therefore, still be required. In an orthogonal arrangement, as is the case in this work, it is possible to some extent to effect mass selection for photo-induced dissociation (PID) by TOF discrimination – pulse acceleration of selected ion into the second mass analyser. This would, however, be useful only in a sparse spectrum, say containing only a few peaks, due to an inherently low mass resolving power. It was the intention in this work to build a versatile instrument, which could be switched to a variety of configurations, e.g. collinear as well as orthogonal. To this effect, an independent mass gating device was perceived to be a key requirement.

The easiest way to achieve mass selection is to introduce deflection plates in the drift region. When a voltage is applied to the deflection plates, the ions are deflected from their trajectory by a perpendicular force $F$:

$$F = E \times q = \frac{V}{d} \times q$$  \hspace{1cm} (5.1)

where $E$ is the electrostatic field between the plates, $q$ is the charge of the ion, $d$ is the distance between the plates and $V$ is the potential difference. This force can also be expressed as:

$$F = m \times a$$  \hspace{1cm} (5.2)

where $m$ is the mass of the ion and $a$ is the acceleration in the direction of the field. Taking the origin at the beginning of the deflecting region, as shown in Figure 5.1, the temporal equation of motion for an ion along the direction of the field (Y-axis) can be derived. Since $a=\frac{d^2y}{dt^2}$, it follows from Equations 5.1 and 5.2 that:

$$y = \frac{1}{2} \frac{Vq}{dm} t^2$$  \hspace{1cm} (5.3)
The temporal equation of motion along the drift region (X-axis) is given by:

\[ x = v_0 \times t \]  \hspace{1cm} (5.4)

From Equations 5.3 and 5.4, the trajectory of the ion can be deduced:

\[ y = \frac{Vq}{2dmv_0^2} x^2 \]  \hspace{1cm} (5.5)

The trajectory is a parabola.

An ion \( M \), of mass \( m \), at the exit of the deflecting field region has co-ordinates \( M(x_{\text{def}}, y_{\text{def}}) \), and ceases to be subjected to any electrostatic force. Its trajectory in the drift region now follows the tangent to the parabola at point \( M \):

\[ y - y_{\text{def}} = \frac{Vq x_{\text{def}}}{dmv_0^2} (x - x_{\text{def}}) \]  \hspace{1cm} (5.6)

The path of the ion can thus be followed and the angle of deflection \( \alpha \), shown in Figure 5.1 is approximately:

\[ \tan(\alpha) = \frac{x_A}{y_A} \]  \hspace{1cm} (5.7)
Figure 5.1: Schematic diagram showing the trajectory of an ion deflected between a set of deflection plates.
Deflection plates can thus eliminate all unwanted ions before the time of arrival of the ion of choice. In order to let the precursor ion through unimpeded, the plates must be briefly pulsed to the field-free potential of the time-of-flight drift region, usually ground potential. As soon as the precursor ion is through, the voltage on the deflection plates must be re-applied to eliminate all ions following the precursor ion.

The mass selection capability of an ion gating device depends on its physical dimensions, such as the length of the deflection plates, its position in the time-of-flight drift region, and the characteristics of the pulse applied to the plates (e.g. rise and fall time, minimum width). The angle of deflection is also dependent on the initial velocity of the ions, which is related to the extraction voltages used in the source, and the voltage applied to the mass gate itself. The mass resolving power is usually expressed as \( m/\Delta m \), or \( t/2\Delta t \) in time-of-flight mass spectrometry. The width is taken at 50% of the maximum peak intensity, and is referred to as the full width at half maximum (FWHM). The resolving power of the mass gate can also be expressed in those terms.

Calculations were performed in a Microsoft Excel spreadsheet using the time-of-flight equations introduced in Chapter 2. Typical experimental parameters were chosen, e.g. the dimensions of the ion optics described in Chapter 3 were employed, and an ion of \( m/z \) 100 was accelerated using a total extraction voltage of 2 kV. Assuming that deflection plates of length 15 mm were placed 1 m from the point of ionisation, the time-of-flight at the entrance (TOF1), in the middle (TOF) and at the exit (TOF2) of the deflection plates could be calculated. The resolution of the mass gate can then be expressed as:

\[
\frac{m}{\Delta m} = \frac{t}{2\Delta t} = \frac{TOF}{2(\text{TOF}_2 - \text{TOF}_1)} \quad (5.1)
\]

For an ion of \( m/z \) 100 and 2 keV kinetic energy, the calculated mass resolution of the deflection plates is \( m/\Delta m = 36 \). Even with shielding electrodes, a substantial field penetration outside the deflection plates is inevitable, which, in reality, would result in much lower resolution. With the fastest electronics available in our laboratory, a
pulse width of 100 ns, rise and fall times of 12 ns could be applied to a mass gating device. Taking the same ion parameters as above, the limit placed on the achievable mass resolution using such a pulse is $m/\Delta m = 76$. Therefore, the use of simple deflection plates limits the maximum resolution attainable. A substantial gain in resolving power can be obtained by improving the geometry of the ion gating device.

A number of groups have used deflection plates for mass selection [2-4,7,8]. There is little detail provided in terms of the performance of the ion gate, the emphasis of the articles being on the results of the experiments. LaiHing et al. [8] pointed that the limiting factor controlling the resolution of their mass gate was the long switching time (1 µs) of the pulse from high voltage to ground. Under those circumstances there was no possible gain in trying to improve the geometry of the mass gate. By using faster switching electronics, Haberland et al. [9] demonstrated a useful improvement with a double set of deflection plates. The first set of plates is used to deflect all ions until the arrival of the ion of chosen mass. The second set is pulsed from ground to a high voltage, immediately after the precursor ion has passed through the gate, thus deflecting all the heavier ions. The rise time of the pulses used was 30 ns. The advantage of this approach is that the limiting factor imposed by having a square pulse of a certain temporal width is removed. It is also easier to make a long electric pulse with a short rising, or falling, edge than a square pulse with two sharp edges. Haberland et al. [9] claim a resolving power of $m/\Delta m = 50$ for their particular design of mass gate. Beck et al. [10] have used an alternative device for mass selection. It consists of a wire placed between two shielding grids at ground potential. The wire is pulsed from a high potential to ground during the passage of the ion of interest. Beck et al. [10] also claim a resolution of $m/\Delta m = 50$ for their device.

In recent years, electronics have improved so much that short pulses with very sharp edges have become more attainable, so that the electronics are no longer the factor limiting the mass resolution. A novel mass gate design was introduced by Weinkauf et al. [6]. It consists of interleaved wires arranged perpendicular to the ion path. Adjacent wires, separated by only 1 mm, are placed at opposite potentials, so that a strong field is created between them. Provided the wires are exactly co-planar,
there is little field penetration into the time-of-flight drift region. Using a similar
design, Vlasak et al. [11] have achieved a resolution of \( \frac{m}{\Delta m} = 167 \). Recently,
Stoermer et al. [12] have described a dual mass gate based on the same principle as
that of Haberland et al., but using interleaved wires. With their design a mass
resolution of \( \frac{m}{\Delta m} = 280 \) was achieved.

The aim in the present work was initially to build a tandem time-of-flight mass
spectrometer using a laser for PID, with the possibility of incorporating a collision
cell for CID. It was, therefore, necessary to build an ion gating device in order to
perform mass selection on the ions before they entered the collision cell. Initially, a
gating device with interleaved wires, which required dual pulse voltage supplies, to
pulse a second, negative, voltage to ground was designed. Problems in actually
assembling this device resulted in the adoption of an alternative design. The
construction and characterisation of this gating device are described in Sections 5.3
and 5.4. Simulations of both approaches described in the literature, namely gating
devices using deflection plates and interleaved wires, were calculated using the
computer program SIMION described in Chapter 4, to give an indication of their
relative performance.

5.2 SIMION Modelling Calculations

The various mass gate designs, described above, were modelled in order to assess
their relative performance. In particular, one design employing two sets of deflection
plates, and a device incorporating interleaved wires, were compared using the
program SIMION. Instead of applying both positive and negative voltages, the
elements that would normally be at a negative potential were set at ground potential.

For the former device, the deflection plates were taken to be 16 mm long,
separated by 25 mm, and shielded by electrodes at ground potential. In addition,
shorter deflection plates (4 mm length across the path of the ions) were also
modelled to test to what extent this would improve the mass resolution. The design,
consisting of interleaved wires, described by Vlasak et al. [11], was also modelled.
For this device the wires were separated by 1 mm, and represented by lines of point-
size thickness in the simulation, to reflect the small diameter of the wires. This resulted in 100% transmission of the ions, which is a feature of SIMION for instances of point size, but this did not matter for the study of deflection performance. However, the choice of wire diameter in reality would be important to optimise the effects of deflection against transmission.

The parameters for the simulations were chosen to reflect a typical experiment. Ions of m/z 300, accelerated to 2 keV kinetic energy, were flown through the mass gates. The simulated workbench was sized to the instrument dimension, assuming the gating device was situated 1 m from the point of ionisation and 46 cm from the centre of the interaction chamber (IC). There, the selected ions would be subjected to photo-induced dissociation. A beam stop of diameter 22 mm was placed 46 cm from the mass gate, and the aim of the simulation was to test the ability of the mass gate to deflect ions away from this target.

The results for the simulations for the mass gate based on deflection plates are shown in Figures 5.2 and 5.3. It can be seen from Figure 5.2 that deflection plates, what dimension was 16 mm in length, were effective in deflecting all ions from the target, with a voltage of 250 V applied to one plate. When reducing the length of the deflection plates to 4 mm, the voltage had to be increased to 600 V to achieve the same degree of deflection, see Figure 5.3.

The corresponding simulation for the mass gate incorporating interleaved wires is shown in Figure 5.4. For this design, most ions are deflected when a potential of 500 V is applied to alternate wires. Some ions, whose trajectory would normally be stopped by hitting a wire, travel through unimpeded and reach the detector unaffected by the electrostatic field. This is a consequence of a feature of SIMION for point size electrodes, and should be disregarded. It should be noted that opposite voltages on alternate wires would increase the deflection substantially, but only one positive voltage supply was used here, so alternate wires were grounded.

Also examined in the simulations was the field penetration of the different devices, which would have an effect on the ion flight times. Potential contours were calculated and are shown in Figure 5.5. For the mass gate based on deflection plates
the field extends over a distance of 68 mm for the 16 mm long deflection plates, and over a distance of 40 mm for those 4 mm in length. The field penetration of the device, incorporating the interleaved wires, was substantially lower (27 mm), although much higher than claimed in reference [11], where a value of 1 mm either side of the wires was quoted. From these simulations it can be seen that reducing the length of the deflection plates does not reduce the field penetration substantially. Compared with the calculations of the effective mass resolution presented in Section 5.1, the mass resolution of the deflection plates would be considerably less due to the field penetration. A narrow design based on interleaved wires seems to produce the best performance in terms of deflection capability and potential contours.
Figure 5.2: SIMION simulation for mass gate based on deflection plates. 23 ions with m/z 300 and 2 keV kinetic energy were flown through shielded deflection plates of length 16 mm. The distance to the target is 46 cm, and represents the actual distance between the mass gate and the interaction region in the tandem time-of-flight mass spectrometer.
Figure 5.3: SIMION simulation for mass gate based on deflection plates. 23 ions with m/z 300 and 2 keV kinetic energy were flown through shielded deflection plates of length 4 mm. The distance to the target is 46 cm and represents the actual distance between the mass gate and the interaction region in the tandem time-of-flight mass spectrometer.
Figure 5.4: SIMION simulation of mass gate incorporating interleaved wires. 23 ions with m/z 300 and 2 keV kinetic energy were flown through the wires set at alternate voltages of 500 V and ground potential. The distance to the target is 46 cm and represents the actual distance between the mass gate and the interaction region in the tandem time-of-flight mass spectrometer.
Figure 5.5: SIMION simulations showing the potential contours for the devices modelled: a) deflection plates of length 16 mm, b) deflection plates of length 4 mm, c) interleaved wires, d) staggered wires, using one voltage supply. Potential contours are drawn at 10 V intervals. An indication of the field penetration outside the devices (in mm) measured in the SIMION workbench is given.
Based on the earlier simulations it was thought that the deflection performance of a mass gate incorporating interleaved wires could be improved by placing the wires in a series of planar sets over a small distance. Such a design was created and modelled using SIMION. A 3-D representation taken from the SIMION simulation is shown in Figure 5.6. The wires at ground potential formed a series of parallel lines, separated by 2 mm, running orthogonal to one another. Between this set of wires, was a second set of wires, held at high potential, also running orthogonal to one another. These two sets of wires were staggered, so that when looking along a plane containing the device, the lines of the second set of wires appear between adjacent lines of the first set, with a spacing of 1 mm. Thus two sets of wires at a high potential are sandwiched by two sets of wires at ground potential. The criss-crossing of wires, with sets 1 and 2 at right angle to sets 3 and 4, would improve the effect of deflection in all directions.

A SIMION simulation was run using the same parameters as in the previous three cases studied, i.e. 23 ions, m/z 300, 2 keV kinetic energy, and the results are shown in Figure 5.7. It can be seen that this mass gate effectively deflects ions away from the target with a voltage of 500 V applied to the inner wires, whilst keeping the outer wires at ground potential. The field penetration, illustrated by the potential contours shown in Figure 5.5, extends over a substantially smaller distance (10 mm) than for the designs based on deflection plates (68 mm and 40 mm), and is also less than that for the design incorporating interleaved wires (27 mm). From these simulations it appeared that such a device with multiple sets of wires was a suitable design, in terms of deflection performance and resolution, and required the using of only one positive pulse voltage supply. In the following Section the transformation of this model design into a real device is described.
Figure 5.6: Schematic diagram showing: a) a 3-D representation of the sets of wires in the SIMION model, with two sets orthogonal to the other two. b) the staggered pattern of the wires and the voltage applied to each set.
Figure 5.7: SIMION simulation of staggered wires. 23 ions with m/z 300 and 2 keV kinetic energy were flown through the sets of wires. The inner wires are set at 500 V and the outer wires are at ground potential. As in Figure 5.2 and Figure 5.4, the distance to the target is 46 cm
Chapter 5. Mass Selection Using an Electronic Ion Gating Device (Mass Gate)

5.3 Construction of Mass Gate

The mass gate consisted of the device itself and the electronics required for its operation. Based on the ideas that emerged from the modelling studies, a device incorporating four sets of wires, as described in the previous Section, was designed. The initial design, described below, based on a custom built aluminium support frame, proved difficult to assemble in the latter stages of construction. It was replaced by a different device based on electrical board as a supporting material, which happened to be easy to shape into a frame that was also convenient for winding wire around it. A high voltage pulser capable of switching a high voltage to ground was also built.

5.3.1 Initial Design

The mass gating device, incorporating four sets of orthogonal wires, was not straightforward to translate into a workable design. The requirement for each planar set of wires was for them to be held parallel and separated by 2mm. To accomplish this, the wires needed to be held in position with sufficient tension to retain their alignment, a bit like the strings of a guitar. The spacing between the wires was also important, especially since the first two sets of wires were to be staggered, so that the distance between the wires would appear to be 1 mm when looking from the side in the plane containing them. The third and fourth sets of wires were held in a similar fashion, but had to be mounted perpendicular to the first two sets. Finally, the inner sets had to be electrically isolated to hold a potential of up to 1 kV, while the outer sets could be part of some grounded metallic frame.

To accommodate all these constraints, the design was initially based on metal frame onto which a set of threaded rods could be mounted. Stainless steel M3 studding is readily available and has a spacing of 0.5 mm between the threads. It was intended that a series of M3 rods would be screwed into the frame in the appropriate position. Wire could then be wound around the M3 studding forming a series of parallel lines. The spacing between the wires would be reproducible by leaving a gap of four M3 threads between them.
With this in mind, an aluminium frame in the shape of a cross was constructed, as shown in Figure 5.8. The central part of the cross was the effective area of the device, a square section with sides of 40 mm in length. On the side of each branch of the cross, threaded holes were drilled and tapped to accommodate the M3 studding. In order to isolate the inner sets of wires electrically, a bigger M5 hole was drilled to allow insertion of a nylon liner between the M3 rod and the frame. For each planar set of wires, two M3 rods were situated at each end. The wire was wound in such a manner that it would line up across the top rod, wind three times around the bottom rod, and go back across the top rod again, lining up parallel to the adjacent wire. The spacing between the wires could be set at 1.5 mm or 2 mm, and the distance between two sets of wires was fixed at 2 mm, resulting in a total working width of 6 mm for the device. The width of the supporting frame was 8 mm, making it a very compact design.

Unfortunately, this design proved impossible to assemble. After the first planar set of wires was attached, there was very restricted access around the device. Winding of the wire, without upsetting the arrangement of the one already fixed in place, was virtually impossible. Several types of wire, of various diameters and stiffness, were tried. However, the lack of space to weave more than one planar set was the main handicap. Moreover, it was difficult to fix the wire with sufficient tension to obtain a perfect plane. Tightening the wire applied a force on the threaded rods, which was compensated by a movement of the rods within the frame. Attempts were made to secure the rods firmly onto the frame by blocking each end with a piece of Teflon, but this proved futile in the face of the problems with winding more than one set of wires. Another approach was needed.
Figure 5.8: Schematic diagram showing the construction of the cross-shaped ion gating device. The top view shows the threaded rods. It can be seen from the side views how little space there was to wind the wire around the M3 studding.
5.3.2 Final Design: Stacked Electrical Board Assembly

Following the initial failed attempts to build the mass gate, it was clear that it would be simpler to construct each planar set of wires separately, then join them together. The idea came to use electrical board to build a frame for each individual plane of wires. This type of board is made of fibreglass, which can be easily machined into four frames of the requisite size and stacked together. The copper-coated side of the board would provide good electrical contact with the wires. This idea appeared even more attractive when it was found that the wire could be held firmly into position solely by friction in grooves cut into the fibreglass.

Electrical board (copper-coated fibreglass, 1.5 mm thickness) was cut into square frames of dimension 70 mm, with an inner square cut-out of dimension 50 mm, as shown in Figure 5.9. Tabs were left at the corners of each frame to enable final assembly. Grooves, 2 mm deep, were cut every 1.5 mm on the outside edge of the two opposite sides of each frame. Tungsten wire (Goodfellow, 25 μm diameter and 99.95% purity) was positioned into these grooves to form a single plane of parallel wires. This was achieved by winding the wire across the frame, with the wire traversing always on the same side. The offset between the first two sets, required so that the wires were staggered when looking across the planes of wires, was achieved by careful machining of the grooves.
Figure 5.9: Schematic diagram showing the four electric board frames that were sandwiched together (in the order 1 to 4) to make the final working design of the mass gate. The wires on set 2 are extended towards set 1 on the diagram to show how they fit in a staggered manner when the frames are assembled together.
Figure 5.10: Photograph showing the mass gate inside the time-of-flight drift tube (TOF1). The photograph was taken from the centre of the interaction chamber (IC), which is situated 46 cm from the mass gate.
When the frames were stacked together, the wires appeared regularly spaced, with the wires from the second set placed exactly between those of the first set. In order to electrically isolate the outer wires from the inner ones, thin Teflon sheets (Goodfellow, 0.25 mm thickness) were fitted between the frames. Thus the separation between two planes of wires was 1.75 mm and the total distance between the first and the fourth sets was 5.25 mm. The total width of the device was 6.75 mm. The four frames were sandwiched together so that the wires of the first two frames were orthogonal to those of the other two frames. The area covered by the 28 wires of one single set was calculated to be 28 mm$^2$, for a total effective area of 40.5 x 40.5 mm, giving a ratio of 1.7% occupancy. Thus the calculated transmission of the device, taking into account the surface area of the other three sets of wires, was 93.2%. The whole assembly was held together by nylon screws situated at the corners of the frames. The mass gate was suspended in the time of flight drift region (TOF1) by a metal rod attached to one of the three flanges which could be placed at distances 0.4 m, 0.7 m and 1 m from the point of ionisation. The outer wires were grounded, and the two inner frames were connected to an electrical feedthrough situated on the same flange.

5.3.3 High Voltage Power Supplies and Pulsing Units

Custom High Voltage Pulser

A high voltage pulser module was built for the mass gate in order to switching a high DC voltage to ground for very short periods. The module was based on a high-speed HV-MOSFET switching device (model DEI 102N05) mounted on a DEI 275EK evaluation board. The ratings for this switching device are: 1000 Volts, 40 Amps pulsed. The high voltage was switched to ground via a load resistor. Three options were available: 10 kΩ (safe mode), 1 kΩ (standard mode) and 100 Ω (high speed mode). In the latter mode the fall time was around 20 ns, with rise time <40ns, but the total ON TIME needed to be less than 2 ms to prevent burn out of the components.
Control of the module was via an external TTL pulse into the trigger input. The duration of the pulse to ground could be controlled internally by a 10-turn potentiometer. The delay between the trigger pulse and the negative going edge of the pulse to ground could also be controlled internally by a 10-turn potentiometer. Monitor outputs were available for checking the delay and width of the pulse, as well as the high voltage level (a 1000:1 voltage divider).

**Behlke High Voltage Switch**

A commercial fast high voltage push-pull switching unit (Behlke, Model GHTS 60A) was also used to operate the mass gate. The unit consists of two alternately controlled switches, made of a large number of series and parallel connected MOSFET. It is especially designed for capacitive load elements such as acceleration grids and ion optics. It can be operated up to a voltage of 6 kV and delivers true square-wave pulses of minimum width 100 ns, with rise and fall time of 12 ns.

The pulser was operated with an external power supply (Stanford Research Systems, Model PS350) and controlled by an external trigger provided by a pulse delay generator. The Behlke pulser can be operated in both positive and negative polarities, as well as in different floating mode. This proved especially useful for the photodissociation experiments. However, for the operation of the mass gate, it was not possible to obtain the desired switching voltage polarity, from high voltage to ground, which is probably the only combination not allowed on the otherwise versatile Model GHTS 60A. Instead, the pulser was used to allow the mass gate to suppress peaks from the mass spectrum, which still enabled the device to be tested.

**5.4 Experimental Characterisation of the Mass Gate**

**5.4.1 Mass Selection Using HV Pulser**

A mixture of coronene and 4-phenylazophenol was used to test the mass gate in the linear TOF1 mass spectrometer. The sample was prepared by dissolving a small portion of the solids in acetone. It was then drop-coated using a Pasteur pipette onto the desorption probe and left to dry. The sample was desorbed using the Alltec 861
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CO\textsubscript{2} laser (10.6\ ($\mu$m) and post-ionised using the fourth harmonic (266 nm) of the JK HyperYAG HY750 laser. Ions were accelerated with a repeller voltage of 1500 V and a draw-out voltage of 1100 V. The sample probe was floated at 1266 V.

With the mass gate disabled, a full photoionisation mass spectrum was obtained and is shown in Figure 5.11a. A broad peak is present at m/z 300, corresponding to the molecule ion of coronene, which has a large cross section at 266 nm. The characteristic product ion of coronene at m/z 276, corresponding to the loss of C\textsubscript{2}H\textsubscript{2}, is also present. No peak due to the molecule ion of 4-phenylazophenol at m/z 198 can be seen, but some of its characteristic product ions are present. Cleavage of the azo bond gives rise to product ions at m/z 93 and m/z 109 (barely visible on the spectrum), whereas loss of N\textsubscript{2} gives a peak at m/z 170 [13]. In the middle spectrum, Figure 5.11b, the mass gate has been set to select one of the product ions of 4-phenylazophenol at m/z 93. In this case, a voltage pulse of 900 V was applied to the mass gate. This pulse and the delay between the ionisation laser were adjusted using the 10-turn potentiometer on the high voltage pulser unit to coincide with the passage of the ion through the mass gate. A residual peak at m/z 300 can be seen, but it is relatively small considering the size of this peak in the full mass spectrum of Figure 5.11. In the bottom spectrum (Figure 5.11c) the peaks of coronene were mass selected. In this case, the duration of the high voltage pulse was set to let both the molecule ion and the product ion of coronene through. All ions corresponding to the 4-phenylazophenol were effectively gated out and no residual peaks can be seen in the mass spectrum.

The home built high voltage pulser suffered a mechanical breakdown, which could not be fixed during the project. Fortunately, it was possible to use a commercial high voltage switch to further characterise the mass gate.
Figure 5.11: Mass selection of the molecule and product ions in the photoionisation mass spectrum of coronene and 4-phenylazophenol: a) Full spectrum showing the main peaks characteristic of the two compounds, b) Selected transmission of the product ion at m/z 93, c) Selected transmission of the coronene molecule ion and its product ion at m/z 276.
5.4.2 Peak Suppression Using the Behlke GHTS 60A Switch

The Behlke switch could not be configured to deliver a pulse from high voltage to ground. Instead, it was used to characterise the mass gate by applying a short high voltage pulse to the gate at the appropriate transit time for an ion of interest; thereby suppressing this mass selected ion.

Anisole (MWt = 108 Da) was used for these experiments. This volatile compound was introduced into the ionisation chamber effusively, via a needle valve (Swagelok Nupro, Willoughby, USA, JN Series), from a glass reservoir. The sample was ionised by irradiation with the fourth harmonic (266 nm) of a Continuum Surelite II Nd:YAG laser. Ions were extracted with 1.85 keV kinetic energy towards the mass gate, which was positioned 1 m from the point of ionisation.

The full photoionisation mass spectrum, with the mass gate disabled, is shown in Figure 5.12. The molecule ion of anisole (m/z 108) gives rise to a broad peak. This ion fragments to give a sharp peak at m/z 93 (loss of CH₃). Further fragmentation peaks are present at m/z 78, m/z 66, and m/z 40, as well as peaks of lower intensity centred at m/z 54 and m/z 28. The Behlke switch was used to suppress the most prominent peaks in this spectrum, at m/z 40, m/z 66, m/z 78, m/z 93 and m/z 108, in turn. The resulting spectra are shown in Figure 5.13 to Figure 5.18. For these experiments, a voltage of +700 V was applied to the Behlke switch, which was subsequently delivered to the mass gate as a positive going voltage pulse of width 100 ns.

The experiment was controlled by delay generators (Stanford Research Systems, Model DG535, and EG&G, Model 9650A), which enabled the delay between the ionisation event and the mass gate pulse to be adjusted at nanosecond accuracy. It can be seen from Figure 5.13b that the peak at m/z 40 is completely suppressed, leaving the other adjacent peaks at m/z 39 and m/z 41 unaffected. Similarly, as shown in Figure 5.14b, the peak at m/z 66 can also be suppressed, while the trailing edge of the peak, which is probably due to metastable decay, is still apparent. A longer duration high voltage pulse would be required to suppress the whole peak.
Figure 5.15b shows the spectrum in which the peak at m/z 78 has been suppressed. In this case however, the peak at m/z 77 is also suppressed, while the peak at m/z 79 is still present. By changing the delay of the high voltage pulse, it was possible to suppress the peak at m/z 79, but it was not possible to suppress the central peak only. In Figure 5.16b, the aniline molecular ion peak has been effectively suppressed although there is still a small residual peak. The isotope peak at m/z 94 has also been suppressed. Due to the breadth of the anisole molecule ion peak, the pulse width was increased to 500 ns in order to suppress the peak at m/z 108. As shown in Figure 5.17b, only a small residual signal remains.

Although it wasn't possible to isolate a single mass with the present set-up, the anisole molecule ion could be isolated, by using a long duration (15μs) high voltage pulse to suppress all lighter ions. The effect of this is shown in Figure 5.18: a single peak could be isolated at m/z 108. The peak is narrower than in the full spectrum because there is less saturation, since the sample is relatively quickly pumped away in the ionisation chamber. The needle valve was opened from time to time to allow more of the sample to enter the chamber, causing immediate saturation of the anisole molecule ion peak. The spectrum in Figure 5.18b also shows small residual peaks corresponding to some of the peaks appearing in the full spectrum shown in Figure 5.12, but the abundance of the residual peak at m/z 78 is only 2.5% of the original peak abundance.

In order to further characterise the transmission characteristics of the mass gate, the voltage applied was gradually increased from 0V to +700 V, and the resulting signal intensity for the aniline molecule ion was recorded. A graph of intensity versus mass gate voltage is shown in Figure 5.19. It can be seen that a voltage of about +80 V suppresses the transmitted signal intensity by 50%, but the voltage has to be increased significantly to eliminate all the ions. In fact, even at +700 V, there is still a residual signal intensity of about 1% of the intensity seen when no voltage is applied. This residual transmission persisted even if higher voltages were applied, indicating that the mass gate is not 100% effective at deflecting ions, although a rejection level of 99% would probably be acceptable for many mass gated experiments.
In order to evaluate the resolving power of the mass gate, the narrowest high voltage pulse (100 ns) was centred on the anisole molecule ion peak (m/z 108). Anisole was introduced in large excess to the ionisation chamber, and the photoionisation laser intensity increased, for this particular purpose, in order to obtain a broad peak due to saturation. As can be seen from Figure 5.20 the high voltage pulse (+700 V) has created a sharp notch in the centre of this broad peak. By measuring the width of this feature, it is possible to estimate the mass resolving power of the mass gate, using the formula \( R = \frac{t^2}{2A_t} \). The width of the notch is 520 ns, and the peak is centred at \( t = 31.025 \mu s \), which gives a mass resolving power of \( m/\Delta m = 30 \). From the data obtained in the simulations, it was expected that the mass resolving power would be somewhat higher. Using the spreadsheet calculation described in Section 5.1, assuming a field penetration of 10 mm, a mass resolving power of \( m/\Delta m = 55 \) would be expected. This suggests that the field penetration outside the mass gate is greater than estimated using the SIMION model.
Figure 5.12: Full mass spectrum of anisole obtained using the linear TOF1 mass spectrometer. Photoionisation at 266 nm.
Figure 5.13: Mass spectra showing suppression of the peak at \( m/z \) 40: a) Full mass spectrum. b) A pulsed voltage (+700 V, 100ns) is applied at the appropriate delay to suppress the \( m/z \) 40 ion.
Figure 5.14: Mass spectra showing suppression of the peak at m/z 66: a) Full mass spectrum. b) A pulsed voltage (+700 V, 100ns) is applied at the appropriate delay to suppress the m/z 66 ion.
Figure 5.15: Mass spectra showing suppression of the peak at m/z 78: a) Full mass spectrum. b) A pulsed voltage (+700 V, 100ns) is applied at the appropriate delay to suppress the m/z 78 ion.
Figure 5.16: Mass spectra showing suppression of the aniline molecule ion at m/z 93: a) Full mass spectrum. b) A pulsed voltage (+700 V, 100ns) is applied at the appropriate delay to suppress the m/z 93 ion.
Figure 5.17: Mass spectra showing suppression of the anisole molecule ion at m/z 108: a) Full mass spectrum. b) A pulsed voltage (+700 V, 100ns) is applied at the appropriate delay to suppress the m/z 108 ion.
Figure 5.18: Mass spectra showing suppression of all peaks prior to the molecule ion of anisole at m/z 108. A voltage pulse of +700 V, of 15 μs duration, was applied to the mass gate.
Figure 5.19: Plot showing the transmitted ion intensity for the aniline molecular ion as a function of the voltage applied to the mass gate.
Figure 5.20: Photoionisation mass spectrum for anisole, showing a broad, saturated peak, centred at 31 μs. A pulsed voltage (+700 V, 100ns) was applied to the mass gate in order to suppress the centre part of the peak, creating a notch of width 520 ns in the transmitted molecule ion intensity.
5.5 Further Improvements

The initial results obtained using this novel design of mass gate, consisting of four sets of wires in a staggered configuration, show that it is a suitable device for mass selection of ions up to unit mass resolution of $m/\Delta m = 30$. This is a better level of performance than can be achieved with deflection plates.

Due to failure of the home-built pulser driver unit, further characterisation of the mass gate was carried out in peak suppression mode, using a BEHLKE GHTS 60A switch, as the voltage driver. However, this switch could not be configured to deliver a pulse from high voltage to ground potential. Additional electronics would have been required to achieve this and enable mass selection of a precursor ion. This could be implemented at a later stage.

Ultimately higher mass resolving power can be achieved by using two mass gates in series, in a configuration similar to that of Stoermer et al. [12]. In their system each mass gate is used to clip one end of the spectrum, using a rapid pulse from high voltage to ground and vice versa. This concept has been taken even further by Piyadasa et al., who have shown that such a gate can be used in dynamic mode with dramatic improvement in mass resolution [14].
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References


Chapter 6

Development of a Tandem Time-of-Flight Mass Spectrometer

6.1 Introduction

As explained in the introductory chapter, time-of-flight mass spectrometry lends itself well to the analysis of molecules and metal clusters formed using pulsed sources. However, when the ions created in the source are examined using a single stage of mass analysis, the resulting spectra do not always provide enough information. In some cases, there are rogue peaks, which cannot definitely be attributed to the sample. In other cases, as in complex mixtures, the spectra are congested with peaks from the various components and difficult to interpret. In those circumstances, it would be desirable to select one mass and subject it to a second stage of mass analysis, thus providing additional information on that particular component in the sample.

In order to perform tandem time-of-flight mass spectrometry, one needs two time-of-flight drift regions, separated by an interaction region. In the first time-of-flight drift region, the ion with mass of interest (precursor ion) is selected out of all the ions. This mass selection is commonly achieved by deflecting all unwanted ions out of the path to the detector. An original ion-gating device developed for this purpose
was described in the previous Chapter. The precursor ion is then interacted with either a gas in a collision cell, or a laser beam to induce dissociation. The fragments produced (product ions) are ejected into the second time-of-flight drift region and mass analysed. In this Chapter some of the different possible configurations for the two time-of-flight drift regions are considered. Some of the problems associated with tandem time-of-flight mass spectrometry are highlighted and addressed, and model ion trajectory simulations are presented in support of the choice of photo-induced dissociation using an orthogonal geometry, which was finally adopted for the instrument.

6.2 Time-of-Fight/Time-of-Flight Mass Spectrometers: Which Configuration?

The major problem in tandem time-of-flight mass spectrometry is the mass dispersion in the second drift region. As shown in Figure 6.1, ions that are formed in the source are accelerated to the same kinetic energy:

\[ K_e = \frac{1}{2} m v^2 \]  
\[
(6.1)
\]

The velocity of the ions in the first drift region is thus directly related to the square root of their mass, resulting in mass dispersion, the light ions travelling faster than the heavier ones:

\[ v \propto (1/\sqrt{m}) \]  
\[
(6.2)
\]
Figure 6.1: Schematic diagram showing the two flight regions of a tandem time-of-flight mass spectrometer. Without any post-acceleration, the ions are not mass dispersed in the second analyser.
However, the product ions formed during the fragmentation process retain the velocity of the precursor ion in the second drift region. In this case, the ions are not separated in time, so that all ions arrive at the detector at once and no meaningful mass spectrum is obtained. Here the product ions have a different kinetic energy $K_{e(\text{prod})}$ which is related to the kinetic energy of the precursor ion $K_{e(\text{pre})}$ by the following relationship, derived from Equation 6.1:

$$K_{e(\text{prod})} = \frac{m_{\text{prod}}}{m_{\text{pre}}} K_{e(\text{pre})}$$  \hspace{1cm} (6.3)
Various approaches have been taken to circumvent the mass dispersion problem. The first one is to use a single reflectron time-of-flight mass spectrometer in two ways, as shown in Figure 6.2. Here fragmentation occurs at the turn-around point at the back of the reflectron, where the ions are more or less stationary for a short time. For practical reasons, fragmentation is limited to photo-induced dissociation by a laser, which is fired across the ion path. The only modification required to the reflectron is the addition of two windows to allow passage of the laser beam. Some means of mass selection is also necessary between the extraction optics and the reflectron. After the dissociation event, precursor and product ions are accelerated from the back of the reflectron towards the detector in what is effectively a linear time-of-flight mass spectrometer, with the reflectron acting as a dual extraction optics. By using the reflectron in such a way, there is no problem of mass dispersing the ions in the second time-of-flight stage. This approach has been used by several research groups. Willey et al. [1] describe the use of such an instrument for studying metal-containing ion–molecule complexes. They calculated a typical time window of 2-3 \( \mu \text{s} \) in the back of the reflectron, which is ample time for laser interaction. However, they remark on the difficulty of estimating the exact ion beam shape and were, therefore, unable to measure absolute dissociation cross-sections. Ding et al. [2] have investigated the photofragmentation spectroscopy of \( \text{Mg}_2(\text{CO}_2)^+ \) and \( \text{Mg}_2(\text{CO}_2)_2^+ \). Jia et al. [3] have looked at the photofragmentation of the molecular ion of the amino acid derivatives phenylthiohydantoin (PTH)-tryptophan, PTH-valine and PTH-alanine. Terasaki et al. [4] have used surface-induced dissociation at the back of the reflectron to investigate the dynamic processes involved in the collision of size-selected aluminium cluster anions with a silicon surface.
Figure 6.2: Schematic diagram of a tandem time-of-flight mass spectrometer with photo-induced dissociation at the back of the reflectron.
There is a second approach to using a single reflectron to provide two stages of time-of-flight mass analysis. Instead of positioning the fragmentation laser at the back of the reflectron, it is situated at the space focus of the extraction optics, as shown in Figure 6.3. In this case, the reflectron is used to mass disperse the ions in the second drift region, as well as used for its normal role of energy focusing. This is due to the fact that, after the fragmentation event, the ions have the same velocity but varying kinetic energy according to Equation (6.3). As a result, the time spent in a single stage reflectron by those ions is linearly proportional to their masses. In a dual stage reflectron, the situation is more complicated because of the abrupt change in field gradient between the two linear regions, necessitating more careful calibration. A further complication is that the voltages applied to the reflectron have to be optimised for a particular kinetic energy, normally that of the precursor ion. In order to obtain a mass spectrum with good resolution at lower masses, the voltages of the reflectron must be scanned. Despite these inconveniences, this approach has been used by a number of groups. Incidentally, the reflectron mass analyser has been used extensively in the study of metastable decomposition, because the ions resulting from fragmentation in the drift region have a different arrival time from those formed in the source. Useful information can be deduced from careful analysis of the mass spectrum. This phenomenon of post source decay has been used to probe the fundamental mechanisms of unimolecular dissociation [5,6], and more recently has been employed in commercial instruments used for the sequencing of proteins and peptides [7]. In the tandem time-of-flight configuration, Boesl et al. [8] have pursued their studies of the multiphoton dissociation of organic molecules. Dey et al. [9] have used PID at the second-order space-focus to investigate multiphoton dissociation of the amino acid tryptophan. Papanikolas et al. [10] have studied photodissociation of $I_2^-$ and the recombination dynamics in size-selected $I_2(CO_2)_n$ cluster ions.
Figure 6.3: Schematic diagram of a tandem time-of-flight mass spectrometer using photo-induced dissociation in the first time-of-flight drift region.
Cornish and Cotter [11] have developed a double reflectron tandem time-of-flight mass spectrometer, with a view to investigating the collision-induced dissociation of biomolecules. The path of the ions follows a Z-shape after passage through the two reflectron analysers, as shown in Figure 6.4. Improvements to the design of the instrument have included the replacement of the dual-stage reflectrons by single-stage, gridless reflectrons, to facilitate mass calibration on the one hand, and to increase the sensitivity [12]. A further improvement consisted of the development of a curved-field reflectron for the second time-of-flight analyser, that enabled focusing of all ions onto the detector without the need to scan the voltages of the reflectron [13]. Beussman et al. [14] have also used a double reflectron instrument and demonstrated its application to photo-induced dissociation of simple aromatic molecules. They used retardation of the selected precursor ion and post-acceleration after the dissociation event as a means of bringing about mass dispersion of the product ions. They also developed a novel reflectron with a non-linear second stage that enables concomitant focusing of precursor and product ions despite their varying kinetic energies.
Figure 6.4: Schematic diagram of a tandem time-of-flight mass spectrometer with two reflectron mass analysers.
When two distinct time-of-flight instruments are used in tandem, the only way to mass disperse the product ions is to post-accelerate them. This usually also implies retardation prior to the dissociation event. A number of research groups have developed tandem time-of-flight instruments using a collinear configuration similar to the one shown diagrammatically in Figure 6.5. Jardine et al. [15] have built such an instrument equipped with a fast atom bombardment source. They used a floating collision cell with post acceleration to disperse the product ions. Sublemontier et al. [16] recently published results on collisional studies of hydrated metal cluster ions. They used parabolic optics at both ends of the collision cell to decelerate and reaccelerate the ions. The second mass analyser is equipped with a reflectron. They were also able to increase the mass resolution by means of a double pulse applied to the extraction optics to counteract the loss of the Wiley-McLaren space-focus due to deceleration in the collision cell. Medzihradsky et al. [17] have also used a linear and a reflectron time-of-flight mass spectrometer arranged in a collinear fashion to study the characteristics of peptide collision-induced dissociation. They used a MALDI source with an extraction voltage of 3 kV, and a post-acceleration voltage of 15 kV at the exit of the collision cell. This enabled detection of all secondary ions with relatively high resolution without having to scan the voltages of the reflectron. This approach represents a substantial improvement in speed of analysis compared with the traditional MALDI instruments utilising post-source decay for the sequencing of proteins and peptides.

Figure 6.5: Schematic diagram of a collinear tandem time-of-flight mass spectrometer.
The collinear configuration of the TOF analysers in the instruments described above is well suited to the CID mode of dissociation. For other modes of dissociation, such as SID and PID, there are advantages in using an orthogonal configuration. In SID, the surface onto which the ions are impacted is placed at 45° to the ion path, so that the secondary ions are ejected and re-accelerated at 90° into a second time-of-flight drift region. Schey et al. [18] discussed the factors affecting mass resolution following SID in their orthogonal tandem time-of-flight mass spectrometer. They found that the major contribution to poor mass resolution was the kinetic energy spread of the fragment ions generated by collision with the target surface. By using a reflectron as the second stage analyser, they improved the resolution from $m/\Delta m = 10$ to $m/\Delta m = 74$ in a typical experiment using the molecular ion of benzene. Beck et al. [19] built an apparatus that includes SID at 45° at the end of a linear time-of-flight region, and a rotatable second time-of-flight mass analyser. They used the instrument for experiments involving the scattering of fullerenes and metallofullerenes onto a highly oriented pyrolitic graphite surface. The angle of the second time-of-flight mass analyser is varied in order to measure the angular distributions of the scattered ions.

When PID is used for dissociation, the fragmentation laser beam is directed to interact with the ion beam in the middle of a set of extraction optics. Immediately after the dissociation event, a pulsed voltage is applied to the acceleration optics, so that the product ions are accelerated orthogonally into the second time-of-flight drift region. This configuration is shown diagrammatically in Figure 6.6. O'Brien et al. [20] studied the laser-induced fragmentation of carbon clusters in such a tandem time-of-flight instrument. Yu et al. [21] used a similar instrument configuration to study the photo-fragmentation of iron-sulfur cluster ions.
Figure 6.6: Schematic diagram of a tandem time-of-flight mass spectrometer with orthogonal extraction into the second time-of-flight drift region.
The advantage of orthogonal acceleration is that mass selection of a precursor ion in the first time-of-flight region can be achieved simply by appropriate timing of the dissociation laser and of the subsequent extraction voltage pulse. A primary mass spectrum is easily obtained in TOF1, by switching the optics situated in the interaction chamber to ground and turning off the dissociation laser. One difficulty is that the ions resulting from PID have different kinetic energy, so that the residual velocity component in the TOF1 direction creates an angle of deflection in TOF2, which needs to be corrected by deflection plates. In effect, unless the precursor ions are decelerated to a complete standstill, there is an inherent problem in tandem time-of-flight mass spectrometry because of the residual velocity of the precursor ion. This is true in both the collinear and the orthogonal configurations.

In the present work, the intention, from the outset, was to use PID as the principal mode of parent ion dissociation. In the following section, model calculations, carried out using SIMION, are presented for the orthogonal instrument configuration that was finally constructed.

### 6.3 Modelling Calculations

One reason for the interest in developing a tandem TOF instrument primarily for studies involving photo-induced dissociation was that the laboratory was well equipped with a number of different types of lasers. From the discussion above, it is apparent that there is a distinct advantage in choosing an orthogonal configuration for the two time-of-flight drift regions. This would enable mass selection in the first stage and mass dispersion in the second stage. A simple set of extraction optics was therefore modelled to study the orthogonal acceleration of ions.

#### 6.3.1 Effect of Initial Velocity of Ions using Orthogonal Extraction

In this SIMION simulation, dual extraction optics were modelled. The repeller consisted of a solid electrode drawn to the standard size of 80x80 mm. The draw-out and flight electrodes were entered as 80x80 mm grids. These had 100% transmission, so that the ion trajectories would be unimpeded through the grids. In practice, the electrodes had a hole of 22 mm diameter cut in their middle, that was covered with
90% transmission mesh. The ion transmission was thus restricted compared with the ideal case of the simulation. However, the aim of the simulation was to evaluate the angle of the trajectories resulting from the velocity in the first, linear, time-of-flight drift region. Figure 6.7 shows the effect of the initial ion kinetic energy on the trajectory of ions following orthogonal extraction. Voltages were set to optimum values in the reflectron time-of-flight mass spectrometer. All ions were started at the same spatial position but with varying kinetic energy, from 50 eV and incremented by 100 eV. It is not possible with SIMION to enter the initial velocity as a parameter, but it is possible to impart some kinetic energy to the ions. In any case, the velocity is related to the kinetic energy. It can be seen from the simulation that even for ions with an initial kinetic energy of 150 eV, with the typical voltages used for orthogonal acceleration there is still a substantial residual angular deflection. In fact, it seems that the upper limit for the initial kinetic energy is about 200 eV. Since the ions formed in the first time-of-flight mass spectrometer are extracted typically with a kinetic energy of 2 keV, it can be concluded that some means of retarding these ions to under 200 eV will be essential. Also, it is clear that the ions emerging from the orthogonal extraction optics will need some further deflection to compensate for the angle imparted due to their initial kinetic energy.
Figure 6.7: SIMION simulations showing the trajectories of ions with varying initial kinetic energy in the TOF1 direction being accelerated at right angles using orthogonal dual extraction optics.
6.3.2 Retardation Optics

The most straightforward way to retard the ions was to establish a deceleration field between two planar electrodes. This is shown diagrammatically in Figure 6.8. The retardation optics were modelled using the same design as for the extraction optics, i.e., 80x80 mm electrodes. Again, in practice, these consist of gold-plated aluminium electrodes with a 22 mm diameter aperture in the centre, covered with 90% transmission nickel mesh. The distance between the retardation plates was set at 15 mm. In a typical experiment, using extraction voltages of +2100 V and +1600 V on the repeller and draw-out electrodes, respectively. Deceleration of the ions to 100 eV could be accomplished by applying a voltage of +1750 V on the second retardation plate. The first plate was kept at ground potential to mark the end of the field-free drift region.
Figure 6.8: Diagram showing the electrostatic fields exerted upon an ion from the ion source to the retardation optics. The final kinetic energy of the ion is 100 eV.
Since the final voltage on the retardation optics was +1750 V, the interaction region for PID would need to be set at that potential to remain field-free. Thus the repeller and draw-out electrodes in the orthogonal extraction optics were also set at +1750 V. The idea was to subsequently pulse the repeller electrode to +3000 V to extract the ions. This arrangement was modelled by placing the retardation optics 10 mm before the extraction optics. Figure 6.9 shows a 3D isometric view of the electrodes entered in SIMION. The retardation electrodes were entered as plates with a circular aperture, 22 mm diameter in the centre. In the simulations, illustrated in Figure 6.10, series of ions of m/z = 300 were given 1850 eV initial kinetic energy to represent a typical experiment. Time markers were set every 2 μs. It can be seen from the figure that the time markers are more closely spaced, after the ions have passed through the retardation plates. However, the trajectories of the ions are slightly deflected towards the draw-out electrode, due to small field imperfection resulting from the separation between the two sets of optics. This effect can be seen more clearly on the potential energy view, shown in Figure 6.10b. This view also illustrates the large decelerating step that the ions have to climb before reaching a field-free plateau: ions enter from the right hand side in this view.
Figure 6.9: 3D isometric view from SIMION showing the electrodes placed in the interaction chamber. Prior to the extraction optics are the retardation electrodes. Simulations of the effect of the deflection plates situated above the extraction optics are presented in the following section.
Figure 6.10: SIMION simulations showing the deceleration of ions in the retardation plates: a) The 2D view shows the time markers closely spaced after passage through the retardation plates, b) The 3D potential energy view shows the electrostatic fields exerted on the ions.
The retardation optics were built to the same dimensions as used in the modelling calculations and tried experimentally. It was found that the transmission into the second time-of-flight mass spectrometer was greater when the voltage on the retarding plate was decreased. In fact, the transmission was still at a maximum when the voltage was completely switched off, which seemed quite baffling. However, setting the retarding voltages to ground in the simulation provided the answer. By setting a grounded, planar, electrode in front of the extraction optics floated at a high voltage, the irregularities in the field have a focusing effect on the incoming ion beam (Figure 6.11a. This effect is even more striking in the potential energy view shown in Figure 6.11b, where the “valley effect” between the edges of the extraction plates intuitively leads to a focal point. Incidentally, the position of the focal point can be shifted, by applying a potential on the retardation electrode. In Figure 6.12, potential contours are drawn every 50 V. It can be seen that, at the focal point, the potential is about +1640 V. This corresponds to a final energy of 210 eV for the incoming ions, which is towards the upper limit discussed in the previous Section. During the experimental work, this proved to be an acceptable value, since a greater transmission was achieved with this value into the orthogonal time-of-flight mass analyser. Model simulations showing the orthogonal extraction of ions are illustrated in Figure 6.13, where the time of the pulse applied to the repeller electrode to +3000 V is shown by a time marker. In this figure, potential contours are drawn every 100 V. Despite the presence of the grounded retarding plate, it can be seen that the contours are more or less flat in the region of acceleration of the ions. This simulation also features the subsequent deflection of the ions into the vertical time-of-flight mass spectrometer, which is more fully described in the following Section.
Figure 6.11: SIMION simulations showing the retarding and focusing effect of floating the extraction optics to +1750 V: a) The 2D view, b) The potential energy view showing the "valley effect" of the electrostatic field.
Figure 6.12: SIMION simulations of the deceleration and orthogonal extraction optics showing the potential contours drawn every 50 Volts. At the focus point of the trajectories, the voltage is 1640 V, which corresponds to a retardation of the ions to a kinetic energy of $1850 - 1640 = 210$ eV.
Figure 6.13: SIMION simulations of the deceleration and orthogonal extraction optics showing the potential contours drawn every 100 Volts, after the repeller electrode has been pulsed up to a voltage of +3000 V.
6.3.3 Deflection Optics

A set of deflection plates was modelled in order to simulate their effect on the trajectory of the ions emerging from the orthogonal extraction optics. The flight distance was taken as 90 cm, which corresponded to the actual drift tube length of the apparatus. In the first instance, the deflection plates were tested for a number of ions with varying initial kinetic energy. The voltage on the plates was adjusted to obtain a vertical trajectory that would hit a virtual detector at the end of the drift region. Figure 6.14 shows the trajectory of six ions with an initial kinetic energy of 50, 60, 70, 80, 90, and 100 eV in the horizontal direction. The voltage on the appropriate deflection plate, and the initial starting position of the ions, were adjusted to obtain the best vertical trajectory for all ions. In a real experiment, the initial starting position of the ions would be optimised by adjusting the delay of the pulse applied to the repeller electrode. It can be seen from Figure 6.14 that the ions were successfully deflected onto a vertical path, but ions of differing initial kinetic energy could not be focused onto a single point. Figure 6.15 shows a similar simulation. In this case, six ions were given an initial kinetic energy ranging from 100 eV to 200 eV. The starting position of the ions had to be moved, and the deflection potential increased, in order to compensate for the higher kinetic energy. Here, a better focus at the end of the drift region was achieved. A further simulation, with initial kinetic energies ranging from 200 eV to 400 eV, is illustrated in Figure 6.16. Here, the starting position of the ions was moved as far back as possible. If it were moved further back, the ions would impact on the draw-out electrode instead of going through the circular 22 mm diameter centre aperture grid. A deflection voltage of +430 V was required to direct all the ions up into the drift region. It can be seen from Figure 6.16 that a focal point was obtained in the middle of the drift region, but the ions were somewhat defocused at the detector end. As a conclusion, it could be said that the best trajectories were obtained with a deflection voltage of +350 V, and that the incoming ions should have a kinetic energy ranging from 100 eV to 200 eV.
Figure 6.14: SIMION simulations showing the deflection of ions from the extraction optics vertically into the second time-of-flight drift region. Initial kinetic energy of the ions ranges from 50 eV to 100 eV. Starting position $x = 65$.
Figure 6.15: SIMION simulations showing the deflection of ions from the extraction optics vertically into the second time-of-flight drift region. Initial kinetic energy of the ions ranges from 100 eV to 200 eV. Starting position x = 60.
Initial kinetic energy: 200 eV to 400 eV
Starting position: x = 53

Deflection: +430V
Flight: 0 V
Draw out: +1750 V
Repeller: +3000 V

Figure 6.16: SIMION simulations showing the deflection of ions from the extraction optics vertically into the second time-of-flight drift region. Initial kinetic energy of the ions ranges from 200 eV to 400 eV. Starting position x = 53.
6.3.4 Whole Instrument Simulation

In order to model the performance characteristics and behaviour of the tandem time-of-flight mass spectrometer, its various ions optics were placed in a SIMION workbench with multiple instances. The dimensions and distances were taken to represent the real instrument. A user program was written to enable pulsed acceleration of the ions into the second time-of-flight mass analyser. When running the simulation, the user is prompted to enter the time at which the repeller voltage in the interaction chamber is pulsed from 1750 V to 3000 V.

```
defa switch_time 20
defa rep2_voltage 1750

seg fast_adjust
    rcl switch_time
    rcl ion_time_of_flight
    x<y goto zapit

3000 sto adj_elect02 exit

lbl zapit
    rcl rep2_voltage 1750
    sto adj_elect02
```

A typical simulation of the ion trajectories through the entire tandem time-of-flight instrument is shown in Figure 6.17
Figure 6.17: SIMION simulations showing the trajectory of ions through the whole tandem time-of-flight mass spectrometer. A packet of six ions with 0.2 mm incremental separation in the vertical axis was placed in the source.
6.3.5 Ion Transmission

In this section, the transmission of ions in the reflectron time-of-flight mass spectrometer was simulated. A reflectron drawn to the same scale as the actual analyser available was situated 1 m from the extraction optics. A beam stop, 40 mm diameter, corresponding to the dimensions of the dual micro-channel plate detector was placed at the appropriate position in the ion workbench. The extraction voltages were set at +3000 V and +1750 V for the repeller and draw-out electrodes, respectively. The reflectron voltages were set at +2000 V for the middle grid and +3000 V for the back grid.

In the first instance, ions of varying initial kinetic energy were flown in the workbench. Parameters such as the initial starting position and the deflection voltage were adjusted so that most of the ions would be transmitted through to the detector. Figure 6.18a shows the trajectories of six ions with increasing initial kinetic energy from 50 eV to 100 eV. In Figure 6.18b the kinetic energy increases from 100 eV to 200 eV. It can be seen that in both cases all the ions hit the detector. However, in Figure 6.18a, the ions are diverging and only just manage to reach the detector. In Figure 6.18b, the ions are more focused on the detector. Also, the starting position of the ions and the voltages of the deflection plates have to be significantly altered depending on the initial kinetic energy. Therefore, it is expected that for ions starting with a spread in kinetic energy the transmission would be poor.

In order to simulate the spatial spread of the ions at the photodissociation point, ions were started at varying positions, with same initial kinetic energy of 100 eV. Figure 6.19a shows the effect of varying the position of the ions in the horizontal direction, with a total spread of 6 mm. Figure 6.19b shows the effect of varying the position of the ions in the vertical direction, also with a spread of 6 mm. In both cases a deflection voltage of +200 V was applied. It can be seen that in both cases the transmission of ions to the detector is very good. This indicates that the spread in the initial starting position of the ions would not have too great an impact on the transmission of the ions.
Figure 6.18: SIMION trajectories showing the transmission of ions of varying initial kinetic energy in the second, reflectron, time-of-flight mass spectrometer: a) initial kinetic energy incremented by 10 eV from 50 eV to 100 eV, b) initial kinetic energy incremented by 20 eV from 100 eV to 200 eV.
Chapter 6 Development of a Tandem Time-of-Flight Mass Spectrometer

Figure 6.19: SIMION trajectories showing the transmission of ions of varying initial position in the second, reflectron, time-of-flight mass spectrometer: a) initial horizontal position incremented by 1 mm each side of the photodissociation point, b) initial vertical position incremented by 1 mm each side of the photodissociation point.
6.3.6 Ion Selection

One of the advantages of the orthogonal configuration for the two time-of-flight drift regions is that it allows some mass selection. The timing of the pulse applied to the repeller electrode can be adjusted to coincide with the passage of an ion of a particular mass-to-charge ratio. In order to evaluate the mass range transmitted for each pulse, a calculation was performed using SIMION. In the first instance, the spatial "window" of transmission into the second time-of-flight mass spectrometer was estimated using the same model as described in the previous Section. A series of ions, with incremental starting positions every 2 mm in the horizontal axis, was flown in the workbench. The results of the simulation are shown in Figure 6.20. As can be seen, some of the first, as well as some of the last, ions hit either the draw-out or the flight electrode. In fact, only five ions out of the thirteen flown reach the detector. This corresponds to a spatial window of transmission of 8 mm. This was converted to a time window by calculating the ion velocity at the point of pulse extraction. For a typical ion of m/z = 300, decelerated to 100 eV, the velocity was calculated to be 8040 m s\(^{-1}\). The time window \(\Delta t\) could then be deduced: \(\Delta t = 1 \, \mu s\). The time-of-flight of this ion was obtained using the \textit{record} function of SIMION. A beam stop was placed in the workbench at the point of pulse extraction. The time of impact on this electrode was \(t = 42.4 \, \mu s\). The mass selection capability of the pulse extraction can be expressed in the same as the mass resolution:

\[
\frac{m}{\Delta m} = \frac{t}{2\Delta t} = 21.2
\]  

(6.4)

Although this value is not very high, effective mass selection of a precursor ion could be achieved in many cases by pulse extraction into the off-axis time-of-flight mass analyser.
Figure 6.20: SIMION simulations showing ions with a range of initial position in the horizontal axis. Ions pulsed too early or too late hit the electrodes, thus illustrating the "time gate" during which ions are transmitted into the second time-of-flight drift region.
6.3.7 Mass Resolving power

It was anticipated that the deflection of the ions into the orthogonal time-of-flight mass analyser would affect the mass resolution adversely. In order to test this, a number of ions were flown in the "reflectron" workbench described in the Section above, using time markers.

In the simulation shown in Figure 6.21, a series of ions of m/z = 300 were started at varying positions in the horizontal direction. It can be seen that there is a loss of mass resolution due to the deflection of the ions towards the reflectron. However, by adjusting the voltage on the middle grid of the reflectron, it was possible to time-focus the ions on the detector. In the simulation shown in Figure 6.22, a series of ions of m/z = 300 were started at varying positions in the vertical direction. As can be seen from this figure, this resulted in a significant spread in the arrival time of the ions. Tuning of the reflectron middle grid voltage to +1790 V again enabled the time-focus of the ions onto the detector to be regained.
Figure 6.21: SIMION simulations showing a) the substantial loss of mass resolution resulting from the deflection of ions having a spread in their initial position in the horizontal axis, b) the time focusing obtained by tuning the reflectron middle grid voltage from +2000 V to +1790 V
Figure 6.22: SIMION simulations showing a) the substantial loss of mass resolution resulting from the deflection of ions having a spread in their initial position in the vertical axis, b) the time focusing obtained by tuning the reflectron middle grid voltage from +2000 V to +1790 V
6.4 Experimental Instrument Characterisation

Initial experiments involved verifying that both time-of-flight analysers were operating satisfactorily. For these experiments, aniline was admitted to provide a low background pressure in either the laser desorption/laser ionisation chamber, or the interaction chamber, using a needle valve.

Figure 6.23 shows the photoionisation mass spectrum obtained for aniline using the first linear time-of-flight mass analyser. The aniline was photoionised using the unfocused fourth harmonic output (266 nm) of the Quantel Brilliant Nd:YAG laser. The peak due to the $^{13}$C isotope of the aniline molecular ion can be resolved in this spectrum; the mass resolution ($m/\Delta m$) is approximately 250. Figure 6.24 shows the photoionisation mass spectrum of anisole obtained using the reflectron time-of-flight mass analyser. In this case photoionisation was carried out in the interaction chamber (IC). The mass resolution of this spectrum is substantially higher, approximately 900.

The mass spectrum shown in Figure 6.25 shows the molecular ion of aniline, which has been selected by pulse acceleration into the reflectron mass analyser. Here the mass resolution is about 500, which indicates that it is somewhat degraded during the passage of ions into the second stage of the tandem time-of-flight mass spectrometer.

In terms of sensitivity, it was estimated that the transmission of ions from the first stage analyser to the second stage analyser was about 10%. This was achieved by measuring the absolute intensity of the signal for the aniline molecule ion on the digital oscilloscope. Care was taken to use exactly the same conditions, in terms of sample input, laser power density and detector gain, in order to obtain a meaningful comparison between the linear (TOF1) and the tandem (TOF1/ReTOF2) signal. It appears that there was therefore a substantial loss of ions. This could be explained in part by the loss of ions in passing through successive meshes in the additional ion optics that are present in ReTOF2, e.g. the extraction optics, the reflectron and the detector. However, this does not account for the whole losses, so it is reasonable that conclude that the interaction chamber optics could be improved.
Figure 6.26 shows the linear photoionisation time-of-flight mass spectrum obtained for tryptophan by laser desorption/ laser ionisation. The sample was volatilised by irradiation with the focused output of the Alltec 861 CO₂ laser, and ionised with the fourth harmonic output (266 nm) of the Quantel Brilliant Nd:YAG laser. The base peak in the spectrum corresponds to the dehydroindole fragment ion at m/z = 130. A smaller peak due to the molecular ion is also present at m/z = 204. The signal at m/z = 93 is due to the molecular ion of aniline which was admitted into the laser desorption/ laser ionisation chamber in order to provide a calibration peak.
Figure 6.23: Linear photoionisation time-of-flight mass spectrum of aniline, showing the peak due to the molecular ion and the $^{13}$C isotopomer.
Figure 6.24: Reflectron photoionisation time-of-flight mass spectrum for anisole, showing the peak due to the molecular ion at m/z = 108 and the $^{13}$C isotopomer peak at m/z = 109.

Figure 6.25: Tandem photoionisation time-of-flight mass spectrum for aniline. The molecular ion was selected by pulsed acceleration into the second, reflectron time-of-flight mass spectrometer.
Figure 6.26: Linear photoionisation time-of-flight mass spectrum for tryptophan. The peak at m/z = 93 is due to aniline and was used for calibration purposes.
6.5 Conclusion

The tandem (TOF/TOF) mass spectrometer was successfully developed and used for photodissociation studies of volatile compounds. Mass resolution was satisfactory, but transmission from the first time-of-flight stage to the second was relatively poor. However, practical experimentation confirmed to a large extent the trajectory calculated using SIMION.

Ion transmission could be improved by reducing the number of grids in the ion optics. Fine nickel mesh (Buckbee Mears, 90% transmission) was used to define precisely the electrostatic fields in the extraction and retardation optics, the reflectron, and the detector. In total, an ion had to traverse three grids in the first time-of-flight region and seven grids (including four in the dual-stage reflectron, due to the ions travelling in and out of it) in the second region. This reduces the maximum transmission to 35%. Gridless reflectrons have been designed and implemented [22]. This would improve the transmission substantially, to a maximum of 53%. However, such reflectrons require tight focusing of the ion beam close to the reflectron axis, otherwise substantial losses occur due to the complex equipotential lines. It may also be possible to design gridless extraction optics, but again this has to be balanced against the benefit of having well defined electrostatic field regions.

As shown in the trajectory simulations, there are also substantial losses due to the initial ion velocity in the (TOF1) direction. To compensate for this, the trajectories were corrected by placing deflection plates in the interaction chamber, but the result was not perfect. It was initially intended to decelerate ions to almost zero kinetic energy, thus eliminating completely the velocity component in the (TOF1) direction. Unfortunately, this approach was not successful, probably due to the fact that stationary ions were more susceptible to the small imperfections in the electrostatic field of the interaction region, and diverted off the direction of the ion beam.

In order to further characterise the tandem (TOF/TOF) mass spectrometer, it may be interesting to compare its performance with a collinear configuration. It would be necessary to overcome the problem of mass dispersion in the second part of the
instrument, possibly by using post acceleration and a quadratic ion mirror [23]. It is likely that a higher transmission of ions could be achieved, but the residual velocity from (TOF1) in the axial direction could be detrimental to the mass resolution.

References


Chapter 6 Development of a Tandem Time-of-Flight Mass Spectrometer


Chapter 7

Study of the Photo-Induced Dissociation of Organic Molecules using tandem TOF/TOF-MS

7.1 Photo-Induced Dissociation of Volatile Molecules

7.1.1 Introduction

Molecules undergoing chemical reaction in the gas phase are subjected to a great number of intermolecular collisions. The increase in internal energy resulting from these collisions is quickly dissipated following a Maxwell-Boltzmann distribution curve. In a mass spectrometer, under high vacuum, the probability of collisions between molecules is extremely low, so that any amount of energy imparted to a molecule results in excitation and dissociation, with no possibility of interaction between other excited species. The reactions that are observed are unimolecular fragmentations.
Two theories explaining unimolecular reactions under high vacuum were proposed in the early 1950s: The Quasi Equilibrium Theory (QET), proposed by Rosenstock, Wallenstein, Warhaftig and Eyring [1] was applied to mass spectrometry. The “RRKM” theory, from the initials of its authors, Rice, Rampsberger, Kassel and Marcus [2], described molecules in general. Both theories are very similar and based on several assumptions and postulates:

1st assumption: The rotational, vibrational, translational and electronic movements are independent of each other.

2nd assumption: The movement of the nuclei can be expressed by classical mechanics.

1st postulate: The energy distributes itself among all the degrees of freedom with the same probability

2nd postulate: The system can be described as movements on a multidimensional surface, with the reactants irreversibly crossing a boundary surface to give products.

Both theories lead to the following expression for the rate constant of a unimolecular reaction:

\[
k(E) = \frac{S}{h} \frac{P^a(E-E_0)}{\rho_E}
\]

(7.1)

where \( h \) is Planck’s constant, \( S \) is the statistical factor representing the number of possible equivalent paths for the reaction that is studied, \( P^a(E-E_0) \) represents the total number of states corresponding to the activated complexes between energies 0 and \( E-E_0 \) and \( \rho_E \) represents the density of states of the molecule ion at energy \( E \).

Techniques used to study unimolecular reactions include photoion-photoelectron coincidence (PIPECO) [3], electron-impact coincidence, and excitation of molecule ions by photon [4,5], electron or collisional [6] methods.

Multiphoton ionisation (MPI) has been used by a number of groups for the preparation of polyatomic ions. The technique has been employed to examine dissociation dynamics, including measurement of the rates of unimolecular decay processes. However, the technique has some drawbacks. For example, the molecule
ions generated via MPI can undergo further photon absorption, dissociating to form fragment ions. This so-called "ladder-switching" process is typical for nanosecond excitation of most molecules. Also, in some cases, neutral fragments can be formed during multiphoton excitation, which can then be ionised during the initial laser pulse. Although it is possible to reduce the laser intensity to suppress these effects, this invariably leads to an overall reduction in the yield of the molecule ion.

As has been recognised by others, there are advantages in separating both spatially and temporally the initial multiphoton ionisation step used to create the molecule ion from any subsequent excitation step used, for example, to induce photodissociation. Such an arrangement ensures that no additional precursor ions are produced in the second laser excitation step, helping to define the internal energy of the molecule ions. This can be further improved by employing a molecular beam source to provide a reduced range of internal energy of the target molecule, as well as through the use of resonance enhanced photoionisation schemes to allow more efficient photoionisation at lower laser intensity.

7.1.2 Photo-Induced Dissociation of the Aniline Molecule Ion

Results using the TOF/TOF-MS

There have been a number of previous studies of the photodissociation of the molecule ion of aniline (see structure below in Figure 7.1).

![Figure 7.1: Chemical structure of aniline](image)

Early work by Proch et al. [7], using MPI between 266-300 nm, led to identification of the metastable decay channel \( \text{C}_6\text{H}_7\text{N}^+ \rightarrow \text{C}_5\text{H}_6^+ + \text{HCN} \) (now known to be HNC [8]). The rate-energy dependence for the same reaction was later
obtained, using the photoion photoelectron coincidence (PIPEC0) technique by Baer et al. [9], who employed MPI in the visible at 460 nm. The most comprehensive study to date has been by Kühlewind et al. [10], using UV-MPI, who identified a number of new metastable ion decay channels of the aniline cation using a reflectron time-of-flight mass spectrometer, and proposed a fairly detailed fragmentation pathway following multiphoton excitation. In the most recent work, by Yoon et al. [11], the photodissociation of aniline molecule ions, generated by two-photon ionisation at 266nm, has been studied using mass-analysed ion kinetic energy (MIKE) spectrometry.

In the present work we have also employed two-photon ionisation at 266nm to prepare the molecule ion of aniline. The ions created in this step were accelerated into the first (linear) time-of-flight analyser and then subjected to a second laser pulse at 266 nm in the interaction chamber to induce photodissociation. The resulting product ions were then pulse accelerated into the reflectron time-of-flight analyser.

Figure 7.2 shows the mass spectrum of the ions created in the first (ionisation) step. Both the precursor ion (m/z 93) and a number of fragment ions can be seen. Figure 7.3 shows the corresponding mass spectrum for precursor ions mass-selected by pulsed acceleration into the reflectron time-of-flight mass analyser (TOF2). Figure 7.4 show the reflectron time-of-flight mass spectra following photo-induced dissociation of the precursor ion in the interaction chamber.
Figure 7.2: Linear (TOF1) mass spectrum of aniline.
Figure 7.3: Aniline molecule selectively accelerated into the second, reflectron time-of-flight mass analyser
Figure 7.4: PID spectra of aniline obtained at (a) low laser power density (3.6 x 10^8 W cm^{-2}), b) high laser power density (8.3 x 10^9 W cm^{-2})
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Discussion

At the lowest photodissociation laser intensity, the fragment ions at m/z 66 [C_{5}H_{5}]^{+} and m/z 92 [C_{6}H_{6}N]^{+} are prominent, corresponding to one photon excitation of the molecule ion. Weak peaks are also present at m/z 65 [C_{5}H_{5}]^{+}, m/z 54 [C_{3}H_{4}N]^{+}, m/z 41 [C_{2}H_{3}N]^{+} and m/z 28 [CH_{2}N]^{+}. With increasing photodissociation laser intensity, additional ions, e.g. m/z 65 [C_{5}H_{5}]^{+}, m/z 54 [C_{3}H_{4}N]^{+}, m/z 51 [C_{4}H_{3}]^{+}, m/z 50 [C_{4}H_{2}]^{+}, m/z 39 [C_{3}H_{3}]^{+} and m/z 28 [CH_{2}N]^{+} are visible. At this higher photodissociation laser intensity, the residual molecule ion peak has been substantially depleted, being approximately one third of the intensity of the corresponding peak in the spectrum shown in Figure 7.3(b). These product ions have been previously assigned as arising from two-photon excitation of the molecule ion [10], as shown on the fragmentation tree in Figure 7.5. Kühlewind et al. proposed several mechanisms to rationalise the peak appearance in their metastable ion spectrum. They attributed the presence of product ions at m/z 51 [C_{4}H_{3}]^{+} and m/z 50 [C_{4}H_{2}]^{+} to rapid dissociation of the molecule ion into m/z 77 [C_{6}H_{5}]^{+} and m/z 76 [C_{6}H_{4}]^{+}, respectively, followed by metastable loss of C_{2}H_{2}. However, we observe very weak peak abundance at m/z 77 and m/z 76 in all our spectra, compared with a peak at m/z 66 that shows increased abundance with increased laser power density. Our interpretation is that other mechanisms may be involved, for instance dissociation of the molecule ion into m/z 66 [C_{4}H_{4}N]^{+} by successive loss of H and C_{2}H_{2} with two-photon excitation. Further fragmentation of [C_{4}H_{4}N]^{+} into m/z 51 [C_{4}H_{3}]^{+} and m/z 40 [C_{2}H_{2}N]^{+} by further loss of C_{2}H_{2} and NH, respectively, may occur. The corresponding peaks are indeed present on our photodissociation spectra. The coincidental m/z 66 of [C_{5}H_{6}]^{+} and [C_{4}H_{4}N]^{+} may explain the strong peak intensity observed at that mass-to-charge ratio.

Regarding the internal energy of the molecule ions undergoing photodissociation, we have no direct measurement. The ionisation energy (IE) of aniline is 7.72 eV. For two-photon ionisation at 266 nm, the excess energy available to the molecule ion is 1.60 eV (neglecting the thermal energy of the precursor molecule, <0.05 eV).
Figure 7.5: Fragmentation tree for laser photodissociation of the molecule ion of aniline, based on mechanisms proposed in [11].
However, in the recent PD-MIKE study by Yoon et al. [11], it has been shown that the internal energy of the aniline molecule ions generated by two-photon ionisation is only \( \sim 50\% \) of the available energy \((2hv - IE)\). In their study, as in this work, spatial (1.46 m) and temporal (\( \sim 25 \mu s \)) separation between the point of ion generation and photo-induced dissociation ensures that only ions with this level of internal energy contribute to the PID spectra. Only a fraction (0.03\%) of molecule ions associated with three-photon excitation in the initial laser ionisation step remains after a time delay of 20 \( \mu s \), so that their contribution to the PID spectra is negligible.

**Comparison of Photo-Induced with Collision-Induced Dissociation**

Results for the collision-induced dissociation of the aniline molecule ion, using a commercial mass spectrometer equipped with an atmospheric pressure electrospray ionisation interface, are also presented. These experiments were carried out on a Micromass Quattro LC instrument, equipped with an atmospheric pressure electrospray (ApESI) interface. The number of collisions between the precursor ions and the buffer gas in the ApESI source increases as the cone voltage is increased, resulting in increased fragmentation of the ions. A complete picture of the fragmentation processes can be obtained by collecting mass spectra across a range of cone voltages and combining the data into a map of (cone voltage) versus (mass-to-charge ratio). This visualisation method has been proposed and coined Energy Dependent Electrospray Ionisation (EDESI) [12].
Figure 7.6: EDESI mass spectrum of aniline.
7.1.3 Photo-Induced Dissociation of the Anisole Molecule Ion

Anisole is similar in structure to aniline. It consists of a methoxy, as opposed to an amino group attached to a benzene ring (see structure in Figure 7.7).

![Figure 7.7: Chemical structure of anisole](image)

It was analysed in the TOF/TOF-MS in the same manner as aniline. Figure 7.8 shows the linear (TOF1) mass spectrum obtained by ionisation at 266 nm. The molecule ion (m/z 108) has the greatest intensity, while the other prominent peaks at m/z 93, 78, 65 and 39 correspond to fragments \([C_6H_5O]^+, [C_6H_6]^+, [C_5H_5]^+\) and \([C_3H_3]^+\), respectively. Similar results were obtained by Polevoi et al., also under photoionisation at 266 nm [13].

The molecule ion was selected by pulse acceleration into the second (ReTOF2) mass analyser (see Figure 7.9a). In the PID mass spectrum shown in Figure 7.9b, the molecule ion peak is still prominent, but its intensity has diminished by half compared with the mass spectrum in Figure 7.9a. A relatively low laser power was used to obtain this spectrum, reflected in fragments of relatively high masses. Peaks at m/z 93, 78 and 65 are characteristic of the dissociation into \([C_6H_5O]^+, [C_6H_6]^+\) and \([C_5H_5]^+\).

Polevoi et al. [13] have measured the appearance potentials for the ions formed following stepwise excitation of anisole by laser irradiation at wavelengths between 275 – 300 nm. The appearance potentials (eV) they report are as follows: \([C_6H_5OCH_3]^+ 8.22 \pm 0.05, [C_6H_5O]^+ 11.64 \pm 0.05, [C_6H_6]^+ 11.06 \pm 0.05\) and \([C_3H_3]^+ 12.75 \pm 0.05\). Their data shows that the fragment ions \([C_6H_5O]^+, [C_6H_6]^+\) and \([C_5H_5]^+\) are formed when the molecule ion has absorbed a further single UV photon. The assignment of the smaller peaks at m/z 98, 89 and 74, seen in the mass spectrum shown in Figure 7.9(b), is less obvious.
Chapter 7. Study of the Photo-Induced Dissociation of Organic Molecules using tandem TOF/TOF-MS

The only other published work on the photodissociation of anisole is that by Schmoltner et al., who studied the infrared multiphoton dissociation of anisole at 10.6μm in a molecular beam. [14]. Under these conditions, the only primary process identified was the dissociation into the phenoxy ion and methyl radical.

Figure 7.8: Linear (TOF1) mass spectrum of anisole.
Figure 7.9: Mass spectra showing a) the molecule ion of anisole selected by pulse acceleration, and b) the product ions resulting from photo-induced dissociation.
7.2 L2MS of Involatile Molecules

Figure 7.10 shows the linear photoionisation time-of-flight mass spectrum obtained for tryptophan by laser desorption/ laser ionisation (L2MS). The sample was volatilised by irradiation with the focused output of a Alltec 861 CO₂ laser, and ionised with the fourth harmonic output (266 nm) of a Quantel Brilliant Nd:YAG laser. The base peak in the spectrum corresponds to the dehydroindole fragment ion at m/z 130. A smaller peak due to the molecule ion is also present at m/z 204. The signal at m/z 93 is due to the molecule ion of aniline, which was admitted into the laser desorption/ laser ionisation chamber in order to provide a calibration peak. Similar conditions were used to obtain the mass spectrum of coronene shown in Figure 7.11.

Attempts were made to pulse-accelerate the dehydroindole fragment ion of tryptophan into the reflectron mass analyser, with a view to obtaining a tandem TOF/TOF mass spectrum. Unfortunately, in the present state of the instrumentation, no signal could be seen. This is probably due in part to the poor transmission of ions into the second (ReTOF2) mass analyser. This could be addressed by further optimisation of the ion optics as discussed in chapter 6.

Another reason for failing to transmit desorbed ions through to the second time-of-flight stage resided in the laser desorption process itself. During the experiments in the linear (TOF1) mass spectrometer, it was evident from the monitoring of the signal on the oscilloscope that the intensity was fluctuating wildly from shot to shot, caused by the inhomogeneity of the sample surface. In addition, the sample was rapidly depleted at the desorption target, so that the laser beam had to be frequently directed to a fresh sample spot. In addition to the desorption issues, the ionisation efficiency also varies from molecule to molecule, depending on the relative effects of the processes competing against ionisation [15]. These in turn are dependent on the photon absorption cross-section and the light intensity as explained in Chapter 2.
Figure 7.10: TOF1 mass spectrum of tryptophan. The peak at m/z 93 corresponds to the molecule ion of aniline and was used for calibration purposes.
Figure 7.11: TOF1 mass spectrum of coronene. The peak at m/z 93 corresponds to the molecule ion of aniline and was used for calibration purposes.
In the future, it may be possible to compensate for the inherent instability of the desorption process with a selective accumulation of mass spectra. At present, using the digital oscilloscope, the signal from the detector can be averaged continuously or by summation. It should be possible to collect and store only the intense signals resulting from successful laser desorption events, above a certain threshold below which the desorption is inefficient. One avenue of development in this area would be to use a program such as LabView (National Instruments, Austin, TX, USA) to set up customised control and data acquisition routines.
References


Chapter 8

Development of a Pulsed Arc Cluster Ion Source
(PACIS)

8.1 Elemental Metal Cluster – Background

The difficulty in the generation of significant numbers of elemental metal clusters of the required form has meant that in cluster science the most significant advances have been made as a result of technical developments in improving cluster production [1].

Clusters can be formed from any element in the periodic table, and fall between the limits of the isolated atom and the bulk phase. It is difficult to predict the properties of clusters by extrapolating from models that describe either isolated atoms or bulk systems, because they fall somewhere between the quantum regime of small molecules and the classical regime of condensed matter. Indeed, it has been found that clusters frequently exhibit chemical and physical properties that are not found in the bulk phase. It is these unique properties that could be exploited in a wide number of areas, e.g. catalysis and nanoscale material fabrication. Deposition of mass selected clusters onto a substrate can produce composite materials with novel optical or electronic properties.
Chapter 8. Development of a Pulsed Arc Cluster Ion Source (PACIS)

The cluster regime is broadly accepted as being anything from two to several hundred thousand atoms. There is much debate on where the boundary between the cluster and bulk regime lies - particularly since it often depends on which aspect of the cluster one is considering. However, at the upper end of this regime, the clusters tend to have bulk properties. For medium sized clusters it has been found that the cluster properties tend to be a smoothly varying function of size whereas for small clusters the properties are more dependent on the structure of the molecule. This trend can be explained by considering the surface atoms of a cluster. Compared with the bulk phase, the atoms in a cluster are far more likely to be on or near the surface. Even for a cluster composed of a thousand atoms, about one quarter of these will lie on the surface. As a result of these surface effects then all of the physical properties of a cluster, whether electronic, optical or thermodynamic for example, become essentially size dependent. To fully understand the properties of a cluster it is necessary to get accurate information on its geometric and electronic structure.

There are a variety of different methods that have been developed over the years to produce clusters from a wide range of materials [2]. In general, these cluster sources were optimised for the production of particular types of clusters, with limited control over their characteristics. For example, the gas-aggregation source produces large clusters (1000's of atoms) from low boiling point (less than 2000K) metals, whilst a sputtering source produces clusters, which have high internal energies and are made up of 100's of atoms. A significant advance from these traditional sources was the development of the laser vapourisation source (LVS) [3]. Due to the pulsed nature of the laser, heating of the source block was dispensed with, and furthermore, high carrier gas pressures could be used, into which the expanded plume of ablated material could be seeded to enhance cluster formation and to minimise the internal temperature of the clusters.

A more recent development is the Pulsed Arc Cluster Ion Source (PACIS), which can, in principle, produce clusters from any metal [4]. The main advantage of the PACIS over the LVS is that replacing the vapourisation laser with a high-voltage discharge makes it a much less costly alternative. Furthermore, unlike the LVS, which produces predominantly neutral clusters, the PACIS produces charged
clusters, so post-ionisation is not required. In addition, the abundance of cluster ions produced by the PACIS is much higher than from the LVS. Using the PACIS, the cluster temperatures are expected to be near or below the source temperature, depending on the supersonic expansion conditions. The cluster size distribution has also been found to be dependent on the conditions and geometry of the source.

8.2 Pulsed Arc Cluster Ion Source (PACIS)

8.2.1 Description of the source

The PACIS that was developed and built during the course of this project essentially follows the design of Siekman et al. [4]. It consists of the following main components: (i) the nozzle, which introduces a pulse of helium gas, (ii) the PACIS block, which contained the target electrode (high negative voltage) and the neutral, grounded, electrode, (iii) the expansion cone, and (iv) the high power supply and timing electronics that deliver the pulsed arc through the electrodes.

The source itself is a relatively simple set-up. It consists of the gas supply, the block on which the electrodes are mounted, and the expansion cone, as shown in Figure 8.1. It is mounted on a dual rail system inside the molecular beam (MB) vacuum chamber and can be aligned in X, Y and Z directions using motorised stages.

Helium (BOC Gases, 99.996% pure) was used as the cooling gas. The helium cylinder was connected to a pulsed valve (General Valve Corporation, Series 9) with stainless steel Swagelok tubing to enable safe use at pressures up to 30 bar. The valve was controlled by a pulse driver (General Valve Corporation, Model Iota One), which was used in external mode. A trigger of variable width (5 V amplitude, 180 𝜇s to 300 𝜇s width) was fed into the pulse driver to control the duration of the gas pulse. The valve was fixed onto the PACIS block with four screws and sealed with a Viton O-ring.
Figure 8.1: Exploded diagram of the PACIS, showing the pulsed gas valve, source block and expansion cone.
The PACIS block, a photograph of which is shown in Figure 8.2, was made out of 316 stainless steel. A channel of 10 mm dia. was drilled through it to accommodate the electrodes. The target electrode was usually a metal rod 5 mm in diameter, about 80 mm in length. It was held in a series of boron nitride spacers for electrical insulation inside the stainless steel channel using Viton O-rings to provide a vacuum seal. The rod was accurately secured into position with a Teflon lined brass fitting, through which it emerged, and was connected to the power supply. At the other end, a stainless steel rod was similarly screwed into position. In this case no electrical insulation was needed since the electrode was connected to ground. The spacing between the two electrodes was typically 1.5 mm, and was determined by the end boron nitride spacer that fitted onto the target rod. A hole of diameter 1mm was drilled through this spacer ring in order to let the helium carrier gas in and out. The exit from the PACIS block was through a 2 mm diameter hole. A standard KF25 port at the exit was used to clamp the block to the expansion cone.
The expansion cone was made out of machined brass. It consisted of two cylindrical elements that fitted snugly together. A cone of length 97 mm, 23.6° angle, with an entrance hole of diameter 2.5 mm and an exit diameter of 42.5 mm, was drilled out of the cylindrical elements. The expansion cone fitted into a large aluminium block, which was fixed onto the motorised stage, and which had a KF25 port for clamping onto the PACIS block. An additional element was inserted between the PACIS block and the expansion cone to enhance the clustering process. This so-called "waiting room" consisted of a 10 mm long brass cylinder which fitted into the KF25 flange, into which was drilled a small cavity of 5 mm diameter which tapered down to a 1 mm hole at the exit toward the expansion cone.
8.2.2 PACIS Electronics

To produce the high voltage high current arc necessary for generating clusters the following electronic equipment was built following the design supplied by Meiwes-Broers group: a power supply, a pulse generator, and a high voltage switch. Additionally, the control box contained a board used for driving the X, Y stepper motors onto which the PACIS source was mounted. A circuit diagram for the power supply is shown in Figure 8.3. It consisted of a 12 A Variac, a high voltage transformer (1400V AC, 1 kW), a high voltage bridge rectifier followed by smoothing capacitors and equilibrating and current limiting resistors. The resulting signal was fed into a high voltage capacitor (Maxwell Laboratories Inc., Model 30549) of specifications 50 μF, 3.5 kV. This capacitor would discharge itself during the pulse applied to the high voltage switch. A pulse of suitable delay and duration (typically 5 V amplitude, 30 μs width) could be applied directly to the switch. Alternatively, a trigger pulse could be fed into the control box, which contained a logic board capable of adjusting the delay and the width of the input pulse. The high voltage switch (Behlke Electronics GmbH, Model HTS 51) was made up of a large number of MOSFETs, lying parallel and in series, which were combined in a compact, low inductance bank. It had very short turn-on (rising) and turn-off (falling) times of a few nanoseconds, variable on-time, and a rating of 5 kV and 30 A. It required a 5 V auxiliary voltage, which was supplied by the control box. A suitable trigger was fed into the switch to release the high DC voltage. The switch was protected by a high voltage diode assembly (Behlke Electronics GmbH, Model FDA-50-240). Current limiting resistors mounted on heat sinks were placed between the switch and the target electrode. Additional heat dissipation was provided by two medium-sized fans (Radio Spares, Type 4650 Z). A schematic diagram of the switching circuit is given in Figure 8.4.
Figure 8.3: Schematic circuit diagram for the PACIS power supply.
Chapter 8. Development of a Pulsed Arc Cluster Ion Source (PACIS)

Figure 8.4: Schematic diagram of the circuit for the high voltage switch for the PACIS source.
8.2.3 Experimental Control

The hardware used for the experimental control has been described in detail in Chapter 3, Section 3.7. The timing sequence shown below in Figure 8.5 was achieved using a series of pulse delay generators, shown diagrammatically in Figure 8.6. It was possible to vary the duration of each of the trigger pulses duration (except the one used to trigger the PACIS discharge, which was fixed by the CAMAC modules to 50 μs), as well as the time delays between the trigger pulses to the pulse valve, the PACIS source and the pulse extraction optics. The timing sequence shown in Figure 8.1 corresponds to the typical settings used for experiments involving time-of-flight characterisation of the cluster distribution produced by the PACIS source, see Section 8.3.
Figure 8.5: Timing sequence of trigger pulses for a cluster experiment using only the linear TOF1 mass analyser.
Figure 8.6: Schematic diagram of a typical experimental control set-up for cluster experiments using the PACIS source.
8.3 TOF-MS of Elemental Metal Clusters.

The PACIS source, a photograph of which is shown in Figure 8.7(a), was initially tested using a lead target rod. The generation of a cluster ion beam necessitated careful optimisation of all the voltages and delays. It was not until these were correctly set that the first cluster mass spectrum was observed. The emission from the expanding plasma plume produced by the PACIS is quite intense and easily photographed. Figure 8.7(b) shows one such photograph of the source in operation.

Using this source, cluster ion beams containing clusters with up to 50 atoms were generated. An example of a spectrum recorded for lead clusters is shown in Figure 8.8. The insert shows an expansion of the region of the spectrum in the neighbourhood of Pb$_2^+$, revealing the presence of a number of oxides of lead. Lead is known to readily form clusters in the PACIS source, as reported by Siekman et al. [4]. However, the fact that the peak due to Pb$^+$ has the greatest abundance suggests that the clustering process was not as effective as it could have been. Indeed, if the condition were ideal, it should be possible to obtain an envelope of peaks with the highest peak intensity for a cluster size of 10 to 15 atoms [4]. The most effective way of improving the conditions is to provide some means of cooling the source, e.g. by circulation of water or liquid nitrogen around the source block.
Figure 8.7: Photographs of the PACIS source showing: a) the various components of the source, and b) the supersonic expansion emerging from the PACIS block; on the right hand side, the conical shape of the skimmer is outlined by the beam.
Figure 8.8: TOF mass spectrum for lead cluster cations generated using the PACIS source: a) full spectrum; b) expanded view (x14) for the mass region m/z > 4000
Similar results to those for lead were obtained for platinum. Figure 8.9(a) shows the time-of-flight mass spectrum for platinum cluster ions, which is dominated by the Pt$^+$ peak. Once again, examination of the spectrum at slightly higher resolution reveals the presence of a significant amount of oxides, see Figure 8.3(b), including the mono and di-oxides of platinum, with Pt$_n$O$^+$ being the most abundant species. Further optimisation of the PACIS source is required before the cluster ion intensity is sufficiently high to permit a cluster of a particular size to be selected for tandem TOF/TOF-MS analysis.
Figure 8.9: TOF mass spectrum for platinum cluster cations generated using the PACIS source, a) full spectrum with expanded Y-axis to show cluster ions Pt$_n^+$ up to n=15 in size, b) expanded view of the peaks corresponding to Pt$_2^+$, Pt$_3^+$ and Pt$_4^+$ 2, 3 and 4 revealing peaks due to oxides of platinum.
References


9.1 Summary of Present Work

A novel tandem time-of-flight was successfully constructed, with a view to studying the photodissociation dynamics of organic molecules and metal clusters. It is equipped with a laser desorption/ laser ionisation (L2) source, previously developed by other members of the Edinburgh group, to enable the mass spectrometric analysis of large thermally labile and involatile molecules. A brief review of this technique is given in Chapter 1. The theoretical concepts of laser desorption and ionisation are explained in Chapter 2, which also contains a detailed account of the principles of time-of-flight mass spectrometry. The actual machinery and experimental set-up are described and illustrated in Chapter 3.

An important aspect of the development of the instrument was the optimisation of the ion optics through the use of ion trajectory simulations. In Chapter 4 the computer program SIMION [1], a benchmark for this type of application, is described in some detail. The methods involved in creating potential arrays into which ion optics are defined as electrode points, are explained. The equations used to calculate the electrostatic fields between these electrodes, as well as the trajectory of ions between them, are also given. SIMION is designed to give visual insight into the
behaviour of ions in electrostatic fields. Potential arrays can be projected in a two or three dimension workbench view, and also in a potential energy view that gives a three dimensional visual representation of the electrostatic fields. These features of SIMION are illustrated in practical simulations of ions flying through simple ion optics.

Mass selection of a precursor ion is an essential feature of tandem mass spectrometry. This is easily achieved in quadrupole and magnetic sector instruments. In TOF-MS, however, it is necessary to implement some means of preventing all unwanted ions except the mass of interest from entering the first time-of-flight drift region. In Chapter 5 some consideration is given to this problem. The idea was to place a device, a mass gate, close to the ion beam, and hold it at a certain potential, thus deflecting all ions from their trajectory. This mass gate is then pulsed to ground for a short time to let only the precursor ion through to the next time-of-flight stage. In practice, the width of the mass gate itself must be as narrow as possible to allow maximum mass resolving power. The high voltage pulse to ground must also be very narrow with very short rise and fall times. In this work a novel mass gating device was designed and constructed, using a single high voltage pulser, to achieve a mass resolving power of $m/\Delta m = 30$. A higher performance can be realised by using two such mass gates in series, as recently exemplified by Stoermer et al. [2].

The issues regarding the development of the tandem TOF-MS instrument itself are fully discussed in Chapter 6. The difficulty in implementing mass dispersion in a second time-of-flight drift region is demonstrated, and the approach taken by others researchers to overcome it was discussed and illustrated. It was found that an orthogonal arrangement of two distinct time-of-flight drift regions had some advantages over a collinear arrangement, particularly for photo-induced dissociation. Some degree of mass selection was afforded by pulsed orthogonal acceleration into the ReTOF2. Due to the velocity component in the TOF1 direction, retardation plates were fitted in the interaction chamber. Some residual velocity component was inevitable and had to be compensated for by deflection plates, positioned immediately after the orthogonal acceleration optics. The behaviour of ions travelling through the ion optics was modelled using the program SIMION. Thus the
performance of the instrument could be evaluated in terms of ion transmission and mass resolution, by varying the simulation parameters. The experimental characterisation of the instrument indicated an ion transmission of about 10% from the first to the second time-of-flight stage, and a mass resolving power of \( m/\Delta m = 500 \) for tandem TOF/TOF-MS of aniline and anisole produced by photoionisation at 266 nm and introduced in the form of an effusive beam.

Photodissociation spectra of aniline and anisole were recorded at 266 nm. For aniline, fragmentation occurs predominantly via loss of HNC, or a hydrogen atom, at low laser intensity (corresponding to one photon excitation), while at higher laser intensities, a number of fragment ions are formed following two-photon excitation of the molecule ion. Anisole dissociates by forming the phenyl radical ion. Attempts were made to perform tandem TOF/TOF-MS of tryptophan and coronene, but the inherent instability of the laser desorption step, coupled to the relatively low ion transmission into ReTOF2, prevented any workable signal being detected.

Preliminary results have also been obtained for the generation of some elemental metal clusters, e.g. lead and platinum, using a new Pulsed Arc Cluster Ion Source (PACIS). Although cluster ions containing up to 50 atoms were detected in the linear TOF-MS, the abundance of cluster ions in the interaction chamber was not sufficiently high to perform tandem TOF/TOF-MS.

9.2 Future Work

9.2.1 Tandem L2MS Experiments

The ultimate aim of carrying out tandem L2MS experiments could be reached by directing any further work in two main directions. Firstly, a dedicated data acquisition system, that would selectively pick the relevant signals, should be developed. Secondly, some improvements could be implemented to address the inherent instability of the desorption process.

During the course of the development of the tandem TOF/TOF mass spectrometer, spectra were acquired in real time using a four-channel, 500MHz
digital storage oscilloscope (LeCroy, Model 9344). This was a very useful device for monitoring the effect of each of the parameters affecting the trajectory of ions through the flight regions. However, the only feature available for the accumulation of spectra was averaging of a number of time-of-flight profiles. For the acquisition of spectra in a L2MS experiments, some manipulation of the time profiles would be necessary. In particular, it would be essential to be able to accumulate the signals that contain information about the molecule of interest, and discard those that correspond to rogue laser shots. Thus the dissociation events that are successfully detected, however weakly, in the ReTOF2 analyser, could be added together to produce a meaningful spectrum. Some dedicated software would be required for this, e.g. a program such as LabView (National Instruments, Austin, TX, USA). Other useful features could be included, for instance interdependent mass calibration in the TOF1 and ReTOF2 mass analysers.

The laser desorption of solid material into the gas phase is dependent on the morphology and homogeneity of the sample. The method of drop-coating a sample dispersed in a volatile solvent tends to leave a solid deposit, upon drying on a sample probe, that forms a ring of material at the periphery of the solvent drop. This results in poor reproducibility in the sample desorption step. Sample coating by electrospray was described by McNeal et al. [3] and implemented in the Edinburgh group by Hollingsworth [4]. Addition of a matrix would also enhance greatly the reproducibility of the desorption process. However, in the case of in situ analysis of real world samples, indeed those typically amenable to L2MS, inherent sample inhomogeneity is to be expected. The power density of the desorption laser can also be a source of instability in the process. It was found that too little control over the laser intensity was possible. At low intensity no signal was detected, while a coarse adjustment to higher power (effected by opening an iris) resulted in rapid depletion of the sample. More sophisticated laser optics, e.g. filters and lenses, would provide greater control.
9.2.2  Further Developments of TOF/TOF-MS

In this work tandem TOF/TOF-MS was implemented by performing PID at the intersection of two time-of-flight drift regions in an orthogonal arrangement. Future work could involve instrument development with a collision cell to enable CID, possibly with a collinear arrangement of mass analysers. The implementation of tandem TOF/TOF-MS has received some attention in recent times. During the production of this thesis, Medzihradsky et al. have reported the construction of a MALDI-TOF/TOF-MS [5], in collaboration with the instrument manufacturer Applied Biosystems. Global manufacturer Bruker Daltonics have very recently launched the Ultraflex TOF/TOF-MS, designed for high throughput protein identification and peptide mass fingerprinting using a MALDI source.

Another area worthy of further work would be the installation of an ion storage device, such as an RF quadrupole trap, which could be fitted in the interaction chamber to allow accumulation of ions and to enable measurement of the rates of dissociation processes. Recently, Gabryelski et al. have reported preliminary data acquired on an ion-trap linear TOF mass spectrometer [6]. Their instrument is fitted with an electrospray source and is designed for the analysis of large biomolecules such as peptides and proteins. Their ion trap was developed to enable ion accumulation, isolation, and excitation by either CID or PID, followed by ion ejection into the TOF-MS. These events were controlled by a sophisticated system, centrally operated from a personal computer (PC).

It is encouraging that the tandem TOF/TOF-MS concepts that originally motivated this work are already finding commercial applications in the analysis of biomolecules by MALDI-TOF/TOF-MS, and that the technique has already entered the commercial market place.
References


Courses and Conferences Attended

In accordance with the regulations of the Department of Chemistry, University of Edinburgh, I have attended the following courses during my period of study:

1. Laser Spectroscopy (1)
2. Laser Spectroscopy (2)
3. Ultra-fast Molecular Processes (1)
4. Ultra-fast Molecular Processes (2)
5. "C" Inceptor Course
6. Introduction to Microsoft Windows 95/ Powerpoint for Windows
7. Introduction to Unix
8. Enhancing your Unix Skills
9. Simulating Molecular Processes on Surfaces
10. Visual Design: Building Virtual Instruments

In addition, I have also attended the Laser Chemistry Research Meetings and Physical Chemistry Section Seminars over my period of study.
I also have attended the following conferences:


Appendix B

Publications

Laser photo-induced dissociation using tandem time-of-flight mass spectrometry

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A novel tandem time-of-flight (TOFMS) mass spectrometer has been developed for studying the photo-induced dissociation of large molecules and elemental clusters. It consists of a linear first stage TOF analyser for primary mass separation and precursor ion selection, and a second orthogonal reflecting field TOF analyser for product ion analysis. The instrument is equipped with a large volume throughput molecular beam source chamber allowing the production of jet-cooled molecules and molecular clusters, as well as elemental clusters, using either a pulsed laser vapourisation source (LVS) or a pulsed are cluster ion source (PACIS). A second differentially pumped chamber can be used with effusive sources, or for infrared laser desorption of large molecules, followed by laser ionisation. These primary ions can then be irradiated with a second, high energy laser to induce photodissociation. Detailed information about the fragmentation mechanisms can be deduced from the product ion mass spectra. Preliminary results on the photo-induced dissociation (PID) of the molecule ion of aniline at 266 nm are presented. In this case the molecule ions were generated via two-photon laser ionisation at 266 nm using an effusive source. Results for the collision-induced dissociation (CID) of the aniline molecule ion, using a commercial mass spectrometer equipped with an atmospheric pressure electrospray ionisation interface, are also presented. Copyright © 2000 John Wiley & Sons, Ltd.

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Time-of-flight mass spectrometry (TOFMS) has undergone a remarkable renaissance during the last two decades. An important breakthrough was the invention of the reflecting field, or reflectron (ReTOF), mass analyser by Mamyrin. Since then accurate time control and fast signal processing have rapidly improved alongside advancements in electronics and computer science. The development of new ion sources such as matrix-assisted laser desorption/ionisation (MALDI) and electrospray ionisation (ESI) has further stimulated improvements in TOFMS, which has now become the mass analyser of choice for many applications, particularly in the biosciences. Our group and others have developed the use of laser desorption/laser ionisation TOFMS, or L2MS, for in situ analysis of large organic molecules. Time-of-flight mass spectrometry lends itself well to the study of metal clusters, as the technique is ideally suited to pulsed sources such as laser vapourisation (LVS) and pulsed arc cluster ion sources (PACIS).

For the elucidation of complex mixtures, as well as for studies of photofragmentation mechanisms, it is desirable to perform TOFMS in tandem. This approach enables selection of one ion mass in the first TOF analyser, followed by interaction with a collision gas or a laser to induce dissociation, and subsequent analysis of the resulting product ions in the second TOF analyser. Tandem TOF/TOFMS has been previously carried out using a variety of instrument configurations. One easily implemented method involves firing the dissociation laser across the ion path at the back of the reflectron, where the ions are almost stationary, thus increasing the chance of interaction with the laser beam. The product ions are accelerated and separated in the second part of the reflectron. One drawback of this method is that the drift regions are reduced in length and the resolution is only that of a linear TOF mass spectrometer in both stages. Another method is to fire the dissociation laser at the space-time focus immediately following the ion extraction region. This approach has been used to deduce the fragmentation pathways of molecule ions from studies of metastable decay of the ions produced. A double reflector in a Z-shape configuration has also been used, with laser-induced dissociation, or with a collision cell and a modified reflector in the second stage to allow mass analysis. The instrument described in this paper consists of two separate analysers placed orthogonally. A similar configuration has been used with a laser at the intersection of the two drift regions to induce dissociation. Compared with these other instruments, the present one has the added flexibility of a wide range of sources making it a very versatile tandem instrument.

EXPERIMENTAL

A schematic diagram of the instrument is shown in Fig. 1. The apparatus consists of two differentially pumped vacuum chambers (MB and L2), housing different sources, a linear drift region (TOF1), an interaction chamber (IC) and finally an orthogonal reflectron time-of-flight mass spectrometer (TOF2). The whole system is pumped down to a high vacuum (<10⁻⁶ mbar) by means of oil diffusion pumps.
placed under the main chambers: (MB) chamber: CVC, Rochester, NY, USA; Model PBA1000, 2600 Ls⁻¹, (L2) chamber: Edwards High Vacuum, Crawley, UK; Model E09, 2500 Ls⁻¹, (IC) chamber: Edwards, Model 160, 600 Ls⁻¹, and a turbomolecular pump (Edwards, Model EXT250, 250 Ls⁻¹) placed near the reflectron.

Molecular beam chamber (MB)

The molecular beam chamber houses a variety of different pulsed nozzles for use with a laser vaporisation source (LVS) and a pulsed arc cluster ion source (PACIS) for neutral and charged cluster generation.

Figure 2. SIMION trajectories through the ion optics in the interaction chamber. (a) Workbench view of the ion optics; (b) Potential energy view from an opposite angle. The repeller electrode is floated at the same potential as the draw-out electrode, then pulsed to a higher voltage immediately following the photodissociation laser pulse.

PHOTODISSOCIATION IN TOF/TOFMS

Laser desorption/laser ionisation chamber (L2)
This chamber houses the ion extraction optics for the first linear TOF analyser. These are set up in a conventional Wiley-McLaren configuration with a set of horizontal and vertical deflection plates. Either side flange of the chamber can be equipped with 50 mm quartz windows to admit laser beams into the photoionisation region, at the midpoint between the repeller and draw-out electrodes.

For laser desorption experiments, samples are presented on a probe which is introduced through a simple vacuum load-lock mounted on one of the side flanges. The sample probe is usually floated at an appropriate potential between that used on the repeller and draw-out electrodes. The desorption laser, usually a pulsed CO$_2$ laser (10.6 μm), is introduced through a NaCl window on the top flange of the chamber, and can be focused onto the sample probe using a NaCl lens external to the vacuum chamber. The desorbed neutral species are post-ionised a few mm above the sample probe using a pulsed UV laser, (e.g. 266 nm harmonic of an Nd:YAG laser), which is introduced through the side flange opposite to the one holding the sample probe load-lock. In the preliminary experiments described here, aniline was introduced effusively into the chamber via a capillary connected to a small reservoir placed outside the chamber.

Interaction chamber (IC)
Following the linear TOF1 drift region is the interaction chamber (IC). The ions have to be retarded and any product ions pulse-accelerated into the second mass analyser (TOF2). The retardation and reacceleration optics are mounted on a dual rail system similar to that used for the ion optics in the L2 chamber, allowing easy removal, adjustment and replacement. Figure 2 shows the layout of these ion optics, which were modelled using the program SIMION. The diagram shows a simulation of the ion trajectories through the ion optics. The side flanges of this chamber are equipped with 50 mm quartz windows to allow the introduction of laser beams for PID.

In the experiments described here, mass selection of the precursor ion was achieved by appropriate timing of the photodissociation laser.

Reflectron TOF mass spectrometer (TOF2)
The reflectron TOF mass spectrometer is used for identification of product ions. It can be set up to operate in both linear and reflecting mode.

Experimental control and data acquisition
The experiment was controlled by a CAMAC-based delay generator (Kinetic systems, Lockport, Illinois, USA; Model 3655) which triggered the ionising laser and a second delay generator (EG & G Ortec, Oak Ridge, TN, USA; Model 9650A) which was used to control the second dissociation laser and the pulsed acceleration of ions up into TOF2. A photodiode was used to detect a small portion of the photodissociation laser pulse, and provided the start trigger for the digital storage oscilloscope (Le Croy Corp, Chestnut Ridge, NY, USA; Model 9344) that was used for data acquisition.

CID experiments
The experiments were carried out on a Micromass (Manchester, UK) Quattro LC instrument equipped with an atmospheric pressure electrospray (ApESI) interface. The number of collisions between the precursor ions and the buffer gas in the ApESI source increases as the cone voltage, is increased, resulting in increased fragmentation of the ions. A complete picture of the fragmentation processes can be obtained by collecting mass spectra across a range of cone voltages and combining the data into a map of (cone voltage) versus (mass-to-charge ratio). This visualisation method has been proposed and coined energy dependent electrospray ionisation (EDESI).

RESULTS AND DISCUSSION
Multiphoton ionisation (MPI) has been used by a number of groups for the preparation of polyatomic ions. The technique has been employed to examine dissociation dynamics, including measurement of the rates of unimolecular decay processes. However, the technique has some drawbacks. For example, the molecule ions generated via MPI can undergo further photon absorption, dissociating to form fragment ions. This so-called 'ladder-switching' process is typical for nanosecond excitation of most molecules. Also, in some cases, neutral fragments can be formed during multiphoton excitation which can then be ionised during the initial laser pulse. Although it is possible to reduce the laser intensity to suppress these effects, this invariably leads to an overall reduction in the yield of the molecule ion.

PID results
As has been recognised by others, there are advantages in separating both spatially and temporally the initial multiphoton ionisation step used to create the molecule ion from any subsequent excitation step used, for example, to induce photodissociation. Such an arrangement ensures that no additional precursor ions are produced in the second laser excitation step, helping to define the internal energy of the molecule ions. This can be further improved by employing a molecular beam source to provide a reduced range of internal energy of the neutral target molecule, as well as through the use of resonance enhanced photoionisation schemes to allow more efficient photoionisation at lower laser intensity.

In this paper we describe some preliminary results on the photo-induced dissociation of aniline using the apparatus described above that has been constructed for laser photodissociation studies of large molecules and clusters.

There have been a number of previous studies of the photodissociation of the molecule ion of aniline. Early work by Proch et al., using MPI between 266–300 nm, led to identification of the metastable decay channel C$_6$H$_7$N$^+$ → C$_6$H$_5$ + HCN (now known to be HNC$^+$). The rate-energy dependence for the same reaction was later obtained, using the photoion photoelectron coincidence (PIPECO) technique, by Baer et al., who employed MPI in the visible at 460 nm. The most comprehensive study to date has been by Kühlwind et al., using UV-MPI, who identified a number of new metastable ion decay channels of the aniline cation using a reflectron TOF mass spectrometer, and proposed a fairly detailed fragmentation pathway following multiphoton excitation. In the most recent work, by Yoon et
Photodissociation in TOF/TOFMS

Figure 3. Tandem TOF/TOF mass spectra of aniline showing (a) the molecule ion selected from the TOF mass spectrum (insert) by pulsed acceleration, (b) photo-induced fragmentation at laser power density $3.6 \times 10^8$ W cm$^{-2}$, and (c) a more abundant product ion spectrum produced at laser power density $8.3 \times 10^9$ W cm$^{-2}$.

In the present work we also employed two-photon ionisation at 266 nm to prepare the molecule ion of aniline: The ions created in this step are accelerated into the first (linear) TOF analyser and then subjected to a second laser...
pulse at 266 nm in the interaction chamber to induce photodissociation. The resulting product ions are then pulse-accelerated into the reflectron TOF analyser.

The insert in Fig. 3(a) shows the mass spectrum of the ions created in the first (ionisation) step. Both the precursor ion (m/z 93) and a number of fragment ions can be seen. Figure 3(a) shows the corresponding mass spectrum for precursor ions mass-selected by pulsed acceleration into the reflectron TOF mass analyser (TOF2). The lower two panels (Figs 3(b) and 3(c)) show the resulting reflectron TOF mass spectra following photo-induced dissociation of the precursor ion in the interaction chamber.

At the lowest photodissociation laser intensity, the fragment ions at m/z 66 [C$_5$H$_6$]+ and m/z 92 [C$_6$H$_7$N]+ are prominent, corresponding to one-photon excitation of the molecule ion. Weak peaks are also present at m/z 65 [C$_5$H$_5$]+, m/z 54 [C$_3$H$_4$N]+, m/z 41 [C$_2$H$_3$N]+ and m/z 28 [CH$_2$N]+. With increasing photodissociation laser intensity, additional ions, e.g. m/z 65 [C$_5$H$_5$]+, m/z 54 [C$_3$H$_4$N]+, m/z 51 [C$_4$H$_3$]+, m/z 50 [C$_4$H$_2$]+, m/z 39 [C$_3$H$_3$]+ and m/z 28 [CH$_2$N]+ are visible. At this higher photodissociation laser intensity, the residual molecule ion peak has been substantially depleted, being approximately one third of the intensity of the corresponding peak in the spectrum shown in Fig. 3(b). These product ions have been previously assigned as arising from two-photon excitation of the molecule ion, as shown on the fragmentation tree of Fig. 4. Kühlewind et al. proposed several mechanisms to rationalise the peak appearance in their metastable ion spectrum. They attributed the presence of product ions at m/z 51 [C$_4$H$_3$]+ and m/z 50 [C$_4$H$_2$]+ to rapid dissociation of the molecule ion into m/z 77 [C$_5$H$_7$]+ and m/z 76 [C$_6$H$_6$]+, respectively, followed by metastable loss of C$_2$H$_2$. However, we observed very weak peak intensity at m/z 77 and 76 in all our spectra, compared with a peak at m/z 66 that shows increased intensity with increased laser power density. Our interpretation is that other mechanisms may be involved, for instance dissociation of the molecule ion into m/z 66 [C$_5$H$_6$N]+ by successive loss of H and C$_2$H$_2$ with two-photon excitation. Further fragmentation of [C$_5$H$_6$N]$^+$ into m/z 51 [C$_4$H$_3$]+ and m/z 40 [C$_3$H$_5$N]$^+$ by further loss of C$_2$H$_2$ and NH, respectively, may occur. The corresponding peaks are indeed present on our photodissociation spectra. The coincidental m/z 66 of [C$_5$H$_6$]+ and [C$_6$H$_7$N]$^+$ may

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explain the strong peak intensity observed at that mass-to-charge ratio.

Regarding the internal energy of the molecule ions undergoing photodissociation, we have no direct measurement. The ionisation energy (IE) of aniline is 7.72 eV. For two-photon ionisation at 266 nm, the excess energy available to the molecule ion is 1.60 eV (neglecting the thermal energy of the neutral precursor molecule, <0.05 eV). However, in the recent photodissociation mass-analysed ion kinetic energy (PD-MIKE) study by Yoon et al., it was shown that the internal energy of the aniline molecule ions generated by two-photon ionisation is only ~50% of the available energy (2hv - IE). In their study, as in this work, spatial (1.46 m) and temporal (~25 μs) separation between the point of ion generation and photo-induced dissociation ensures that only ions with this level of internal energy contribute to the PID spectra. Only a fraction (0.03%) of molecule ions associated with three-photon excitation in the initial laser ionisation step remain after a time delay of 20 μs, so that their contribution to the PID spectra is negligible.

CID results

The CID spectrum obtained for aniline is shown in Fig. 5. Most of the product ion peaks present in the PID spectrum (Fig. 3(c)) are also present in the CID spectrum. However, one notable difference, due to the different method of ion production (ESI versus laser photoionisation), is that a protonated molecule ion is formed at m/z 94. Also, an
intense peak is seen at m/z 77, which is barely visible in the PID spectrum. This suggests that dissociation, in this case, occurs via loss of mass 17 (NH$_3$) to form the phenyl ion $m/z$ 77 $[\text{C}_6\text{H}_5]^+$. Further, peaks at $m/z$ 51 $[\text{C}_4\text{H}_2]^+$ and $m/z$ 50 $[\text{C}_4\text{H}_3]^+$ are also very intense, and are likely to result from further dissociation of the phenyl ion at higher cone voltages. The weak peak at $m/z$ 66 $[\text{C}_6\text{H}_5]^+$ indicates that dissociation via loss of HNC is a less favoured fragmentation pathway using ESI.

CONCLUSIONS

Photodissociation spectra of aniline have been obtained using a novel tandem time-of-flight mass spectrometer. Fragmentation occurs predominantly via loss of HNC or a hydrogen atom at low laser intensity (corresponding to one-photon excitation), while at higher intensities, a number of fragment ions are formed following two-photon excitation of the molecule ion. These results corroborate to some extent the dissociation pathways proposed earlier by Kühlwind et al.$^{28}$ However, some additional mechanisms have been suggested. Although aniline has been used primarily to optimise the parameters of the TOF/TOF mass spectrometer, and thus not studied in depth, it is intended that, in future experiments, a supersonic nozzle beam source will be used together with resonant photoionisation using a tunable laser to enable better control over production of the precursor ion. Variation of the PID laser intensity will allow more detailed information on the fragmentation pathways of the aniline cation. The instrument will also be used in future work with a laser desorption source to investigate the PID spectra of large involatile organic molecules. It is envisaged that an ion storage device could be fitted in the interaction chamber to allow accumulation of ions and to enable measurement of the rates of dissociation processes. Finally, the capability of the instrument will soon be deployed to the study of metal clusters produced using LVS and PACIS sources.

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