Applications of Laser Desorption Laser Photoionisation Time-of-Flight Mass Spectrometry

by

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Declaration

This thesis is of my own composition and is based on work carried out in the Chemistry Department at the University of Edinburgh and in the mass spectrometry laboratory of ICI Wilton Materials Research Centre.

Signed :

Date : 15/6/35
To Sharon,
Abstract

This thesis describes the development and application of laser desorption laser photoionisation time-of-flight mass spectrometry (L²TOFMS) for the analysis of polymers and related systems. L²TOFMS has been little used in this area until now. In the past, this technique has been used extensively for the study of high mass, involatile and/or thermally labile species such as biomolecules, porphyrins and dyestuffs. The theory behind the main experimental principles is discussed and the equipment used is described in detail.

The main body of the thesis is concerned with the generation of high quality polymer mass spectra. Utilising several ionisation wavelengths, the mass spectra of several aromatic polymers have been obtained for the first time. For two model polystyrene systems, polystyrene 800 and 2500, a series of intense oligomer peaks and some fragments were observed at each photoionisation wavelength employed. Fragments were shown to occur in the laser desorption event, a phenomenon previously documented. However, an intact oligomer series for these polymers had never previously been observed using this technique. The data obtained allowed a complete and unambiguous characterisation of the polystyrenes to be made. Molecular weight averages were calculated from the spectra. When 193 nm photoionisation was employed, these values compared favourably to those supplied by the manufacturer. However, postionisation using either 248 nm or 266 nm UV radiation resulted in mass spectra which gave lower molecular weight averages. This was primarily due to oligomer fragmentation at these wavelengths. The analysis and characterisation of a fluorinated polystyrene and a phenyl containing siloxane polymer was also carried out.

L²TOF mass spectra were also recorded for several polymer additives in their pure form. Two compound classes of additive were studied, namely UV stabilisers and phenolic antioxidants. Each compound class gave distinctive mass spectra using both 193 nm and 248 nm photoionisation wavelengths. Relatively low detection limits (ca. 50 nmoles) were achieved, thereby indicating that in-situ de-
tection from a polymer formulation was viable using this technique. Furthermore, two polymer additives were detected at the 0.1-1 % level in a polyoxymethylene polymer formulation.

The mass spectra of a series of indole derivatives have also been obtained. The fragmentation patterns observed using multiphoton ionisation (MPI) were consistent with those seen in earlier electron impact mass spectra. The characterisation of electropolymerised 5-substituted indole derivatives was carried out by L²TOFMS. In each case, the results indicated the formation of a cyclic trimer species in the electropolymerisation event with subsequent linking between trimers to form the polymer. In some cases, a pentamer species was also observed. However, no complete polymer distribution was obtained. This is the first observation and characterisation of these polymer types by mass spectrometry. Other spectroscopic (IR, UV-Vis and NMR) and electrochemical techniques have confirmed these findings.

Finally, the development of a vacuum ultraviolet (VUV) radiation source for ionisation is described. The generation of 118 nm VUV radiation was achieved by frequency tripling 355 nm laser radiation in a xenon gas cell. This radiation was used to photoionise several aliphatic compounds in order to characterise the tripling process and optimise the conversion efficiency. In addition, the 118 nm photoionisation mass spectrum of the aliphatic polymer poly(ethylene glycol) was recorded.
Acknowledgements

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Chapter 1

Introduction

Mass spectrometry is perhaps the most widely applicable of all the analytical tools available to the scientist. It is a technique that can provide information on the quantitative and qualitative composition of complex mixtures, the structure of molecular species and the composition of surfaces. This can be accomplished at high sensitivity, and the mass spectrum has a high information content. However, the identification and structural characterisation of small amounts of high molecular weight, involatile and thermally labile organic compounds still presents a difficult challenge, particularly in-situ characterisation of such compounds directly from their host matrix or substrate.

In order to provide a solution to these analytical problems, any mass spectrometric technique used must satisfy a number of criteria. Firstly, the technique should provide information on the molecular weight of the target species, as well as structural information. Clearly, a soft ionisation technique alone is not sufficient as some control over the degree of fragmentation is also necessary. Secondly, the technique should also be sensitive and species selective, enabling the detection of minor components in complex mixtures to be detected, preferably without the need for any pre-separation step. Finally, the technique should provide good mass measurement accuracy with high resolution over a wide mass range.

A number of mass spectrometric techniques are currently available which fulfill at least some of the above criteria. Further enhancement of these mass spectrometric techniques can be provided by coupling them with other separation techniques,
such as high performance liquid chromatography (HPLC) or gas chromatography (GC). Such hyphenated techniques are now commonly used in analytical laboratories worldwide. At present, however, no universal mass spectrometric technique exists which can provide answers to all the problems posed by today’s scientists. Instead, a combination of several techniques is often employed in the repeated analysis of the same sample, which can be very time-consuming and expensive. There is, therefore, a continuing demand for new techniques for accelerated mass spectrometric analysis and characterisation.

Conventional methods of ionisation in mass spectrometry, e.g. electron impact (EI) [1,2] or chemical ionisation (CI) [1], necessitate that the sample under investigation be present in the ion source in the gas phase. For gaseous and volatile materials this presents no serious problem. However, for involatile substances, special techniques must be used. The direct probe inlet system [3] allows the introduction of species with low vapour pressures (< 10⁻⁶ torr) into the ion source of the mass spectrometer. This methodology involves heating the sample in a capillary in order to generate sufficient vapour pressure for analysis. This method, however, is unsuitable for compounds with very low vapour pressure and/or thermally labile materials, where the energy supplied during evaporation exceeds that which is required for thermal degradation.

A number of techniques have been developed over the years to allow mass spectra of involatile and thermally labile species to be recorded. In these so-called desorption methods, the sample is presented in either the solid form or dissolved in a suitable solvent or matrix, and placed in the ion source of the mass spectrometer. Ions are then desorbed/sputtered from the sample surface using particle bombardment desorption methods. The techniques commonly used for this include secondary ion mass spectrometry (SIMS) [4], fast atom bombardment (FAB) [5, 6], ²⁵²Cf - plasma desorption (²⁵²Cf-PD) [7], direct laser desorption (LD) [8,9] and more recently, matrix assisted laser desorption (MALD) [10]. The techniques of field desorption (FD) [11,12] and electrospray [13,14] are also now commonly used for the analysis of high mass species.

In all the above techniques, the energy that is required for ionisation is di-
directly linked to that required to desorb the species from the surface. Therefore, it is difficult to control the ionisation process and hence to control the degree of fragmentation. Often the molecular ion is not observed in the mass spectra, instead a quasi-molecular ion species, formed by the addition of a proton and/or an alkali metal adduct is observed. In addition, the spectra are often contaminated by matrix species or fragments, each of which may have associated adduct species, therefore preventing a readily interpretable spectrum from being obtained.

With many of these techniques, neutral species are desorbed from the surface in a much higher concentration than the nascent ions [15,16]. An alternative approach, therefore, is to ignore the nascent ions and to exploit the high density of gas phase neutrals that are desorbed by using laser post-ionisation.

The development of such a two-step laser mass spectrometric technique in this laboratory, laser desorption laser photoionisation time-of-flight mass spectrometry (L²TOFMS) has been previously described [17,18]. This technique combines the use of infrared laser desorption of intact neutral species with postionisation via multiphoton ionisation using high power ultraviolet lasers, followed by time-of-flight mass analysis of the product photoions. The main advantage of this technique is that the spatial and temporal separation of the desorption and ionisation steps allows independent optimisation of each process, with respect to both laser wavelength and laser fluence.

As previously stated, the pulsed infrared laser desorption event produces many more intact neutral species than nascent molecular ions. Typical ratios of ca. 10⁴:1 have been quoted in the literature [19,20]. Since the rate of surface heating by an infrared laser pulse is typically many orders of magnitude faster than conventional heating methods (ca. 10⁷ Ks⁻¹) then this rapid heating favours intact neutral desorption over decomposition [21]. The high density of intact neutral species are subsequently photoionised by a pulsed ultraviolet laser.

Since the ionisation potential (IP) of many gas phase organic species lies between 7 and 10 eV [22], ionisation can only be accomplished by the absorption of an energetic vacuum ultraviolet (VUV) photon in a single photon ionisation scheme. Radiation at these wavelengths is strongly absorbed by oxygen in the air
and presents several operational problems. The beam paths must be evacuated or purged to remove oxygen and specialised optics must be used for beam steering. In addition, the direct generation of laser radiation at such short wavelengths is difficult. Instead, the production of VUV radiation by higher harmonic generation of ultraviolet (UV) wavelengths in inert gases, e.g. frequency tripling (see Chapter 7) is often used. Due to these drawbacks, an alternative ionisation mechanism that is very commonly employed involves the simultaneous absorption of two, or more, less energetic UV photons in a multiphoton ionisation (MPI) process; the sum of the energies of the individual photons absorbed being greater than or equal to the IP of the target molecule(s). These UV wavelengths are easily generated from a wide variety of lasers and are much more convenient to work with, requiring no evacuation of the beam paths. If an electronic absorption band of the target molecule coincides with the wavelength of the UV radiation employed, then absorption of a second photon by the electronically excited molecule is a highly favourable process resulting in a large photoion yield. This technique is known as resonantly enhanced multiphoton ionisation (REMPI) and can be exploited to provide unique identification and discrimination of molecules in a mixture by wavelength selective photoionisation.

One further advantage of MPI for ion production is the ability to vary the ionising laser beam fluence. At low ionisation laser fluences, predominantly molecular ions are observed in the mass spectra, so-called soft ionisation. Increasing the ionisation laser fluence results in decomposition of the parent ion to form structurally significant fragment species, so-called hard ionisation. At the highest laser fluences, it is possible to fragment molecules down to their constituent atoms [23].

In two-step laser mass spectrometry, both neutral desorption and ion production are pulsed events. Accordingly, the most appropriate type of mass analyser to use is the time-of-flight (TOF) mass spectrometer [24]. The main advantages of such an instrument are its theoretically unlimited mass range, high throughput and low cost. Moreover, for each ionising laser pulse, a complete mass spectrum can be recorded making for short analysis times. The mass resolution of such analysers is generally quite low, although the use of reflecting field instruments
coupled with the use of ionisation lasers with short pulse widths can increase the resolving power to several thousand.

The technique of L^2 TOFMS has been under development in other research groups since the mid 1980's, primarily those of Schlag [26], Lubman [27] and Zare [28]. Both Schlag and Lubman's groups opted for an instrument with entrainment geometry, where the laser desorbed neutrals are transported into the ionisation region of the mass spectrometer by means of a pulsed molecular beam, as shown in the schematic diagram in Figure 1-1a. In this approach, the entrainment stage is utilised, not only as a means for sample transportation, but also for *jet-cooling* of the internal degrees of freedom of the laser desorbed molecules. Such jet-cooling enables the optical selectivity of the REMPI process to be exploited, allowing wavelength resolved photoionisation spectra or wavelength selective mass spectra to be recorded [29,30].

The instrument developed in Zare's group does not use sample entrainment, and is shown schematically in Figure 1-1b. Instead, laser desorption and laser photoionisation are carried out in close proximity in the ionisation region of the mass spectrometer. Typically the laser desorbed neutrals are photoionised a few mm above the sample surface. The main advantage of this approach is that the detection sensitivity of the instrument is considerably enhanced. One disadvantage of this approach is that the optical selectivity for laser post-ionisation provided by jet-cooling with sample entrainment is no longer available.

The instrument in Edinburgh was originally designed with sample entrainment geometry, to exploit the advantages of optically selective laser post-ionisation of jet-cooled laser desorbed samples. However, the instrument has recently been extensively used, with only minor modifications, to allow studies without sample entrainment to be carried out in order to achieve higher detection sensitivity. These modifications were carried out in such a way as to retain the original entrainment capability. At present, the instrument can be easily operated in either entrainment or non-entrainment mode by simply changing the path of the desorption laser.

Since the introduction of L^2 TOFMS by Schlag *et al.* [26] in 1985, the technique has been used to examine a wide range of compounds, including biomolecules [31,
Figure 1-1: Schematic diagram of the two geometries used for L²TOFMS; a) with molecular beam sample entrainment, b) without sample entrainment.
32], peptides [33], nucleosides and nucleotides [34,35], dyestuffs [36] as well as polyaromatic hydrocarbons (PAH's), even directly from their native environments [37,38]. A survey of the analytical applications of L\textsuperscript{2}TOFMS up to 1994 has recently been written [18] and will not be repeated here. Little work on polymers and related systems using this technique has appeared in the literature, and hence, the principal objective of the work described in this thesis was to explore the feasibility of using L\textsuperscript{2}TOFMS to study such compounds.

The layout of the remainder of this thesis is as follows:

In Chapter 2, the principles and the background theory concerning the three fundamental concepts of L\textsuperscript{2}TOFMS, namely laser desorption, laser photoionisation and time-of-flight mass spectrometry are presented. Chapter 3 describes the experimental methods and equipment used in the L\textsuperscript{2}TOFMS experiments carried out during the course of this work.

In Chapter 4, the results obtained using L\textsuperscript{2}TOFMS for the characterisation of a series of polystyrenes and other aromatic polymers are presented. Utilising several ionisation wavelengths, oligomer distributions of several aromatic polymers have been obtained for the first time using L\textsuperscript{2}TOFMS. Furthermore, the fragment species observed, allowed a complete and unambiguous characterisation of the polymers to be made. For the polystyrenes studied, molecular weight averages were calculated from the mass spectra. When 193 nm photoionisation was employed, these values compared favourably to those supplied by the manufacturer.

Chapter 5 describes the results obtained using L\textsuperscript{2}TOFMS to examine a series of polymer additives, both as pure compounds and directly from polymer formulations. Two compound classes of additive were studied, namely UV stabilisers and phenolic antioxidants. Each compound class gave distinctive mass spectra using both 193 nm and 248 nm photoionisation wavelengths. Relatively low detection limits (ca. 50 nmoles) were achieved, thereby indicating that in-situ detection from a polymer formulation was viable using this technique. Further to this work, two polymer additives were detected at the 0.1-1 % level in a polyoxymethylene polymer formulation.
In Chapter 6, the L²TOF mass spectra obtained for a series of substituted indole monomers, some of which can be electropolymerised, are presented. For the monomers studied, the fragmentation patterns observed using multiphoton ionisation (MPI) were consistent with those seen in earlier electron impact mass spectra. The polymerisation products have also been analysed using L²TOFMS and the results are presented along with complimentary data obtained using other mass spectrometric techniques. In each case, the results indicated the formation of a cyclic trimer species in the electropolymerisation event with subsequent linking between trimers to form the polymer. In some cases, a pentamer species was also observed. However, no complete polymer distribution was obtained. This is the first observation and characterisation of these polymer types by mass spectrometry.

Finally in chapter 7, the use of laser vacuum ultraviolet (VUV) radiation for post-ionisation is described along with the background theory and experimental details of a VUV source (118 nm) based on frequency tripling of UV laser radiation (355 nm) in inert gases. This radiation was used to photoionise several aliphatic compounds in order to characterise the tripling process and optimise the conversion efficiency. In addition, the 118 nm photoionisation mass spectrum of the aliphatic polymer poly(ethylene glycol) was recorded.
Bibliography


Chapter 2

L²TOFMS Background Theory

2.1 Introduction

Laser desorption laser photoionisation time-of-flight mass spectrometry (L²TOFMS) is the technique whereby infrared (IR) laser radiation at a wavelength of 10.6 µm, is used to desorb intact neutral species which are subsequently photoionised by an ultraviolet (UV) laser pulse, then mass analysed by a time-of-flight mass analyser. It is the first step, namely the laser desorption event, which is critical in allowing the L²TOFMS methodology to be an effective mass spectrometric technique. The other two events, namely laser multiphoton ionisation (MPI) and time-of-flight (TOF) mass spectrometry, have been used independently in research for many years. Indeed, with the comparatively recent invention of matrix assisted laser desorption/ionisation (MALDI), TOF is now in its Renaissance period. It is the coupling of these three individual techniques, however, that has made L²TOFMS a successful methodology for the analysis of involatile and/or thermally labile, high molecular weight species.

In the following sections of this chapter, the processes and mechanisms involved in laser desorption, laser multiphoton ionisation and time-of-flight mass spectrometry, respectively, are outlined. In addition, the use of molecular beam entrainment for the purpose of sample transportation is also briefly discussed.
CHAPTER 2. L²TOFMS BACKGROUND THEORY

2.2 Laser Desorption

2.2.1 Background

The earliest use of lasers in mass spectrometry date from the early 1960's. These studies involved the vaporisation of coal [1] and graphite [2], and the pyrolysis of non-volatile compounds to form volatile fragments [3]. The elemental analysis of solids, also figured prominently in early work [4,5]. In each case, the ions formed in the laser desorption event were mass analysed. The analysis of organic compounds using laser desorption (LD) mass spectrometry was first reported in 1968 by Vastola and Pirone [6]. They reported that large molecular ion signals could be obtained from a series of conjugated aromatic compounds, using the pulsed output from a ruby laser at ca. 6.9 \( \mu \text{m} \). In subsequent work [7,8], Vastola and coworkers reported the laser desorption mass spectra for various salts. Here, they observed cation attachment of alkali metals to the parent molecules. No fragmentation or decomposition products were observed in the mass spectra. It was this work which pioneered the use of lasers for the desorption of intact molecular or quasi-molecular ions.

In 1978, Posthumus et al. [9] published a ground breaking paper which sparked great interest in the LD technique. Using a pulsed CO\(_2\) laser, at 10.6 \( \mu \text{m} \), they obtained the mass spectra for several oligosaccharides, glycosides, nucleotides, amino acids, peptides and other biological molecules. In each case, intense cation-attached molecular ions were observed in the mass spectra. This was the first observation of intact species being generated from high molecular weight, involatile and thermally labile species.

Since then, many groups have utilised the LD mass spectrometric technique for the analysis of a diverse range of molecular species. Furthermore, numerous experiments have been performed in order to try to understand the exact nature of the LD mechanism. In the following sections, the current theories concerning the various LD processes will be reviewed.
2.2.2 Mechanisms

The exact nature of the LD mechanism is difficult to determine due to the many experimental parameters that can be varied, such as laser power and wavelength, pulse duration, substrate type, matrix, sample thickness and orientation of the incident laser beam. Any description of the laser desorption mechanism must answer two major questions:

- What is the nature of the laser-induced process leading to the transition from the solid phase to the gas phase?

- How can large molecules escape fragmentation in an environment abruptly energised by the laser pulse?

Furthermore, the mechanism must also account for a number of experimental observations:

- high kinetic energy particles (tens of eV), such as ions, fragments and atomic species, are desorbed immediately after the laser pulse,

- many of the desorbed species are protonated or cationised and have relatively low kinetic energies,

- many more neutral species than ions are desorbed and the release of neutral particles occurs over a long time period (several hundred microseconds) after the laser pulse.

Vertes and Gijbels [10] have recently summarised the efforts made to understand the different desorption mechanisms. They focused upon the role that restricted energy transfer had upon the volatilisation of intact large molecules. The laser desorption mechanisms proposed, have mainly centred on energy transfer mechanisms to the analyte and the subsequent disintegration mechanisms [11], i.e. desorption of the analyte. In order to desorb intact large molecules, the timescale of the desorption process must be relatively short. However, if the desorption
process occurs too slowly, then energy equilibration can produce intra-molecular vibrational excitation, resulting in fragmentation of the molecules.

Several possible mechanisms have been proposed for the LD event which take into account some of the points previously raised. These range from resonant desorption [12], and thermal desorption [13] to shock wave models [14]. The first of these mechanisms occurs when the analyte itself undergoes electronic excitation under laser irradiation, and is commonly used to describe the mechanism in MALDI. In the thermal model, desorption occurs as a function of substrate temperature whilst the shock wave models are used to describe the non-thermal explosive ablation of target species. Since a wide range of desorption conditions are generally used for LD mass spectrometry, it is generally accepted that one or more of these mechanisms is responsible for the desorption of intact species.

From experimental evidence, it is clear that only a small fraction of the desorbed species are ions, the majority being intact neutrals. However, the majority of the LDMS studies performed directly analyse the nascent ions. L²TOFMS analysis relies solely upon the desorption of neutral species and for this reason, the following discussion will mainly consider the mechanisms proposed for the desorption of neutral species. When the mechanism of ion formation is relevant, it will be included to provide a more complete picture of the desorption mechanism.

**Resonant Desorption**

It is generally accepted that the wavelength used for desorption is a parameter of some importance [15,16]. Although it should be realised that the majority of compounds studied, exhibit only negligible absorption at the desorption laser wavelength. For example, Southon et al. [17] demonstrated that pyrolysis products of organic materials were observed using 532 nm laser desorption, whereas 266 nm laser desorption produced structurally significant fragments. Karas et al. [18] have reported lower laser power thresholds for the detection of aliphatic and aromatic amino acids, a larger working range of desorbing laser powers and an increase in the ratio of molecular-to-fragment ion intensities when resonant desorption was used.
The observation of predominantly radical cations of PAH's, desorbed using 266 nm radiation, provided support for a resonant desorption mechanism initiated by electronic excitation of the sample [19]. Furthermore, LD studies of amino acids have shown that use of a desorption laser wavelength which coincides with the presence of a molecular absorption band of the analyte, can dramatically improve the molecular ion to fragment ion ratio [18,20,21,22]. However, Kissel and Kruger [23] have suggested that the resonant enhancement observed for the direct LD of ions was more a function of the ion formation process than a requirement for efficient sample desorption.

Observation of an increased ion yield for non-absorbing molecules when presented in an absorbing mixture has more recently been exploited for the technique of matrix assisted laser desorption/ionisation (MALDI). Here, the analyte molecules are dissolved in a matrix material prior to analysis. This matrix material strongly absorbs the desorption laser wavelength and is electronically excited, transferring energy to the analyte molecules and causing them to be desorbed. This methodology was first reported by Tanaka et al. [24] and Karas et al. [25] in 1988 and has now rapidly expanded into a large area of research. The mechanisms involved in MALDI remain poorly understood and therefore the technique has mainly developed empirically. A detailed discussion of the possible mechanisms has been given by Vertes and Gijbels [10]. It is clear, however, that resonant absorption of the matrix plays an important role in the mechanism.

The resonant desorption mechanism requires efficient energy transfer to the analyte molecules, either by direct absorption or via the substrate or matrix. Consequently, UV laser radiation, which can couple directly to electronic states, or far IR laser radiation which can couple directly to rovibrational states, has been shown to give the best results. Overberg et al. [26,27] showed that resonance conditions could be met at almost any wavelength between the UV and IR (200 nm to 10 μm) provided there was a sufficiently large energy coupling probability to the sample. Above the threshold laser fluence for desorption, the energy transfer between the incident radiation and the analyte occurs via non-linear absorption [21]. Excitation with a resonant wavelength, permits direct transfer of energy into
the target molecules. The use of UV photons for resonant desorption is not without drawbacks, since a wide range of physical processes can occur. The absorption of such high energy photons results in electronic excitation of molecules, which in turn, may lead to the formation of electrons, excitons and holes in the conduction band of the organic crystals. In addition, direct photofragmentation may occur as a consequence of electronic singlet state excitation of the target molecules.

Resonant desorption has also been investigated for the desorption of neutral species. Using an L²TOFMS methodology, Beavis et al. [28,29] investigated the desorption efficiency of neutral molecules, using a CO₂ laser at 10.6 μm, by incorporating the analyte in a matrix. They found that strong sample/matrix absorption was detrimental to the desorption process, since the rate of thermal decomposition processes was enhanced, causing a reduction in the postionised neutral signal intensity of the parent molecule. In contrast, 10.6 μm LD of the pure peptides studied, produce intense molecular ion peaks. However, this work is contradictory to the theory of MALDI.

In order to determine whether absorption of the desorption laser wavelength by the analyte was desirable for the LD of intact neutral molecules, Kinsel et al. [30] carried out a series of experiments involving LD of a large group of test compounds at the four harmonic wavelengths of an Nd:YAG laser, namely 1064 nm, 532 nm, 355 nm and 266 nm. They found that, in a manner similar to the direct LD of ions, resonant desorption of neutrals could be achieved at lower thresholds and with stronger yields of postionised molecular ion signals. Furthermore, they found that under resonant desorption conditions, rapid heating of the substrate after absorption plays a minor role in the desorption process. Instead, they suggested that the best description of the mechanism was one where the LD energy was non-linearly coupled directly into the sample bulk, resulting in efficient neutral desorption. In contrast, non-resonant desorption requires the participation of the substrate material as the energy uptake medium for the desorption process to occur. As a result higher laser powers are required for desorption.

In the context of the experiments described in this thesis, where desorption is performed using CO₂ laser radiation at 10.6 μm, resonant desorption is unlikely
to be the principal desorption mechanism. This is due, most importantly, to the analyte molecules having little or no appreciable absorption at the infrared wavelength used. Instead, the resonant desorption mechanism may be more relevant for the analysis of materials embedded in host matrices, such as polyaromatic hydrocarbons in soil, dyestuffs on fabrics, or polymer additives in polymer formulations.

**Shock-Wave Model**

Under high laser fluences ($> 10^{10} \text{ Wcm}^{-2}$), laser desorption proceeds without interaction from the substrate, and hence is not driven by temperature. This model, proposed by Lindner and Seydel, is termed the shock-wave model [14], and is a suitable explanation for transmission type laser desorption geometries, i.e. where the laser beam is incident upon a thin substrate with the sample coated onto the other side. In the experiments that Lindner and Seydel performed, cationised molecular ion signals from 20 $\mu$m thick layers of saccharides and alkali salt mixtures, were obtained under high laser fluence conditions, ca. $10^{11}$ Wcm$^{-2}$. At these high laser fluences, the substrate heating rate was calculated to be approximately $10^{11}$ Ks$^{-1}$. This rate exceeds the limit of approximately $10^9$ Ks$^{-1}$ above which an explosive vaporisation or phase explosion can occur. The result of this thermal ablation, is a shock-wave which traverses the solid and leads to the desorption of intact molecules and alkali ions from the opposite surface via vibrational disturbance of the binding potentials. Since the molecules are not coupled to the lattice long enough to absorb sufficient internal energy, then thermally labile species can be ejected as intact neutrals and do not undergo fragmentation. The sample is also thought to be desorbed one monolayer at a time [14].

The shock wave or phase explosion mechanism has also been used to explain other direct ionisation techniques such as FAB and SIMS [32,33]. For example, experiments utilising thin layers of alkali metal salts on the back of thick analyte layers, have shown that cationisation of the desorbed neutrals occurs, even although the incident particles did not fully penetrate the thick analyte layer.
It is unlikely that the shock wave model of laser desorption is predominantly relevant in the context of the experiments carried out in this thesis. This is primarily due to the desorption laser power densities used, being somewhat lower than the $10^{10} \text{ Wcm}^{-2}$ required to initiate the process. It is possible, however, that it might play a part in the desorption from thick samples or matrices.

**Thermal Desorption**

The mechanism of thermal desorption is thought to dominate under low laser fluence conditions, ca. $10^8 \text{ Wcm}^{-2}$. In this regime, the desorption of intact molecular species, proceeds as a function of substrate temperature. It is this mechanism which is thought to be the most relevant in the context of the experiments carried out in this thesis, where the infrared laser power densities used are typically between $10^6$ and $10^8 \text{ Wcm}^{-2}$.

It should be noted that the thermolability of organic molecules is a relative concept and is dependent upon the heating rate. Thus, the liberation of intact, thermally labile molecules from the bulk solid state is not necessarily incompatible with the high temperatures attained by ultrafast heating during laser desorption. Daves *et al.* [34] and Beuhler *et al.* [13] exploited this in the flash desorption technique. This was developed as an alternative to resistive heating. They rationalised the phenomenon by applying an Arrhenius-type equation to the desorption of intact neutrals and thermal degradation products.

\[ k = A e^{-\frac{E_a}{kT}} \]  

(2.1)

The parameter $k$ is the rate of desorption or thermal degradation, $E_a$ is the activation energy for this process, and $T$ is the temperature. A nonvolatile compound can, therefore, be defined as a species for which the activation energy for desorption is greater than that for decomposition. A plot of the logarithmic rate of desorption and the logarithmic rate of decomposition against $1/T$ gives two straight lines. The point of intersection between these lines is the critical value where, at higher temperatures, desorption of intact species is favoured over decomposition; at lower temperatures, the reverse is true. More specifically, the fast
heating approach means that the time spent in the low temperature regime, where decomposition prevails, is minimised and, therefore, the relative number of intact molecules in the gas phase is increased.

The absorption of an infrared laser pulse by a solid results in rapid surface heating, which is normally very localised due to the low thermal diffusivity of most materials. The rate of heating has been calculated to be ca. $10^8$ Ks$^{-1}$ by Zare et al. [35] for Macor ceramic and glass substrates using pulsed CO$_2$ laser irradiation at a power density of ca. $1.5 \times 10^4$ Wcm$^{-2}$. Heating rates in excess of $10^8$ Ks$^{-1}$ have also been observed in glass and quartz [36]. In comparison, heating rates of only between 1 and $10^3$ Ks$^{-1}$ can be attained using conventional resistive or electron bombardment heating methods. Furthermore, Zare and coworkers have modeled the surface temperature rise in fused silica on irradiation with an infrared laser pulse from a CO$_2$ laser [37]. Using a finite difference method, they found temperature increases of ca. 1100 K in less than 10 μs. Dale et al. [38] used a similar approach to simulate the transient temperature profiles induced in stainless steel, brass and fused silica. Brand and George [39] investigated the effect of laser pulse characteristics and thermal desorption parameters on the laser desorption event. Using one and two dimensional models, with spatial and temporal Gaussian laser pulse profiles, they determined a series of relationships between the laser pulse length, the peak surface temperature and the desorption activation energy. In each case, however, it is the rapid jump in substrate temperature during the desorption laser pulse, that facilitates the liberation of intact neutrals from the substrate. These methods are particularly applicable for thermally labile species where the species-substrate bond is broken before energy can flow into the internal modes of the molecule.

In 1982, Kistemaker and coworkers [40] proposed a model for the IR laser desorption of organic species on a surface. They assumed that the substrate had a high thermal absorptivity and that the organic film on the surface did not affect the substrate temperature distribution, i.e. the organic film was optically transparent to the IR radiation. It was observed that lower laser powers were required to desorb ions from non-absorbing organic films on metal surfaces, which had high thermal
conductivities, rather than from non-absorbing organic films on substrates with poor thermal conductivities. Their results suggested that the laser energy was absorbed by the substrate and subsequently transferred to the organic overlayer. Subsequently, both Burgess et al. [41] and Simpson et al. [42] have provided experimental evidence that rapid substrate heating facilitates the desorption of internally cold intact molecules.

Zare and Levine [43] have proposed a mechanism for the thermal desorption of intact, internally cold molecules based upon the rapid substrate heating model. A molecule physisorbed on a surface is bound by a weak van der Waals type bond, which has a low vibrational frequency, similar to that of the surface phonons\(^1\). During rapid IR laser heating of the substrate, this physisorption bond is expected to be readily pumped. At this stage, however, a bottleneck in the energy flow from the surface-adsorbate van der Waals bond to the chemical bonds in the physisorbed molecule may occur. This is due to the chemical bonds having higher vibrational frequencies that are not well matched the low frequency van der Waals physisorption bond. The energy flow out of this physisorption bond will therefore be slow, resulting in the desorption of relatively cold molecules, i.e. it is possible by rapid laser-induced thermal desorption to break the surface-adsorbate bond, even if this is not the weakest bond in the free molecule. Zare and Levine have suggested a simple quantitative criterion for the desorption of internally lukewarm molecules as,

\[
\tau \nu \exp(-\zeta) < 1 \tag{2.2}
\]

where \(\tau\) is the time required for the transfer of energy to the physisorption bond in excess of its dissociation energy, \(\nu\) is the frequency of the physisorption bond and \(\zeta\) is the adiabaticity parameter [44], which represents the ability of the adsorbate molecule to resist changes in vibrational excitation. Molecules can still be desorbed if the criterion in Equation 2.2 is not satisfied. However, they will generally be desorbed with excess energy in their internal degrees of freedom. Values of \(\zeta >

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\(^1\) A phonon is one quantum unit of lattice vibrational energy
11 have been experimentally measured from the decomposition of van der Waals adducts [45,46,47]. Indeed, for $\zeta > 10$, heating rates of $10^{11} - 10^{12} \text{ Ks}^{-1}$ can be used to selectively desorb even reasonably strongly bound molecules with low internal energies. Heating rates in excess of $10^{15} \text{ Ks}^{-1}$ have been obtained with femtosecond laser pulses [48] suggesting the possibility of thermally desorbing molecules from even tighter binding surfaces.

It is clear that the infrared laser fluences of between $10^8$ and $10^8 \text{ Wcm}^{-2}$, that are routinely use for desorption, fall into this low/medium fluence regime. Hence, the desorption mechanism that most likely predominates is that of thermal desorption. In addition to the low desorption laser fluences used, the analyte is most commonly presented for desorption as a thin film on a metal surface. These conditions are similar to those used by Zare and Levine [43] in their thermal desorption model. Since the samples are not all presented in the same manner, and different desorption laser powers are used, it is difficult to determine exactly which desorption mechanism is occurring. Most likely, a combination of two or more of the mechanisms previously discussed contribute.

### 2.2.3 Laser Desorption of Intact Neutral Species

In the original LD experiment performed by Vastola and Pirone [6], it was found that neutral molecules were the major product of the desorption process, with neutral emission occurring over a much longer period than that of ions. Since then, many other observations of this phenomenon have been made [49,50,51]. This result is predicted by the thermal desorption mechanism.

The rate of desorption of ions or neutrals depends only on the provision of sufficient energy to remove them from the surface:

$$\frac{dn^{(+)}}{dn} \propto [c] \exp(-E_d/KT)$$

where $n^{(+)}$ is the number of ions or neutrals in the gas phase, $[c]$ is the concentration of surface species, $E_d$ is the activation energy for desorption and $T$ is the surface temperature. The activation energy for the desorption of a neutral molecule will
generally be lower than that of ions, hence neutrals will be emitted for longer times and at lower surface temperatures [50].

The ratio of ions to neutrals in a laser induced desorption experiment is determined by the rapid jump in surface temperature. This is given, to a first approximation, by the Langmuir-Saha equation [52].

\[
\frac{n^+}{n^o} = \exp[(W - I)/KT] \tag{2.4}
\]

where \(W\) is the work function of the substrate, \(I\) is the ionisation potential of the sample species, and \(T\) is the substrate temperature. This equation, which describes a gas phase thermal equilibrium process between ions and neutrals, has been applied with some success, even in cases where non-equilibrium processes dominate. The ratio of ions to neutrals varies with laser power density [53] since the peak surface temperature depends on the laser power density. The ratio of ions to neutrals is approximately \(10^{-5}\) at a typical desorption laser power density of \(10^8\) Wcm\(^{-2}\), whilst at higher laser power densities of ca. \(10^9\) to \(10^{10}\) Wcm\(^{-2}\) this ratio can be as high as 0.01 - 0.1. Studies by Cotter and coworkers [49,50] using a 40 ns, 700 mJ pulse from a CO\(_2\) laser, revealed that ions were emitted from the surface for ca. 1 \(\mu s\) while neutrals were desorbed over a period of ca. 100 \(\mu s\). The laser power density employed was in the region of \(10^8\) Wcm\(^{-2}\).

Since the majority of the species produced under typical desorption conditions are neutrals, then it is clearly advantageous to post-ionise these neutrals in order to improve the detection sensitivity. The instrument developed in Edinburgh employs both spatial and temporal separation of the desorption and entrainment events in order that they may be independently optimised with respect to both laser wavelength and laser power. In order to transport the desorbed neutrals into the ionisation region of the mass spectrometer, a supersonic molecular beam is normally used to entrain the molecules, as described in the following section. However, in order to improve the detection sensitivity of the instrument, this entrainment step can be easily removed, resulting in the desorption and ionisation events occurring in close proximity. Both of these instrument geometries have been employed in the experiments described in this thesis.
2.3 Molecular Beam Entrainment of Desorbed Neutral Species

The L²TOFMS experiments described in this thesis fall into two categories, those performed with molecular beam sample entrainment, and those carried out without any sample entrainment. In the former case, the desorption and ionisation events are spatially and temporally separated by ca. 40 cm and 250 \( \mu \text{s} \), respectively. The desorbed species are transported into the ionisation region of the mass spectrometer using a supersonic molecular beam.

The flow of gas from a high pressure reservoir through a small hole into a vacuum chamber creates a molecular beam [54,55,56]. The dynamical processes involved depend on the magnitude of the Knudsen number, \( K \), which is defined by the equation,

\[
K = \frac{\lambda_o}{D}
\]

(2.5)

where \( \lambda_o \) is the mean free path of the source gas, and \( D \) is the diameter of the nozzle orifice through which the expansion takes place. Two distinct processes can occur depending on the relative magnitude of these two parameters.

For \( K \gg 1 \), i.e. \( \lambda_o \) is on the order of, or larger than \( D \), very few collisions between the expanding gas molecules occur and effusive flow through the nozzle results. In contrast, for \( K \ll 1 \), i.e. \( \lambda_o < D \), the molecules undergo many collisions with one another as they flow through the orifice. The gas acquires a net velocity in response to the pressure gradient across the nozzle, and the gas leaves the nozzle as a supersonic expansion [57].

The advantages of a supersonic molecular beam over an effusive beam are many-fold. Firstly, since the divergence of a supersonic beam is less than that of an effusive beam then the relative flux through a given area, perpendicular to the direction of flow, is higher for a supersonic source. Secondly, in a supersonic molecular beam, many collisions take place as the gas exits the nozzle orifice. These collisions cool the internal degrees of freedom of the expanding gas, allowing the
conversion of translational, rotational, and vibrational energy into directed mass flow, with a corresponding increase in beam velocity [58] and a lowering of the temperature of the beam. Monatomic gases, which have no internal (rotational and vibrational) degrees of freedom can reach the lowest translational temperatures, e.g. 0.03 K for He and 2K for Ar [57]. For a polyatomic gas, typical beam temperatures are of the order: $T_{\text{trans}} = 0.5 - 20$ K, $T_{\text{rot}} = 2 - 50$ K, and $T_{\text{vib}} = 10 - 100$ K. Rotational relaxation by collisions is an efficient process therefore the rotational temperature of the molecules follows quite closely, the translational temperature. Collisional vibrational relaxation is a less efficient process, which is reflected in the higher vibrational temperature of the molecular beams.

The fully expanded molecular beam is characterised by its high degree of directionality and small spread in velocity. The velocity spread in the molecular beam can be calculated from the Maxwell-Boltzmann velocity distribution [59]. Figure 2–1 shows these distributions for a beam of helium atoms at 300 K and 5 K. At 300 K, a wide velocity distribution is observed. However, at 5 K, the distribution of velocities is very much narrower. In addition, the most probable velocity in the beam has increased to around 1700 ms$^{-1}$.

In order to transport the laser desorbed neutral molecules into the ionisation region of the mass spectrometer, they must be 'seeded' into the molecular beam. This involves pick-up and entrainment of the desorbed molecules. As the molecular beam expands into the low pressure vacuum chamber the desorbed neutrals are swept along in the gas expansion, and two-body collisions cool their internal degrees of freedom in a manner similar to polyatomic carrier gases.

One effect of a seeded supersonic expansion that must be noted, is that of velocity slippage. When, for example, a polymeric material with wide range of molecular weights is desorbed, two-body collisions between the carrier gas and the polymer causes an acceleration of the polymer species to, ideally, the same velocity as the carrier gas. For low carrier gas pressures, however, the acceleration of the seeded molecules may be incomplete, resulting in velocity differences between the heavier oligomers and the lighter carrier gas atoms [60]. This effect can be overcome if higher carrier gas densities are used.
Figure 2-1: Maxwell-Boltzmann velocity distributions for molecular beams of helium at 300 K and 5 K.
In addition to the purpose of transportation of laser desorbed molecules, the supersonic expansion also has the effect of cooling the internal degrees of freedom of the entrained molecules. This makes spectroscopic analysis of the entrained species, a straightforward process [61], since only a few quantum states are populated. Consequently, the spectral features are dramatically simplified, and are therefore, more easily assigned. For the experiments in this thesis, however, this high degree of internal cooling for spectroscopic work was not exploited.

Spectral simplification also causes the ionisation laser wavelength to play an important role. For example, by tuning the ionising laser wavelength to a resonance in the molecules, an enhancement in the photoionisation yield can be obtained. Therefore, in a mixture of two, or more components, selective ionisation of one of the species can be achieved by tuning the ionising laser to an appropriate wavelength. This will be described more fully in the following section.

For the experiments described in this thesis which involved sample entrainment, the molecular beam expansion was not optimised for achieving the lowest beam temperatures. The molecular beam was used primarily as a 'pick-up' source, for the transportation of the desorbed neutrals into the ionisation region. The degree of internal cooling of the laser desorbed molecules was never measured, but it was expected to be insufficient to provide a high degree of optical selectivity.

### 2.4 Laser Photoionisation

Laser photoionisation can proceed via a number of different schemes and these are summarised in Figure 2-2. For many gas phase molecules, the minimum energy required to remove an electron, known as the ionisation potential (IP), is typically on the order of 7 to 10 eV [62,63]. Therefore, single photon ionisation (SPI), as illustrated in Figure 2-2a, can only be accomplished by the absorption of an energetic vacuum ultraviolet (VUV) photon [64,65]. In this case, the photon energy is greater than the IP of the molecule and the process is strongly allowed. The ejected electron carries away the excess energy and the angular momentum
Figure 2-2: Schematic diagram of the main photoionisation schemes used in conjunction with TOFMS.

- **SPI**
- **Non-Resonant MPI**
- **Resonant MPI (REMPI)**
- **2-Colour REMPI**
- **[2+1] REMPI**
- **Ionisation Continuum**

**Virtual Excited State**

**Real Excited State**
leaving a singly charged molecular ion. However, radiation at these wavelengths is difficult to work with, since they are strongly absorbed by the oxygen in the air, necessitating that the beam paths have to be evacuated or purged. In addition, VUV lamps only produce low output intensities, and therefore the ion yields are too low for sensitive mass spectrometric work. Higher photon fluxes can be obtained from synchrotron sources but there are no laser sources that will directly produce intense VUV radiation.

Recently, the generation of 10.5 eV, 118 nm VUV radiation by frequency tripling the third harmonic wavelength of an Nd:YAG laser at 355 nm in a phase-matched mixture of xenon and argon has been reported [66,67]. This technique enables the production of higher photon fluxes suitable for use in mass spectrometric studies [68,69]. A more detailed description of this technique, which has been successfully used in exploratory studies on VUV photoionisation of non-aromatic polymers, is given in Chapter 7.

In order to circumvent the main problems of working with VUV radiation, namely evacuated beam paths, specialised optics and low photon fluxes, the technique of multiphoton ionisation (MPI) [70,71,72] is more commonly used. This technique relies upon the absorption by a molecule of several photons of ultraviolet (UV) or visible radiation, such that the sum of the energies of the individual photons is greater than or equal to the IP. The practical advantages of this technique are that UV and visible photons are available from a wide variety of laser systems, capable of producing a high photon flux and no beam path evacuation is necessary.

A number of possible multiphoton ionisation schemes are shown in Figure 2-2. The rate equation for an n-photon absorption is generally given as

$$W_n = \sigma_n I^n$$  \hspace{1cm} (2.6)

where $W_n$ is the transition rate for an n-photon process, $\sigma_n$ is the cross-section for n-photon absorption ($\text{cm}^2\text{s}^{-n-1}$) and $I$ is the instantaneous photon flux ($\text{cm}^{-2}\text{s}^{-1}$).

When this equation is transformed into a logarithmic form, thus;

$$\ln W_n = \ln \sigma_n + n \ln I$$  \hspace{1cm} (2.7)
it can be readily seen that a power dependence plot, using a fixed photoionisation wavelength, gives a crude estimate of a molecule's IP. Therefore, a plot of \( \ln W_n \) (or more practically, the logarithm of the photoion yield) versus \( \ln I \) should give, for low photon fluxes, a straight line of gradient \( n \) [73]. In this way, the IP of the molecules can be found in the region

\[
(n - 1)E < IP < nE
\]  

(2.8)

where \( E \) is the energy of a single photon. Deviations from linearity at higher photon fluxes result from resonance saturation effects or volume saturation effects at the laser focus.

The simplest multiphoton process is two-photon non-resonant MPI, shown in Figure 2-2b. This involves the simultaneous absorption of two photons via a 'virtual' intermediate state of the molecule. This virtual state is not a real eigenstate of the molecule. The interaction time required for this coherent two-photon process is on the order of the fly-by time of a photon, ca. 1 femtosecond. Consequently, this process can only occur if the photon flux is sufficiently high.

Typical values for the absorption cross-sections for SPI and non-resonant MPI are \( \sigma_1 \approx 10^{-18} \text{ cm}^2 \) and \( \sigma_2 \approx 10^{-50} \text{ cm}^4 \text{s} \) [74]. UV arc lamps can provide a photon flux of \( 10^{15} \text{ photons cm}^{-2} \text{s}^{-1} \), but these are not powerful enough to drive such a non-resonant process. However, a typical narrow bandwidth pulsed laser, can provide photon fluxes in excess of \( 10^{28} \text{ photons cm}^{-2} \text{s}^{-1} \), when tightly focussed. This is sufficient to drive a simultaneous two-photon absorption process. At such high fluxes, ionisation or fragmentation of background contaminants and/or residual gas in the mass spectrometer can occur, both of which are undesirable.

If the energy of the first photon absorbed in a two-photon process is equivalent to the energy of a real excited intermediate state of the molecule, then the MPI process is radically different, see Figure 2-2c. Such a phenomenon is known as resonance enhanced multiphoton ionisation (REMPI), or resonant two-photon ionisation (R2PI). Since the lifetime of a real excited state is typically \( 10^{-6} \) to \( 10^{-9} \text{ s} \), then the probability of absorbing a second photon is increased by at least six orders of magnitude [75,76] compared to the non-resonant case. As a result,
such a REMPI process requires much lower laser powers to produce the same photoionisation yield as a non-resonant process.

One advantage of the REMPI process is its selectivity. For example, in a mixture of two or more components, by tuning the energy of the first photon to a resonance in one of the molecular species, see Figure 2-2d, then this species can be selectively ionised over the others present in the mixture. This optical selectivity has been used for the characterisation of a mixture of species in a drug formulation [77].

The two REMPI schemes shown in Figures 2-2c and 2-2d, are the most widely used for sample photoionisation in mass spectrometric studies. In each case, the first photon excites a real excited state of the molecule and the second photon is used for ionisation of this excited state. In the scheme in Figure 2-2c, the two photons used are of the same wavelength, whereas for that in Figure 2-2d, the two photons have different wavelengths. Experimentally, the latter scheme is more difficult, since it requires both the spatial and temporal overlap of two laser beams.

The last MPI scheme shown in Figure 2-2e involves two-photon absorption to a real intermediate state of the molecule, before a third photon ionises it. This process has a lower ionisation efficiency than R2PI, due to the involvement of the intermediate non-resonant two-photon step. Such [2+1] REMPI schemes, have been used for spectroscopically probing the electronic states of a molecule that are forbidden in a single-photon process by symmetry restrictions [76,78].

Two extremes of behaviour at the resonant excited state have been classified by Gedanken et al. [79], namely photochemical decomposition or ionisation. They proposed two types of system; ‘Class A’, which exhibits ionisation followed by fragmentation, and ‘Class B’, in which dissociation to yield neutral fragments precedes the ionisation. The behaviour observed depends upon the relative rate of up-pumping. The majority of compounds studied in this thesis exhibit Class A behaviour, and are generally organic aromatic species. However, for some compounds, no molecular ion was observed in the mass spectrum and this is indicative of a Class B compound, which dissociates before ionisation.
Multiphoton ionisation results in the formation of a molecular ion in a well defined vibronic level, usually the vibrationless level of the ground electronic state of the ion [80]. The excess energy supplied in the ionisation step is removed as kinetic energy by the ejected electron, leaving the molecular ion with a narrow energy spread. With increasing laser intensity, the molecular ion may absorb further photons which induces fragmentation. Several mechanisms have been proposed to explain the fragmentation of the molecular ion [81,82,83,84,85]. Of these, the mechanism proposed by Deitz et al. [85] is now recognised as being the most widely accepted. Furthermore, experimental evidence has been obtained in support of this model [86,87].

The model proposed by Deitz et al. [85] is known as the 'ladder-switching' mechanism and is shown schematically in Figure 2-3. In this model, the neutral molecule absorbs two or more photons on its absorption ladder and is ionised. If the photon density in the laser pulse is high enough, then the molecular ion may absorb one or more photons. Fragmentation by absorption of further photons occurs once certain energy thresholds are exceeded, which is in common with the quasi-equilibrium theory of conventional mass spectrometry [88]. At sufficiently high excitation energies, the unimolecular dissociation rate (≈ 10^{-11}s) can compete effectively with photon absorption over the duration of the laser pulse (5 - 10 ns). This places an effective maximum energy on the molecular ion absorption ladder, thereby causing the system to switch to a new ladder of product ions. These product ions can then in turn absorb further photons, until their maximum energy is reached when they themselves undergo ladder switching.

This absorption-fragmentation mechanism may occur several times during a laser pulse leading, at sufficiently high laser intensities, to total fragmentation of the molecule [86,89]. In this manner, complete control over the degree of fragmentation may be obtained by simply controlling the intensity of the ionising laser pulse. For example, Figure 2-4 shows the L²TOF mass spectra of perylene, a polycyclic aromatic hydrocarbon, obtained using photoionisation at 266 nm with laser power densities of 0.025 MWcm^{-2} and 5 MWcm^{-2}. The spectrum in Figure 2-4a shows only the molecular ion at m/z 252, so-called 'soft ionisation', while
Figure 2-3: Schematic representation of the ladder switching mechanism for fragmentation.

$E_1 =$ 1st Ionisation Energy

$F =$ Fragment Species
Figure 2.4: L2TOF mass spectra of perylene under a) soft and b) hard ionising conditions, using 266 nm laser photoionisation.
Figure 2-4b shows complete fragmentation of the perylene molecule, in this case down to C\(^+\), so-called 'hard ionisation'. Under hard ionisation conditions it is possible to obtain structural information from the fragment species [80].

The absorption of UV photons by a molecule is controlled by the Franck-Condon principle i.e. there will no change of the nuclear co-ordinate during the electronic transition. Furthermore, only transitions to certain electronic states will be allowed, which limits the nature of any fragmentation observed. In contrast, electron impact (EI) ionisation, employing 70 eV electrons (which corresponds to a wavelength of 0.15 nm) strongly perturbs the molecules. As a result, many more states are accessible to the energy, producing more interesting fragmentation pathways [90]. In EI, however, the 70 eV of energy is deposited in the molecules instantaneously, leaving the different dissociation pathways to compete with each other. As a result, there is little or no control over the degree of fragmentation in EI, unlike laser photoionisation where complete control can be achieved.

2.5 Time-of-Flight Mass Spectrometry

2.5.1 Introduction

In the previous sections the mechanisms for laser desorption and laser multiphoton ionisation have been discussed. The main feature that these processes have in common is their pulsed nature. Therefore, in order to successfully mass analyse the photoions produced, a pulsed analyser is required. The type of mass analyser best suited to recording mass spectra from pulsed laser events is the time-of-flight (TOF) mass analyser, which, unlike other scanning mass spectrometers, can record a complete mass spectrum for every ionisation event.

TOFMS is one of the simplest, yet most versatile of the mass spectrometric techniques, with the separation of ions being solely dependent on their flight times in a field-free drift tube. The small size, low cost and ease of construction have made it the primary choice of mass analyser by researchers in the laser ionisation
field. This trend is highlighted by the number of citations given in recent reviews of the subject [91,92,93,94]. The great interest and success of the technique led Price and Milnes to entitle their recent review, 'The Renaissance of Time-of-Flight Mass Spectrometry' [95].

The concept of TOFMS is not new, indeed it was originally proposed in 1948 by Camerona and Eggers [96]. However, the principles upon which most of today's TOF systems are based, were first published by Wiley and McLaren in 1955 [97]. The principal disadvantage of TOF instruments, is their inherent low mass resolution, compared to that of sector instruments. The reasons behind these limitations and the methods available to counteract them are discussed in the following sections together with a brief review of the TOF technique. A more complete description of the TOF instruments in Edinburgh and a consideration of their operational limitations can be found elsewhere [98].

### 2.5.2 The Linear TOF Mass Analyser

The basic principle underlying the time-of-flight technique is very simple, and relies on the fact that all the ions are created at the same point and at the same time in an electric field. In this way, the electric field imparts the same amount of kinetic energy to all ions, i.e.

\[
KE = \frac{1}{2}mv^2 = zeE_s s
\]  

(2.9)

where \(e\) is the charge on an electron, \(z\) is the number of charges on the ion (normally 1), \(E_s\) is the magnitude of the electric field and \(s\) is the separation between the repeller and ground plates. The ions are accelerated to different velocities depending on their mass-to-charge ratio. They then enter a field-free drift region, and are finally detected. This simple single-field linear TOFMS is shown schematically in Figure 2-5 along with a schematic diagram for the more commonly used two-field Wiley-McLaren type linear TOF mass spectrometer. The advantage of this two-field design is that it provides first-order focusing of the ion packets, i.e. ions of the same mass created at different positions in the extraction field will
Figure 2-5: Schematic diagram of the a) single-field and b) two-field Wiley-McLaren type linear TOF mass spectrometers.
arrive at the detector simultaneously, thereby increasing the mass resolution of the instrument.

The equations which govern the flight time of ions created in the source region are given below. The velocities of ions, which have the same kinetic energies as they enter the field-free drift region, depend on their mass, $m$: \[ v = \sqrt{\frac{2zeEs}{m}} \] (2.10) Therefore, the time required to traverse the drift region, length $D$, is given by \[ t = D\sqrt{\frac{m}{2zeEs}} \] (2.11) The arrival time spectrum of the ions can, therefore, be converted directly to a mass spectrum; \[ \frac{m}{z} = 2zeEs \left( \frac{t}{D} \right)^2 \] (2.12) i.e. lighter, faster moving ions reach the detector before heavier ions. Therefore, a time-of-flight mass spectrum is merely a record of the signal intensity versus the arrival time of the ions at the detector.

Mass calibration of the time-of-flight mass spectra for unknown masses can be carried out directly from equation 2.12, or, more commonly, by fitting the time-of-arrival of ions of known mass using Newton's equations of motion. Unknown masses can be obtained from the empirical equation \[ m = a + bt^2 \] (2.13) where $a$ and $b$ are constants for the particular instrument. These coefficients can be obtained by means of a least squares fit to the time-of-arrival and exact mass of at least two species. Calibration is usually performed by the addition of an internal standard, or the accumulation of a mass spectrum containing two known compounds, one of high mass and the other of low mass.

2.5.3 Resolution in a TOF Mass Spectrometer

The mass resolving power or resolution of a TOF mass spectrometer is defined as \[ R = \frac{m}{\Delta m} = \frac{t}{2\Delta t} \] (2.14)
where \( m \) is the ion mass, \( \Delta m \) is the FWHM spread in the ion packet mass, \( t \) is the time-of-arrival of the ion, and \( \Delta t \) is the FWHM temporal width of the ion packet.

Schlag and coworkers [99] introduced an alternative definition of mass resolution.

\[
R = m \frac{(t_2 - t_1)}{\Delta t}
\]  

(2.15)

where \((t_2 - t_1)\) is the difference in flight time for two neighbouring mass peaks, of mass \( m \) and \((m + 1)\), and \( \Delta t \) is the temporal width of the ion packets. The resolution, therefore, depends on the difference in arrival time of ions whose masses differ by 1 amu. Since the ion flight times are proportional to \( m^{3/2} \), then, at high masses, the resolution of the instrument is degraded since the arrival times of the adjacent ions becomes so short that it is no longer possible to resolve ions separated by 1 amu.

The maximum resolvable mass is increased by a narrow ion packet width and long flight time. Design parameters will dictate the flight time, whilst the temporal width of an individual ion packet is limited by the initial temporal, spatial, and kinetic energy distributions of the ions and also the properties of the electronic data recording system. The mechanisms which broaden the ion packet length are further considered and discussed in the following sections.

### 2.5.4 Spatial Resolution

Under ideal conditions in a TOF mass spectrometer, all ions formed in a single laser pulse will gain the same amount of kinetic energy (KE) from the electric field. For this to happen, the ions must be formed in a plane perpendicular to the electric field gradient. However, since it is impossible to focus a laser beam to a single point, or an infinitely thin plane, then ions will be created over a finite spatial volume in the ion source. Therefore, if two ions are created at exactly the same time, but at two different positions along the spectrometer axis, they will be extracted from the ion source with different kinetic energies and enter the drift region with different velocities. In this manner, an ion which starts further away
from the draw-out grid will acquire greater KE and therefore arrive at the detector before the other ion. This limiting effect is known as spatial resolution.

This type of energy spread is the main limiting factor on the achievable resolution of simple single-field linear TOF instruments. The use of a focused or apertured laser beam for ionisation will clearly limit the range of potentials over which ions are created, and therefore reduce the spatial broadening. However, tight focusing of the laser beam can introduce other broadening mechanisms, such as space-charge effects, which are caused by coulombic repulsion when high ion densities are created by the laser pulse. These effects are normally only significant if ion densities exceed $10^7 \text{ cm}^{-3}$ [70]. The densities in the ion source of our instrument, however, rarely exceed $10^6 \text{ cm}^{-3}$ under typical experimental conditions [100]. In order to improve the spatial resolution of TOF analysers, Wiley and McLaren [97] introduced the double-field ion source.

In a single-field ion source, there is a point in the field-free drift region at which the faster ion will catch up to the slower ion. This point is known as the 'space-focus'. If the detector is placed at this point then the optimum spatial resolution is achieved. For a single-field mass spectrometer, however, the space-focus position is given only by the geometric condition $D = 2s_0$, where $D$ is the distance from the detector to the ion source, and $s_0$ is the distance from the point of creation of the ions to the front plate in the ion source (see Figure 2-5a). These conditions limit the resolution of high mass species since the flight times are too short. The introduction of a second acceleration field allows the position of the space-focus to be shifted by simply varying the electric fields in the ion source [97]. In this way, longer flight times can be obtained.

2.5.5 Temporal Resolution

It is impossible to create an ion packet which has a temporal width shorter than that characteristic of the ionisation technique used. Consider the most extreme case in which two ions are formed, one at the leading edge of the ionising laser pulse and one at the trailing edge. They would both have the same initial velocities,
since they were formed at the same spatial position, but they would arrive at the
detector separated in time by Δt, the width of the ionisation laser pulse. This
effect remains constant even if all the other broadening mechanisms are ignored.
With the advent of pulsed lasers with pulse widths on the order of 5 - 20 ns, laser
ionisation has become an ideal ion source for use in conjunction with TOFMS.

In order to minimise the effect of timing resolution, the overall flight time of
the ions may be extended. This can be achieved by either increasing the drift
tube length or reducing the accelerating voltage. Increasing the drift tube length,
however, makes the velocity components of the ions perpendicular to the flight
tube axis more significant, thereby reducing ion transmission. Decreasing the
acceleration voltage also has the effect of reducing the ion transmission and also
degrades the energy focusing conditions. A more effective way of reducing the ion
packet temporal width, would be to use shorter ionisation pulses from picosecond
or femtosecond lasers. Although this is an expensive option, such systems are
becoming more widespread in use.

2.5.6 Kinetic Energy Resolution

The initial velocity distribution of ions parallel to the spectrometer axis is another
factor affecting the resolution of TOF instruments. Consider two ions with the
same mass-to-charge ratio formed at the same position in the ion source, but with
equal and opposite initial velocities along the spectrometer axis. These initial ve-
locities are derived from the velocities of the neutral precursor molecules. Clearly,
the two ions will reach the detector at two different times. This time difference is
due to the 'turn-around time' of the ion initially travelling away from the detector,
which has to be slowed down, stop and then be re-accelerated by the electric field.
In this way, a distribution of kinetic energies for the initial neutral molecules will
result in ion packets with finite width. This limiting resolution factor is known as
energy resolution.

For simple single-field linear TOF instruments, the use of high extraction fields
will minimise the energy resolution contribution. This requires a long flight tube
to ensure sufficient time separation between adjacent masses. An alternative approach is to utilise the narrow velocity distribution afforded by a supersonic molecular beam propagating either parallel or perpendicular to the flight tube axis.

Wiley and McLaren [97] described a technique known as 'time-lag focussing' in their double field ion source to improve the energy resolution of the instrument. However, this was offset by a loss of spatial resolution since their instrument had to be operated away from space-focusing conditions. A more complete summary of energy resolution correction methods is given by Boesl et al. [91].

2.5.7 The Reflectron TOF Mass Analyser

An alternative method of correcting for the effects of the initial kinetic energy distribution was introduced by Mamyrin et al. [101]. They used an ion mirror or 'reflectron' which consisted of two fields, one to decelerate / accelerate the ions and the other to reflect the ions. The ion mirror was placed at one end of the field-free drift region. Using the first-order space-focus position of a set of Wiley-McLaren [97] ion optics as a 'pseudo ion source', there then followed a second field-free drift region of length equal to the space-focus to reflectron distance; the detector was placed at this point. A schematic diagram showing the characteristic features of a reflectron time-of-flight mass spectrometer is shown in Figure 2-6.

The reflectron is generally constructed from a series of ring electrodes, the first being grounded to maintain the field-free drift region. The second grid is generally set to about 10% of the reflectron depth and at a voltage of approximately two-thirds of the accelerating voltage. Over this short distance the incoming ions are decelerated by about two-thirds of their entry velocity. The remaining electrodes provide a uniform field gradient whose maximum potential is usually set slightly higher than the initial accelerating voltage.

The reflectron operates in the following manner. Consider two ions of the same mass-to-charge ratio but with different initial kinetic energies. The ion with the greater kinetic energy will travel faster than the other, and hence arrive at the reflectron first. This ion will penetrate deeper into the reflecting field than the
Figure 2-6: Schematic diagram of the reflectron time-of-flight mass analyser.
ion with lower kinetic energy and as a consequence, it will have a longer residence time in the reflectron. By judicious choice of the geometry and potentials on the reflectron grids, the two ions will arrive at the detector simultaneously due to the shorter flight time of the high kinetic energy ion in the field-free drift region being compensated for by a longer residence time within the reflectron.

The design of the reflectron used in the present work is based on that of Boesl et al. [102]. This design is slightly different from that described by Mamyrin et al. [101] since the detector and ion source are tilted by $4^\circ$ off the reflectron axis. The drift regions are therefore symmetrical about the axis of the reflecting ion mirror. Using such a geometry, no extra turning ion optics are required to focus the ion trajectories into the reflectron, like those previously used by Mamyrin et al. [101].

The reflectron only compensates for the kinetic energy spread in the ions and not for temporal distributions, i.e. the reflectron images the flight-time distributions at the space-focus of the ion source directly onto the detector. In this way, the peak widths remain narrow, whilst the time interval between adjacent masses is increased due to the extended length of the field-free drift region. High resolution can therefore be obtained without the need for altering the fields in the ion source.

### 2.6 Concluding Remarks

The L$^2$TOFMS methodology consists of three separate techniques, namely laser desorption, laser multiphoton ionisation and time-of-flight mass spectrometry. The subsidiary technique of molecular beam entrainment is also occasionally employed.

Pulsed CO$_2$ laser desorption using infrared radiation (10.6 μm) facilitates the volatilisation of fragile, involatile molecules as intact neutral species which can be photoionised. The entrainment of these neutral species in a supersonic molecular beam has several advantages. Firstly, it helps to minimise fragmentation and secondly it cools the internal degrees of freedom of the entrained molecules which can be useful for wavelength selective and spectroscopic analysis. However, removal
of the molecular beam entrainment stage can improve the instrument sensitivity, and this is described in more detail in Chapter 3.

Pulsed laser multiphoton ionisation has a number of unique analytical properties:

- wavelength selectivity in ionisation,
- control over the degree of fragmentation
- high sensitivity.

The time-of-flight mass analyser complements these pulsed laser techniques. It has high sensitivity and transmission, a theoretically unlimited mass range and the ability to collect a complete mass spectrum from every ionising laser pulse. Furthermore, the development of reflectron time-of-flight instrumentation has further increased the resolution attainable using TOF analysers.

On the whole, it is the combination of these techniques which makes the L²TOFMS methodology so successful for the mass spectral analysis of high molecular weight, involatile and/or thermally labile species. The following chapter contains a description of the methods and equipment used in the L²TOFMS experiments carried out during the course of this work.


Chapter 3

L²TOF Mass Spectrometry: Instrumentation

3.1 Introduction

The experimental work described in the following chapters was principally carried out on a purpose built mass spectrometer [1]. The instrument, shown schematically in plan and elevation views in Figures 3-1 and 3-2 respectively, is based upon a modular differentially pumped [2] design, consisting of three independently pumped vacuum chambers; the desorption chamber, the laser ionisation chamber and a third chamber housing a reflecting geometry time-of-flight (RETOF) mass spectrometer. The instrument was originally designed to have interchangeable linear and reflectron TOF analysers but the linear TOF analyser and associated cryopumps, described in detail later, were removed in order to facilitate easy interchange between entrainment and non-entrainment modes of operation.

In the entrainment mode of operation, neutral molecules are desorbed from a sample probe in the source chamber (SC) using a pulsed CO₂ laser and transported using a pulsed molecular beam into the ionisation chamber (IC). There, the neutral species are photoionised using a second pulsed UV laser and the resulting product photoions are extracted into the reflectron for mass analysis. In the non-entrainment mode of operation, the neutral molecules are desorbed from a probe mounted directly in the ionisation chamber; photoionisation, ion extraction and mass analysis are carried out as before. The main advantage of this second mode of operation is the much higher detection sensitivity which can be achieved.
Figure 3.1: Plan view of the RETOP mass spectrometer.
by removal of the entrainment stage. However, the majority of the results presented in this thesis were obtained using sample entrainment, since this mode of operation generally provided adequate detection sensitivity. The use of each mode of operation will be noted in the text, where appropriate.

In the following sections of this chapter, a brief description of the vacuum system, lasers, as well as data acquisition and control hardware and software used in the operation of the RETOF mass spectrometer is given. In addition, an outline of the different modes of operation of the instrument is given, highlighting, where appropriate, the changes required to switch between operation using sample entrainment and non-entrainment.

3.2 The Vacuum System

The entire vacuum system is constructed from 304 stainless steel, with the exception of the side flanges on the source chamber, which were constructed from aluminium to reduce weight. All vacuum seals are made using viton O-rings. As shown in Figure 3-1, the instrument consists of three vacuum chambers separated from each other by manually operated gate valves (VAT Series 8 and 11).

The source chamber (SC), which is a stainless steel cube (external dimension of 14.5") with a volume of 47.3 l, houses the laser desorption source, molecular beam valve and molecular beam skimmer. It is pumped by a 10" oil diffusion pump (CVC PMC-10, Convoil 20 pump fluid) equipped with a half chevron water cooled baffle, which reduces the unbaffled pumping speed (for air) from 5250 l/s \(^{-1}\) to 2600 l/s \(^{-1}\). To speed up roughing out of the SC, the diffusion pump was backed by a mechanical rotary / booster combination (Edwards E2M40/EH250), capable of pumping 8.5 mbar l/s \(^{-1}\) at a typical foreline pressure of 0.1 mbar. The source chamber pressure was monitored by an Edwards CP25EK Penning gauge head attached to an Edwards 505 analogue gauge. The base pressure in the chamber was typically 5 x 10\(^{-6}\) mbar. During operation of the pulsed valve (3 atmospheres
stagnation pressure of helium, repetition rate 10 Hz) the base pressure rose to ca. 5 x 10^{-4} \text{ mbar}.

The SC could be isolated from the diffusion pump by a manually operated gate valve (Vacuum Research Company LP series), and the diffusion pump itself could be isolated from the foreline by means of a pneumatically operated gate valve (Airco Temescal 5230). This enabled access to the SC which could be rapidly evacuated by the rotary/booster combination via an independent roughing line. This roughing line could be isolated from the SC using an Edwards SP40K valve. This set-up dispensed with the need to cool the diffusion pump oil during sample interchange. The foreline pressure was monitored during roughing by an Edwards PRH 10 Pirani gauge head attached to one port of an Edwards 1005 digital Pirani/Penning controller. During pump-down, the foreline pressure was typically allowed to fall below 2 x 10^{-3} \text{ mbar} before the diffusion pump was opened up to the SC.

The ionisation chamber (IC) is a cube (external dimension 11.2") with a total volume of 26 l. This chamber is pumped by an Edwards Diffstak 160/700 diffusion pump (Edwards L9 pump fluid), with a pumping speed (for air) of 700 l s^{-1}. The Diffstak is backed by an Edwards E2M18 rotary pump which is also used to back the diffusion pump on the reflectron chamber via a common foreline. The IC houses the ion extraction optics for the time-of-flight mass spectrometer. The pressure in this chamber was monitored by an Edwards PRL 10 Pirani gauge and an Edwards CP25K Penning gauge, both connected to an Edwards 1005 Pirani/Penning digital controller. The background pressure in this chamber was typically less than 10^{-7} \text{ mbar}, rising to ca. 1 x 10^{-6} \text{ mbar} under normal operating conditions. A 113 cm long linear TOF drift tube, together with a 65 cm high double-skinned liquid nitrogen dewar can be mounted on the top flange of the IC. The base of the dewar protrudes 38 mm into the IC and is connected to a series of copper cryoplates mounted onto the base of the dewar. These cryoplates surrounded the ion extraction optics on four sides and are effective in reducing the pressure in this chamber by an order of magnitude.

The chamber housing the reflectron (63.5 cm long with an i.d. of 19 cm) is
connected to the IC via a manually operated gate valve, by a 31.2 cm long, 6.3 cm o.d. stand-off tube. The reflectron ion mirror is mounted on the rear flange of the chamber, tilted at an angle of $4^\circ$ to the common molecular beam / ion extraction axis. This enables the ions to be reflected along the second flight path of the reflectron towards the MCP detector. The axis of the second drift region is set at an angle of $8^\circ$ to the first. A second stand-off section consisting of two short tubes, 5.1 cm long (6.3 cm o.d.) and 8.9 cm long (5.1 cm o.d.) connects the MCP detector to the RC. This vacuum chamber is pumped by an Edwards Diffstak CR 160/700 diffusion pump (Edwards L9 fluid) equipped with a liquid nitrogen-cooled cryotrap and a quarter-swing butterfly valve, and backed in parallel by the Edwards E2M18 rotary pump used to back the IC. In addition a double-skinned liquid nitrogen dewar is located on top of this chamber to provide some cryopumping. The vacuum pressure in the main chamber is measured by an Edwards CP25K Penning gauge head connected to an Edwards 1005 Pirani/Penning digital controller. The base pressure is typically below $1 \times 10^{-7}$ mbar and rises to ca. $5 \times 10^{-7}$ mbar under normal operating conditions.

On first changing over to the non-entrainment mode of operation, several instrument modifications were made, see Figure 3-3. Since the source chamber was no longer required, an additional roughing line from the IC was attached to the E2M40/EH250 rotary/booster combination to provide faster pump down times following sample introduction. The linear TOF analyser and associated liquid nitrogen dewar and cryoplates were removed from the top of the IC, and replaced with a blanking flange with a central 50 mm hole. The two Edwards Diffstak 160/700 and CR 160/700 diffusion pumps, which were originally used to pump the IC and RC respectively were swapped around in order to try and minimise any backstreaming of diffusion pump oil into the ionisation chamber. In addition, the quarter-swing butterfly valve on the the CR 160/700 diffusion pump could be used to isolate the IC from the diffusion pump, which allowed for rapid sample turnaround. Finally, the Edwards L9 fluid in the CR 160/700 diffusion pump was replaced by Edwards Santovac 5 fluid in order to try and further minimise the likelihood of any contamination in the ionisation chamber due to pump
Figure 3.3: Elevation and plan views of the RETOF mass spectrometer using the non-entrainment mode of operation.
3.3 Laser Desorption Source

3.3.1 Sample Entrainment

Desorption is carried out in the SC when sample entrainment is employed, as shown schematically in Figure 3-4. The infrared laser enters the SC through a 50 mm diameter NaCl window, mounted on the side flange of the chamber. The window is held in place by four PTFE clamps and sealed to the flange by a viton O-ring. The desorbed neutrals are entrained in a synchronised molecular beam pulse and transported through a skimmer to the ionisation chamber.
The molecular beam valve is mounted on an XYZ translator, which allows for alignment of the molecular beam with the skimmer. The axis of the instrument is therefore defined by the molecular beam axis. A commercial molecular beam valve (General Valve Corporation Series 9) was generally used, consisting of an iron actuator attached to a teflon plunger which was seated against a 1 mm orifice and sealed by spring action. The valve was opened by the application of a current pulse to a single solenoid which pulled back the actuator. The duration of the gas pulse was determined by the length of time that the current pulse was applied. Typically pulse duration settings of between 450 $\mu$s and 600 $\mu$s were used, with a stagnation pressure of 3 - 4.5 bar of helium.

Two different sample probes were employed, see Figure 3-4. The first consisted of a cylindrical stainless steel rod, ca. 20 cm long and 6 mm in diameter. The sample was drop coated from solution onto the rod, which was set spinning in a horizontal geometry. Solvent evaporation ensured even coverage of the rod by the solid residue. The probe was then mounted in the source chamber and connected to an externally mounted stepper motor via a screw mechanism which slowly rotated and translated the rod to ensure that a fresh area of sample was presented to each pulse from the desorption laser. This extended the sample lifetime and reduced the need for frequent sample replacement. Typically, 10 to 15 minutes of continuous operation could be achieved from a sample of this type. The sample rod was secured vertically by means of a brass guide attached to the bottom of the molecular beam valve faceplate. This ensured accurate and constant positioning of the rod relative to the molecular beam and laser axes. The stepper motor (RS No. 332 082) was controlled by a variable speed unit consisting of an RS unipolar 2A driver board and an RS model 320-24A power supply. The stepper motor was generally operated on the slowest speed, at half step intervals, to increase the sample lifetime.

The second type of sample probe employed consisted of a square-faced stainless steel bar, ca. 20 cm long and 6 mm thick. A shallow slot, ca. 1.5 mm wide and 40 mm long, was cut into one face of the rod into which the sample was placed. Three different sample preparation methods could be employed with this type of probe.
As before, the sample could be deposited from solution into the slot, providing a thin uniform sample layer. Alternatively, the sample could be deposited in a matrix material, e.g. glycerol, and dropped into the slot. A fine dusting of activated alumina (Type H) was used to thicken the mixture to prevent it from running out of the slot. Finally, the pure sample could be firmly pressed into the slot, providing a thick uniform sample layer. Generally, good shot-to-shot stability from thin sample layers was difficult to achieve. The use of thick samples improved the shot-to-shot stability. However, large amounts of sample were consumed using this method. Most of the experiments carried out in the following chapters were performed using relatively thick sample layers, built up by repeated application of thin layers of material from solution. The sample probe was, as before, mounted in the source chamber and connected to an externally mounted linear actuator (RS No. 318 711) controlled by the same stepper motor controller. Vertical movement of the sample rod, by the linear actuator, was again employed to extend the sample lifetime; approximately 10 minutes of continuous operation could be achieved. The sample rod was secured vertically by the use of a brass sample guide attached to the bottom of the molecular beam valve faceplate.

The sample probe guides were used to, prevent the target probes from moving out of the focus of the desorption laser during their vertical range of travel. In addition, they fixed the position of the probe relative to both the molecular beam axis and the nozzle orifice. Both these parameters are important for efficient entrainment of the sample. At short distances from the nozzle orifice, there is a strong likelihood of setting up shock waves in the molecular beam as the desorbed species enter the high density region of the molecular beam [3], resulting in a reduction in the signal intensity. The distance from the probe to the molecular beam axis is also an important experimental parameter. A compromise between the ability to obtain good entrainment conditions without disrupting the molecular beam must be achieved. Typical values for the distances between the nozzle orifice and the point of desorption, and the molecular beam axis and the point of desorption, were 4.5 mm and 5 mm, respectively.

The desorbed and entrained neutrals then pass through a skimmer before en-
tering the ionisation region of the mass spectrometer. Several skimmers with different orifice diameters were used (2 mm to 5 mm). For most experiments, however, a 5 mm orifice skimmer was used in order to maximise the signal intensity. The skimmer (Beam Dynamics, 50° included angle [4]), was attached to a brass mount, which was fixed to the inner wall of the SC opposite to the molecular beam nozzle. The mount protruded ca. 9 cm into the source chamber to prevent any disruption of the molecular beam caused by back reflection from the source chamber bulkhead wall [5]. The nozzle to skimmer distance was ca. 3 cm. Use of such a skimmer allowed a pressure differential of approximately 500 between the SC and IC to be maintained under normal operating conditions.

3.3.2 Non-entrainment

In the non-entrainment mode of operation, sample desorption is carried out in the ionisation chamber and the source chamber is not used. A schematic diagram of the desorption source used for this mode of operation is shown in Figure 3–5. The sample probe itself is constructed from stainless steel or Macor (an insulating ceramic material). The probe is attached, with a small nut and bolt, to a plastic holder which itself is held onto the arm of a UHV XYZ manipulator by two small grub screws. For ease of use when removing the probe, the whole probe/holder assembly is normally removed from the instrument. The manipulator arm is an aluminium rod (ca. 250 mm long, 10 mm dia.) welded onto a 70FC flange. This flange is mounted on the end of the XYZ manipulator (VG Instruments, model XYZ75) to allow accurate positioning of the probe within the ionisation chamber. The manipulator allows movement of the probe in the X and Y directions to a resolution of 0.01 mm, and in the Z direction to a resolution of better than 1 mm over a pressure differential of better than 10⁶ mbar (i.e. atmosphere on one side and ca. 10⁻⁶ mbar on the other). The manipulator was mounted on one of the side flanges of the ionisation chamber, such that the Z axis of the manipulator is perpendicular to the desorption laser beam.

Samples were deposited from solution onto small Macor disks (5 mm dia.)
Figure 3-5: Schematic diagram of the desorption source used in the non-entrainment mode of operation.

which could be inserted in holes bored into the sample probe (see Figure 3-5), or directly onto the surface an unbored probe. The probe was then inserted into the sample holder, which in turn was attached to the XYZ manipulator, as described above. Access to the sample probe was gained through the top flange of the instrument, in the non-entrainment mode of operation. When using non-entrainment, only a small amount of sample (ca. 0.05 g) is required, much less than that required for operation with sample entrainment, reflecting the higher sensitivity of the instrument.

The sample probe sits horizontally in the ionisation chamber, approximately halfway between the repeller plate and the draw out grid of the ion optics see Figure 3-6. The desorption laser beam enters the ionisation chamber through a 50 mm diameter NaCl window in the center of the top flange. The window was held in place, as before, by four PTFE clamps and sealed to the flange by a viton O-ring. The ionisation laser enters the ionisation chamber, through a Spectrasil B window (50 mm diameter), mounted on the side flange opposite the
Figure 3–6: Schematic diagram of the RETOF ion extraction optics mounted in the ionisation chamber of the mass spectrometer. (All dimensions in mm)

XYZ translator. This window is held in place by PTFE clamps and sealed by a viton O-ring. Ionisation takes place approximately 5 mm above the sample probe surface and the resultant photoions produced are then extracted into the RETOF mass spectrometer.

3.4 Time-of-Flight Ion Optics

The ion optics used for ion extraction following photoionisation are shown schematically in Figure 3–6. They are based upon the design of Wiley and McLaren [6] for a double-field spatially focussing TOF mass spectrometer. The ion optics consist of three electrodes, the repeller, the draw-out grid and the flight tube grids, followed by two sets of (X and Y) deflection plates. For most experiments, only the horizontal deflectors were used.

The extraction optics were fabricated in-house from gold plated aluminium. The repeller, draw-out and flight tube electrodes are 1.8 mm thick and 80 mm x 80 mm square. The deflection plates are 5 mm thick and 30 mm x 30 mm square. The repeller electrode has a 7.7 mm diameter hole in the centre to admit the molecular beam into the ionisation region. The draw-out and flight tube electrodes have
22.4 mm diameter circular apertures, both covered in a fine nickel mesh (Buckbee Mears 90% transmission) attached by conducting metallic paint. The mesh was used to improve homogeneity of the electric field gradient in the ionisation region. The repeller plate had no mesh over the central 7.7 mm hole as this was found to reduce the transmission of the molecular beam dramatically. The electrodes were supported by aluminium rods insulated with precision machined Delrin spacers. The whole assembly was supported on an aluminium base which rested on a set of bed-bars attached to the front and rear bulkheads of the ionisation chamber. Once the extraction optics had been placed in position, they could be locked to the bed bars by a screw mechanism on the base plate.

The ion mirror, used to reflect the ions into the second arm of the reflectron TOF analyser are shown schematically in Figure 3-7. The ion mirror consists of six concentric stainless steel rings (120 mm o.d., 60 mm i.d.). The backplate is a solid stainless steel plate 120 mm in diameter. The apertures in the two front rings were covered by fine nickel mesh (Buckbee Mears 90% transmission) attached by
### Table 3–1: Power supplies and corresponding voltages used for the ion extraction and reflectron optics.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Power Supply</th>
<th>Voltage / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeller</td>
<td>Stanford PS 350</td>
<td>+3780</td>
</tr>
<tr>
<td>Draw out grid</td>
<td>Stanford PS 350</td>
<td>+2595</td>
</tr>
<tr>
<td>Horizontal Deflectors</td>
<td>Stanford PS 325</td>
<td>-0-50</td>
</tr>
<tr>
<td>Retarding field (ion mirror)</td>
<td>Stanford PS 350</td>
<td>+2319</td>
</tr>
<tr>
<td>Reflecting field (ion mirror)</td>
<td>Stanford PS 350</td>
<td>+3817</td>
</tr>
</tbody>
</table>

conducting metallic paint, whilst those in the remaining rings are left uncovered. The ion mirror is split into two distinct regions, corresponding to the two fields in the reflectron, namely the retarding and reflecting fields. The retarding field is applied between the first two electrodes of the reflectron, and the reflecting field is applied between the third electrode and the back plate via a resistor chain across the intervening guard rings. The voltages for both these fields were supplied by independent power supplies. The voltages applied to both the ion extraction optics and the ion mirror are given in Table 3–1 along with the power supplies used. With these voltages, the resolution of the instrument was ca. 1200 at m/z 477. The mass accuracy in the spectra shown is within 1 Da unless otherwise stated.

### 3.5 Ion Signal Detection

Product photoions were detected by a dual microchannel plate detector (R.M. Jordan) [7,8] of a dual chevron design, consisting of two Galileo MCP-18B plates with an active area of 2.5 cm². Each microchannel plate consists of a honeycomb array of 10 μm diameter channels separated from each other by ca. 2.5 μm. The lead glass from which the microchannel plates are constructed was developed to ensure optimum secondary emission characteristics from each channel, and to be sufficiently semiconducting to allow charge replenishment from an external voltage source [7]. A voltage divider was used to provide a maximum voltage drop of 1000
V across each plate. The MCP detector has a typical gain of $10^2$ at 700V rising to $10^3$ at 1KV.

The detector was operated in grounded anode mode, thereby allowing easy coupling to the transient digitiser. This mode of operation required that the front channel plate be maintained at a large negative potential, but had the added advantage of increased gain for positive ions, which are accelerated towards this plate. The disadvantage of this mode of operation is that a grounding grid (82 % transmission) is required before the MCP to define the end of the field-free drift region. This also means that negative ions cannot be detected. The ion signal at the MCP anode was further amplified by a factor of ten using a LeCroy Model 134 Linear Amplifier before being fed into the low level input of a transient digitiser.

3.6 Laser Systems

In order to conduct L²TOFMS experiments a minimum of two lasers systems are required; one for sample desorption and a second laser to ionise the desorbed neutral molecules. In all the work described in this thesis, a pulsed CO₂ laser operating at 10.6 μm was employed for sample desorption. Photoionisation was achieved using the three fixed UV laser wavelengths: 266 nm, 248 nm and 193 nm. These were generated from the fourth harmonic of an Nd:YAG laser and the KrF and ArF lines of an excimer laser respectively. The laser systems employed are described in more detail below.

3.6.1 Alltec 854MS CO₂ Laser

The CO₂ laser is a gas laser driven by an electric discharge in which the lasing action occurs between rotation-vibrational levels in free CO₂ molecules. Laser emission occurs at long wavelengths, 10.6 μm, well into the infrared. The lasing medium consists of a mixture of 12% CO₂, 4% CO and 84% He. Population inversion occurs in the CO₂ molecules following collision with CO molecules that
are vibrationally excited by discharge pumping. This is a very efficient energy transfer process since the energy levels in the two molecules are so close. Emission in CO$_2$ occurs by radiative decay from the (001) state ($\nu_3$ antisymmetric stretching mode) to rotational sublevels of the (100) state ($\nu_1$ symmetric stretching mode).

The Alltec 854MS laser used in this work was a transverse excitation atmospheric (TEA) CO$_2$ laser, capable of generating 100 ns pulses of 10.6 $\mu$m radiation at a maximum repetition rate of 50 Hz. The laser was of modular design with the electronic components physically separated from the HV power supply, thyratron and laser cavity by means of a bulkhead. The laser beam traveled in a hermetically sealed system, which also housed the electrode assembly used to initiate the discharge. This sealed system provided laser radiation safety for the user and protection for the laser optics. The laser gas mixture was automatically admitted into the laser cavity when required via a demand valve. The maximum laser output of 400 mJ was rarely, if ever used, with more typical pulse energies of ca. 100 mJ or less (at a repetition rate of 10 Hz) usually employed. Pulse energies were measured using a Gentec power meter (Model ED100, 10 mV per mJ) attached to an oscilloscope. The laser could be manually controlled via a remote control module on a long umbilical cord. In order to fire the laser remotely a 5V, 50 $\mu$s pulse was required.

For experiments using sample entrainment, the output from the CO$_2$ laser was steered into the source chamber through a NaCl window via two gold plated mirrors, and focused using a 30 cm focal length NaCl lens mounted external to the chamber. The laser spot size on the sample probe was typically 1 mm square. When using the non-entrainment mode of operation, the laser beam was steered through a NaCl window on the top flange of the ionisation chamber using four gold coated mirrors and focused by a 25 cm focal length NaCl lens mounted external to the chamber. The laser spot size in this case was approximately 0.6 mm square. The laser beam was attenuated using a combination of fine nickel mesh and plastic attenuators. Taking into account the losses at the gold mirrors, lens and NaCl window, the desorption laser power density for studies using sample entrainment was typically 2.5 x10$^7$ Wcm$^{-2}$, and 5 x 10$^5$ Wcm$^{-2}$ for non-entrainment studies.
CHAPTER 3. L\textsuperscript{2}TOF MASS SPECTROMETRY: INSTRUMENTATION

3.6.2 JK HyperYAG HY750 Nd\textsuperscript{3+}:YAG Laser

The gain medium in an Nd:YAG laser is the isotropic crystal Y\textsubscript{2}Al\textsubscript{5}O\textsubscript{12} (yttrium-aluminium garnet, YAG) in which approximately 1% of the yttrium in the crystal is replaced by neodymium. Lasing action occurs between the energy levels of the Nd\textsuperscript{3+} ion within the YAG crystal lattice at 1064 nm. Second or higher order, harmonic generation can be achieved by use of a angle-tuned phase matched non-linear harmonic generating crystals mounted external to the laser cavity.

The JK HyperYAG Model HY750 laser used in this work has a folded-geometry oscillator-amplifier configuration. The oscillator and amplifier rods consisted of two 3" long Nd:YAG rods, 4 mm and 8 mm in diameter respectively, in close coupled pumping chambers excited by xenon flashlamp pumping. Both the oscillator and amplifier stages contained a x2 Galilean telescope which helped to compensate for thermal lensing effects. The oscillator cavity contained a plane output coupler with a 5 m radius of curvature, concave rear mirror. A Pockels cell was used to Q-switch the YAG output. This consisted of a dielectric polariser with a Brewster-angled KD\textsuperscript{*}P crystal and an optical rhomb which corrected for any beam deviation. The oscillator output was steered through the amplifier using two high reflectivity mirrors before passing through the thermally stabilised ovens containing the non-linear harmonic generation crystals. The Q-switched fundamental output (1064 nm) of this laser was specified as 800 mJ per pulse, at a repetition rate of 10 Hz.

Generation of higher harmonics required positioning of the appropriate ovens containing the non-linear harmonic generation crystals into the beam path. The second (532 nm) and third (355 nm) harmonics were generated using CD\textsuperscript{*}A and KD\textsuperscript{*}P crystals with typical pulse energies of ca. 320 mJ and 170 mJ respectively. Separation of the desired 532 nm or 355 nm wavelengths from the fundamental was achieved using two Brewster-angled gull wing prisms located after the harmonic generating crystals. Generation of fourth harmonic (266 nm) radiation was achieved using a KDP crystal to frequency double the second harmonic (532 nm) radiation. The fundamental, and second harmonic radiation were separated from
the 266 nm output using a Pellin Broca prism assembly. Typically, ca. 90 mJ pulse\(^{-1}\) of fourth harmonic radiation could be obtained.

In order to externally trigger the YAG laser, two trigger signals were required, one to trigger the flashlamps and the other to trigger the Q-switch. The Q-switched pulse energy could be varied by altering the time delay between these two pulses. The optimal time delay was around 180 \(\mu\)s. Alternatively, the laser power output could be altered by either increasing or decreasing the amplifier charging voltage.

The 266 nm fourth harmonic output was most commonly used for photoionisation purposes, although in later studies the third harmonic output at 355 nm was used to generate VUV radiation at 118 nm via frequency tripling in xenon (see Chapter 7). The 266 nm output was steered into the ionisation chamber using 90° UV quartz turning prisms. The beam diameter was normally reduced using an iris to give a typical spot size of 2 mm dia. The fourth harmonic pulse energy was measured with a Scientech (Model 672) power meter. Typical values of 2-3 mJ pulse\(^{-1}\) were employed. Higher pulse energies could be obtained by increasing the amplifier voltage or focusing the beam with a 30 cm quartz lens. Laser power densities in the range 10\(^5\) - 10\(^8\) Wcm\(^{-2}\) could then be achieved. When the 30 cm focal length lens was employed, the laser spot size was estimated to be 250 \(\mu\)m [1].

### 3.6.3 Lumonics TE-861T-4 Excimer Laser

Excimer lasers, like the CO\(_2\) laser, are also gas discharge lasers. The gain medium in this case is an excited dimer formed on discharge pumping. Lasing action occurs between an electronically excited, bound, state of the excimer and a dissociative, or weakly bound, ground state. The most common excimer lasers are based upon the rare gas halides or rare gas dimers. These molecules provide an ideal gain medium since a population inversion between the upper bound state and the lower lower dissociative state can be easily maintained. However, since the radiative decay is fast, the pumping process is the bottleneck. This problem can be overcome by the use of fast transverse electric discharges. In addition, the use of high gas densities increases the number of collisions allowing the excimer molecules to combine very
quickly, in times of the order of $10^{-8}$ s [9]. The laser wavelength emitted, however, depends upon the gas mixture used.

The Lumonics TE-861T-4 excimer used was primarily operated on the ArF or KrF lines, producing 193 nm (6.4 eV) or 248 nm (5.0 eV) radiation respectively. A thyratron-switched electric discharge at ca. 40 kV is used to stimulate laser action. The laser is fired by means of two 15 V trigger pulses. The first pulse initiates the capacitor charging cycle, called 'charge on demand', and the second pulse triggers the thyratron after approximately 12 ms. The output pulse energy could be controlled by either varying the charging period of the capacitor bank, or, more commonly, by adjusting the peak charging voltage. The laser is filled with the required excimer gases, F₂ and Ar or Kr, along with an excess of helium buffer gas to take the pressure within the cavity to more than 3 atmospheres. The cavity gases are continually circulated by means of an internal fan through an exhaust gas filter containing various molecular sieves. This helps to increase the lifetime of the gas fill.

The laser cavity was initially set up using stable resonator optics, consisting of a totally reflecting, flat rear mirror and a fully transmitting, MgF₂ front optic. The measured output at 193 nm was ca. 70 mJ pulse⁻¹ in an 8-10 ns pulse. At 248 nm, the output was typically 90 mJ pulse⁻¹ in a 12-16 ns pulse. These pulse energies were measured using a Coherent 210 power meter with the laser was operating at 10 Hz.

At a later stage the stable resonator optics were replaced with unstable resonator optics. The rear optic was replaced by a slightly concave rear mirror with a wedged front surface, and this was arranged confocally with the front optic. The same front optic as used in the stable resonator configuration was employed. Feedback was provided by an aluminium coated 3 mm diameter mirror mounted on a rod external to the laser cavity. The position of this mirror was easily adjusted to allow optimisation of the beam energy, shape and divergence. The use of unstable resonator optics enabled much lower output beam divergence to be achieved, which in turn meant that much tighter focusing conditions could be
used for more efficient multiphoton ionisation. However, the laser output energy was somewhat reduced using these optics.

The majority of experiments were carried out using the excimer fitted with unstable resonator optics. In this configuration the laser output took the form of a well collimated beam with a cross-section of $3 \times 15 \text{ mm}^2$ at 193 nm and $6 \times 15 \text{ mm}^2$ at 248 nm. The measured output energy at 193 nm was ca. 16 mJ pulse$^{-1}$, and ca. 45 mJ pulse$^{-1}$ at 248 nm. Normally the laser beam was further collimated using a set of razor edged slits of varying width before it entered the ionisation chamber.

3.7 Experimental Control

In order to control the many events in a typical L$^2$TOFMS experiment such as triggering and synchronisation of the pulsed molecular beam valve, desorption and photoionisation lasers as well as to record and process the data obtained in real time, a sophisticated data acquisition and control system is necessary. The system used is based on the CAMAC (Computer Automated Measurement And Control) [10] protocol, and employs a number of CAMAC modules that are housed in a CAMAC crate. This crate provides both power and communication lines allowing the transfer of data to and from the individual modules. The crate itself is linked, via a crate controller, to a Dell system 325 PC which runs the control software that was written by a former research student in this laboratory [11].

The Dell system 325 PC containing an Intel 386 microprocessor with an added maths coprocessor, is linked to a high resolution 17" monitor which displays the data obtained in real time. The computer software, known as THOR, was written in the C programming language with some assembler language routines to speed up the operation when commands are issued to the crate units. The crate controller (Hytec 1331) provides the interface between the computer and the CAMAC crate for communication with and read-out from the control and acquisition hardware.
3.7.1 Control Hardware

The IEEE CAMAC standard [10] defines a common dataway to which a number of instruments can be interfaced. The CAMAC modules are housed in a crate (Standard Engineering Corporation PCS 1410) which supplies them with power and 24 read/write data communication lines via the backplane. The data lines are used to direct commands from the software platform running on the Dell system 325 PC to the correct module and to transmit acknowledgment of receipt of these commands or requests for attention to the microprocessor in the PC. The control hardware is set up as shown in Figure 3-8.

The crate controller (Hytec 1331/Turbo PC Interface Module) is located in the first station on the right of the CAMAC crate. This is connected, via a 3 m long 50 core ribbon umbilical, to an IBM 1331 personality card (Hytec Electronics Ltd. Iss4) located in one of the 16 bit expansion slots of the Dell 325 PC. This module accepts commands from the PC and passes the information onto the relevant modules in the CAMAC crate. It also passes the recorded data back from the crate to the PC.

The timing of specific experimental events such as firing the pulsed valve or the lasers are critical. Therefore two CAMAC modules in the crate are used to provide trigger control pulses at the appropriate times, as instructed by the THOR program running on the PC. The first module, shown next to the crate controller in Figure 3-8, is a Kinetic Systems Model 3655 pulse delay generator (PDG) providing eight separate TTL level output signals, 200 ns wide, with a timing resolution of 1 μs and jitter of approximately 1 ns. The minimum possible interval between pulses from successive channels is 1 μs. This unit is used to provide trigger pulses for the molecular beam driver, whenever sample entrainment was used, the CO₂ laser and the COD trigger for the excimer lasers. In addition, it was used to trigger the second PDG (LeCroy Model 4222).

The LeCroy 4222 PDG can generate four 100 ns wide TTL pulses with timing resolution of 1 ns. Each channel of the 4222 is independent and can be used in any order, or even simultaneously. The jitter between pulses is less than 170 ps. This
Figure 3-8: Schematic of the CAMAC based experimental control and data acquisition system used for a typical L²TOFMS experiment.
module was therefore used to trigger devices which required more precise timing control such as the thyratron of the excimer laser and the transient digitiser trigger. The output signals from the two PDG’s are of insufficient magnitude and duration to drive the external trigger relays of the lasers. For this reason, the output from the PDG’s are connected to home-built line driver units, which are used to boost the output signals to higher voltages and duration. The line drivers each contain 8 channels capable of providing either 5 V, 50 μs or 15 V, 10 μs output pulses. These line driver units are housed in a separate NIM bin, which supplies the units with power and also houses the linear pre-amplifier used to amplify the MCP output.

3.7.2 Transient Digitiser

The arrival of ions at the microchannel plate detector results in the production of a negative going waveform. This waveform is first amplified by a LeCroy Model 134 Linear Amplifier. The amplifier contains two channels, each providing amplification by a factor of 10, or 100 if used in series.

The resulting amplified signal is digitised by means of a fast sampling Joerger TR200 transient digitiser (TD). The unit is capable of digitising 512 mV signals, at 8 bit resolution, with a maximum sampling rate of 200 MHz. The digitising rate was set using the THOR program running on the PC. The input offset can be altered via a front panel trimpot and can be monitored by the offset test point. In addition, a monitor output is provided which reconverts the digitised input to an analogue form via an onboard DAC to generate an output signal which tracks the input signal.

Once the TD is armed by the CAMAC crate controller using a CAMAC dat-away command, the input signal is continuously sampled and stored. This data is continuously overwritten, until the module receives an external trigger stop pulse from the 4222 PDG. Following this trigger pulse, the module accumulates the required number of post-trigger samples. For all the experimental work described in this thesis, the record length of the TD was constrained to 2 Kbytes. These 2048 bytes constitute a mass spectrum.
CHAPTER 3. L²TOF MASS SPECTROMETRY: INSTRUMENTATION

Since the maximum record length was set at 2Kb, only ca. 10 µs portions of the entire mass spectrum can be recorded using the highest resolution sampling speed of 200 MHz. The flight times of ions in the RETOF analyser range from 2 to 100 µs. Therefore in order to record a complete mass spectrum for every laser shot, a slower sampling rate is used. However, this results in the loss of mass spectral resolution. An alternative method of obtaining high resolution spectra that was frequently employed, was to record spectra at the highest sampling rate but changing the delay between the trigger pulse to the ionisation laser and the TD stop trigger pulse, in order to ensure that the mass region of interest fell within the 2 Kb capture window of the digitiser. This however meant that the spectra recorded did not show the entire mass range.

3.8 Software Control

The executive program THOR was written by A.M. Butler [11] using the C programming language together with some assembler language routines. The program runs on a Dell system 325 PC platform incorporating an Intel 386 processor and maths coprocessor, and allows control of the experiment to be carried out in real time as well as providing an immediate on-screen view of the acquired data. The program runs the experimental cycle at a repetition rate of 10 Hz. This is accomplished by employing the interrupt mechanism of the PC to ensure that any changes made to the experimental parameters are executed in the dead time between data cycles. The interrupt is operated at twice the experimental repetition rate in order that the software can toggle between the software routines used for controlling the experiment and those used for downloading and processing the data. These two main software routines are known as TIC and TOC respectively. The TIC routine arms the digitiser, loads the required experimental time delays in the pulse delay generators and triggers the first channel of the Kinetic Systems 3655 PDG to start the experimental cycle. The TOC routine is executed after a TIC, and controls downloading of the acquired waveform from the transient digitiser memory to the PC. The data is then inverted to a positive going waveform
and summed with those from previous data cycles as required. A typical experimental timing cycle is shown in Figure 3–9 for both sample entrainment and non-entrainment modes of operation.

### 3.8.1 Data Acquisition Modes

There are three types of experiment which THOR allows the user to carry out. The simplest and most common experiment involves recording a TOF mass spectrum. The program permits a user defined number of experimental data cycles to be accumulated before displaying the summed total on the monitor of the PC. Successive single shot spectra can be accumulated before the screen is refreshed or alternatively, the shots can be displayed individually as they are collected and summed. The mass spectra are typically summed until a satisfactory signal-to-noise ratio has been attained. The spectra are normally recorded on a time-labelled axis and after summation these can be re-calibrated to show a mass-labelled axis. The intensity scale is usually normalised to the intensity of the largest peak.

The collection of TOF mass spectra relies upon synchronisation and optimisation of a number of events. The time delay between the desorption laser and the ionisation laser is one of the most critical and needs to be carefully optimised in order to achieve the best signal. THOR therefore, allows a second type of experiment to be carried out in which the intensities of up to ten different species can be monitored as a function of any one of the time delays shown in Figure 3–9. In this case, the screen display plots the intensity of any chosen species as the time delay between any two trigger events is varied, such as the time delay between the desorption and ionisation lasers. The peak of the distribution represents the optimum timing position for the ionisation laser. Figure 3–10a shows the variation in the helium carrier gas signal monitored on the $\He^+$ signal generated using the 193 nm output of the excimer laser for photoionisation, as a function of the excimer laser trigger delay. This clearly maps out the profile of the helium pulse from the molecular beam valve. The timescan in Figure 3–10b shows the optimum arrival time of indole-3-acrylic acid in the ionisation region of the mass
### Nd:YAG laser for ionisation

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ valve</td>
<td>450</td>
</tr>
<tr>
<td>Laser</td>
<td>40</td>
</tr>
<tr>
<td>JK lamps</td>
<td>180</td>
</tr>
</tbody>
</table>

- PC triggers 3655
- PDG via CAMAC dataway

### Excimer laser for ionisation

<table>
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<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>CO₂ valve</td>
<td>450</td>
</tr>
<tr>
<td>Laser</td>
<td>250</td>
</tr>
</tbody>
</table>

- 4222 Trigger

**Figure 3-9:** A schematic of the trigger pulse timing set-up for L²TOFMS experiments using either the Nd:YAG or excimer laser in a) sample entrainment and b) non-entrainment modes of operation. (All times are in microseconds)
Ion of indole-3-acrylic acid was monitored. Upper profile, the He + signal was monitored and in the lower profile, the molecular excitation profile of indole-3-acrylic acid, using sample preparation, photolysis, and the electronic profile of the helium carrier gas pulse and (b) the delay.

Figure 3-10: (a) Temporal profile of the helium carrier gas pulse and (b) the delay.

Relative intensity / arb. units

Excimer laser delay / microseconds

0 50 100 150

0 20 40 60 80 100

100 200 300 400 500 600 700 800

500 400 300 200 100

Excimer laser delay / microseconds

(b) (a)
spectrometer recorded by monitoring the molecular ion signal generated using 193 nm photoionisation as a function of excimer laser trigger delay.

The third type of experiment which can be carried out involves the accumulation of wavelength resolved photoionisation spectra. In this case, one or more chosen ion signals can be monitored whilst using a computer driven stepper motor to control the wavelength of a tunable laser, such as a Nd:YAG or excimer pumped dye laser. Such wavelength resolved photoionisation spectra have been recorded in this laboratory for a number of species using CO₂ laser desorption with sample entrainment and jet-cooling, such as tryptophan and perylene [1].

3.9 Sensitivity Enhancement using Non-entrainment

In order to weigh up the merits of both the sample entrainment and non-entrainment modes of operation, the instrument sensitivity and resolution was optimised for each configuration. High instrument sensitivity is a requirement for the direct analysis of complex systems. One such system which clearly illustrates the advantages of removing the entrainment stage is the analysis of aerosol particulate matter for polyaromatic hydrocarbons (PAH's) directly from the bulk particulate matter. When the particulate matter, collected on a polycarbonate filter was examined using sample entrainment, the mass spectrum in Figure 3-1a was obtained. Using 248 nm photoionisation, the base peak in the spectrum at m/z 202 corresponds to pyrene, a volatile PAH. No other peaks due to PAH contamination are observed. On changing over to the non-entrainment mode of operation, an identical piece of the same polycarbonate filter was examined. The mass spectrum in Figure 3-1b was recorded by Scott Wright. Again, the base peak in the mass spectrum is at m/z 202 corresponding to pyrene, however, several other intense peaks have appeared. These correspond to other PAH's that are in the sample but were of too low a concentration to be detected before. Using this non-entrainment methodology has clearly resulted in a dramatic improvement in
mass spectra were recorded under similar conditions using 248 nm photolysis. The (a) sample enrichment and (b) non-enrichment modes of operation. The mass spectrum of cloud water illustrate sample obtained.

**Figure 3.11:** Ion Top mass spectrum of cloud water.
instrument sensitivity. It has been estimated that an improvement in sensitivity of between $10^3$ and $10^4$ has been attained for some species [12].

Although the sensitivity of the instrument in the sample entrainment mode of operation is lower than that in the non-entrainment mode, it should be noted that the detection sensitivity of such a sample entrainment set-up is not particularly low. For example, de Vries et al., using a laser desorption and sample entrainment set-up, have examined the concentration profiles of entrained perylene vapour [13]. They determined the concentration profiles in a molecular beam expansion, as a function of desorption laser position, variation of source gas pressure and variation of source gas. Under the optimum conditions, they determined that 1 % of the desorbed material could be extracted through the skimmer, and therefore concluded that the sample entrainment technique would be sensitive enough for the detection of molecular species adsorbed on surfaces. In a further publication, they used the information previously obtained, to determine a detection sensitivity for their time-of-flight instrument [14]. For the compound perylene, which had a known (and high) ionisation efficiency at the photoionisation wavelength used, they determined that $(5\pm1)$ perylene ions were detected for every $10^6$ perylene molecules desorbed. They further demonstrated this sensitivity by recording a two-colour (1+1) REMPI spectrum of perylene using less than 30 picograms of material.

Since PAHs have large absorption cross-sections at the laser wavelengths routinely employed for photoionisation, they are generally very easy to detect. For this reason, peaks due to PAH contamination are often observed in the mass spectra of other species. Where appropriate throughout the rest of this thesis, attention will be drawn to any PAH contaminant peaks by labelling them with an asterisk (*).
Bibliography


Chapter 4

L²TOFMS of Aromatic Polymers

4.1 Introduction

Over the last three decades, mass spectrometry has become an increasingly important technique for the analysis of polymers. The high sensitivity and dynamic range of the technique, provide a powerful method for the structural characterisation of polymeric systems. However, in order to obtain a mass spectrum of a polymer, several criteria must be met. Firstly, the polymer must be vaporised intact, if possible, into the gas phase before ionisation can occur. This enables a more accurate representation of the polymer distribution to be obtained. The need to vaporise or desorb intact species into the gas phase poses obvious limitations for high mass, thermally labile polymer species. Only since the comparatively recent advent of more novel mass spectrometric techniques, such as field desorption [1,2,3,4], laser desorption [5,6,7,8,9] electrospray [10,11] and matrix-assisted laser desorption / ionisation (MALDI) [12,13,14,15,16] has polymer mass spectrometry progressed significantly. These new techniques, with enhanced sensitivity, mass accuracy and increased mass range have also dramatically enlarged the variety of polymeric systems that can be studied.

The advantages of mass spectrometry for polymer characterisation over other more conventional techniques are manyfold. For example, small sample requirement, the ability to directly obtain molecular weight and / or structural information, complex mixture analysis and rapid analysis time are some of the advantages. A detailed and fundamental review of this topic can be found in the excellent text by Schulten and Lattimer [17]. More recently their work has been updated in
For a polymeric system, mass spectrometry could be expected to provide information on the following parameters from a very small amount of sample:

- Molecular weight distributions and average molecular weight values.
- Fingerprint patterns for polymer identification.
- The sequence of monomer units.
- Branching, crosslinking or sidechain substitution.
- Copolymer structure.
- Additives or impurities present.

No single mass spectrometric technique, however, can provide an answer to all of these questions for a typical polymer system.

The unique property of mass spectrometry is the ability to produce intact molecular ion species and to accurately measure their molecular mass. In addition, the intensity of each peak present in the mass spectrum, is indicative of the relative amount of each species present. Using a soft ionisation technique, such as field desorption [1], where little or no excess energy is imparted to the ionised species, the accurate mass of the molecular ion produced can be readily ascertained. The ability to produce these intact molecular or quasi-molecular ions for each oligomer in a polymer sample then allows direct calculation of the molecular weight averages, since the accurate mass and relative intensity are known. The mass spectrum also provides a unique view of the shape and width of the oligomer distribution, which provides additional and complimentary information for the polymer scientist.

The ability to observe fragmentation products is an extremely powerful feature. This facility is most commonly found on sector and multiple quadrupole
instruments, where tandem mass spectrometry or MS/MS experiments can be carried out. More recently the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometers for MS/MS experiments has been highlighted [19]. In an MS/MS experiment, one molecular ion or fragment is selected in the first MS step. With the aid of a gas collision cell, it is then fragmented and the fragments are mass analysed using the second MS stage. This is called a product or daughter ion scan. This technique is extremely useful for the analysis of copolymers, where the entire monomer sequence of the copolymer oligomers can be easily ascertained.

Even if the degree of fragmentation observed in a mass spectrum is difficult to control, the technique can still be useful in providing data on polymeric systems. Techniques, such as electron impact (EI) and secondary ion mass spectrometry (SIMS), where the energy of the desorption/ionisation event is fixed, are often used to provide a unique polymer fingerprint. Using modern computer based systems, a mass spectrum of a polymer unknown can be compared to a library of polymer fingerprint mass spectra. The closest matches can therefore be displayed and the unknown identified.

The need to obtain a representative mass spectrum with a minimal amount of sample is particularly important. Since many new polymeric compounds are initially produced on a very small scale, analysis must be carried out on as little sample as possible. Typically, micrograms of material or less are required for modern mass spectrometer systems which have high sensitivity. Unfortunately, due to the inherent destructive nature of mass spectrometry, the sample cannot be recovered. However, the destruction of small amounts of analyte in order to obtain important information is often an effective compromise.

The ability of a mass spectrometric technique to ionise selectively or non-selectively also has major implications for polymer analysis. For example laser photoionisation has been employed, where the ionisation wavelength was varied to selectively ionise the aromatic species in a polymer blend [20,21]. In comparison, non-selective ionisation techniques, such as VUV laser postionisation, have the advantage of being able to ionise all the species present in a polymer blend.
Clearly, such selectivity can be of major importance for the analysis and characterisation of commercial polymer formulations.

In the following sections, the use of L²TOFMS for the analysis and characterisation of aromatic polymers is described. In particular, the feasibility of using L²TOFMS for determining oligomer distributions, end group information, molecular weight averages and structural information of several aromatic polymers is discussed, as are the more general factors governing the applicability of the technique for polymer analysis. This work was carried out since very few reports concerning L²TOFMS analysis of polymers have been published. Furthermore, the few publications available have generally failed to obtain oligomer distributions of significant intensity. A number of polystyrene standards have been studied using three laser photoionisation wavelengths, 266 nm, 193 nm and 248 nm. A fluorinated polystyrene sample and an aromatic siloxane polymer were also examined. Where appropriate, complimentary results for these samples, obtained using other mass spectrometric techniques are presented.

4.2 Molecular Weight of Polymers

4.2.1 Introduction

In any polymerisation process it is virtually impossible for all polymer chains to be terminated at the same length. Instead a range of chain lengths are formed (called oligomers) and one must deal, therefore, with an average molecular weight for the polymer. The molecular weight is an extremely important variable because it relates directly to the properties, performance and processing of the polymer. In general, the higher the average molecular weight, then the tougher the polymer and the more difficult it is to process. As a consequence, accurate measurements of molecular weight distribution must be made both during the production, and of the final product, to ensure that the desired properties are obtained. The terms low molecular weight and high molecular weight are very subjective. There is no simple answer to the question, where does low molecular weight stop and
high molecular weight start? In this thesis, however, it is assumed that polymers of average molecular weight, ≤5000 Da, will be classed as low molecular weight species.

### 4.2.2 Methods of Molecular Weight Determination

There are many methods employed for the determination of molecular weight distributions of polymers, including size exclusion chromatography (SEC) [23], osmometry [24], scattering methods [24,25], ultracentrifugation [26], and mass spectrometry [27]. The two molecular weight averages most commonly determined, are the number average molecular weight, $M_n$, and the weight average molecular weight, $M_w$. These are expressed mathematically in Equations 4.1 and 4.2.

\[
M_n = \frac{\sum N_i M_i}{\sum N_i}
\]

\[
M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}
\]

Where $N_i$ and $M_i$ are the number of moles and molecular weight respectively of each oligomer $i$. The techniques of end group analysis [28], cryoscopy [29], ebulliometry [24,29], viscosity [30], and other colligative properties [24,25,31] such as osmotic pressure, are used to determine the number average molecular weight, because the number of molecules of each weight in the sample are counted. In contrast, methods for determining the molecular weight based upon the mass or polarizability of a polymer, such as ultracentrifugation [26], or light scattering [32] are used to determine the weight average molecular weight. In these techniques, the greater the mass of the oligomer then the greater the contribution it makes to the measurement.

When calculating $M_n$ and $M_w$ for a polymer, it is found that $M_w$ is always greater than $M_n$. The reason for this lies in the measurement methods. For colligative properties, each molecule in the sample contributes equally, regardless of its molecular weight. However, in light scattering methods, for example, the larger molecules will contribute more because they scatter light more effectively. Consequently, the narrower the molecular weight range, the closer the values of $M_w$.
and $M_n$ become. The ratio of $M_w/M_n$ may, therefore, be used as an indication of the molecular weight range of the polymer. This ratio is called the *polydispersivity* of the polymer.

Mass spectrometry can be used for determining average molecular weight values, since the spectra generally contain information on both the mass of the oligomer and the amount present in the sample. The technique can therefore provide both number average and weight average molecular weight information, and hence also polydispersivity values. In addition, the range of oligomers present in the sample can generally be seen directly from the mass spectrum.

### 4.3 L²TOFMS Analysis of Polystyrene

#### 4.3.1 Introduction

To date, use of two-stage laser desorption laser photoionisation mass spectrometry (L²TOFMS) for the analysis of high molecular weight species has been rather limited. Schlag and coworkers have obtained mass spectra of large biomolecules up to mass $m/z$ 5729 [33] and of peptides with masses below $m/z$ 2000 [34,35]. With the exception recent work by Anex *et al.* [36], the number of groups that have studied polymers using a two step methodology, have generally failed to detect oligomeric species with any significant intensity. In the recent study by Anex *et al.*, REMPI was used to examine laser desorbed and entrained polymer distributions of perfluorinated polyethers. Intense oligomer peaks extending up to $m/z$ 7000, with little fragmentation were obtained. A study of rubber vulcanites by Lykke *et al.* [22] showed that low mass polymer fragments and polymer additives could easily be detected from complex polymer systems, using an L²TOFMS methodology. However, no complete oligomer distribution was observed.

Polystyrenes have been studied by a number of groups using a two-stage desorption / ionisation technique. For example, Feldmann *et al.* [37] used 193 nm UV laser desorption for the ablation of polystyrene, followed by 118.4 nm pho-
to ionisation of the neutral species liberated. An intense styrene monomer peak at m/z 104 together with several characteristic fragments were observed, however no oligomer distribution was seen. Similarly, Pallix et al. [38] used ion and/or electron bombardment followed by 118.4 nm laser postionisation. Again, an intense styrene monomer peak at m/z 104 was detected, as well as several fragment peaks to lower mass. In addition, small ion peaks up to m/z 265 were observed, but no distribution of higher oligomers was present. Laciprete and Stuke [39] used 248 nm photoablation and picosecond UV laser photoionisation at 290 nm for the analysis of polystyrene and other polymers. The dominant peak observed in the mass spectrum was the styrene monomer peak at m/z 104, but smaller peaks to higher mass were observed which were attributed to fast chemical and/or photochemical processes occurring during ablation. Lustig and Lubman [20] analysed a series of polystyrenes blends along with polycarbazole and polyamide. They used CO₂ laser desorption followed by 266 nm UV laser postionisation, with entrainment of the desorbed species in a molecular beam. The spectra for the polystyrene samples all showed the monomer molecular ion peak at m/z 104, along with characteristic molecular ion fragments. No oligomer distributions were observed with significant intensity. However, they demonstrated the ability of the technique to selectively detect target aromatic polymers in aliphatic blends. The other samples examined, showed predominantly molecular ion peaks of the monomer. In later work, Lustig and Lubman [21] reported a more complete study of polystyrene, polystyrene blends, EPON epoxyresins and polyamides. For polystyrenes with average molecular weights below 1000 Da, intense styrene monomer peaks were observed with only a few small peaks corresponding to higher mass oligomers. For higher average molecular weight polystyrenes, ca. 3000 Da, only the styrene monomer peak was observed.

It is clear from this brief summary, that the L²TOFMS technique has had only limited success for the analysis and characterisation of polymers, in particular polystyrenes. For this reason, the following section describes the use of L²TOFMS for the characterisation of several low molecular weight polystyrene standards. This was carried out in order to discover both the strengths and limitations of
the technique for polymer analysis. The effect of ionising laser wavelength upon the relative intensity of peaks corresponding to oligomers and fragments in the mass spectra is discussed. Furthermore, the effect of both entrainment and non-entrainment methodologies on the mass spectra is examined. Mass spectra with oligomeric distributions up to ca. m/z 3800 have been observed. The factors which govern the applicability of the L²TOFMS technique for the analysis of high molecular weight polymers are also discussed.

4.3.2 Materials

Two polystyrene standards, polystyrene 800 and 2500 were obtained from Aldrich Chemical Co. A further polystyrene 1300 standard was obtained from Polymer Laboratories. The polystyrene standards were previously characterised by size exclusion chromatography (SEC), vapour pressure osmometry, NMR and intrinsic viscosity. The average molecular weight values quoted by the manufacturers are shown in Table 4-1. Unless otherwise stated, the samples were drop coated onto a stainless steel rod from acetone solution. A relatively thin sample layer was deposited in order to produce a uniform coating.

4.3.3 Polystyrene 800

Figure 4-1 shows the L²TOF mass spectrum for the polystyrene 800 standard obtained using photoionisation at 266 nm. The sample was desorbed from a stainless steel substrate, and sample entrainment was employed. The power density of the photoionisation laser was ca. 3.75 MWcm⁻². The spectrum shows a series of intense peaks separated by 104 Da. This mass separation corresponds to the styrene repeat unit mass, clearly identifying the peaks as oligomers. The oligomer distribution is bell-shaped, indicating that the polymer has been formed statistically in a typical polymerisation process. The oligomer peaks range from n=1, at m/z 162, to n=10, at m/z 1099. The distribution peaks at m/z 474, corresponding to the n=4 oligomer. To low mass, a series of less intense fragment peaks are observed, which are of structural significance; these are tabulated in Table 4-2.
substrate and the sample entrapment mode of operation were used.

266 nm photolysis of a power density of 3.73 MW cm⁻². A stainless steel

FIGURE 4-1: I2TOP mass spectrum of polystyrene 800 standard obtained using

Relative intensity / arb. units

mass / Da.

0.0 0.2 0.4 0.6 0.8 1.0

91 92 105 196 117 162 300 266 474

1099 1200
Table 4-1: Table of molecular weight average values for the polystyrene standards. Data supplied by the manufacturers.

The fragments observed are consistent with those seen in the electron impact (EI) mass spectrum of polystyrene 800, shown in Figure 4-2. A few of the most intense fragments can be assigned as m/z 91 [C₆H₅CH₂]⁺, m/z 92 [C₆H₅CH₃]⁺, m/z 117 [C₈H₉]⁺, m/z 131 [C₁₀H₁₁]⁺ and m/z 196 [C₆H₅(CH₂)₃C₆H₅]⁺.

The EI mass spectrum, of the same polystyrene 800 sample, was obtained using a Kratos MS 902 sector mass spectrometer with a source temperature of 100°C. The mass range of the instrument was ca. 800 Da. Two series of peaks can be seen in the mass spectrum, both separated by 104 Da, the styrene repeat unit mass, as outlined in table 4-3. Pairs of peaks in series A and B differ by 70 Da and this separation corresponds to a pentene group. Any given mass in series A can be viewed in terms of a molecular ion containing n styrene units (n104 Da) + butane (58 Da). The masses in series B can be arrived at via a McLafferty rearrangement as shown in Figure 4-3. From this information one can deduce that the polymer contains a butyl terminal group. This behaviour has been observed before by Beckwitz and Heusinger [40].

From the masses of the fragments observed in the 266 nm photoionisation mass spectrum of the polystyrene 800 standard (Figure 4-1), it is clear that several
<table>
<thead>
<tr>
<th>Technique</th>
<th>m/z observed fragments</th>
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<tr>
<td>EI (70 eV)</td>
<td>79 (1), 91 (100), 92 (13), 103 (3), 104 (25), 105 (19), 116 (2), 117 (36), 118 (6), 128 (1), 129 (3), 130 (1), 131 (6), 132 (1), 160 (1), 161 (19), 162 (12), 163 (2), 193 (7), 194 (3), 195 (9), 196 (17), 197 (3), 265 (1), 266 (4), 267 (1), 300 (6), 301 (2)</td>
</tr>
<tr>
<td>L²TOFMS (266 nm)</td>
<td>66 (19), 71 (9), 77 (3), 91 (79), 92 (100), 104 (15), 105 (34), 117 (54), 118 (13), 131 (10), 142 (10), 152 (6), 161 (29), 162 (38), 196 (19), 266 (82), 300 (4)</td>
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<tr>
<td>L²TOFMS (193 nm)</td>
<td>91 (100), 92 (57), 104 (15), 105 (25), 117 (31), 118 (21), 131 (12), 161 (27), 162 (18), 175 (2), 181 (9), 192 (1), 193 (7), 194 (3), 195 (9), 196 (12), 300 (3), 404 (2), 508 (1), 612 (1)</td>
</tr>
<tr>
<td>L²TOFMS (248 nm)</td>
<td>55 (73), 91 (93), 92 (30), 104 (77), 105 (60), 117 (77), 131 (12), 161 (83), 162 (100), 191 (57), 196 (87), 300 (37)</td>
</tr>
</tbody>
</table>

**Table 4-2:** Comparison of the fragments observed for polystyrene 800 using electron impact mass spectrometry (EI MS) and laser desorption laser photoionisation time-of-flight mass spectrometry (L²TOFMS). The L²TOFMS data was obtained using 266 nm, 193 nm and 248 nm photoionisation wavelengths. The relative intensities, normalised to the largest fragment observed, are given in parenthesis.
Figure 4.2: EI (70 eV) mass spectrum of polystyrene 800 standard. Source temperature ca. 100°C.
<table>
<thead>
<tr>
<th>Series A</th>
<th>Series B</th>
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<tbody>
<tr>
<td>162 (12)</td>
<td>92 (13)</td>
</tr>
<tr>
<td>266 (4)</td>
<td>196 (17)</td>
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<tr>
<td>370 (2)</td>
<td>300 (6)</td>
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<td>474 (1)</td>
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</table>

**Table 4-3:** $m/z$ of principal ion series from the El (70 eV) mass spectrum of polystyrene 800. Relative intensities are in parenthesis.

**Figure 4-3:** Scheme showing the McLafferty rearrangement of polystyrene that occurs in order to obtain series A and B masses as shown in Table 4.1
B series fragments are present, indicating that the polymer is butyl terminated. Therefore, from the L²TOFMS data alone, it is possible to unambiguously characterise the polymer as a butyl terminated polystyrene. Furthermore, the observation of a series of intense oligomer peaks using 266 nm photoionisation contradicts Lustig and Lubman’s earlier work [21] on polystyrene in which they stated that larger oligomer units are rarely observed with any significant intensity.

Figure 4–4a shows the mass spectrum obtained for polystyrene 800 using 193 nm photoionisation and sample entrainment. This mass spectrum is markedly different from that obtained using 266 nm photoionisation, in that the intensity of the oligomer series is much reduced in comparison to the low mass fragment species. Again, the series of peaks to high mass are separated by 104 Da, the styrene repeat unit mass, and the distribution is bell-shaped. The oligomer series ranges from n=1, at m/z 162, to n=12, at m/z 1306, and peaks at n=6, m/z 578. The fragment peak intensities are greatly enhanced in the 193 nm photoionisation mass spectra, with the base peak at m/z 91. This m/z 91 peak is not shown in Figure 4–4a, in order that the complete oligomer distribution could be observed instead. The fragment species present in the 193 nm spectrum are again consistent with those observed in the El mass spectrum, and are listed in Table 4–2. Furthermore, the B series peaks formed via a McLafferty rearrangement, extend up to m/z 612 with significant intensity.

Figure 4–4b shows the 248 nm photoionisation mass spectrum of the polystyrene 800 standard, obtained using the sample entrainment mode of operation. It exhibits a series of oligomer peaks, separated by m/z 104, the styrene repeat unit mass. The distribution is bell-shaped, which is consistent with both the 266 nm and 193 nm mass spectra, and the oligomer peaks range from n=1, at m/z 162, to n=13 at m/z 1410. The distribution peaks at m/z 370, which corresponds to n=3, although both the n=4 and n=5 oligomers are almost as intense as the base peak. The intensities of the fragment species are low relative to the oligomer peaks in the spectrum, particularly in comparison to the 193 nm and 266 nm spectra. Again the fragment species, listed in Table 4–2, are consistent with those observed in the El mass spectrum, shown in Figure 4–2.
Relative intensity / arb. units

Figure 4. (a) TOP mass spectrum of polystyrene 800 standard using a 193 nm photolysis. Figure 4. (b) TOP mass spectrum of polystyrene 800 standard using a 193 nm photolysis.
For each of the ionisation laser wavelengths used, several facts must be noted. Firstly, in each case the fragments observed correspond directly to those observed in the electron impact mass spectrum, the only difference being that the relative intensities of the peaks vary with ionisation wavelength. Both the 266 nm and 248 nm mass spectra exhibit fragment peaks which are of relatively low intensity compared to the oligomer peak intensities. This is not surprising since the two ionisation laser wavelengths are relatively close and one would expect little, if any, differences in the mass spectra obtained. The 193 nm photoionisation mass spectrum is dramatically different, in that the intensities of the fragment peaks are large relative to the oligomer peaks.

Varying the desorption laser power density over two orders of magnitude (10^6 - 10^8 MWcm^(-2)) produced no significant effect on the mass spectra obtained. Furthermore, reducing the ionising laser intensity only resulted in reducing the overall peak intensities, and the relative intensity of the oligomers with respect to the fragment peaks. This suggests that at least some of the fragment species are formed during the CO_2 laser desorption event, with the intensity differences observed at the different ionisation wavelengths being due to different absorption cross-sections for the fragments. Lustig and Lubman [21] also reported that no significant changes were observed in the mass spectra when the desorption laser fluence was altered. Since their spectra showed predominantly a styrene peak at m/z 104, with little or no higher oligomers, they suggested that large oligomers desorbed from the bulk, either photochemically or thermally decompose upon desorption whether laser vaporisation or particle beam sputtering is utilised.

The shape of the oligomer distribution also changes between the 266 nm and 248 nm mass spectra, which are similar, and the 193 nm mass spectrum. In the former case, a slightly skewed distribution is observed, with the low mass oligomers of greater intensity than would be expected for a bell-shaped distribution. The 193 nm data, however, shows little or no such skewing. There are four possible explanations for this skewing effect. Firstly, thermal decomposition of the higher oligomer species may occur during desorption, leaving only lower molecular weight oligomers intact. Secondly, the longer ionisation wavelengths can selectively ionise
the low mass oligomers over the higher mass species, i.e. the absorption cross-
sections at these wavelengths varies as the oligomer size increases. If this effect
occurs, then it would be impossible to obtain accurate average molecular weight
values, since only a small contribution from the higher molecular weight oligomers
will be included. Alternatively, the longer ionisation wavelengths may fragment
the higher oligomeric species in such a manner that the resulting fragments have
the same mass as the lower mass oligomers. That is, intact styrene repeat units
are fragmented from the higher mass oligomers. Again, if this mechanism was oc-
curring, then varying the intensity of the ionisation laser would affect the shape of
the distribution observed. This effect has not been encountered. Finally, velocity
slippage in the molecular beam can occur, whereby inefficient momentum transfer
from the molecular beam carrier gas to the larger oligomers takes place. In this
case, all the oligomers do not arrive in the ionisation region at the same time and
instead, the higher mass oligomers are delayed by a few microseconds. Optimising
the time delay of the ionisation laser would correct this problem. However, for
the spectra obtained, the time delays were fully optimised. This velocity slippage
phenomenon is described in more detail later.

It is difficult to speculate which, if any, of these mechanisms is operating under
the conditions used. Indeed, more than one may be in operation. However, it may
be possible to obtain a clearer picture by analysing a mixture of two, or more,
single oligomer samples in an equimolar mixture. In this way, it would be easier
to determine the mechanism(s) involved from either the fragments observed or the
relative intensity of the oligomers.

Although a skewed oligomer distribution was observed, it is clear from the data
obtained that L²TOFMS in the sample entrainment mode of operation is useful
for the characterisation of polystyrenes. At each photoionisation wavelength, both
oligomer and fragment peaks were observed. From the fragment peaks observed,
it is clear that the polystyrene is terminated by a butyl end group. Furthermore,
from the higher mass peaks, it is clear that intact oligomers are being detected,
and the repeat unit in the chain is styrene.
Non-entrainment

Figure 4-5 shows the mass spectrum obtained for the polystyrene 800 standard using the non-entrainment mode of operation and 248 nm photoionisation. As observed in the sample entrainment spectra, a distribution of oligomers is observed, separated by 104 Da. The distribution is slightly skewed and ranges from n=1, at m/z 162 to n=12 at m/z 1306 and peaks at n=4, m/z 475. As in the corresponding sample entrainment mass spectrum (Figure 4-4b), the relative intensities of the fragment species are much reduced compared to the oligomer peak intensities. The fragments observed are again typical EI-type fragment species. As described previously, removal of the sample entrainment step provides higher instrument sensitivity. Due to this increase in sensitivity, only 10 laser shots were required to produce this mass spectrum compared to 250 shots for the sample entrainment spectra.

In Figure 4-5, the distribution would appear to be slightly more skewed towards low mass than was previously observed in the corresponding sample entrainment mass spectrum. This is most likely, a consequence of thermal decomposition in the desorption step, since the desorption laser fluence is always more critical in the non-entrainment mode of operation. Most likely, the CO₂ laser fluence was somewhat higher than the threshold required for sample desorption. In order to observe all the high mass oligomers in the distribution, the low mass end of the spectrum was discriminated against during data collection.

4.3.4 Polystyrene 1300

The mass spectrum of polystyrene 1300 obtained using 248 nm postionisation in the non-entrainment mode is shown in Figure 4-6. Oligomer peaks ranging from n=3 at m/z 370 to n=14 at m/z 1516 and peaking at n=8, m/z 891, are clearly visible, with a bell-shaped distribution. However, an increase in the relative intensity of the fragment peaks to the oligomer peaks is also observed compared to those seen in the 248 nm photoionisation of polystyrene 800 in the non-entrainment mode, Figure 4-5. This is possibly caused by a higher desorption laser power
Figure 4-5: $I_2$TOF mass spectrum of the polystyrene 800 standard obtained in the non-entrainment mode of operation using 248 nm photoionisation. A CO$_2$ desorption laser power density of 1.6 MW/cm$^2$ was employed.
Figure 4.6: $L_2$TOF mass spectrum of polystyrene 1300 standard using the non-entrainment mode of operation and 248 nm photoionisation. A CO$_2$ desorption laser power density of 2.5 MW cm$^{-2}$ was employed. Desorption was performed from a Macor substrate. Peaks labelled with an asterisk (*) are due to PAH contamination.
density (2.5 MWcm$^{-2}$), employed to study this sample compared to that used (1.6 MWcm$^{-2}$) for the polystyrene 800 sample. Again, the fragments observed are consistent with those observed in the El mass spectrum of polystyrene 800. In addition to these fragment species, several peaks present in the mass spectrum are due to contamination from polyaromatic hydrocarbon species. These are labelled with an asterisk (*) where appropriate.

It is clear from these results obtained in the non-entrainment mode, that the desorption laser power density has a profound effect upon the mass spectra observed. Some initial results using this instrument mode have indicated that at low CO$_2$ desorption laser powers, only a relatively small degree of fragmentation is observed. At higher desorption laser powers, for a constant ionising laser power density, a much higher degree of fragmentation is observed. This correlates well with the data obtained for these polystyrenes in the entrainment mode, where the sample was cooled in the jet before ionisation. Since varying the CO$_2$ laser power had such little effect on the shape of the distribution, or on the intensity of the fragments observed, then it is clear that the power densities employed were well above threshold for the system. It is only in this non-entrainment regime that careful control and monitoring of the desorption laser powers becomes critical, and desorption mechanisms can be more easily elucidated.

### 4.3.5 Polystyrene 2500

In order to determine the high mass capabilities of the instrument, using the sample entrainment mode of operation, a polystyrene 2500 standard was examined. The sample was desorbed from a sintered glass disc, and photoionised using 193 nm UV laser radiation. The sintered glass disc source was used to extended the sample lifetime. However, the higher substrate temperatures achieved during laser desorption facilitated the desorption of higher mass oligomers. In addition, the higher substrate temperatures attained would increase the degree of thermal decomposition occurring in the desorption step. The sample was deposited onto the disk from acetone solution as before; a relatively thick layer was applied. The
L²TOF mass spectrum obtained is shown in Figure 4–7. A series of peaks separated by 104 Da are observed corresponding to intact polystyrene oligomers. The distribution ranges from n=10, at m/z 1099, to n=36 at m/z 3807 and is bell-shaped. The shape of the distribution does not appear to be skewed, as in the lower mass polystyrene spectra, indicating that the molecular weight averages calculated from the data may be quite accurate. To lower molecular weight, below 600 Da, intense fragment peaks are present in the mass spectrum. However, in order to obtain the complete oligomer distribution, the low mass region was discriminated against during data collection. These low mass fragment peaks are, however, of much greater intensity than the oligomer peaks. This is consistent with the results found for the polystyrene 800 spectra using 193 nm photoionisation. The intensity of these low mass fragment species are, however, somewhat greater than would be expected on the basis of the ionisation wavelength alone. This may be due to the higher substrate temperature achieved during desorption from the sintered glass disk. This increased substrate temperature will increase the degree of thermal decomposition produced during the desorption process as was suggested by Lustig and Lubman [21].

From Figure 4–7 it is clear that species up to ca. m/z 3800 may be photoionised. It has previously been thought that photoionisation of large molecular species would be very difficult, due to the large number of internal degrees of freedom in the molecule in which the energy may randomise. For this reason, Boesi speculated that photoionisation would be limited to molecules with masses below ca. m/z 2000 [43]. As has been shown, this hypothesis has been proven unfounded.

As the mass of each oligomer increases, then there is an increasing contribution to the oligomer peaks from isotopes [41]. This is particularly important when unit mass resolution is unattainable, as in the present case. For example, the n=100 oligomer of polystyrene has a molecular formula which can be expressed as C₈₀₆H₈₁₀, with a nominal mass of m/z 10458. Since there are also contributions from the ¹³C and ²H isotopes, then the molecular ion peak in a time-of-flight mass spectrum will be an average of all the isotopic contributions. Matsuo et al. [41] have defined an approximate relationship which allows the calculation of the
Desorption was performed from a sintered glass disk.

Figure 4-7: L_2 TOF mass spectrum of polystyrene 2500 standard using sample entrainment and 193 nm photolionisation at a power density of 5.2 MW/cm^2. Desorption was performed from a sintered glass disk.
CHAPTER 4. L²TOFMS OF AROMATIC POLYMERS

strongest isotope peak which would be observed for the molecule C₅H₆ as:

\[ K_{max} = 0.01108i + 0.007825j \] (4.3)

where the coefficients 0.01108 and 0.007825 are correction factors for the \(^{13}\)C and \(^2\)H isotopes respectively. Using this relationship, the most abundant isotope of the n=100 oligomer of polystyrene has a mass of m/z 10473.2.

Yergey et al. [42] have calculated the nominal mass, monoisotopic mass, most abundant mass and average mass for a series of polystyrene oligomers. As the size of the oligomers increases, the mass shift between the monoisotopic mass and the nominal mass becomes progressively larger and the average mass is again somewhat larger. In addition, the shape of the group of peaks becomes increasingly non-symmetrical. These phenomena have been observed in the L²TOF mass spectra of the high mass polystyrenes. Table 4-4 lists the mass shift between the nominal and average mass for the polystyrene 2500 oligomers observed in Figure 4-7.

4.4 Field Desorption MS of Polystyrenes

4.4.1 Introduction

In order to further characterise the polystyrene samples studied previously by L²TOFMS, field desorption mass spectrometry was carried out on the same samples. The following sections briefly describe the field desorption technique, the equipment used, and the results obtained.

4.4.2 The Field Desorption Technique

The term Field Desorption (FD) implies the removal of a substance from an emitter surface, including the desorption of any adsorbed solid or liquid layers. Field desorption has long been considered to be an offspring of field ionisation (FI), and has tended to be treated in the same vein, i.e. the mechanism for FD has been treated similarly to that for FI. Field ionisation more specifically, is the
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Table 4-4: Oligomer molecular masses for the polystyrene 2500 standard peaks observed by L\(^2\)TOFMS. \(^1\) Nominal mass based upon C=12 and H=1. \(^2\) Average molecular weight for the isotopic cluster. \(^3\) Peak mass from L\(^2\)TOF mass spectrum of polystyrene 2500.
process whereby ions are formed solely by quantum mechanical tunneling of an electron through a potential barrier formed by the molecular potential, the image potential and the applied electric field. Because of the complexity of the field desorption phenomena, the interpretation of experimental observations in terms of mechanisms of ion formation is still a controversial issue. As a result many models have been proposed for the FD mechanism.

A theoretical model for field desorption and field evaporation was originally developed from the theory for field ionisation, which itself was based upon the mathematical derivations of Müller [44] in 1956 and Gomer [45] in 1959. The treatment considers atoms on clean metal surfaces or in their lattice. This, and other models are described in detail by Prókai [46].

Field desorption and field ionisation are both inherently soft ionisation techniques, which produce mainly molecular ions or pseudo molecular ions, such as [M+H]+ or [M+Na]+. The molecular or pseudo molecular ion intensities are normally very large compared to fragment ion intensities and this makes FD an attractive technique for the analysis of oligomeric mixtures.

### 4.4.3 Experimental

A schematic diagram of the field desorption source is shown in Figure 4-8. It consists of an anode (called an emitter) with sharp tips at a high positive potential, and a cathode at a negative potential. These act as an extraction lens to produce a potential difference of about 10 to 12 kV. This arrangement is followed by a series of ion lenses to focus the ions produced into the mass analyser. The most commonly used emitters are 10 μm diameter tungsten wires onto which have been grown carbon micro-needles. These micro-needles are called dendrites and are normally 20 to 40 μm in length. They are grown onto the wire using a high temperature activation technique. The role of the emitter is chiefly to produce a high electric field focused on the tip of the dendrites due to their very small radius of curvature. Typically, electric field strengths of ca. 10^8 Vcm^{-2} are obtained at the tip of the dendrites.
All the field desorption mass spectra shown in this thesis were recorded at ICI Wilton Materials Research Centre, Cleveland, using either a model ZAB-2SE reverse geometry mass spectrometer or ZAB-T four sector instrument of similar design. A schematic diagram of the ZAB-2SE is shown in Figure 4–9. This instrument was manufactured by VG Analytical Ltd (Wythenshawe, UK) and was equipped with the standard VG combined field desorption/fast-atom bombardment (FD/FAB) source. The samples were analysed using 10 μm activated carbon FD emitters supplied by Linden ChroMasSpec (Bremen, Germany), and the sample was applied to the emitter using the standard syringe technique. The samples were prepared as solutions in volatile solvents, usually chloroform or acetone, then drawn into a small syringe and the bubble of liquid on the tip of the needle was brushed lightly over the surface of the emitter. The emitter current applied was typically in the range 0 to 50 mA, or until the signal intensity disappeared. All data were acquired at a resolution of 1000. Data were acquired into the VG Opus data system in multichannel analysis (MCA) mode.
Polymer Analysis

In a multicomponent sample, such as a polymer with many oligomers, or a mixture of compounds, then for FD mass spectrometry each component will have a Best Anode Temperature (BAT) at which it will desorb from the emitter. The BAT is the temperature at which predominantly molecular ions are generated and thermally and field induced fragmentation is minimised. Lower mass oligomers tend to desorb even with no heating, while higher mass oligomers may require fairly strong heating conditions. Mass spectra are therefore normally acquired in profile mode, where the emitter current is raised slowly while the polymer desorbs. The observed mass spectra are normally averaged after data acquisition is complete. Low temperature spectra of volatile impurities and high temperature scans obtained from decomposition products, if any, can then be subtracted from the averaged mass spectrum.

The relative ionisation, transmission and detection efficiencies must be strictly evaluated for the calculation of molecular weight averages, but numerous reports
have shown that molecular weight and intensity parameters derived directly from FD spectra compare favourably with those values obtained by conventional techniques such as GPC and intrinsic viscosities [2].

Figure 4-10 shows a typical set of spectra for the polystyrene 800 standard obtained during data acquisition as the emitter current is raised from 0 to 50 mA. Only the most intense peaks are shown. As the emitter current is raised (a-e), higher oligomer species are desorbed. During this run the emitter current was slowly increased at a rate of ca. 2 mA per minute, and the entire spectrum was obtained in approximately 40 minutes.

4.4.4 FD of Polystyrenes

In the last decade, FD has been used extensively for the qualitative characterisation of complex oligomer systems, including the determination of distinct oligomer series [47,48], end group determination [49], the investigation of oligomerisation mechanisms [50] and structural/compositional characterisation of block copolymers [49]. Many polymer systems have been studied by FD including polyglycols (PEG’s [51], PPG’s [52] and PFPO’s [53]), polyesters [47] and resins [54,55,56].

Several groups have used FD for the analysis of polystyrenes [2,3,4,49]. Saito et al. [49] used FDMS to determine the mechanism of thermally initiated polymerisation of styrene using several different solvents. In each case, the mass spectrum showed a series of peaks with masses corresponding to characteristic head and tail groups attached to the styrene oligomers. Previous to this, Matsuo et al. [4] had used both polystyrene and polyethylene glycol as mass references for FD. Polystyrene oligomers up to ca. m/z 10000 were detected with significant intensity. Lattimer et al. [3] subsequently used FDMS to determine molecular weight averages for a series of polystyrenes up to ca. m/z 5300. The calculated $M_n$ and $M_w$ values compared favourably with the values obtained by conventional techniques. They concluded that the relative intensities of the molecular ions obtained by FDMS could be used directly to give accurate relative concentrations of
Figure 4-10: FD mass spectra of polystyrene obtained during data acquisition at emitter currents of a) 0 mA, b) 22 mA, c) 28 mA, d) 34 mA and e) 46 mA. Only the significant peaks are bar plotted.
the oligomers after the appropriate corrections for the isotopic abundances were made.

Rollins et al. [2] have extended the mass range and increased the resolution of FDMS over previous studies. A series of polystyrenes were examined up to average molecular weight m/z 12500. In each case, a series of singly charged oligomer species were observed up to m/z 15000. In addition, doubly charged and occasionally triply charged polystyrene oligomers were observed in the mass spectra.

Figure 4-11 shows the FD mass spectrum of the polystyrene 800 standard obtained using the ZAB-2SE mass spectrometer at ICI Wilton. It exhibits a series of singly charged oligomer peaks separated by 104 Da, the styrene repeat unit mass. The oligomer series begins at n=3, m/z 370, and ends at n=17, m/z 1826, peaking at n=8, m/z 890. No peaks due to the n=1 or n=2 oligomers were observed during the collection of the spectrum. The masses of the peaks correspond to oligomers terminated by a butyl group, and, therefore, the series has masses which follow the formula \((104n) + 58\). The shape of the distribution is bell-shaped with the
maximum occurring at \( n=8, \ m/z \ 890 \). In agreement with FDMS being a soft ionisation technique, no fragmentation is observed in the spectrum.

Figure 4-12 shows the FD mass spectrum of the higher molecular weight polystyrene 2500 standard. Two distinct features are present. Firstly intact, singly charged molecular ion species are observed, between \( m/z \ 890 \) and \( m/z \ 4500 \), separated by 104 Da, with a maximum in the distribution occurring at ca. \( m/z \ 2000 \). These peaks correspond to a series of singly charged styrene oligomers terminated, as before, by a butyl group. The oligomers range from \( n = 8 \) to \( n = 43 \). Secondly, an additional discrete envelope of peaks can be seen between \( m/z \ 600 \) and \( m/z \ 2200 \), separated by 52 Da, which correspond to doubly charged oligomer species.

One odd feature of the mass spectrum is a discrepancy in the shape of the singly charged and doubly charged oligomer distributions. The shape of the distribution would normally be identical for the singly and doubly charged species. However, the singly charged oligomer distribution appears to have a flattened top, whilst the doubly charged distribution is more like the classic bell-shaped or Gaussian oligomer distribution. One possible explanation for this effect is saturation of the
detector. This is obviously not the case, however, as several mass spectra were recorded under varying conditions and each spectrum was identical. In addition, the intensity of the ion signal is also recorded on the mass spectrum along the right-hand axis. The maximum intensity value for the polystyrene 2500 standard mass spectrum is much lower than that recorded for the polystyrene 800 mass spectrum in Figure 4-11. Therefore, detector saturation has obviously not occurred. As yet, apart from this being the true shape of the distribution, we have no other explanation for this phenomenon.

It can be concluded that FD is a powerful technique for polymer analysis. In each case, representative mass spectra of the polystyrene standards were easily obtained. The spectra contained intact singly charged oligomer species of significant intensity and no fragment species were observed. Some doubly charged oligomers were also observed.
4.5 Determination of Molecular Weight Averages

From the FD mass spectrum of polystyrene 800, it is clear that no peaks are present due to the n=1 and n=2 oligomers. Since the accuracy of the FD data is in no doubt, and only the oligomers observed in the mass spectrum are actually present in the sample, then clearly the presence of both n=1 and n=2 oligomers in all the L²TOF mass spectra is due to fragmentation. Therefore, two calculations of the molecular weight averages were performed, the first taking into account the first two oligomer species, and the second neglecting these peaks and starting from n=3. The average molecular weight values for the other polystyrene samples were calculated for all the peaks present.

4.5.1 Polystyrene 800

Table 4–5 summarises the results obtained on calculation of the average molecular weight values of the polystyrene 800 standard at each photoionisation wavelength.

From Table 4–5 it is clear that when the n=1 and n=2 oligomers are not included in the calculations, the average molecular weight values are closer to those obtained by the manufacturer using GPC, than the corresponding data incorporating all the oligomers observed in the spectra. This provides further evidence that these oligomers are produced as fragments, either during the desorption or ionisation events. The values calculated from the 193 nm photoionisation mass spectrum would appear to be in excellent agreement with the GPC data given by the manufacturers. This suggests that the intense fragment peaks observed in the spectrum do not significantly affect the distribution of oligomers observed. In every case, the 248 nm and 266 nm photoionisation data give low molecular weight averages, even although the degree of fragmentation in these mass spectra is significantly lower than in the 193 nm photoionisation mass spectrum. From
<table>
<thead>
<tr>
<th>Technique/laser wavelength used</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>Polydispersivity ( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPC</td>
<td>700</td>
<td>794</td>
<td>1.13</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 266 nm entrainment(^1)</td>
<td>472</td>
<td>559</td>
<td>1.13</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 266 nm entrainment(^2)</td>
<td>546</td>
<td>589</td>
<td>1.08</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 193 nm entrainment(^1)</td>
<td>448</td>
<td>687</td>
<td>1.53</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 193 nm entrainment(^2)</td>
<td>710</td>
<td>786</td>
<td>1.11</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 248 nm entrainment(^1)</td>
<td>598</td>
<td>710</td>
<td>1.19</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 248 nm entrainment(^2)</td>
<td>662</td>
<td>745</td>
<td>1.13</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 248 nm non-entrainment(^1)</td>
<td>576</td>
<td>675</td>
<td>1.17</td>
</tr>
<tr>
<td>( \text{L}^2\text{TOFMS} ) 248 nm non-entrainment(^2)</td>
<td>650</td>
<td>732</td>
<td>1.13</td>
</tr>
<tr>
<td>( \text{FDMS} )(^1)</td>
<td>880</td>
<td>949</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 4-5: Comparison of the number average molecular weight, the weight average molecular weight and the polydispersivity values quoted by the manufacturers and calculated from \( \text{L}^2\text{TOFMS} \) and FD data for the polystyrene 800 standard.\(^1\) Data calculated from all oligomer peaks observed in the mass spectrum. \(^2\) Data calculated from oligomer \( n=3 \) upwards.
this, it is possible to conclude that 193 nm photoionisation is clearly better for polystyrene analysis.

A comparison of the molecular weight averages for the polystyrene 800 standard using 248 nm ionisation with and without entrainment shows that the non-entrainment mass spectrum has a lower molecular weight average than the entrained spectrum data. This is most likely due to an increase in the degree of fragmentation produced during the desorption event. Using the non-entrainment mode of operation results in an increased amount of internally hot oligomers being desorbed, which under entrainment conditions, would have been cooled by the molecular beam prior to photoionisation. Therefore, the distribution is skewed towards the low mass region and correspondingly, low molecular weight averages are obtained.

The molecular weight averages calculated from the FDMS data in Figure 4–11 are $M_n = 880$, $M_w = 949$ and polydispersivity = 1.07. Both $M_n$ and $M_w$ are considerably higher than the values obtained by GPC quoted by the manufacturer ($M_n = 700$, $M_w = 794$ and $M_w/M_n = 1.13$). The most likely reason for this is that since oligomers are desorbed when no anode heating current was applied, then the smaller oligomers will desorb quickly, resulting in only high mass oligomers remaining on the probe. Since the probe temperature is elevated for a long time during the mass spectrum acquisition, then a greater contribution from the high mass oligomers will be observed in the spectrum and hence the calculated molecular weight averages will be higher. This effect has been observed before for low molecular weight polymers [3].

4.5.2 Polystyrene 1300

The average molecular weight values calculated from the 248 nm photoionisation mass spectrum are $M_n = 892$ and $M_w = 962$. These values correlate poorly with the GPC values quoted by the manufacturer of $M_n = 1260$ and $M_w = 1346$. As with the polystyrene 800 standard, the most likely reason for the low values obtained are a greater degree of fragmentation caused by higher substrate temperatures
Table 4-6: Comparison of the number average molecular weight, the weight average molecular weight and the polydispersivity values quoted by the manufacturers and calculated from L²TOFMS and FD data for the polystyrene 2500 standard.

<table>
<thead>
<tr>
<th>Technique/laser wavelength used</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Polydispersivity $M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPC</td>
<td>2300</td>
<td>2514</td>
<td>1.09</td>
</tr>
<tr>
<td>L²TOFMS 193 nm entrainment</td>
<td>2290</td>
<td>2529</td>
<td>1.10</td>
</tr>
<tr>
<td>FDMS</td>
<td>2300</td>
<td>2552</td>
<td>1.11</td>
</tr>
</tbody>
</table>

on using the non-entrainment mode of operation and a failure to efficiently ionise the high mass oligomers in the sample. It would be interesting to examine this sample using 193 nm photoionisation in both the sample entrainment and non-entrainment modes of operation.

### 4.5.3 Polystyrene 2500

Table 4-6 lists the average molecular weight values calculated from the FD and L²TOF mass spectra of the polystyrene 2500 standard. Calculation of the molecular weight averages from the FD data gives values of $M_n = 2300$ and $M_w = 2552$. These values are in excellent agreement with those obtained by the manufacturers, using size exclusion chromatography (SEC), $M_n = 2300$ and $M_w = 2514$. Clearly, for higher mass polymers, the FD technique presents no problems in determination of accurate molecular weight values.

Surprisingly, as in the polystyrene 800 case, calculating the average molecular weight values from the 193 nm photoionisation mass spectrum produces values which are in excellent agreement with the manufacturers. This is despite the relatively low signal-to-noise ratio and the ragged baseline in the spectrum. It would appear, that 193 nm photoionisation and the sample entrainment mode of operation is the wavelength and instrument mode of choice to use for the most accurate characterisation of polystyrene samples.
4.5.4 Factors Affecting the Molecular Weight Determination

It is clear from the data presented, that a great deal of information can be obtained on aromatic polymers using L²TOFMS. In every case, both an oligomer distribution and structurally significant fragments were observed in the spectra, enabling a complete characterisation of the polymer to be made. In addition, by judicious choice of the ionisation wavelength, a relatively accurate average molecular weight value can be obtained. However, it is clear that in the majority of cases, the molecular weight averages calculated from the L²TOFMS data, are lower than the values obtained by other techniques. For this reason, a number of factors must be considered that may affect the oligomer distribution observed, and hence, give inaccurate molecular weight averages. These are:

1. desorption efficiency of large molecules
2. ionisation efficiency of large molecules
3. mass/velocity slippage in molecular beam entrainment
4. detector response

These factors, and their implications will be discussed more fully in the following sections.

Desorption Efficiency of Large Molecules

In other laser mass spectrometric techniques, such as MALDI, or direct laser desorption, high mass ionic species have been detected for a variety of systems. In these techniques, the energy required to both evaporate and ionise the molecules is much greater than that required to just desorb intact neutrals. For this reason, it is expected that the desorption efficiency of intact, high mass neutral species, would not pose a significant problem to polymer analysis by L²TOFMS. Indeed, it has been shown that high mass polystyrene oligomers, up to m/z 3800, and
biomolecules with masses up to m/z 5729 [33] can be desorbed as intact neutrals. As yet, it is uncertain how high in mass, the L²TOFMS technique can detect. However, in the low mass regime, below ca. m/z 5000, the L²TOFMS technique is not expected to be limited by the desorption efficiency of intact neutrals.

**Ionisation Efficiency of Large Molecules**

As the size of the oligomers increases, the number of internal vibrational modes and degrees of freedom in the molecule rapidly increases, and the ionisation efficiency rapidly decreases. Schlag *et al.* [57,58] have discussed the factors which can impede the photoionisation of large molecules and consequently limit the size of molecule that can be photoionised. They proposed that the origin of this limitation is related to the number of vibrationally excited levels that are coupled to the ionising level. For a large molecule there are a very large number of non-ionic, super-excited states which are isoenergetic with the initially excited ionic state. They proposed that the loss of electronic energy (needed to eject the electron and form the ion) to vibrational degrees of freedom, as a result of coupling to these states, can interfere with ionisation.

These molecules, excited above their ionisation threshold, but having their energy in the wrong degrees of freedom for ejecting the electron may undergo other processes. Firstly, the molecules may autoionise, resulting in delayed ionisation. Secondly, the energy rich molecules may undergo bond dissociation which can compete with ionisation. Thirdly, the ejected electron may re-attach itself to a remote part of the molecule, thereby forming a zwitterion. Another factor cited was the possibility of unfavourable Franck-Condon factors. In order to counteract these effects, the use of picosecond lasers for ionisation has been employed. These short laser pulses are thought to reduce these energy randomisation effects and allow for larger oligomers to be ionised by MPI. Boesl [43], has also speculated that for similar reasons, photoionisation would be limited to molecules with masses below ca. m/z 2000. This has been disproven by Grotemeyer and Schlag [33] who have published the mass spectra of photoionised biomolecules with masses up to m/z 5729. Although experimentally difficult, we have shown that intact neutral
polystyrene oligomers up to m/z 3800 can be photoionised using non-resonant MPI.

Mass/Velocity Slippage in Molecular Beam Entrainment

One other possible factor which may affect the distribution of oligomers observed in the mass spectrum, is the mass slippage of large oligomers in the molecular beam. During entrainment of the desorbed neutral oligomers, it is possible that inefficient momentum transfer from the helium buffer gas occurs. Therefore the oligomers do not all arrive at the photoionisation source at the same time. Instead larger oligomers are delayed by several microseconds. It has been seen that early ionisation laser firing times, produce spectra with little or no high mass peaks, whilst late firing times, produce spectra containing mainly high mass peaks. It is obvious, therefore, that in order to obtain a representative mass spectrum of the sample, the photoionisation laser must be fired at some intermediate time, between the arrival of the maximum amount of low mass species and the higher mass species, in the photoionisation source region.

The use of the timescan function in the control and data acquisition software provides an effective means of monitoring this effect. Simply timescanning one low mass oligomer and one high mass oligomer provides a best time-of-arrival plot for each species. Setting the postionisation laser delay to an intermediate time between each of the maxima, is usually sufficient to provide a representative mass spectrum and also prevent the low or high mass oligomers dominating the mass spectrum.

Detector Response

As the mass of the ions increases the time-of-flight becomes longer and the ions travel more slowly due to their lower kinetic energies. As a consequence, the number of secondary electrons liberated upon ion impact with the MCP detector is reduced. The resulting signal is therefore smaller than would normally be expected. This phenomenon has the effect of skewing the oligomer distribution towards lower
masses, which results in lower calculated values of the molecular weight averages. Several methods of circumventing this phenomenon exist namely, use of higher extraction fields, different types of detector, or use of a post-acceleration stage before the detector. Alternatively, a computer program which models the oligomer distribution obtained and corrects it by accounting for the transmission and detection efficiencies of the apparatus could be used. We have rarely found this effect to pose a significant problem. However, whenever it has occurred, simply increasing the voltage on the MCP detector has been sufficient to counteract these effects.

Despite these factors which can affect the oligomer distribution observed in an L²TOF mass spectrum, it is clear from the data presented that aromatic polymer analysis has been successful. In this work, we have mainly found that the degree and type of fragmentation have a significant effect upon the mass spectra of polystyrenes. Furthermore, the fragmentation observed is wavelength dependent, therefore judicious choice of the photoionisation wavelength employed must be made, in order to obtain an accurate average molecular weight value. For the polystyrene standards examined, a series of oligomer peaks have been observed and any fragment species present, have assisted in providing a more complete characterisation of the polymer structure.
CHAPTER 4. L^2 TOFMS OF AROMATIC POLYMERS

4.6 L^2 TOFMS Analysis of Other Aromatic Polymers

The L^2 TOFMS results for the polystyrenes showed that contrary to previous work, oligomer distributions of aromatic polymers could be obtained. Encouraged by these results, two other aromatic polymers were studied, namely a fluorinated polystyrene sample and a polymethylphenyl siloxane. The following sections describe the results obtained.

4.6.1 Fluorinated Polystyrenes

A fluorinated polystyrene sample of nominal mass 576 was obtained from ICI Wilton Materials Research Centre. It was previously characterised by field desorption mass spectrometry (FDMS) [60].

The fluorinated polystyrene standard, with the structure shown in Figure 4-13, was examined by L^2 TOFMS, in the non-entrainment mode of operation using a Macor substrate. The mass spectrum obtained using 193 nm photoionisation is shown in Figure 4-14a. The base peak in the mass spectrum at m/z 367 corresponds in mass to loss of OH from the dimer. However, the dimer peak itself is not observed. In addition, an intense monomer peak at m/z 192 and a fragment peak at m/z 178 are observed. In contrast, EI data has shown that peaks are observed at m/z 193 and m/z 179 [59]. To higher mass, a series of peaks

\[
\text{[CH-CH}_2\text{]}_n
\]

\[
\text{F} \quad \text{F}
\]

\[
\text{OH}
\]

Figure 4-13: Structure of fluorinated polystyrene.
Figure 4-14: L₂TOF mass spectrum of fluorinated polystyrene sample using a) 193 nm photoionisation and b) 248 nm photoionisation. The non-entrainment mode of operation, and a Macor substrate was used. Insets: high mass regions of 193 and 248 nm photoionisation mass spectra showing oligomeric species up to m/z 1916 and m/z 2880 respectively. The peak labelled with an asterisk (*) is due to PAH contamination. The peak labelled with an n=10 at m/z 1916 and n=15 at m/z 2880 respectively.

Relative intensity / arb. units

mass / Da.

0.0 0.2 0.4 0.6 0.8 1.0

0 300 600 900 1200 1500 1800 2100 2400 2700 3000

386 * 372

(b) (a)
separated by 192 Da are observed with very low intensity. This is seen more clearly in the expansion of the high mass region shown in the inset. This mass separation corresponds to the monomer repeat unit mass. This oligomer series terminates at ca. m/z 1916 which corresponds in mass to n=10, although at this mass, the mass calibration of the spectrum may be slightly out. However, it is clear that oligomers are present in the sample up to around n=10. This data compares favourably with the FDMS spectrum which shows oligomers present up to n=9 at m/z 1792 [60, 61].

The mass spectrum shown in Figure 4-14b was obtained using 248 nm photoionisation. In addition to an intense monomer peak at m/z 192 and a smaller fragment peak at m/z 178, the spectrum also exhibits a dimer peak at m/z 386. The base peak in the mass spectrum is at m/z 372. As in the 193 nm photoionisation spectrum, to higher mass a series of peaks separated by 192 Da are present, although the relative intensity of the peaks is greater in this mass spectrum. In addition, the peaks are narrower and better defined. The intensity of this oligomer series drops off slowly to higher mass and a typical bell-shaped oligomer distribution is not observed. Oligomeric species are present up to n=15 at m/z 2880. FDMS data suggests that oligomeric species exist only up to n=9 at m/z 1728 [61], and that the distribution peaks at the trimer, m/z 576. However, the intensity of the higher oligomers diminishes in the same way as observed by L^2TOFMS.

The L^2TOFMS data has shown that oligomeric species of higher mass are present in the sample than was previously observed by FDMS. However, as in the case of polystyrene, careful choice of the photoionisation wavelength is necessary in order to observe the complete oligomer distribution with significant intensity.

4.6.2 Aromatic Siloxanes

The most commonly used high temperature silicone fluids are the phenyl containing siloxanes, which are characterised by their high stability. For example, polymethylphenyl siloxanes are stable for thousands of hours in a closed oxygen-free system at 230°C [63]. This high stability makes these compounds particularly
suitable as heating bath oils, lubricant base oils and dielectric coolants. Furthermore, the low surface tension of siloxane fluids permits them to spread easily over irregular surfaces. For this reason they are extensively used in hair products to promote easier application. Polymethylphenyl siloxanes also exhibit good radiation resistance by remaining serviceable up to 200 megarads exposure [63].

Polymethylphenyl siloxane (PMPS) of average molecular weight 2600 Da was obtained from Fluorochem Ltd. and studied by L$^2$TOFMS. The structure is shown in Figure 4-15. The sample was supplied as a low viscosity fluid, and was prepared by dropping a small amount (<10μl) on the Macor sample probe, and dried by dusting the probe with alumina (Type H). The excess alumina was removed prior to the sample being placed in the mass spectrometer.

Figure 4-16 shows the L$^2$TOF mass spectrum of PMPS 2600 obtained using 193 nm photoionisation and the non-entrainment mode of operation. To low mass, below 300 Da, several intense fragments peaks are present at m/z 73, 135, 197 and 209. The fragmentation scheme in Figure 4-17, shows the origin of a number of these peaks, which have been observed before in the mass spectra of high molecular weight PMPS's [63]. A large potassium peak at m/z 39 is also present in the spectrum. To higher mass, a series of very low intensity peaks, separated by m/z 136, the polymer repeat unit mass are observed. These correspond to intact oligomers and terminate above ca. m/z 700.

The mass spectrum in Figure 4-18 obtained following 248 nm photoionisation is markedly different. To low molecular weight, below 300 Da, a different series
Figure 4.16: L2TOF mass spectrum of the poly(methylphenyl) siloxane 26000 sample using 193 nm photolysis. The non-entrainment mode of operation and a Macor substrate were used.
Figure 4-17: Fragmentation scheme of polymethylphenyl siloxane showing the origin of a number of the more intense fragment peaks.

<table>
<thead>
<tr>
<th>Fragment mass</th>
<th>Possible structural assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>([\text{C}_6\text{H}_6]^+)</td>
</tr>
<tr>
<td>166</td>
<td>([\text{Phenyl}-\text{O}-\text{Si}-(\text{CH}_3)_3]^+)</td>
</tr>
<tr>
<td>254</td>
<td>([(\text{CH}_3)_3-\text{Si}-\text{O}-\text{Phenyl}-\text{O}-\text{Si}-(\text{CH}_3)_3]^+)</td>
</tr>
</tbody>
</table>

Table 4-7: Possible assignments of some of the more intense fragment peaks observed in the 248 nm photoionisation mass spectrum of polymethylphenyl siloxane 2600.

of fragments to those observed using 193 nm photoionisation are seen. Some of the more intense peaks are tabulated in Table 4-7. To higher mass, two separate series of peaks are present, with the peaks within each series being separated by \(m/z\) 136, the polymer repeat unit mass. The two series are tabulated in Table 4-8. Series A starts at \(m/z\) 408 and ends at \(m/z\) 952. This series corresponds to bare repeat unit clusters without any end groups. The most intense peak is at \(m/z\) 680 and corresponds to the pentamer in the series. This is possibly the most stable since the other peaks are of much lower intensity. A cyclic structure for this series has been proposed with less than 3 repeat units being unable to form a ring, whilst greater than 7 repeat units being unstable.
Figure 4-18: L2TOF mass spectrum of the poly(methylphenyl)siloxane 2600 sample using 248 nm photoionisation showing a) the low mass fragments and b) the high mass region. The non-entrainment mode of operation and a Macor substrate were used. The peaks labelled A and B correspond to the two series of peaks listed in Table 4.8. The peaks labelled with an asterisk (*) are due to PAH contamination.
<table>
<thead>
<tr>
<th>SERIES A</th>
<th>SERIES B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>Assignment</td>
</tr>
<tr>
<td>408</td>
<td>3 RU’s</td>
</tr>
<tr>
<td>544</td>
<td>4 RU’s</td>
</tr>
<tr>
<td>680</td>
<td>5 RU’s</td>
</tr>
<tr>
<td>816</td>
<td>6 RU’s</td>
</tr>
<tr>
<td>952</td>
<td>7 RU’s</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4–8:** Assignments of the peak series observed in the L²TOF mass spectrum of polymethylphenyl siloxane 2600 using 248 nm photoionisation. RU’s = repeat units, SG’s = both side groups.
The second set of peaks, series B, correspond to complete oligomer units with intact side groups. The series ranges from m/z 706, n=4, to m/z 1930, n=13, and again the peaks are separated by m/z 136. The small satellite peaks to the left of these oligomers may be due to fragmentation. No molecular weight averages were calculated for this polymer for a number of reasons. Firstly, the average molecular weight of the polymer is 2600 Da and only oligomers up to m/z 1931 are observed. Secondly, the oligomer series rises sharply then tails off to higher mass. MALDI MS data has shown that the oligomer series is a bell shaped distribution peaking at ca. 2500 Da [64]. Clearly the L$^2$TOFMS data does not show the complete oligomer distribution. However, the polymer structure can be easily characterised from the oligomer and fragment species observed.

4.7 Concluding Remarks

The use of L$^2$TOFMS for the mass analysis of a variety of aromatic polymers has been shown to be of considerable analytical utility. The technique has allowed a range of aromatic polymers of different type, average molecular weight, functionality and polarity to be studied successfully. The data presented have unequivocally shown that high mass polystyrene oligomers, up to m/z 3800, can be desorbed as intact neutral species and successfully photoionised. This result contradicts Lustig and Lubman's earlier work [20,21], and has significantly improved upon the range of oligomers observed by other groups, using similar techniques.

For the polystyrenes studied, each photoionisation wavelength used produced an oligomer distribution of singly charged molecular ions. On photoionising with 193 nm laser radiation the mass spectra obtained show significant and intense EI-type fragments. However, this observation does not significantly affect the oligomer distribution. Indeed, the molecular weight averages calculated from the 193 nm photoionisation mass spectra of the polystyrenes are in good agreement with the values quoted by the manufacturers.
CHAPTER 4. L²TOFMS OF AROMATIC POLYMERS

Changing the ionising laser wavelength to 248 nm or 266 nm results in a dramatic change in the mass spectra. Principally, the relative intensity of the fragments is significantly reduced and the intensity of the oligomer series dominates. Oligomers in the low mass range, from \( n = 1 \) to around \( n = 5 \), have significantly higher than expected intensities at these ionisation wavelengths. One of the possible explanations for this discrepancy is fragmentation to lower oligomers by the 248 nm or 266 nm radiation, although it is not observed at 193 nm. The resultant molecular weight averages calculated for these spectra are lower than the manufacturers data since the distributions are skewed to lower mass. For every ionisation wavelength used, however, a complete structural characterisation of the sample could be achieved on examination of the fragment species obtained.

Data obtained using the non-entrainment mode of operation has assisted in determining that the fragments species observed in the mass spectra were attributable to both the desorption process and the photoionisation wavelength. Generally, a larger degree of fragmentation was observed in the polystyrene mass spectra obtained by this method. Further work in this field is necessary to completely elucidate these mechanisms.

The fluorinated polystyrene data obtained by L²TOFMS is in slight conflict with the data obtained by FDMS, in that a series of oligomers up to \( n=15 \) is present in the L²TOFMS spectrum, whilst oligomers up to only \( n=9 \) are observed in the FDMS data. Again, careful selection of the photoionisation laser wavelength is required in order to obtain a representative mass spectrum for the sample. In contrast to the pure polystyrene samples, 248 nm photoionisation proved to be more effective than 193 nm photoionisation in obtaining an oligomer distribution for the fluorinated polystyrene sample.

The analysis of polymethylphenyl siloxane is similar to that of the fluorinated polystyrene, in that 248 nm proved to be the best ionising wavelength for analysis. Two principal series of peaks appear in the mass spectra each with their peaks separated by \( m/z \ 136 \), the repeat unit mass. In addition, a series of fragment peaks that are commonly observed in siloxane polymer mass spectra are present in the L²TOFMS data obtained using 193 nm photoionisation. Using the data
from both photoionisation wavelengths, the structure of the polymer could be elucidated, although no molecular weight average information could be obtained.

It is acknowledged that, at present, the analysis of aromatic polymers by L$_2$TOFMS is difficult experimentally. It is also uncertain during data collection, that the spectrum is a faithful representation of the oligomer distribution of the polymer. In general, however, the fragment species present in the L$_2$TOF mass spectra can be utilised for structural, and end group characterisation, and the oligomers present can be used to determine the repeat unit of the polymer. These data are as important to the polymer scientist as molecular weight information and, therefore, the L$_2$TOFMS technique may prove useful for the rapid analysis of polymer formulations.

Future studies of polymers using L$_2$TOFMS will require an improvement in the mass range of the instrument, in order to obtain complete oligomer distributions of low mass polymers. At present, the largest oligomer species observed using the Edinburgh instrument have a mass ca. 3800 Da. Using a similar sample entrainment instrument, Anex et al. [36] have observed oligomers up to ca. 7000 Da, for a perfluorinated polyether polymer. The photoionisation of high mass species was previously thought to be a severe limitation of the L$_2$TOFMS technique, however, clearly intact neutral oligomer species can be ionised in this manner. The use of a resonant photoionisation wavelength, for the analysis of polystyrenes, may prove to be advantageous for ionising the larger oligomers. An important advance would be to perform tandem TOF experiments to determine the pathways for the complex fragmentation processes. UV laser ionisation somewhat restricts the analysis to aromatic polymers of relatively low molecular weight. Employing a laser generated VUV photoionisation source, currently under development (see Chapter 7) will enable aliphatic polymer systems to be studied. It may also enhance the data already obtained by providing a further ionising wavelength for the analysis of these aromatic systems.
Bibliography


Chapter 5

L²TOFMS of Polymer Additives

5.1 Introduction

The commercial formulation of rubbers and plastics include many ingredients. In addition to various polymers they also contain a number of compounding ingredients or additives, which are added to give specific chemical or physical properties. Typical additive types include plasticisers, extender oils, carbon black, organic and inorganic fillers, antifatigue agents, heat and light stabilisers, antioxidants, anti-ozonants, tactifying resins, crosslinking agents, accelerators, retarders, adhesives, pigments and smoke and flame retardents.

The direct analysis of additives in polymers is often difficult due to a number of factors:

1. The wide variety of additive type. Thousands of additives are commercially available with widely differing molecular weights and properties.

2. Many additives are thermally labile and therefore are difficult to analyse. Some are specifically designed to decompose during processing.

3. Generally many additives are found in even the simplest commercial polymer formulations.
4. Additive concentrations are usually present at less than percent level concentrations in the polymer matrix.

These factors usually necessitate an extraction procedure, to remove the additive from the polymer matrix, before analysis. This is often followed by a chromatographic separation step. However, even after extraction, gas chromatographic separation is often difficult due to the reactive nature and high molecular weight of many additives. Thin layer chromatography (TLC) [1] and high performance liquid chromatography (HPLC) [1,2,3,4] have also been used, but both are limited in resolution and the difficulty in identifying unknown components.

In order to successfully analyse polymer formulations it is necessary not only to be able to distinguish the number of mixture components but also to provide characteristic structural information about each additive. Lattimer [5] recently described how mass spectrometry could be used as an alternative to traditional methods, for the analysis of polymer additives.

Mass spectrometric analysis of polymer additive extracts has previously been carried out using fast atom bombardment (FAB) [6,7], field desorption (FD) [8], laser desorption (LD) [6,9], and chemical ionisation (CI) [8]. Liquid chromatography in tandem with mass spectrometry (LCMS) has been used to identify antioxidant and UV stabilisers in plastics [10].

Due to the difficult and time consuming nature of the extraction procedures, direct determination of additives from polymer samples by mass spectrometry has also been investigated. Early work involved thermal desorption of additives directly from polymers, using electron impact (EI) ionisation of the volatiles [11, 12]. This method, however, is limited to additives that are volatile. Many additives are large, involatile species and therefore more elaborate desorption and ionisation methods are generally required. Some of the methods used include CI [13], time-of-flight secondary ion mass spectrometry (TOF SIMS) [14,15], FAB [8], LD [6] and multiple ion detection mass spectrometry (MID) [16].

Mass spectrometry has also been used to analyse raw polymer additive samples. For example, direct laser desorption of ions coupled to Fourier transform ion
cyclotron resonance mass spectrometry (LD FTICR MS) has been used to study a series of antioxidant and UV stabilisers [9] and others [6].

Until now, the laser desorption experiments performed on additives have generally involved single-step desorption/ionisation, which often leads to complicated fragmentation patterns and quasi-molecular ions. Asamoto et al. [9] described how LD FTICR MS of polymer additives showed intense quasi-molecular ions containing either Na\(^+\) or K\(^+\) adducts and fragments which were structurally informative. One group however, have examined phosphite polymer stabilisers using Nd:YAG laser desorption of neutral species followed by electron impact (EI) ionisation [17].

In the following sections, the results of exploratory studies into the use of \(L_2\)TOFMS for the analysis of both pure polymer additives and the \textit{in-situ} detection of additives are described. The aim of this work was to evaluate the use of the technique for the direct analysis of polymer formulations without the need for any lengthy pre-separation steps. In previous work from this laboratory [18], it has been shown that \(L_2\)TOFMS is a useful technique for the analysis of polynaphatic hydrocarbons (PAH's) directly from environmental matrices. These PAH's were detected at concentrations around the ppm level. Therefore it was expected that polymer additives could be similarly characterised. The \(L_2\)TOFMS technique may provide a novel approach to screening of polymer samples for additives. In addition, the technique may circumvent many of the problems associated with more conventional analytical techniques, thereby detecting semi-volatile, involatile and/or thermally labile species without the need for extraction or separation procedures.

Two classes of polymer additive were studied, namely UV stabilisers and phenolic antioxidants, using two fixed laser photoionisation wavelengths, 193 nm and 248 nm. As discussed below, the mass spectra obtained show significant differences depending on the ionisation wavelength employed. All the mass spectra presented were obtained using the non-entrained laser desorption mode. This mode of operation was used primarily to improve the detection sensitivities. The additives studied in this work were analysed as supplied from ICI Wilton, without any further preseparation or purification.
For each sample, approximately 0.1 g of material was dissolved in ca. 2 ml of acetone and approximately 0.2 ml of this solution was deposited onto a Macor probe. The area of the probe covered by the solution was ca. 2 cm$^2$. The CO$_2$ laser spot size was 0.27 mm$^2$. In general, for most samples analysed using L$^2$TOFMS, several tens of laser shots are accumulated to acquire a mass spectrum with reasonable signal-to-noise ratio. However, for these additives, typically only 10 laser shots were required for each mass spectrum. The sample was kept stationary throughout the data collection cycle. Generally, complete sample removal from the substrate was observed after 10 laser shots. Each ten shot mass spectrum typically corresponds to ca. 50 nanomoles of material.

The ionising laser power density was usually maintained at a relatively low level in order to maximise the intensity of the molecular (or in some cases pseudo-molecular) ion. Typical laser power densities of ca. $7 \times 10^4$ Wcm$^{-2}$ were used for the studies at 193 nm, and ca. $3 \times 10^4$ Wcm$^{-2}$ for those at 248 nm.

5.2 UV Stabilisers

One of the most common types of polymer additive are UV stabilisers, the function of which is to protect the polymer from the harmful effects of near UV radiation. One class of these UV stabilisers is the Tinuvin series. Three compounds of this class were studied, namely Tinuvin 326, Tinuvin 327 and Tinuvin P. Their structures, molecular weights and IUPAC compound names are shown in Figure 5-1.

Tinuvin 326

Figure 5-2 shows the L$^2$TOF mass spectra obtained for Tinuvin 326 using 248 nm and 193 nm photoionisation. Using photoionisation at 248 nm, Figure 5-2a, a reasonably intense molecular ion peak is seen at m/z 315, with the $^{37}$Cl isotope peak at m/z 317. The smaller fragment peaks at m/z 300 and m/z 302 correspond to loss of CH$_3$ from the molecular ion, whilst the relatively intense fragment peak
Figure 5-1: Structures, molecular weights and the trade and IUPAC compound names for the three Tinuvin UV stabilisers examined using L²TOFMS.
Figure 5-2: LTOF mass spectra of Tinuvin 326 polymer additive using photoionization at (a) 248 nm and (b) 193 nm. Macor substrate.
<table>
<thead>
<tr>
<th>Compound or Element</th>
<th>Percentage Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>46</td>
</tr>
<tr>
<td>MgO</td>
<td>17</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16</td>
</tr>
<tr>
<td>K₂O</td>
<td>10</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>7</td>
</tr>
<tr>
<td>F</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5-1: Composition of the Macor substrate.

at m/z 258 corresponds to [M-C₄H₉]⁺. A small potassium adduct peak of the molecular ion can also be seen at m/z 354. The base peak in the mass spectrum is at m/z 39 and corresponds to potassium liberated from the Macor substrate.

In comparison, the 193nm photoionisation mass spectrum of Tinuvin 326, Figure 5-2b, is markedly different. No molecular ion peak or fragments are observed, however, the peak at m/z 354 corresponds to the potassium adduct of the molecular ion. Again, the base peak in the spectrum is due to potassium from the Macor substrate. Clearly, cation attachment to Tinuvin 326, is more favourable than direct ionisation to form the molecular ion using 193 nm photoionisation. Asamoto et al. [9], using single-stage LDMS, previously noted that hydrogen cations attached more readily to Tinuvin UV stabilisers than alkali cations. However in most cases, the cationised molecular ions formed by alkali metal attachment, were still observed with significant intensity.

Potassium is present at a relatively high concentration, in the form of K₂O, in the Macor substrate, see Table 5-1, and commonly appears in most mass spectra recorded using this substrate. It was never intentionally added to the sample. Potassium is generally observed even with the lowest photoionisation laser fluences since the IP of this element is quite low, at 4.34 eV. Photons at 248 nm and 193 nm have energies of 5.0 eV and 6.4 eV, respectively, and therefore potassium can be ionised in a one-photon process at both wavelengths. In addition to potassium, a small peak centered near m/z 44 is seen in the 193 nm photoionisation mass
spectrum of Tinuvin 326. This wide and unresolved peak can be attributed to a number of fragment species desorbed from the Macor substrate, most notably $BO_2$ at $m/z$ 43, $AlO$ at $m/z$ 43 and $SiO$ at $m/z$ 44.

Another notable feature of the 193 nm photoionisation mass spectrum of Tinuvin 326, is the width of the peaks. Since the sampling interval of the digitiser was set at 40 ns per bin, then the resolution of the instrument was degraded, and the chlorine isotopes of the cationised molecular ion peak are unresolved.

Tinuvin 327

Tinuvin 327 behaves in a similar fashion to Tinuvin 326. The structures of these two compounds are very similar, the only difference being the replacement of the methyl group on the phenyl ring in Tinuvin 326 with a tertiary butyl group. Figure 5-3 shows a high resolution mass spectrum of Tinuvin 327 using photoionisation at 248nm, in the neighbourhood of the molecular ion. The molecular ion is the base peak in the spectrum at $m/z$ 357 with the $^{37}Cl$ isotope at $m/z$ 359. An intense potassium peak is also present, although it is not shown, which has an intensity of approximately 90 % of the molecular ion. The molecular ion peak intensities are in good agreement with the values calculated from the natural isotopic abundances. The small peak seen at $m/z$ 380, corresponds to the sodium adduct of the molecular ion. The fragment peak at $m/z$ 342 corresponds to $[M-C_3H_7]^+$, surprisingly however, no $[M-C_4H_9]^+$ fragment is seen. The peak at $m/z$ 352 is due to contamination from diffusion pump oil, a commonly observed contaminant in L$^2$TOF mass spectra using the non-entrainment methodology.

On ionising with 193 nm laser radiation a similar mass spectrum to that seen for Tinuvin 326 is observed, in that no molecular ion peak or fragments are observed. Instead, an intense quasi-molecular ion corresponding to the potassium adduct is seen at $m/z$ 396. Again, the base peak in the spectrum is potassium, however a sodium peak of low intensity, ca. 3 % of the base peak, is also present. The sodium is likely to be a surface contaminant on the substrate, since it is not a constituent of Macor. The observation of sodium, as a contaminant, may account
Figure 5-3: L$_2$TOF mass spectrum of Tinuvin 327 using photoionisation at 248nm. Macor substrate. Peaks labelled with an asterisk (*) are due to diffusion pump oil contamination.
for the small sodium adduct peak observed in the 248 nm photoionisation mass spectrum.

**Tinuvin P**

A soft ionisation mass spectrum of Tinuvin P using photoionisation at 248 nm is shown in Figure 5–4a. It exhibits an intense molecular ion peak at m/z 225 with little fragmentation. A small potassium adduct peak is also seen at m/z 264. By simply increasing the ionising laser fluence from 0.03 MW cm\(^{-2}\) to 0.12 MW cm\(^{-2}\), fragmentation can be induced in Tinuvin P to yield a series of structurally significant fragments. This partially hard ionisation mass spectrum is shown in Figure 5–4b. It provides another example of the unique properties of laser MPI as an ionisation mechanism. The fragmentation pathway most likely proceeds via \(N_2\) elimination from the molecular ion to form the m/z 197 species, followed by further fragmentation. Two alternative possible fragmentation schemes for this initial step are shown in Figure 5–5. However, it would be difficult to distinguish between these two schemes even using MS/MS. The first common step, elimination of \(N_2\) has previously been observed in L\(^2\)TOF mass spectra of azodyes [19,20].

Table 5–2 lists the fragments observed in the soft and partially hard ionisation mass spectra of Tinuvin P. In both the soft and partially hard ionisation mass spectra, the base peak corresponds to the molecular ion. In both spectra, small peaks due to diffusion pump oil contamination are seen at m/z 254 and m/z 260.

The L\(^2\)TOF mass spectrum of Tinuvin P obtained using photoionisation at 193 nm is shown in Figure 5–6. As in the case of Tinuvin 326, an intense peak due to the potassium adduct is seen at m/z 264. The base peak in the spectrum is again due to potassium. However, in this case, a small molecular ion peak at m/z 225 is also observed.

For all three of these UV stabilisers, a reasonably intense molecular ion peak is observed when photoionising at 248 nm. Also, in all cases, an alkali adduct peak, together with some fragmentation of the molecular ion is seen. In contrast, the spectra obtained using photoionisation at 193 nm usually only exhibit adduct
Figure 5-4: a) Soft and b) partially hard ionisation L2-TOF mass spectra of Tinuvin P using photoionisation at 248nm. Macor substrate. Peaks labelled with an asterisk (*) are due to diffusion pump oil contamination.
Figure 5-5: Possible fragmentation schemes for Tinuvin P.

Table 5-2: L²TOF mass spectral peaks of Tinuvin P using photoionisation at 248 nm. The relative intensities are in parenthesis.
Figure 5-6: L²TOF mass spectrum of Tinwin P using photolysis at 193nm.

- **Relative intensity / arb. units**
- Mass / Da.

- **K⁺** at mass 264
- **M⁺** at mass 225
- **[M+K]⁺** at mass 264

Macor substrate.
peaks, with little or no evidence of the molecular ion or, indeed fragments of significant intensity.

5.3 Phenolic Antioxidants

Antioxidants are an important class of additive often added to polymer formulations. Their function is to prevent deterioration due to oxidative degradation of polymer bonds. The Irganox class of phenolic antioxidants are amongst some of the most commonly used additives. Two compounds of this class, together with one sulphonated phenolic antioxidant were studied; their structure, molecular weights as well as trade and IUPAC compound names are shown in Figure 5–7.

Irganox 1076

Figure 5–8a shows the $L^2$TOF mass spectrum of Irganox 1076 obtained using photoionisation at 248 nm. A relatively intense peak due to the molecular ion can be seen at $m/z$ 530 together with a fragment corresponding to $[M-CH_3]^+$, at $m/z$ 515. The prominent peaks at $m/z$ 408, 352, 260 and 254 are due to diffusion pump oil contamination and are labelled with an asterisk (*). The base peak in the spectrum corresponds to potassium, which is desorbed from the Macor substrate.

The mass spectrum for Irganox 1076 obtained using photoionisation at 193 nm, is shown in Figure 5–8b. The base peak corresponds to the potassium adduct of the molecular ion, at $m/z$ 569. Apart from the strong signals at $m/z$ 39 and 44 from substrate constituents, no other significant peaks are present in the spectrum.

Irganox 1098

The structure of Irganox 1098 is different from that of Irganox 1076 in that the molecule has two phenolic end groups. The mass spectrum obtained for this compound using photoionisation at 248 nm is shown in Figure 5–9a. The spectrum
Figure 5-7: Structures, molecular weights and trade and IUPAC compound names for the phenolic antioxidant additives examined by L²TOFMS.
Figure 5-8: L 2 TOF mass spectra of Irganox 1076 obtained using photoionisation at (a) 248 nm and (b) 193 nm. Macor substrate. Peaks labelled with an asterisk (*) are due to diffusion pump oil contamination.
differs from that of Irganox 1076 in that the potassium adduct of the molecular ion, at m/z 675, is the more intense than the molecular ion itself, at m/z 636. Again, the base peak in the spectrum corresponds to potassium at m/z 39.

In comparison, the mass spectrum obtained using photoionisation at 193 nm, shown in Figure 5-9b, exhibits two adduct peaks. The molecular ion peak, at m/z 636, is relatively intense, unlike the molecular ion peak in the 193 nm photoionisation mass spectrum of Irganox 1076, which was absent. Also, the peak corresponding to \([\text{M+K}]^+\), at m/z 675, is not the base peak, although it is quite intense. The additional peak at m/z 714, corresponds to \([\text{M+2K} ]^+\). This is one of only a few examples where double adduct peaks have been observed in an \(L^2\)TOF mass spectrum.

**Bis-S**

The third phenolic antioxidant additive studied was Bis-S, a sulphonated biphenol compound. Figure 5-10 shows the \(L^2\)TOF mass spectrum of Bis-S obtained using photoionisation at 248 nm under partially hard ionisation conditions. The base peak is at m/z 250 and corresponds to the molecular ion. In addition, a series of lower molecular weight fragments are also observed. These fragments, at m/z 141, 110 and 94 correspond to \([C_6H_5O_2S]^+\), \([C_6H_6S]^+\) and \([C_6H_6O]^+\) respectively. A relatively small potassium signal is also seen. On decreasing the ionisation laser power density, only the molecular ion peak is observed in the mass spectrum.

In comparison, using photoionisation at 193 nm, the mass spectrum of Bis-S shows no evidence for potassium adduct peaks, as observed for the Irganox phenolic antioxidants and Tinuvin UV stabilisers. Instead, a strong molecular ion peak, is observed in the mass spectrum.
Relative intensity / arb. units

Figure 5-9: L2 TOF mass spectra of Irganox 1098 obtained using photoionisation at (a) 248 nm and (b) 193 nm. Macor substrate.
Figure 5-10: LiTOF mass spectrum of Bis-S obtained using photoionisation at 248 nm. Macor substrate.

Relative intensity / arb. units

mass / Da.

M+ 250

[CH$_5$SO$_2$]$^+$ 141
[CH$_6$]$^+$ 110
[CH$_6$O]$^+$ 94
K$^+$ 65

$^{11}$AATIVIOU
5.4 *In-situ* Detection of Polymer Additives

The primary aim of the work in the previous sections, was to demonstrate that \( \text{L}^2 \text{TOFMS} \) mass spectra of low concentrations of polymer additives could be easily obtained. In each case, intense molecular and/or quasi-molecular ions were detected, depending upon the laser photoionisation wavelength employed. In addition, low detection limits, ca. 50 nanomoles, were recorded for all the additives studied. This initial work was carried out as a prelude to direct, *in-situ* analysis of additives from polymer formulations.

The *in-situ* analysis of additives is of major interest, not least since preseparation of additives from polymers prior to analysis is very labour intensive and time consuming. Another important question that *in-situ* analysis may address is the spatial distribution of additives within the polymer, and throughout the lifetime of the polymer. For example, some additives may migrate, forming regions of higher concentration within the material, or diffuse to the surface during formulation or moulding of the polymer. Since such migration or diffusion processes can significantly influence the properties of the polymer, then selective analytical methods are needed to follow such changes. \( \text{L}^2 \text{TOFMS} \), with its high degree of selectivity and spatial resolution available in the desorption step, may be a useful technique for examination of such systems.

Three polyoxymethylene polymer samples were obtained from DuPont. One sample was pure polymer and the others contained between 0.1 and 1 % of either a Tinuvin UV stabiliser or phenolic antioxidant additive. The Tinuvin additive used was Tinuvin 320 and the phenolic antioxidant additive was known as santo white powder. The structures of these compound are shown in Figure 5-11. Initially, a spectrum of each pure additive was recorded. As before, approximately 0.1 g of each additive was dissolved in 2 ml of acetone, and approximately 0.2 ml of this solution was deposited onto a Macor probe, completely covering an area of about 2 cm\(^2\).
CHAPTER 5. L²TOFMS OF POLYMER ADDITIVES

Figure 5-11: Structures and molecular weights of the Tinuvin 320 UV stabiliser and the santo white powder phenolic antioxidant additives added to the polyoxymethylene polymer.

Figure 5-12a shows a 10 shot, L²TOF mass spectrum of a pure sample of Tinuvin 320, recorded using photoionisation at 248 nm. A relatively intense molecular ion peak at m/z 323 is seen, together with a smaller fragment peak at m/z 308, corresponding to [M-CH₃]⁺. The peak at m/z 362 corresponds to the potassium adduct of the molecular ion, [M+K]⁺. This behaviour is identical to that observed for the other Tinuvin UV stabilisers examined. In addition to these peaks, the spectrum also contains a series of peaks between m/z 150 and m/z 280, which are due to PAH contamination. The base peak in the spectrum is the PAH, carbazole at m/z 167.

Figure 5-12b shows the mass spectrum obtained, using photoionisation at 248 nm, for the polyoxymethylene polymer sample containing between 0.1 and 1 % Tinuvin 320. The moulded polymer bar was simply cut to a manageable size and attached to the Macor sample probe with double-sided tape. High desorption laser intensities produced neatly drilled holes in the polymer bar. Consequently, the CO₂ laser intensity was attenuated such that no surface pitting was seen. As in the case of the pure Tinuvin sample, the mass spectrum is dominated by PAH contaminant peaks. However, the small peak at m/z 323 indicates the presence of Tinuvin 320 in the polymer bar. The characteristic [M-CH₃]⁺ fragment peak at m/z 308 is also seen in the spectrum. The peaks labelled 'background' in Figure
Figure 5-12: L2 TOF mass spectra of a) pure Tinuvin 320 from a Macor substrate and b) polyoxymethylene polymer containing 0.1% Tinuvin 320 additive. Both spectra were obtained using photoionisation at 248 nm. Peaks labelled with an asterisk (*) are due to diffusion pump oil contamination.
5–12b, are also seen in the mass spectrum of the pure polyoxymethylene sample, which shows no evidence for any peaks due to Tinuvin 320.

Figure 5–13a shows the L^2 TOF mass spectrum of a pure sample of the santo white powder antioxidant additive, recorded at 266 nm, the fourth harmonic output from a Nd:YAG laser. An intense molecular ion peak is present at m/z 382, along with two fragment peaks at m/z 339 and 345. The small peak at m/z 65 is a Macor contaminant.

The L^2 TOF mass spectrum of the pure polyoxymethylene (POM) polymer sample is shown in Figure 5–13b. No peaks are seen which can be attributed to a polymer distribution. This is an unsurprising result, since the polymer is aliphatic and contains no UV chromophore. The base peak in the spectrum at m/z 167 is due to carbazole, a PAH used for mass calibration. The small peaks between m/z 180 and 300 are due to other PAH background contaminants.

The mass spectrum of the POM polymer sample containing between 0.1 and 1 % of the santo white powder antioxidant additive is shown in Figure 5–13c. The base peak in the spectrum again corresponds to carbazole, at m/z 167. The peaks at m/z 339, 345 and 382 clearly indicate the presence of santo white powder in the polymer formulation. Clearly, under these conditions, the santo white powder antioxidant additive can be easily observed in-situ from a commercial polymer formulation.

It is clear from the data obtained that both the Tinuvin 320 and santo white powder polymer additives can be easily detected, at the 0.1 - 1 % level, from a polyoxymethylene polymer. It would be interesting to further examine both the raw additive and the polymer formulation using a resonant ionisation process in which the laser wavelength is tuned to match absorption features in the UV/visible spectrum of the additive. This should significantly increase the signal intensity from the additive, relative to the contaminated background. Clearly, these early non-optimised results suggest that this technique could be routinely used as a rapid sample screening technique.
CHAPTER 5. L2 TOFMS OF POLYMER ADDITIVES

Figure 5-13: L2 TOF mass spectra of a) pure santo white powder b) pure polyoxymethylene (POM) polymer and c) POM polymer containing between 0.1 and 1% santo white powder antioxidant additive. All the spectra were obtained using photoionisation at 266 nm. Peaks labelled with an asterisk (*) are due to diffusion pump oil contamination. Peaks labelled with an asterisk (*) are due to diffusion pump oil contamination. All the spectra were obtained using photoionisation at 266 nm. Peaks labelled with an asterisk (*) are due to diffusion pump oil contamination.
5.5 Concluding Remarks

From the data presented earlier, there are clear and distinct differences in the mass spectra obtained for the pure polymer additives when photoionisation at 248 nm and 193 nm is employed.

For all the Tinuvin UV stabilisers studied, a reasonably intense molecular ion peak is observed, when photoionising at 248 nm. A much weaker alkali adduct peak is also seen together with some fragmentation of the molecular ion. In contrast, the spectra obtained using photoionisation at 193 nm, usually only exhibit intense alkali adduct peaks, with little or no evidence of the molecular ion or, indeed fragments of significant intensity.

For the Irganox additives, photoionisation at 248 nm generally produced relatively intense molecular ion peaks. Only for Irganox 1098 was an alkali adduct peak also observed. Photoionisation at 193 nm, resulted in relatively intense alkali adduct peaks, with little or no evidence for the molecular ion. Again Irganox 1098 was anomalous, in that a double alkali adduct peak was also observed. In the spectrum of the Bis-S phenolic antioxidant, the molecular ion was found to be the base peak using either 248 nm or 193 nm photoionisation. No potassium adduct peaks were observed at either photoionisation wavelength.

This marked difference in behaviour at the two laser wavelengths employed, suggests that the dominant ionisation mechanism using 193 nm photoionisation is alkali cation attachment. At 248 nm, direct photoionisation is a more effective competing process. Clearly it would be of interest to examine the wavelength dependent photoionisation channels for these compounds using other substrates, such as stainless steel, where desorption would result in a much lower concentration of alkali atoms.

In these preliminary studies, relatively intense molecular or quasi-molecular ion peaks were observed for each 10 laser shot mass spectrum. These spectra correspond to the detection of approximately 50 nanomoles of material. However,
since the signal to noise ratio is relatively high for the molecular or quasi-molecular ion peaks, then a ten-fold reduction in the amount of additive present would still produce reasonably intense mass spectra. Therefore, the detection limit for these additives may be as low as 5 nanomoles or less, indicating that the L^2 TOFMS technique is capable of additive detection at the levels commonly found in polymer formulations. Further work is necessary in order to determine the true detection limit for each species, most likely by using the method of standard additions.

The *in-situ* detection of polymer additives from commercial polymer formulations is an important problem, which mass spectrometry so far, has had relatively little success in solving. The detection of one Tinuvin UV stabiliser and one phenolic antioxidant additive at the 0.1 - 1 % level in a polyoxymethylene polymer by L^2 TOFMS, is one small step on the route to using the technique as a rapid sample screening method. Further work is required to improve the detection limits for these additives, most likely by employing resonant laser photoionisation. This resonant photoionisation technique may also have the further advantage of rejecting all the background signal arising from the polymer, thereby producing relatively simple spectra, showing predominantly polymer additive molecular ion peaks.
Bibliography


Chapter 6

L^2TOFMS of Indole Monomers and Polymers

6.1 Indole Monomers

6.1.1 Introduction

The development of indole chemistry began in the mid-nineteenth century with extensive research into the dye indigo. From then until the beginning of the twentieth century, indole continued to be used in the dyestuff industry until it was superseded by newer dyes. During the 1930's, research on indole chemistry was significantly increased following recognition that the essential amino acid tryptophan had a structure based upon the indole nucleus. This research led to the development of many new and important methods of indole synthesis. The basic indole structure and numbering system used is shown in Figure 6-1.

Mass spectral analysis of indole and indole derivatives has previously been carried out. Primarily, electron impact has been the preferred ionisation method.

![Figure 6-1: Structure and IUPAC numbering system used for the indole nucleus.](image-url)
Some of the first work was carried out by Beynon and Williams [1,2], who obtained the EI mass spectra of 11 alkyl indoles. They concluded that for the compounds studied, the intense molecular ion peaks present in the spectra were indicative of a conjugated ring structure, and furthermore, in each mass spectrum an intense m/z 103 rearrangement peak was observed. In addition, many of the most prominent fragment peaks corresponded to ions retaining the nitrogen atom. Indoles substituted with alkyl groups at the 2 and/or 3 positions readily undergo simple \( \beta \) cleavage and this resulted in a fragment peak at m/z 130 being observed. Beynon et al. [3] have postulated that this fragment ion rearranges to a more stable quinoline structure, shown in Figure 6-2, before further fragmentation occurs by the loss of HCN to form the C\(_8\)H\(_7\)+ fragment at m/z 103.

Subsequently, Powers [4] obtained the EI mass spectra of a series of substituted indoles. In addition to studies of the 1 - 7 methyl substituted indoles, Powers also studied several indole aldehydes, ketones and carboxylic acids. From examination of the fragmentation patterns observed in the spectra, Powers concluded that the indole substituent preferentially directed the fragmentation and he suggested a scheme for predicting which substituent was present.

More recently, several groups have used L\(^2\)TOFMS and other laser spectroscopic techniques for the analysis of indole derivatives. Behrson et al. [5] recorded the laser induced fluorescence (LIF) spectra of indole, 3-methyl indole (skatole) and indole-3-acetic acid in a supersonic expansion and found the origin transitions (\( S_1 \leftarrow S_0 \)) to be at 283.82, 286.64 and 293.74 nm respectively. Later, Levy et al. [6] studied the REMPI spectrum of tryptophan in a jet expansion with detection by time-of-flight mass spectrometry and recorded the origin band at 286.75 nm.
Levy *et al.* also discovered that the shift in the indole origin band depended upon the particular substituent group and its electron-donating or electron-withdrawing abilities. Generally, the further away a group is from the indole center, then the smaller the expected effect on the shift of the origin transition. In general, the broad absorption contour observed in the UV spectra of the indole derivatives are similar and are thought to be due to $\pi - \pi^*$ transitions which are expected to span the region 280 - 295 nm. The spectra reported by Levy *et al.* [6] were subsequently obtained at higher resolution over a slightly wider wavelength range by Costello *et al.* [7] in Edinburgh, using laser desorption instead of thermal desorption prior to molecular beam entrainment.

Tembreull and Lubman [8,9] have studied a series of indole derivatives and other clinically important molecules and recorded their mass spectra by ionising with a dye laser tuned to a wavelength near the origin band transition. They employed CO$_2$ laser desorption instead of thermal desorption and obtained the soft ionisation mass spectra which revealed intense molecular ion peaks with little fragmentation. In the case of tryptophan, simple $\beta$ cleavage of the side chain was found to be facile and was difficult to prevent even at low ionising laser fluences.

Gormally *et al.* [10] have more recently reported L$^2$TOF mass spectra for some indole derivatives and alkaloids. They studied indole-3-butyric acid, tryptamine and tetrahydrocarbazole using ionising laser wavelengths near 280 nm, i.e. close to the $S_1 \leftarrow S_0$ origin transition. The samples were desorbed from a glass substrate using a CO$_2$ laser and entrained in a pulsed molecular beam. The photoionisation mass spectra of two larger indole alkaloids, yohimbine and reserpine were also recorded at 280 nm. In each case, under soft ionisation conditions molecular ions were observed as the base peak the spectrum.

In a further publication, Gormally *et al.* [11] cited an anomaly in the L$^2$TOF mass spectrum of indole-3-acrylic acid recorded at an ionising laser wavelength of 280 nm. The molecular ion for this molecule should occur at m/z 187 but was never found to be the base peak. However, two intense peaks at m/z 271 and m/z 286 were observed. These peaks of anomalously high intensity were attributed to an association reaction between molecules of 3-vinyl indole (m/z 143) that are
formed in the thermal decarboxylation of indole-3-acrylic acid that occurs in the course of IR laser desorption. Gormally et al. reported that decarboxylation of indole-3-acrylic acid, to form 3-vinyl indole occurred preferentially over the laser desorption of the intact neutral molecule [12].

The following chapter describes the use of L²TOFMS for the mass spectrometric analysis of several 3-substituted and 5-substituted indoles. This work both extends and supplements the earlier studies carried out by Gormally et al. [10,11, 12]. In this work, instead of ionising with a laser wavelength close to the origin band, i.e. 280 nm, the two fixed wavelengths at 193 nm and 248 nm from an excimer laser were employed. As will be discussed, this non-resonant ionisation scheme provides both structural and molecular ion information. Unless otherwise stated, the laser power densities used to record the 193 nm and 248 nm photoionisation mass spectra were 0.7 MWcm⁻² and 0.86 MWcm⁻² respectively.

As well as the different photoionisation wavelengths that were employed, some samples were also desorbed from a glass substrate, as opposed to a stainless steel (s/s) substrate. This was done to provide a closer comparison with the results obtained by Gormally’s group (who used a glass substrate), in particular for indole-3-acrylic acid. All the experiments were carried out using the entrainment mode of the mass spectrometer.

Although it was of some interest to compare the results obtained at different ionisation wavelengths and from different substrates with earlier work, the principal reason for studying this series of substituted indoles was to provide characteristic fingerprint mass spectra of the monomers prior to L²TOFMS analysis of the products formed by electropolymerisation of these indoles. The analysis of these polymers is described in detail and comprises the majority of the remainder of the chapter.

6.1.2 3-Substituted Indoles

The 3-substituted indole monomers that were examined were indole-3-acetic acid, indole-3-carboxaldehyde and indole-3-acrylic acid. Their structures and molecular
weights are shown in Figure 6-3. These compounds were obtained from Aldrich, and used as received without further purification or separation. The samples were run in entrainment mode and were deposited onto the stainless steel or glass substrates from an acetone or chloroform solution. An interesting point to note is that recently it has been reported that indole-3-acrylic acid has a possible use as a matrix material for MALDI-MS at 337 nm [13].

**Indole-3-acetic acid**

Figure 6-4a shows the L²TOF mass spectrum of indole-3-acetic acid obtained at 248 nm following desorption from a stainless steel substrate. This partially hard ionisation mass spectrum exhibits several distinct features. The base peak in the mass spectrum is the molecular ion at m/z 175, and a small $^{13}\text{C}$ isotope peak is also present. The major fragment peak at m/z 130 corresponds to simple $\beta$ cleavage of the side chain (see Figure 6-5), which upon rearrangement, probably forms the more stable quinolinium ion structure as proposed by Beynon [1]. The formation of this quinolinium ion helps to explain the loss of HCN to form the small fragment at m/z 103. Two subsequent losses of C$_2$H$_2$ result in the formation of the fragment ions at m/z 77 and 51. This fragmentation scheme has been observed before by Powers [4] for the EI mass spectrum of 3-methyl indole. A small peak at m/z 57 due to iron from the substrate is also visible in the spectrum.
Relative intensity (arb units)

Figure 6-4: L2TOF mass spectra of indole-3-acetic acid obtained using photoionisation at a) 248 nm and b) 193 nm.
Figure 6–5: Fragmentation scheme for indole-3-acetic acid.
On reducing the ionising laser intensity, the soft ionisation mass spectrum of indole-3-acetic acid at 248 nm shows predominantly the molecular ion peak at m/z 175. A small fragment peak due to the β cleavage product at m/z 130 is also present; this does not disappear even at the lowest laser fluences used. This effect is similar to that observed in the 280 nm photoionisation mass spectrum of the related molecule, tryptophan [8], where even at low ionisation laser intensities, the fragment ion at m/z 130 corresponding to β cleavage was still visible. However, it has been reported that if a photoionisation wavelength of 280 nm is employed, the mass spectrum of indole-3-acetic acid shows no β cleavage fragmentation under soft ionisation conditions; only an intense molecular ion is observed [9].

The mass spectrum obtained for indole-3-acetic acid using a photoionisation wavelength of 193 nm is shown in Figure 6-4b. In contrast to the 248 nm photoionisation mass spectrum, the base peak now corresponds to the β cleavage fragment and only a small molecular ion peak is observed. The other much weaker fragment peaks in the spectrum correspond to those observed in the 248 nm L²TOF mass spectrum. When the ionising laser intensity at 193 nm is reduced, the relative intensity of the molecular ion peak to the m/z 130 fragment, which remains the base peak, is not affected. At very low ionisation laser intensities only the m/z 130 fragment peak is observed.

It is clear that following 248 nm photoionisation, indole-3-acetic acid fragments in a manner consistent with the ladder switching mechanism previously proposed by Deitz et al. [14]. In contrast, photoionisation at 193 nm results in prompt fragmentation by β cleavage on absorption of the second photon. Consequently only the m/z 130 fragment is observed under soft ionisation conditions. Only under higher 193 nm laser intensities does the molecular ion channel show significant intensity. Surprisingly, however, both of the ionisation wavelengths employed show fragments that are consistent with the EI fragments observed by Powers for the structurally similar 3-methyl indole compound [4].
Table 6–1: Relative intensities of the peaks observed in the EI\textsuperscript{a} and L\textsuperscript{2}TOF mass spectra\textsuperscript{b} of indole-3-carboxaldehyde and indole-3-acetic acid. \textsuperscript{a} J.C. Powers, J. Org. Chem., 33, 2044, (1968), \textsuperscript{b} this work.

**Indole-3-carboxaldehyde**

The photoionisation mass spectra of indole-3-carboxaldehyde obtained at 193 nm and 248 nm from a s/s substrate are shown in Figure 6–6. Using photoionisation at 193 nm, an intense m/z 144 peak is present in the spectrum. This is the base peak and corresponds to [M-H]\textsuperscript{+}. A small molecular ion peak at m/z 145 can also be seen. For photoionisation at 248 nm, only a small peak at m/z 144 is observed and the base peak is now the molecular ion. Fragmentation to m/z 116 via loss of HCO is observed using both ionisation wavelengths and then further fragmentation occurs via loss of HCN to m/z 89. This behaviour was observed before by Powers [4] in the EI spectrum of indole-3-carboxaldehyde where the fragmentation proceeded as in Figure 6–7.

Table 6–1 summarises the fragment peaks together with their relative intensities observed in the EI [4] and L\textsuperscript{2}TOF mass spectra of indole-3-carboxaldehyde, and also the L\textsuperscript{2}TOF mass spectra of indole-3-acetic acid. On reducing the ionising
Figure 6-6: L$_2$TOF mass spectra of indole-3-carboxaldehyde obtained at a) 193 nm and b) 248 nm.

**a)**
- [M-H]$^+$ at 144
- [M-HCO]$^+$
- [C$_5$H$_3$]$^+$
- [C$_7$H$_5$]$^+$

**b)**
- M$^+$ at 145
- [M-H]$^+$ at 144
- 89, 90

Relative intensity (arb units)

mass / Da.
laser intensity, the degree of fragmentation is reduced for both ionising laser wavelengths. The only peak observed in the 193 nm photoionisation mass spectrum corresponds to \([M-H]^+\) at m/z 144 whilst the soft ionisation mass spectrum at 248 nm shows only the molecular ion peak at m/z 145. Using both 193 nm and 248 nm photoionisation, it is clear that, in a similar manner to indole-3-acetic acid, indole-3-carboxaldehyde fragments by the mechanism seen in EI ionisation. In addition, 193 nm photoionisation induces prompt fragmentation to \([M-H]^+\) which is the base peak in the spectrum, whilst 248 nm photoionisation accesses this fragmentation channel to a much lesser degree. It is possible that the 12.8 eV of energy deposited into the molecules by two 193 nm photons is higher than the threshold energy for this fragmentation channel whilst 10 eV (corresponding to two 248 nm photons) is very close to this threshold energy. One other interesting point to note is that the fragmentation observed in the EI mass spectrum [4] is sequential, as would occur for a multiphoton ionisation process and not random or statistical as would be expected.

**Indole-3-acrylic acid**

Figure 6-8 shows the 193 nm photoionisation spectra of indole-3-acrylic acid following desorption from both stainless steel and glass substrates. In both cases a small molecular ion peak is seen at m/z 187 and an adduct peak at m/z 188, corresponding to \([M+H]^+\). For desorption from the stainless steel substrate (Figure 6-8a), the base peak in the mass spectrum is at m/z 170, corresponding to \([M-OH]^+\). Three small metastable peaks, centered around m/z 135, 143 and 160 are also present. In addition, two small peaks at m/z 130 and m/z 116 can be seen corresponding to a quinolinium ion rearrangement and the complete loss of the acrylic acid side-chain respectively. No peaks to higher mass at m/z 270 and m/z
Figure 6-8: L²TOF mass spectra of indole-3-acrylic acid obtained using photodissociation at 193 nm following desorption from a) stainless steel and b) glass substrates.
286 are observed as has been reported by Gormally et al. [11]. These peaks to higher mass than the molecular ion were reported to be due to the Diels-Alder [4+2] cyclo-addition products of 3-vinyl indole formed by decomposition of the indole-3-acrylic acid during sample desorption. Gormally et al., however, used a glass rod as the substrate for their laser desorption experiments and this is unlikely to be directly comparable with the results obtained here using a stainless steel substrate, since the temperature of the glass substrate during desorption will be markedly higher. Under the desorption conditions that were employed to record the mass spectrum in Figure 6-8a, it is clear that there is no formation of any Diels-Alder [4+2] cyclo-addition products. Furthermore there is no intense peak at m/z 143 corresponding to the formation of 3-vinyl indole.

On re-examination of indole-3-acrylic acid using glass as the sample substrate for desorption, the mass spectrum shown in Figure 6-8b was obtained. The CO₂ and UV laser power densities were similar to those used to record the spectrum obtained using the s/s substrate. In this spectrum, the base peak corresponds to the quinolinium ion, at m/z 130. In addition, two peaks at m/z 142 and 144 indicate the formation of 3-vinyl indole. As in the case for desorption from the s/s substrate, an intense [M-OH]⁺ fragment at m/z 170 is present together with the molecular ion and protonated molecular ion peaks at m/z 187 and m/z 188 respectively. To low mass, both sodium and potassium ions are seen which come from the glass substrate itself and an intense sodium adduct peak of the molecular ion at m/z 210 can also be seen. Two small peaks in the baseline at m/z 270 and m/z 286, which are often observed with greater intensity, signify the presence of the Diels-Alder [4+2] cyclo-addition products of 3-vinyl indole, as observed by Gormally et al. [11]; these peaks are related to the presence of the peaks at m/z 142 and m/z 144 due to 3-vinyl-indole.

Clearly the occurrence of these extra peaks to high mass must be due to some substrate effect, since they were only observed when a glass substrate was employed. Dale et al. [15] have previously examined the effect of the thermal properties of substrates on the desorption efficiencies of poly-atomic molecules. Using a one-dimensional heat diffusion model, the transient temperature profile produced
in several substrates, following CO$_2$ pulsed laser irradiation were simulated. For laser power densities of 10 to 60 MWcm$^{-2}$, that are typically used for desorption, the surface temperature and the temperature at various depths in the substrate were calculated. The peak induced surface temperature in stainless steel, brass and fused silica were found to be 1050 K, 1600 K and 4750 K respectively. The simulations were then compared to experimental observations.

Since the peak surface temperature of the glass substrate is around 3700 K higher than that for the s/s substrate following pulsed CO$_2$ laser irradiation then two mechanisms can be proposed for the origin of these anomalous Diels-Alder [4+2] cyclo-addition products, observed by Gormally et al. [11] and ourselves using glass substrates. Firstly, the higher surface temperature may lead to thermal decomposition of indole-3-acrylic acid prior to desorption from the surface. Alternatively, the desorbed indole-3-acrylic acid molecules may have higher internal energies, which leads to facile thermal decomposition. At this time, it is impossible to determine which mechanism predominates. In addition to the observation of cyclo-addition products in the mass spectrum obtained using a glass substrate, the resolution has been slightly degraded. Again this may be attributed to the effect of increased internal energy of the molecules following desorption from the glass substrate.

6.1.3 5-Substituted Indoles

Three 5-substituted indoles have also been examined by L$^2$TOFMS namely indole-5-carboxylic acid, 5-cyano indole and 5-chloro indole. These compounds were used as received from Aldrich without further purification or separation; their structures and molecular weights are shown in Figure 6-9. The samples were run in entrainment mode and were deposited onto stainless steel or glass substrates from either acetone or chloroform solution. These 5-substituted indoles were examined primarily to obtain fingerprint mass spectra as a prelude to more extensive studies of their electropolymerised products studied for their electrochemical characteristics by Dr. Mounts group at Edinburgh (see Section 6.2).
indole-5-carboxylic acid  cyano indole  5-chloro indole

Figure 6-9: Structures and molecular weights for the 5-substituted indoles studied by L2TOFMS.

**Indole-5-carboxylic acid**

Figure 6-10 shows the L2TOF mass spectra for indole-5-carboxylic acid obtained following photoionisation by 193 nm and 248 nm laser radiation; desorption was performed from a s/s substrate. In both spectra the base peak is at m/z 161 and this corresponds to the molecular ion. Several fragment peaks are also present, the most prominent being at m/z 144. The peaks at m/z 145 and 147 are most likely due to an impurity in the sample. Figure 6-11 shows the possible fragmentation schemes that can account for these fragment ions. The other lower mass fragments, at m/z 116 and m/z 89, correspond to the complete loss of the side-chain and further fragmentation via loss of HCN to [C7H5]+ respectively. Under soft ionisation conditions fragmentation to m/z 144 readily occurs but no further fragment peaks are visible in the mass spectrum. The molecular ion at m/z 161 remains the base peak. Table 6-2 summarises the peaks and their intensities observed in the EI [4] and the L2TOF mass spectra of indole-5-carboxylic acid.

The 248 nm photoionisation mass spectrum recorded for this compound is shown in Figure 6-10b. This was obtained using a similar UV laser fluence to that employed to record the 193 nm photoionisation spectrum above. Again, the base peak is the molecular ion, and an intense fragment corresponding to [M-OH]+ at m/z 144 is observed; no other intense fragments are visible. However, small peaks at m/z 117, 116, 90, 89 and 63 can be seen close to the baseline.
Figure 6-10: L2TOF mass spectra of indole-5-carboxylic acid obtained using photoionisation at a) 193 nm and b) 248 nm (s/s substrate).
Figure 6-11: Possible fragmentation scheme for indole-5-carboxylic acid using 193 nm photoionisation
CHAPTER 6. \( L^2 \) TOFMS OF INDOLE MONOMERS AND POLYMERS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Technique</th>
<th>( m/z ) observed ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>indole-5-carboxylic acid</td>
<td>EIMS(^a)</td>
<td>161 (100), 144 (69), 117 (7), 116 (50), 115 (7), 90 (4), 89 (21), 63 (10)</td>
</tr>
<tr>
<td></td>
<td>( L^2 ) TOFMS 193 nm(^b)</td>
<td>161 (100), 147 (53), 145 (18), 144 (22), 117 (1), 116 (7), 90 (1) 89 (3)</td>
</tr>
<tr>
<td></td>
<td>( L^2 ) TOFMS 248 nm(^b)</td>
<td>161 (100), 147 (1), 145 (2), 144 (26), 117 (2), 116 (3), 90 (1), 89 (4), 63 (1)</td>
</tr>
<tr>
<td>5-cyano indole</td>
<td>( L^2 ) TOFMS 248 nm(^b)</td>
<td>142 (100), 116 (8)</td>
</tr>
<tr>
<td>5-chloro indole</td>
<td>( L^2 ) TOFMS 248 nm(^b)</td>
<td>154 (5), 153 (47), 152 (13), 151 (100), 118 (2), 117 (3), 116 (3), 90 (2), 89 (2)</td>
</tr>
</tbody>
</table>

**Table 6-2:** Relative intensities of the peaks observed in the \( EI^a \) and \( L^2 \) TOF mass spectra of indole-5-carboxylic acid, 5-cyano indole and 5-chloro indole.

\(^a\) J.C. Powers, J. Org. Chem., 33, 2044, (1968), \(^b\) this work.

Unlike in the 193 nm photoionisation mass spectrum, the impurity peaks at \( m/z \) 145 and 147 are very small. This fragmentation pattern is very similar to that observed in the \( EI \) mass spectra reported by Powers [4].

5-cyano indole

Figure 6-12a shows the \( L^2 \) TOF mass spectrum of 5-cyano indole obtained using photoionisation at 248 nm from a s/s substrate. An intense molecular ion peak at \( m/z \) 142 is seen together with a small fragment peak at \( m/z \) 116. This fragment corresponds to loss of the CN side-chain. No further fragmentation is observed. The \( L^2 \) TOF mass spectrum obtained using photoionisation at 193 nm, using a similar UV laser power density is almost identical. The only significant difference is a reduction in intensity of the molecular ion signal by around 60 %. The 5-cyano indole monomer is very easily detected at both ionising laser wavelengths and this proved to be advantageous when the electropolymerisation products were studied.
Figure 6.12: L$^2$TOF mass spectra obtained using 248 nm photoionisation of a) 5-cyano indole and b) 5-chloro indole (both s/s substrate).

5-Cyano Indole

5-Chloro Indole
Table 6-3: Comparison between the observed and expected chlorine isotope abundances for the molecular ion peaks of 5-chloro indole.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Calculated Isotopic Abundance (%)</th>
<th>L²TOFMS Isotopic Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>151</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>152</td>
<td>8.98</td>
<td>11</td>
</tr>
<tr>
<td>153</td>
<td>32.40</td>
<td>38</td>
</tr>
<tr>
<td>154</td>
<td>2.90</td>
<td>4</td>
</tr>
</tbody>
</table>

5-chloro indole

The mass spectrum of 5-chloro indole obtained using photoionisation at 248 nm following desorption from a s/s substrate, is shown in Figure 6-12b. It is very similar to the spectrum for 5-cyano indole, in that the base peak corresponds to the molecular ion and a small fragment is observed at m/z 116, corresponding to loss of the side-chain. The isotopic distribution of the molecular ion peak is consistent with that expected on the basis of the natural $^{35}\text{Cl}/^{37}\text{Cl}$ isotope abundance, given that the digitisation rate can affect the intensity and width of the peaks observed. The insert region in Figure 6-12b shows an expansion of the isotopic distribution of the molecular ion. A comparison between the observed and expected isotopic abundances is given in Table 6-3. The observed values were obtained from Figure 6-12b and calculated from the overall peak areas. Surprisingly, no signals could be detected for this compound when photoionisation at 193 nm was attempted. This is most likely due to a poor absorption cross-section at this laser wavelength.

6.1.4 Concluding Remarks

The spectra recorded for the 3-substituted indoles using photoionisation at both 248 nm and 193 nm generally contain molecular ion peaks with some degree of fragmentation. For the compounds examined, the fragments observed in the 248
nm photoionisation mass spectra correspond closely to those observed in the electron impact (EI) mass spectra, previously obtained [4]. This is surprising since the two ionisation methods are widely different; multiphoton ionisation (MPI) generally induces fragmentation when the molecular ion absorbs further photons. This is commonly referred to as the ladder switching mechanism [14]. The EI mechanism proceeds by depositing 70 eV of energy directly into the molecule. Under normal circumstances, this energy explores all the possible fragmentation channels available, resulting in complex mass spectra. Clearly, however, both the EI and L²TOFMS spectra show fragmentation and/or loss of the side-groups followed by sequential fragmentation of the indole nucleus.

The 248 nm photoionisation mass spectra all show intense molecular ion peaks and, on increasing the ionising laser intensity, the intensity of the fragment peaks increase in a manner consistent with the ladder switching mechanism. Photoionisation using 193 nm, however, produces intense fragment peaks and smaller molecular ions. Reducing the ionising laser intensity has the effect of reducing the overall intensities of the molecular ion and fragment peaks until the base peak is the promptly formed molecular ion. More specifically, the β cleavage product of indole-3-acetic acid at m/z 130 and the m/z 144 fragment of indole-3-carboxaldehyde, corresponding to [M-H]⁺ dominate the spectra under soft ionisation condition.

Desorption of indole-3-acrylic acid from a stainless steel substrate, followed by photoionisation at 193 nm shows no evidence for the Diels-Alder [4+2] cycloaddition products previously observed by Gormally et al. [11]. These products, observed to higher mass than the molecular ion were thought to originate when 3-vinyl indole was formed by thermal decomposition during the desorption step. Under similar desorption and ionisation conditions, the spectrum recorded using a glass substrate (as used by Gormally et al.) did show evidence for these cycloaddition products, albeit at very low intensity. Clearly, the occurrence of these peaks must be due to the use of the glass substrate. Since the peak surface temperature induced by a CO₂ laser pulse is around 3700 K higher for a glass substrate than a stainless steel substrate [15] then the observation of thermal decomposi-
tion and cyclo-addition products can be attributed to these higher temperatures reached during desorption event.

The 5-substituted indoles studied generally show intense molecular ion peaks using photoionisation at both 193 nm and 248 nm. The exception is 5-chloro indole, for which no signals were recorded using 193 nm photoionisation. The most likely explanation is that the absorption cross-sections are unfavourable at this wavelength. Again the fragmentation appears to proceed in a manner similar to EI, with initial side-chain fragmentation and/or loss, followed by sequential fragmentation of the indole nucleus. Since the 5-substituted species all show intense molecular ions then there should be no difficulty in detecting residual monomers in the electropolymerisation products of these species.
6.2 L²TOFMS of Electropolymerised Indoles

6.2.1 Introduction

Over the last 15 years there has been considerable interest in the electropolymerisation of heterocyclic molecules such as pyrroles, thiophenes and indoles to form electronically conducting polymer films [16,17]. Waltmann et al. [16] have listed several potential applications for these polymer films including polymer electrodes, electro-optical display devices, battery applications and information storage devices. The formation of substituted polymers from substituted monomers has received considerable interest, since variation of the substituent may allow changes in the properties of the polymers [16,17,18].

Recent attention has focussed on conducting polymers which contain pendant carboxylic acid groups. Bartlett et al. [19] have recently polymerised indole-5-carboxylic acid and have observed a dependence on the the current passed on the pH of the aqueous solution. They have therefore proposed that this polymer could be used as a fast response pH sensor [20]. Poly (indole-5-carboxylic acid) electrodes can also be used for the direct oxidation and reduction of cytochrome c [21]. Despite the potential importance of this and other electropolymerised indoles, there has been little work reported to date on the structural characterisation of the polymers formed. This is chiefly because conducting polymer layers are typically inherently insoluble and intractable.

In particular, there has been little or no mass spectrometric characterisation of any electropolymerisation product films. This is due to several reasons. Firstly, the high molecular weight of the polymers generally prohibits mass spectrometric characterisation by standard techniques e.g. EI, CI, FAB or SIMS. Secondly, the films have the ability to strongly adhere to surfaces. Application of pyrolysis techniques, which involve heating the source to high temperatures are commonly used to study high molecular weight polymers, however, this leads decomposition of these electropolymerised films.
By contrast, using L²TOFMS, it has been possible to desorb intact, the polymer building blocks as neutral species and in this manner research the polymer structure. The rapid substrate heating of ca. \(10^6 \text{ Ks}^{-1}\) that is induced by the CO₂ laser pulse results in desorption from the surface rather than complete thermal breakdown of these polymer films. This, coupled with the high ionisation efficiency for the liberated neutral species makes L²TOFMS a powerful tool for the analysis of electropolymerised indole films. A further advantage is the exclusion of background peaks in the mass spectra due to the electrolyte.

Recently, O'Malley et al. [22] showed the electropolymerisation products of imidazole and its derivatives could be characterised by single-step laser desorption/ionisation mass spectrometry. A series of peaks were observed at low mass (ca. \(m/z\) 200 - 1000), with the electropolymerisation products being slightly more intense than the background. Although the mass spectra were rather poor in terms of signal-to-noise ratio, oligomers up to \(n = 10\) could be detected. O'Malley et al. suggested that the poor spectra were due to the fact that the ions observed were fragments of larger oligomeric species, consisting of perhaps hundreds or even thousands of repeat units. Similarly, Wilkins et al. [23] have examined the electrochemical polymerisation products of 2-vinylthiophene by laser desorption Fourier transform mass spectrometry. For the three polymers studied, namely, the chemically polymerised form, the precipitate formed after electropolymerisation and the film formed during electropolymerisation, a polymer distribution of strong intensity was observed. The distributions ranged from ca. \(m/z\) 500 to 5000. On the basis of the masses and intensities of the peaks observed, several possible polymerisation mechanisms were proposed.

In this section, the L²TOF mass spectra that have been obtained for a series of 5-substituted electropolymerised indoles are discussed. These indole polymers were produced and characterised both electrochemically and by other spectroscopic techniques by the electrochemistry group in the Department of Chemistry at The University of Edinburgh under the supervision of Dr. Andrew Mount. As will be discussed later, from the data obtained it has been possible to unambiguously characterise one of the major products, formed during electropolymerisation, as a
cyclic trimer species. In each case the spectra obtained were simple and exhibited intense molecular ion peaks with little fragmentation.

### 6.2.2 The Electropolymerisation Process

The chemicals used for the electropolymerisation experiments were of AnalaR grade or equivalent and were used as received unless otherwise stated. The background electrolyte solution used for every experiment consisted of 0.1 M anhydrous lithium perchlorate (Aldrich) in acetonitrile (Fisons, dried, distilled).

The polymerisation studies and the electrochemical characterisation were carried out by Mackintosh and Mount [24] using the following procedure. A 2 cm² platinum gauze was used as a counter electrode with a 0.387 cm² rotating-disc electrode (Oxford Electrodes) as the working electrode. The reference electrode was constructed in-house and consisted of a silver wire dipped into a solution of silver perchlorate (0.01 M) in background electrolyte solution. All the potentials reported are measured with respect to this electrode, which has a potential of 0.437 V with respect to the saturated calomel electrode.

The polymerisation experiments typically involved the oxidation of a 20 mM solution of indole or substituted indole, with the electrode at a positive potential with respect to the reference electrode. Table 6-4 lists the indole compounds that have been successfully polymerised by Mackintosh and Mount and the potential at which the electropolymerisation was carried out. Polymerisation was carried out on the rotating-disc electrode (platinum) rotating at 4 Hz. Steady state conditions were reached within a few seconds with a constant current being passed. Electropolymerisation was generally terminated after 30 mC of charge had been passed in order to ensure a reproducible film thickness. The films were then scraped from the electrode after washing in acetonitrile. For indole-5-carboxylic acid and 5-cyano indole, the films were washed in acetonitrile prior to purification by extraction. The films formed by the other indoles were soluble in acetonitrile and were column separated and extracted.
<table>
<thead>
<tr>
<th>Compound used</th>
<th>Potential /V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indole-5-carboxylic acid</td>
<td>+ 1.46</td>
</tr>
<tr>
<td>5-cyano indole</td>
<td>+ 1.64</td>
</tr>
<tr>
<td>5-chloro indole</td>
<td>+ 1.34</td>
</tr>
<tr>
<td>indole</td>
<td>+ 1.00</td>
</tr>
<tr>
<td>Co-polymer (5-cyano indole &amp; indole-5-carboxylic acid)</td>
<td>+ 1.64</td>
</tr>
</tbody>
</table>

Table 6-4: Indoles used for polymerisation and the potentials at which they were electropolymerised.

6.2.3 Poly(indole-5-carboxylic acid)

Initial experiments by Mackintosh and Mount [24] on the electropolymerised film of poly(indole-5-carboxylic acid) (I5CA) established its complete solubility in dimethyl-sulphoxide (DMSO, Aldrich, 99+ % anhydrous). However, on using N,N-dimethyl formamide (DMF, Aldrich, 99 %) as the solvent, incomplete dissolution of the polymer occurred; indeed after several washings with DMF, an insoluble fraction remained. The residual DMF-insoluble material was, however, soluble in DMSO. These results indicated the presence of two different species in the electropolymerised film which could be separated by their differential solubility in DMF. Neither of these fractions could be unreacted monomer as they were both found to be insoluble in acetonitrile.

Examination of the DMF soluble fraction of the electropolymerisation products of I5CA, resulted in the L²TOF mass spectrum shown in Figure 6-13a; photoionisation was carried out using 248 nm radiation. The base peak in the mass spectrum is at m/z 477. Given that the molecular weight of the I5CA monomer is m/z 161, then this is consistent with a trimeric species. Furthermore this mass is exactly equal to the expected molecular weight for a trimer in which all the indole monomers have coupled, with each monomer losing 2 hydrogen atoms and each forming 2 new bonds. This indicated a cyclic structure for the trimer, for which
Figure 6-13: 248 nm photoionisation L^2 TOF mass spectra for the DMF soluble fraction of poly(indole-5-carboxylic acid) obtained under a) soft and b) hard ionisation conditions.

Relative intensity (arb units)

mass / Da.

250 300 350 400 450 500

345 389 433

M^+ 477

mass / Da.

250 300 350 400 450 500

345 + Li 389 + Li 433 + Li 477

+2Li + 3Li +2Li
there are several possible structural isomers, as shown in Figure 6-14. Waltmann et al. [16,18] had previously thought that the indoles would polymerise through the 3-position and the nitrogen on the 5-membered ring. If this had occurred, the \( L^2 \)TOF mass spectrum of a linear trimer would have shown a peak at \( m/z \) 479.

Three fragment peaks to lower mass than the trimer can also be seen at \( m/z \) 433, \( m/z \) 389 and \( m/z \) 345, separated by 44 Da. These correspond to fragmentation of the trimer by successive loss of \( CO_2 \) from the carboxylic acid side-groups. No peaks to higher mass than the trimer are observed. Moreover, there is no peak due to the monomer species seen in the spectrum or any other peaks to lower mass than \( m/z \) 345.

Under hard ionisation conditions using photoionisation at 248 nm, the mass spectrum shown in Figure 6-13b was obtained. Again, the base peak in the spectrum is at \( m/z \) 477, and corresponds to the cyclic trimer. The three fragment peaks corresponding to loss of \( CO_2 \) are greatly enhanced in intensity relative to Figure 6-13a, however little or no fragmentation below \( m/z \) 345 is observed. This is indicative of the particular stability of the cyclic structure for the indole trimer. The additional peaks at \( m/z \) 439, 401, 395, 363, 357 and 351 correspond to lithium adduct peaks of the fragmentation products; for the loss of each carboxyl group, a lithium atom can recombine with the fragment ion. The lithium is present in the base electrolyte solution but is rarely observed in the mass spectra.

Using photoionisation with 193 nm UV laser radiation, a similar mass spectrum to that shown in Figure 6-13a is obtained, the only major difference being the presence of small lithium adduct peaks associated with the fragments. Photons of wavelength 193 nm have an energy of 6.4 eV, sufficiently energetic to ionise lithium (I.P. 5.14 eV) in a one photon process. Photons at 248 nm, however, only correspond to an energy of 5.0 eV and cannot ionise lithium in a one photon process. Consequently, lithium adducts are only observed in the 248 nm photoionisation mass spectra under high laser intensity conditions, as shown in Figure 6-13b.

From this data it is clear that there is only one component in the DMF-soluble fraction and this is the cyclic trimer. This was confirmed by NMR studies performed by Reid et al. [25], which are described in detail elsewhere. The NMR
Figure 6-14: Possible isomeric structures for the cyclic poly(indole-5-carboxylic acid) trimer of mass 477 Da.
Figure 6–15: Structure of the asymmetric cyclic trimer of I5CA.

data conclusively shows that the trimer has the asymmetric structure (v) shown in Figure 6–15.

Figure 6–16 shows the L²TOF mass spectrum of the DMF-insoluble (DMSO-soluble) fraction of the electropolymerisation products of I5CA. Using photoionisation at 248 nm, with a laser fluence similar to that used to record the spectrum in Figure 6–13a, only the trimer and associated fragment peaks are seen. No peaks to higher mass are observed. This mass spectrum was obtained from the accumulation of 500 laser shots (c.f 20 shots to obtain the spectrum shown in Figure 6–13a). The overall intensity of the trimer peak, is much reduced although the relative intensities of the fragment peaks are similar. Since no trimer band was observed in the TLC of this fraction, then the presence of a peak due to the trimer in the spectrum is attributed to fragmentation, indicating that the polymer may have discrete trimer units in the chains.

Both the DMF-soluble and DMF-insoluble fractions were examined by field desorption mass spectrometry (FDMS) at ICI Wilton using a ZAB 2E reverse geometry instrument. However, no spectra could be obtained showing the trimer or polymer.

From the L²TOF mass spectra, it is clear that the DMF-soluble fraction of electropolymerised I5CA is a cyclic trimer species as further confirmed by NMR studies [25]. In addition, the DMF-insoluble (DMSO-soluble) species exhibited a similar mass spectrum, albeit at an overall reduced intensity, indicating the
Relative intensity (arb units)

Figure 6-16: LTOF mass spectra of the DMF-insoluble (DMSO-soluble) face under soft ionization conditions.
presence of trimer units in the polymer chain. Mackintosh's UV-vis, IR and fluorescence spectra [26], are all very similar for the DMF-soluble and DMF-insoluble (DMSO-soluble) fractions, although the spectra for the monomer are completely different. This would also indicate that the trimer unit is a major constituent of the polymer. Given this, the most likely structure for the polymer is that it consists of linked trimer units. The IR spectra of the trimer and polymer indicate that the polymer contains fewer N-H units. Therefore it is possible that, to a large extent, the polymer is linked via the indole ring nitrogens in the trimer. One further piece of evidence to support a linked trimer structure for the polymer is that electropolymerisation of either I5CA monomer or the DMF-soluble trimer results in the formation of a polymer film which exhibits the same electrochemical and spectroscopic properties [24].

6.2.4 Poly(5-cyano indole)

The characterisation of the electropolymerisation products formed from 5-cyano indole (5CI) was of considerable interest not least, because it was important to establish if the electropolymerisation mechanism that was found for indole-5-carboxylic acid was generally applicable to other 5-substituted indoles. Furthermore, the greater electronegativity of the CN group might affect the properties and/or processing of the 5-cyano indole polymer. The most important reason, however, for studying the 5CI polymers, was the possibility of functionalisation of the cyano substituent. This would allow the production of highly specific polymers with tailored electrochemical and conducting properties.

As was found with indole-5-carboxylic acid, Mackintosh and Mount found that the electropolymerisation of 5-cyano indole also leads to the deposition of two products which can be separated by their differential solubility in DMF [27]; one DMF-soluble (DMSO-soluble) fraction and one DMF-insoluble (DMSO-soluble) fraction. The DMF-soluble fraction was expected to be a trimeric species as found for indole-5-carboxylic acid.
Figure 6–17 shows the high resolution L²TOF mass spectra of the DMF-soluble fraction of poly(5-cyano indole) (poly(5Cl)). These were obtained using 248 nm photoionisation under soft and hard ionisation conditions. The soft ionisation mass spectrum (Figure 6–17a) shows only the molecular ion at m/z 420, corresponding to the trimer of poly(5-cyano indole). The peaks to higher mass which are present in the following natural abundance, 32.4 % (421), 5.1 % (422) are due to the ¹³C containing species of the molecular ion. Under harder ionisation conditions the spectrum shown in Figure 6–17b was obtained. As well as the intense molecular ion peaks, this spectrum also exhibits a small peak centered upon m/z 394, which can be attributed to the fragment ion resulting from the loss of one CN substituent from the molecular ion. This [M-CN]⁺ fragment peak is very wide and of low intensity, and most likely is due to metastable decay. At even higher laser power densities, low intensity metastable peaks which are several mass units wide can be seen centered upon m/z 368 and m/z 342. These arise from the loss of two and three CN side-groups from the trimer respectively. The loss of three CN groups results in the formation of the unsubstituted polyindole trimer which is stable to further fragmentation. The high stability of the molecular ion of the 5Cl trimer towards the loss of the CN substituents has been confirmed in further studies using field desorption mass spectrometry at ICI Wilton.

The FDMS spectra were recorded on a VG ZAB-T, 4-sector mass spectrometer at ICI Wilton. Figure 6–18 shows the FD mass spectrum for the DMF soluble fraction of poly(5-cyano indole). It is almost identical to the soft ionisation L²TOF mass spectrum (Figure 6–17a), with peaks of similar relative intensity. The only difference in the two spectra is the presence of small sodium and potassium adduct peaks at m/z 443 and m/z 459 respectively, in the FD mass spectrum. The intensity of the molecular ion signal for the 5Cl trimer was sufficiently intense to enable an FD MS/MS spectrum to be recorded. Using collision induced dissociation (CID) to examine the daughter (or product) ions formed from this ion, the spectrum in Figure 6–19 was recorded. The spectrum was obtained using argon as the collision gas under the standard operating conditions where the pressure was increased until the intensity of the molecular ion peak was reduced to ≈ 10
Figure 6-17: 248 nm photoionisation L$_2$TOF mass spectra of the DMF-soluble fraction of poly(5-cyano indole) obtained under (a) soft and (b) hard ionisation conditions.

Relative intensity (arb units)

- Mass (Da): 330, 360, 390, 420, 450
- Relative intensity: 0.0, 0.2, 0.4, 0.6, 0.8, 1.0

(a) [Graph showing mass spectra under soft ionisation conditions]

(b) [Graph showing mass spectra under hard ionisation conditions]
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Figure 6-18: Field desorption mass spectrum of the cyclic trimer of poly(5-cyano indole).
Figure 6-19: Field desorption (FD) tandem mass spectrum (MS/MS) of the molecular ion at m/z 420 under collision with argon. The spectrum is a collision induced dissociation (CID) daughter (or product) ion scan showing the fragments obtained from cyclic trimer of poly(5-cyano indole). The spectrum is a collision induced dissociation (CID) daughter (or product) ion scan showing the fragments obtained from cyclic trimer of poly(5-cyano indole).
The most intense fragment peak is at m/z 394.1 and corresponds to the loss of one CN group from the trimer. There are no other fragment peaks of significant intensity.

It is interesting that the CN groups are much harder to remove from the 5-cyano indole trimer than the corresponding CO₂H groups from the indole-5-carboxylic acid trimer. MPI of the cyclic trimers using 248 nm photoionisation, results in rapid formation of the singly charged M⁺ ion, which can be further fragmented by the absorption of further photons via the ladder switching mechanism [14]. In the case of indole-5-carboxylic acid, fragmentation proceeds via decarboxylation. However, for the 5-cyano indole trimer, the CN substituent is highly electronegative and is less easily lost. This is probably because it is less likely to cleave from the molecular ion as a neutral species, and the result is metastable decay from the trimer. In addition only one CN cleavage product is observed with significant intensity in either the L²TOF or FD MS/MS spectra indicating the difficulty in removing two or more CN groups.

The mass of the molecular ion peak at m/z 420, seen in both the L²TOF and FD mass spectra, is exactly 6 mass units less than that for three 5Cl molecules and this is again indicative of the cyclic nature of the trimer. The structure of this cyclic trimeric species i.e. whether it is symmetric or asymmetric cannot be established from the mass spectral data alone. Once again, however, other NMR data conclusively shows that the trimer has the same asymmetric structure (v) in Figure 6-14, as for indole-5-carboxylic acid [27].

As with poly(indole-5-carboxylic acid), the mass spectra recorded for the DMF-insoluble (DMSO-soluble) fraction of poly(5-cyano indole) were essentially identical to those of the trimer, the only differences being a decrease in the overall intensity of the spectra recorded. This is indicative that the polymer consists of linked trimer species. The observation of the trimeric species in the mass spectra of the DMF insoluble fraction is therefore most probably due to fragmentation of the polymer. Further evidence that supports the linked trimer structure of the polymer has been obtained by other workers in Dr. Mounts group using UV-vis and fluorescence spectroscopy, and electrochemical analyses [27].
Functionalisation of poly(5-cyano indole) to poly(5-methyl amino indole)

Figure 6-20 shows the L²TOF mass spectrum of the 5-methyl-amino indole trimer fraction formed after the reduction of the 5-cyano indole trimer by LiAlH₄. This work was carried out by Alastair Thomson. The mass spectrum was recorded using 248 nm photoionisation, under soft ionisation conditions. The base peak in the spectrum is at m/z 387 and corresponds to a cyclic trimer of 5-methyl indole, an expected by-product of the functionalisation step. A small molecular ion peak at m/z 432 corresponding to the cyclic trimer of 5-methyl-amino indole is also observed. This is the expected product in the reaction. The fragment peak at m/z 402 is due to the loss of one CH₂NH₂ group from the molecular ion. The other fragment ion peaks are due to successive loss of side chain groups. The two intense peaks at m/z 408 and m/z 352 (labelled * in the spectrum) are due to diffusion pump oil contamination. Below the peak due to the 5-methyl indole trimer, m/z 387, three fragment peaks are present at m/z 373, 359 and 345. These correspond to the loss of one, two and three methyl groups, respectively. This fragmentation pattern is expected and is consistent with the fragmentation seen in the spectrum of the indole-5-carboxylic acid trimer.

Below m/z 345 no further fragments are observed, again due to the great stability of the indole trimer core. The small peaks between m/z 160 and m/z 300 are due to PAH contamination in the ionisation chamber of the mass spectrometer. The peak at m/z 146 corresponds to the 5-methyl-amino indole monomer and the peak at m/z 117 is due to indole itself. These peaks, however, are contaminants in the trimer solution and are not caused by fragmentation.

6.2.5 Poly(5-chloro indole)

The electropolymerisation mechanism for indole-5-carboxylic acid and 5-cyano indole, two electron withdrawing substituents, has been determined. However, in order to determine the mechanisms universality, a wider variety of 5-substituted indoles must be studied with a range of functionality. In order to ascertain that
The spectrum was recorded under soft ionisation conditions at 248 nm. The spectrum formed after reduction of the 5-cyano indole trimer with LiAlH4. The spectrum was recorded at 248 nm.

**Figure 6.20:** LTOF mass spectra of the functionalised 5-methyl-amino indole trimer formed after reduction of the 5-cyano indole trimer with LiAlH4. The spectrum was recorded under soft ionisation conditions at 248 nm.

![Mass Spectrum Graph](image-url)
the polymerisation mechanism held for a weakly electron donating group, the 5-chloro indole (5CLI) monomer was polymerised. As in the case of 5-cyano indole, functionalisation of the Cl group is relatively straightforward, thereby allowing for the production of novel conducting polymer layers.

Mackintosh and Mount showed that the electropolymerisation of 5-chloro indole leads, as before, to the deposition of a polymer film on the electrode surface. This time the electropolymerised film was completely soluble in DMF. This DMF soluble fraction was therefore examined by L²TOFMS using photoionisation at 193 nm and the resulting spectrum is shown in Figure 6-21a. The base peak in the spectrum near m/z 447 corresponds to the cyclic trimer of poly(5-chloro indole). The molecular ion consists of a number of peaks due to the high natural abundance of both chlorine isotopes ($^{35}\text{Cl}$, 75.4 % and $^{37}\text{Cl}$, 24.6 %). Figure 6-21b shows an expansion of the molecular ion region at higher resolution. The solid vertical bars represent the expected intensities for the trimer calculated on the basis of the natural isotopic abundances. The relative peak intensities are listed in Table 6-5. Given that the resolution for this mass spectrum is approximately 850, the peaks are not baseline resolved. The observed intensities, measured from the peak areas are in good agreement with the calculated intensities.

The exact structure of the 5-chloro indole trimer has not been ascertained by NMR. However, from the L²TOFMS data it is obvious that the trimer has a cyclic structure since the molecular ion peak is 6 mass units short of the mass of three 5-chloro indole monomers. The structure is expected to be asymmetric like that found for the 5-cyano indole and indole-5-carboxylic acid trimers.

Fragmentation of the trimer of 5CLI follows a similar pattern to that seen in the spectra of the 5-cyano indole and indole-5-carboxylic acid trimers, namely, via loss of the side-groups and is terminated by the loss of all three. Unlike the other indoles studied, the mass spectrum of poly(5-chloro indole) shows a small monomer peak at m/z 151-153. This peak is not due to fragmentation since under soft ionisation conditions, no trimer fragments are observed and the small monomer peak is still present. This peak is therefore most likely due to the presence of unreacted monomer in the DMF-soluble mixture.
Figure 6-21: $L_2$ TOF mass spectra of poly(5-chloro indole) obtained at 193 mm showing a) the complete spectrum and b) expansion of the molecular ion region. Solid vertical bars indicate the trimer intensities calculated from the natural abundance of $^{35}Cl$ and $^{37}Cl$ isotopes.
### Table 6-5

<table>
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<tr>
<th>m/z</th>
<th>Calculated relative intensity</th>
<th>Observed relative intensity</th>
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<tr>
<td>447</td>
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<td>31.5</td>
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<tr>
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<td>8.5</td>
<td>14</td>
</tr>
<tr>
<td>453</td>
<td>3.4</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 6-5: Relative intensity of the calculated and observed chlorine isotope peaks for the trimer of 5-chloro indole.

In addition to the monomer peak, the spectrum shown in Figure 6-21a exhibits a small peak centered on m/z 745. Under higher resolution conditions, this peak is split into several peaks, the most intense being at m/z 743, 745, 747 and 749. This is indicative of a pentamer species and is not observed for the other indoles studied. There are two possible explanations as to the origin of this species. Firstly, this pentameric species is produced as a separate entity in the electropolymerisation event. This could be confirmed by TLC and fluorescence studies which are presently being undertaken by the electrochemistry group. Secondly, the pentamer could be formed as a fragment from the larger oligomers in the polymers either during laser desorption or laser ionisation. Further work is necessary in order to ascertain the structure and origin of this species.

### 6.2.6 Poly(indole)

Of all the indoles originally studied by Waltmann et al., [18], the 5-substituted indole-5-carboxylic acid and 5-cyano indole yielded the best films, closely followed by indole itself which deposited a green-black film on the anode surface. Initial experiments on this indole film by Mackintosh in the electrochemistry laboratory
determined that it consisted of several components; the whole film being completely soluble in DMSO and a DMF-soluble fraction.

The DMF soluble fraction was studied by L$^2$TOFMS using photoionisation at 248 nm and the spectrum obtained is shown in Figure 6-22. The base peak in the spectrum at m/z 345, corresponds to the cyclic trimer of poly(indole). No fragment peaks are visible in the spectrum since there are no side-groups to lose. Under higher ionisation laser power densities, no fragmentation is observed, again this is indicative of the high stability of the molecular ion of the cyclic trimer.

This stability was further confirmed by FDMS studies carried out at ICI Wilton. Figure 6-23 shows an FD MS/MS spectrum of the daughter (or product) ions formed during CID of the indole trimer at m/z 345. Under normal conditions, using argon as the collision gas there was no discernible fragmentation of the indole trimer. Substituting the argon for the heavier xenon gas, greatly increases the collision energy. A normal MS/MS spectrum would typically show several major fragments of structural significance. However, the spectrum in Figure 6-23 shows the complete destruction of the trimer. This only occurred under the severest collision conditions, further indicating the stability of the cyclic trimer.

The other intense peak seen in the L$^2$TOF mass spectrum of the DMF soluble fraction of poly(indole) is at m/z 573. This is 12 Da. short of the mass of five indole monomer units, and therefore most likely corresponds to a pentameric species. The relative intensity of the peak suggests that it is present in the DMF-soluble fraction at a high concentration. In order to determine whether the pentamer was a real species, and not an adduct formed in the mass spectrometer, Mackintosh performed TLC on the DMSO-soluble fraction. For this fraction, three bands were observed, unlike poly(I5CA) in which only two TLC bands were found. Two of these bands eluted up the TLC plate ($R_f \approx 0.3$) and the other band was not eluted ($R_f = 0$). The two bands eluted at $R_f \approx 0.3$ were completely soluble in DMF. Clearly therefore, the pentamer species is formed as a separate entity in the electropolymerisation event, and is observed in the L$^2$TOF mass spectra of the DMF-soluble fraction. Further confirmation of pentamer production during electropolymerisation is provided by the fluorescence excitation spectra [28]. The
Fig. 6-22: L$_2$TOP mass spectra of the DMF soluble fraction of poly(indole) obtained using 248 nm photoionisation.
Figure 6-23: FD MS/MS spectrum of the trimer of poly(indole) obtained using CID with xenon as the collision gas.

CHAPTER 6. LIGNANS OF INDOLE MONOMERS AND POLYMERS
pentamer has a distinctly different excitation spectrum from either that of the trimer or the polymer, which are very similar. This suggests that the polymer is formed from linked trimer units. At present, however, the role of the pentamer in the polymerisation event is unclear. The structure of this pentamer is still to be elucidated. Initial studies by L²TOFMS on a pure pentamer sample indicate the presence of a cyclic trimer as well as the pentamer. At this time it is not clear whether the sample was completely pure or whether the pentamer fragments to form the cyclic trimer. If the sample was pure, then the observed fragmentation pattern would indicate that the structure of the pentamer is based upon that of the cyclic trimer, although at present this is purely speculation.

Examination of the DMF-insoluble (DMSO-soluble) fraction of poly(indole) by L²TOFMS using photoionisation at 248 nm revealed the presence of the cyclic trimer at m/z 345, and only a very small pentamer peak at m/z 573. No fragment peaks below m/z 345 were observed and furthermore, no peaks indicative of an oligomer distribution at high molecular weight were observed. Again the overall intensity of the peaks in the spectrum was much reduced compared to the DMF-soluble fraction. This is indicative that the polymer is comprised of linked trimer, and possibly some pentamer, units, that fragment from the polymer chains during either the laser desorption or laser photoionisation events.

6.2.7 Co-Polymers

To date, no spectroscopic evidence has been obtained that indoles may be copolymerised using the electropolymerisation technique. Therefore, since the best polymer films were found to be produced by 5-cyano indole and indole-5-carboxylic acid, Mackintosh and Mount decided to co-polymerise these monomers. The two compounds were mixed in solution in a 1:1 ratio and electropolymerised at a potential of +1.64 V with respect to the reference electrode. As for the single component polymers, they obtained two fractions, namely a DMF-soluble (DMSO-soluble) fraction and a DMF-insoluble (DMSO-soluble) fraction. The DMF-soluble fraction was examined by L²TOFMS.
Figure 6–24a shows the soft ionisation mass spectrum of the DMF-soluble fraction of the co-polymerisation products obtained using photoionisation at 248 nm. Four intense molecular ion peaks are present corresponding to the four possible products. The two peaks at m/z 420 and m/z 477 correspond to the cyclic trimers of 5-cyano indole and indole-5-carboxylic acid, respectively. Their intensities are approximately in a 1:1 ratio as expected; the discrepancy may be due to different absorption cross-sections for the trimers. The two central peaks at m/z 439 and m/z 458 are separated from each other, and the homo trimers, by 19 amu (the difference in mass between a CN group and a COOH group). These peaks correspond to the cyclic trimers formed from two (5-cyano indole) and one (indole-5-carboxylic acid) monomers and one (5-cyano indole) and two (indole-5-carboxylic acid) monomers, respectively. Since there are two ways of making these two co-polymers, then the intensity ratio of the four trimer peaks should be 1:2:2:1. This is indeed the approximate relative intensity ratio that is observed indicating that the composition of the trimers is statistical with respect to the monomers, i.e. there is no preference expressed for incorporating either of the indole monomers into the trimer. Further electrochemical and spectroscopic studies are being carried out by Mackintosh and Mount in order to determine the properties of these co-polymer products.

Figure 6–24b shows the L^2TOF mass spectrum of the same DMF-soluble fraction obtained using higher ionisation laser power density. Fragmentation can now be seen from the cyclic trimers, via loss of the side groups as is observed for the homo polymers. However, complete fragmentation to the bare indole trimer is not observed at this laser power density. At least one fragment is observed from each of the four cyclic trimer species. These are tabulated in Table 6–6. From the 5CI trimer, only one fragment is observed, corresponding to loss of one CN side-group whereas, the trimers formed by co-polymerisation and the 15CI trimer all show loss of two side-groups. Fragmentation by loss of a CO_2 group is easier than loss of a CN group (as is observed in the spectra for the homo polymers) and therefore these fragments are observed as the dominant daughter ion peaks in the mass spectrum.
Figure 6-24: L_2 TOF mass spectra of the DMF soluble fraction of the co-polymerisation products of 5-cyano indole and indole-5-carboxylic acid obtained using photoionisation at 248 nm ionisation under (a) soft and (b) hard ionisation conditions.

(a) (5Cl)_3 420
(b) (5Cl)(I5CA) 439
(c) (5Cl)(I5CA)_2 458
(d) (I5CA)_3 477
|   |             | Table 6-6: Fragment ions observed from the cyclic trimers of A - (5-cyano indole)$_3$, B - (5-cyano indole)$_2$(indole-5-carboxylic acid), C - (5-cyano indole) (indole-5-carboxylic acid)$_2$, D - (indole-5-carboxylic acid)$_3$. data taken from Figure 6-24b. |
Figure 6-25: Structure of the asymmetric cyclic trimer for the indoles studied. R = COOH, CN, H, or Cl. Only for R = COOH and CN have the structures been confirmed by NMR.

6.2.8 Concluding Remarks

From the data presented in this section, it is clear that L²TOFMS is an excellent technique for the analysis of electropolymerised indoles. In each case, for the low molecular weight fractions (usually DMF-soluble), using either 193 nm or 248 nm photoionisation very simple spectra containing an intense molecular ion signal, indicative of a cyclic trimeric species were obtained; no contamination due to background electrolyte species present in the sample was seen. This cyclic structure for the trimer, shown in Figure 6-25, has been confirmed by NMR by Reid et al. [25] as asymmetric for 5-cyano indole and indole-5-carboxylic acid. The evidence suggests that a similar asymmetric cyclic structure is formed in all cases.

Fragmentation from the trimers occurs via the sequential loss of the three side groups to form the stable unsubstituted indole trimer at m/z 345. In the case of indole-5-carboxylic acid, these carboxyl side groups are easily removed under soft ionisation conditions. For the trimer of 5-cyano indole, cleavage of the side-group is a much more difficult process, and even under hard ionisation conditions, loss of more than one side-group is rarely observed.
The high stability of the unsubstituted indole cyclic trimer, inhibits fragmentation of this species. This can be seen from the hard ionisation spectra for the indole-5-carboxylic acid trimer and the indole trimer, where no fragment peaks below m/z 345 are observed in the spectra. Moreover, in FD MS/MS studies of the indole trimer using CID with argon as the collision gas, no structurally significant fragments were observed under normal conditions. Changing the collision gas to xenon, only resulted in complete destruction of the trimers.

The structure of the pentamer species, observed in the spectra of poly(indole) itself and, to a lesser extent poly(5-chloro indole), and its role in the polymerisation process has still, however, to be elucidated. A recently recorded L²TOF mass spectrum of a purified pentamer fraction of poly(indole), revealed the presence of a cyclic trimer peak at m/z 345 [29]. One possible explanation is that the pentamer structure is based upon a central trimer core and that it fragments via loss of a cyclic trimer. Alternatively the sample may not have been 100 % pure and the residual trimer in the fraction was detected. Hopefully, future FD MS/MS studies may be able to help elucidate the structure of this species.

The mass spectra recorded for the DMF-insoluble fractions generally only showed evidence of cyclic trimeric species, at a much reduced overall intensity. This could be taken to indicate that the larger polymers are formed from linked trimer units, with trimers appearing as the dominant daughter ion fragments of these larger polymer chains. Additional mass spectrometric information together with data from other spectroscopic and electrochemical techniques will be required in order to confirm this hypothesis.

The co-polymerisation products of 5-cyano indole and indole-5-carboxylic acid have been successfully characterised by L²TOFMS. This is the first evidence for copolymers being formed electrochemically from more than one indole monomer. To date, no other evidence for their existence exists and further work on their electrochemical and spectroscopic properties is required. Clearly, there is great scope for the preparation of novel conducting polymers based upon the co-polymerisation technique. L²TOFMS will undoubtedly remain an important technique for the
analysis of these novel compounds which are of considerable potential commercial interest.

Further mass spectrometric studies of these electropolymerised indoles are clearly necessary in order to try and ascertain some of the answers to questions left unresolved in this initial work. For example these studies will require an improvement in the mass range, resolution sensitivity and mass accuracy for characterisation of the higher molecular weight polymeric species, already seen in the electropolymerisation products of indole and 5-chloro indole, such as the pentamers. In this context, the ability to perform tandem time-of-flight mass spectrometric studies using LDMS would be an important advancement, enabling perhaps the determination of the fragmentation pathways in the pentamer and ultimately its structure.

As described in Chapter 3 and further exemplified by the results presented in Chapters 4 and 5, the removal of the entrainment stage results in a very large improvement in the sensitivity of L²TOFMS. This enables much smaller sample sizes to be examined. One particular advantage, in the context of the present studies on the characterisation of these electropolymerised indoles, has been the ability to examine the products formed after derivatisation or chemical functionalisation of the indole trimers or polymers, where often only a small amount of sample is recovered. The use of small desorption laser spot sizes would also enable the examination of these compounds directly from the TLC plates, a technique that would be of major importance in further studies of the co-polymers.
Bibliography


Chapter 7

Vacuum Ultraviolet (VUV) Ionisation

7.1 Introduction

Laser photoionisation has been used in conjunction with mass spectrometry for a number of years. A variety of ionisation schemes have been employed as discussed in Chapter 2. They all broadly fall into one of two categories namely multiphoton ionisation (MPI) or single-photon ionisation (SPI). Multiphoton ionisation has many unique properties, the most notable being the high optical selectivity and the control that is possible over the degree of fragmentation.

One drawback of the MPI technique is that only molecules which have a large absorption cross-section at the photoionisation wavelength employed (normally in the UV) may be photoionised efficiently. This criterion restricts the use of MPI to aromatic molecules which contain a UV chromophore. Fortunately, the majority of compounds of interest to the analytical chemist or mass spectroscopist are either aromatic in nature or contain a suitable aromatic chromophore.

Increasingly, however, the analysis of non-aromatic and/or inorganic species is required and it would be useful to be able to generate intense, soft ionisation mass spectra using a laser based ionisation method in a similar manner. Since non-aromatic species generally do not contain a suitable UV chromophore, MPI using UV wavelengths is not a suitable technique. The most efficient photoioni-
sation method for these types of molecule is direct photoionisation with vacuum ultraviolet (VUV) radiation using a SPI scheme.

The VUV region of the electromagnetic spectrum extends from 200 - 0.2 nm [1]. As the name VUV suggests, radiation with such short wavelengths can only be propagated through a vacuum (or purged beam path) since it is strongly absorbed by oxygen in the air. The VUV wavelengths employed for photoionisation in most mass spectrometric studies are typically around 120 nm, corresponding to photon energies of around 10 eV. At these energies, most organic molecules and metal atoms can be one-photon ionised.

The SPI process promotes ground state molecules directly to the ionisation continuum without accessing any intermediate electronic states. Consequently, the cross-sections for ionisation of different molecular species are generally of the same order of magnitude. This makes SPI a less selective ionisation method than MPI for analytical analysis [2]. However, this loss of ionisation selectivity is offset by the fact that SPI provides an improved method for quantitation of unknown molecules since the absorption cross-sections at VUV wavelengths are relatively similar so that the ion yield is a much truer reflection of the concentration of the neutral precursors. Furthermore, since the ionisation efficiency using VUV radiation is high, then only low photon intensities are required. As a consequence, two-photon (or higher) absorption processes do not play a major role and the degree of fragmentation observed in the resulting photoionisation mass spectra is generally low; in the main only molecular ion species are detected.

Because of these features, photoionisation with VUV radiation can be considered to be a ‘universal’ ionisation method. No detailed knowledge of the electronic spectra of the molecular species under investigation is required, as is the case for resonantly enhanced MPI. This is a major advantage, particularly when no prior knowledge of the compounds or mixtures of compounds present in the sample under investigation is available.

As mentioned earlier, the use of VUV radiation in mass spectrometric studies dates back many years. In 1956, Lossing and Tanaka [3] used a krypton discharge lamp for the photoionisation of selected alkanes using 123.6 nm and 116.5 nm
(10.03 eV and 10.64 eV) radiation. They observed mostly parent molecular ion peaks for these compounds. Their early results demonstrated that light could be used as an ionisation source in mass spectrometry.

This pioneering work was soon followed by a more comprehensive study by Steiner et al. [4]. They dispersed the radiation from a hydrogen discharge lamp using a monochromator to examine the photoionisation mass spectra of a series of alkanes. By recording the mass spectra as a function of VUV wavelength, they were able to obtain ionisation efficiency curves for the species studied, enabling the determination of the ionisation potentials for these species and also appearance potentials for fragment ions. They demonstrated that SPI yielded a high abundance of molecular ions from saturated hydrocarbons. Similarly, Arimura and Yoshikawa [5], in much more recent studies, have used a hydrogen discharge lamp to obtain the VUV photoionisation efficiency curve and appearance potential for the more complex molecule \( N,N \)-dimethylformamide and its fragment ions.

VUV radiation continued to be generated using discharge lamps until, in 1973, Kung et al. [6,7] reported the successful generation of VUV radiation at 118.2 nm by frequency tripling the third harmonic output (355 nm) of a Nd:YAG laser. They achieved this by means of gas cell containing a phase-matched mixture of Xe and Ar, into which the laser was focused. Using this set-up, they achieved a conversion efficiency of 2.8 %. Zare et al. [8] subsequently published a further instrumental modification for VUV and extreme UV (XUV) generation. Instead of focussing the laser beam into a gas cell, the laser radiation was focused into a pulsed free jet supersonic expansion of xenon. In this manner, greater conversion efficiencies and higher order frequency generation could be obtained.

The use of laser generated VUV radiation for photoionisation in mass spectrometric studies has been quite limited. Indeed, relatively few articles have been published using this ionisation method compared to ionisation by MPI using UV radiation. There are, however, several experiments where soft, non-selective laser ionisation is desirable. For example, Welge et al. [9,10] have identified neutral products of unimolecular decomposition reactions induced by infrared laser ra-
CHAPTER 7. VACUUM ULTRAVIOLET (VUV) IONISATION

They examined several compounds and used 118.2 nm (10.5 eV) VUV radiation for the blanket ionisation of all species.

The majority of VUV photoionisation experiments have involved direct introduction of volatile samples into the ionisation region of the mass spectrometer. For example, Arps et al. [11] used SPI for the analysis of mixtures of volatile organic compounds. In each case, the most intense peak in the spectra obtained corresponded to the molecular ion.

In a similar manner, Kistemaker et al. [12] have studied the VUV photoionisation mass spectra of a series of hexane isomers. They compared the fragmentation of hexane as a function of temperature with predictions from quasi-equilibrium theory. In each case little or no fragmentation was observed at room temperature and molecular ions dominated the spectra. However, at elevated temperatures, the degree of fragmentation observed in the VUV photoionisation mass spectra was significantly increased.

Van Bramer and Johnston [13] have carried out the most comprehensive study to date of aliphatic molecules from many compound classes containing six to eight carbon atoms. They showed that n-alkanes, alkenes, ketones, carboxylic acids and esters formed predominantly molecular ions, whilst the spectra for aldehydes and amines showed strong molecular ion peaks but also extensive fragmentation. Branched-chain alkanes, alcohols and esters gave either very weak or no molecular ion peaks but commonly exhibited a single dominant fragment peak. In a further study [14], these authors generated tunable VUV radiation over the wavelength range 118 - 129 nm (10.5 - 9.6 eV) and recorded photoionisation mass spectra for the same compound classes. For those species which previously had not yielded intense molecular ion peaks, it was found that molecular ion peaks could be obtained when photoionisation wavelengths close to the ionisation thresholds were employed.

Studies involving the use of VUV radiation to photoionise desorbed neutral molecules, using an \( L^2 \)TOFMS type methodology have been less common. Becker et al. [2] have employed Ar\(^+\) ion beam bombardment as a means of desorbing neutral molecules followed by postionisation with 10.5 eV (118.2 nm) VUV radiation.
to record SPI mass spectra for a series of organic species, which had shown little or no signal when using UV MPI photoionisation; ionisation using VUV radiation, however, gave intense spectra. In more recent work [15], they used this approach to examine a series of non-aromatic and aromatic polymers and obtained characteristic and readily interpretable mass spectra for the bulk polymer samples. They have also used SPI to determine the effects of desorption technique upon the molecular fragmentation of two test biomolecule compounds [16]. Recently, Köster and Grotemeyer [17] have recorded SPI mass spectra for a series of biomolecules using infrared laser desorption with subsequent postionisation by 10.5 eV (118.2 nm) VUV radiation. They compared the mass spectra to those obtained previously using a multiphoton ionisation scheme and found that unique information about the ionisation process could be obtained.

It is clear that VUV photoionisation is a powerful technique that can be used effectively in conjunction with mass spectrometry. In the following section, a brief outline of the theory behind the generation of VUV radiation at 118.2 nm via frequency tripling of 355 nm laser radiation is given. This is followed by a description of the frequency tripling cell designed and built in Edinburgh. Finally the performance characteristics of the tripling cell are presented together with some initial results on the SPI mass spectra of poly(ethylene glycol) PEG 600.

7.2 Theory

The theory behind third-harmonic generation has been discussed in detail by Bjorklund [18] and Mahon et al. [19]. In simple terms, when the incident radiation (355 nm third harmonic output from the Nd:YAG laser) is focused into a cell containing the nonlinear medium (xenon gas), a collinear third-harmonic beam (118.2 nm VUV radiation) is generated. Conversion takes place mainly near the focus of the incident beam where the photon density is sufficiently high. In order to produce the third-harmonic radiation, three photons have to be added together. This is shown schematically in Figure 7-1. The momentum of the
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Figure 7-1: Vector diagrams showing the addition of three 355 nm photons, wave vector \( \vec{k}_1 \), to produce one 118.2 nm VUV photon, wave vector \( \vec{k}_3 \).

Photons is given by

\[
\vec{p} = h \vec{k}
\]

(7.1)

where \( \vec{k} \) is the wave vector with length given by

\[
k = \frac{2\pi n \nu}{c}
\]

(7.2)

where \( n \) is the refractive index in the medium at the frequency of light \( \nu \) and \( c \) is the velocity of light in vacuum. Conservation of momentum requires that

\[
k_3 \vec{e}_4 = k_1 \vec{e}_1 + k_1 \vec{e}_2 + k_1 \vec{e}_3
\]

(7.3)

where \( k_1 \vec{e}_{1,2,3} \) are the wave vectors of the incident radiation with frequency \( \nu_1 \) and \( k_3 \vec{e}_4 \) is the wave vector of the frequency tripled radiation of frequency \( \nu_3 \). Since the incident radiation is focused, then the three unit wave vectors, \( \vec{e}_i \) will have slightly different directions. Consequently,

\[
k_3 < 3k_1
\]

(7.4)

as shown in Figure 7-1. The difference

\[
\Delta k = k_3 - 3k_1
\]

(7.5)

is called the phase mismatch.
Energy conservation requires that

$$\nu_3 = 3\nu_1$$

(7.6)

therefore, in order to conserve momentum

$$n_3 < n_1$$

(7.7)

i.e. the refractive index must be lower for the generated third-harmonic wavelength than the incident wavelength. This effect is called ‘negative dispersion’ and it occurs only in specific regions of the spectrum, near an allowed dipole transition. In the case of xenon, negative dispersion occurs near 118.2 nm [19].

The power of the generated third-harmonic radiation, $P_3$, is given by the expression

$$P_3 \propto N^2 |\chi^{(3)}|^2 P_1^3 F(b\Delta k)$$

(7.8)

where $N$ is the number density of Xe, $\chi^{(3)}$ is the third-order nonlinear susceptibility at $\lambda_3$, $P_1$ is the incident laser pump power and $F(b\Delta k)$ is a phase matching function, which depends on the confocal parameter, $b$, and the wave vector mismatch $\Delta k$. The confocal parameter, $b$, is defined as

$$b = \frac{2\pi w_o^2}{\lambda}$$

(7.9)

where $w_o^2$ is the diffraction-limited beam waist radius and $\lambda$ is the wavelength in the non-linear medium. The diffraction limited beam waist radius is given by the expression

$$w_o = \frac{1.22\lambda f}{D}$$

(7.10)

where $f$ is the focal length of the lens used to focus the incident 355 nm laser radiation and $D$ is the diameter of the incident laser beam on the lens.

Under tight focussing conditions, where $b$ is short in comparison to the length of the cell and the entire focal region is contained within the cell, $F(b\Delta k)$ is non-zero only when $\Delta k$ is negative, i.e. only when the medium is negatively dispersive. Only under these conditions can third-harmonic radiation be generated.

The parameters $P_1$, $F(b\Delta k)$, and $N$ must be optimised to maximise the third-harmonic power at a given wavelength. $|\chi^{(3)}|^2$ is determined by the wavelength
and gas used for harmonic generation, and is essentially a constant. The upper limit of $P_1$ is determined by the onset of Kerr-induced dispersion [20] and dielectric breakdown. Zych and Young [20] calculated this limit to correspond to an irradiance of ca. $10^{12}$ Wcm$^{-2}$ at the focal point, for xenon gas. The parameter $b$, is fixed by the optical system. However, $F(b\Delta k)$ can be optimised by adjusting $\Delta k$. Since $\Delta k$ is the product of the wave vector mismatch per atom and the number density of the gas, it can be optimised by adjusting the pressure of the gas in the cell. An alternative method of adjusting the value of $\Delta k$ is by mixing a second, ‘positively dispersive’ gas with the negatively dispersive third-harmonic generation medium.

Optimisation of $\Delta k$ by adjusting the pressure of the third-harmonic generation gas (xenon) is simple, but the conversion efficiency is low since $N$ is dependent upon the optimisation of $\Delta k$. When a positively dispersive gas such as argon is mixed with the xenon, $\Delta k$ is adjusted and $N$ can be increased while the positively dispersive gas compensates for excess negative dispersion. Although this method is more involved, it has the advantage that $N$ and $F(b\Delta k)$ can both be optimised, thereby increasing the amount of incident radiation that is frequency tripled.

From the above discussion, it is clear that VUV generation via frequency tripling is a relatively simple process and, as a consequence, a VUV tripling cell was constructed which could be used in conjunction with the L$^2$TOFMS apparatus. In the initial work presented here, frequency tripling in xenon was employed in order to generate preliminary data. In future studies, a phase-matched xenon/argon gas mix will be used to generate higher VUV photon fluxes. The following section describes the tripling cell that was constructed.

### 7.3 Apparatus

The mass spectrometer and laser systems have been described in detail in Chapter 3. The third-harmonic wavelength of the Nd:YAG laser at 354.7 nm (355 nm) is frequency tripled in a xenon gas cell to yield 118.2 nm (10.5 eV) VUV radiation.
This VUV radiation enters the ionisation chamber of the mass spectrometer along the same beam path as that for the UV laser radiation more commonly used for recording MPI mass spectra. Figure 7-2 shows a schematic diagram of the tripling cell.

The cell consists of a 280 mm long stainless steel tube with o.d. 25.5 mm and i.d. 20 mm. One end of the tube is welded to a stainless steel flange, 62 mm dia., on which a standard 50 mm diameter Spectrasil B UV window is mounted. The window is held in place by a delrin ring which is secured by six screws. The vacuum seal is made by two O-rings, one on each side of the window.

Close to this end of the tube, three gas ports (1/4" dia. s/s tube) are mounted 120° apart. A fourth port, mounted equidistant between two of these, is attached to a 1/8" dia. s/s tube which is spot welded to the inside of the main tube. This 1/8" dia. tube runs along the entire length of the inside wall of the gas cell and is designed to allow continuous circulation of the gas via one of the other 1/4" dia. gas ports. All the gas ports are terminated by Cajon VCO fittings. The xenon (and argon) gas supply line and vacuum pump for evacuating the cell are attached to one of the 1/4" dia. ports, whilst another is attached to an Edwards total pressure transducer (Model EPS10) and digital controller (Model EMV 251). The other two gas ports, are sealed by Cajon VCO blind nuts when the gas recirculating system is not in use.

Approximately 60 mm from the flange carrying the window, the tube is welded through the center of a standard 70FC conflat flange (Vacuum Generators). This allows the entire cell to be mounted on an XYZ translator (Vacuum Generators Model XYZ75) which permits fine adjustment of the position of the VUV beam within the ionisation region of the mass spectrometer.

The opposite end of the 1" dia. tube is connected to a stainless steel flange assembly which houses a 38 mm dia. MgF₂ lens (Crystran Ltd.). The flange assembly consists of two parts. The first, a 48 mm dia., 6.5 mm thick stainless steel ring with a 26 mm dia. hole in the center. This is attached by three screws to a second 48 mm dia. 14 mm thick stainless steel ring, which holds the MgF₂ lens. A circlip, located between these two rings prevents the lens holder from slipping
VACUUM SIDE

Standard 8" o.d. flange

1/8" dia. tube welded to inner wall of main tube

AIR SIDE

Fused Silica UV window
50 mm dia.

70 FC Flange welded to 1" dia. tube

1" dia. tube

3 gas ports
1/4" dia. tube welded
CAJON VCR fittings
120 degrees apart

1/8" dia. tube

VG XYZ translator
Model XYZ75

38 mm dia. MgF₂ lens

30 mm focal length in VUV
off the end of the 1" dia. tube. The ring holding the MgF₂ lens is sealed against the 1" dia. tube by means of a compression O-ring seal. The lens is plano-convex and has a 30 mm focal length at 118 nm. The lens itself is sealed against an O-ring in the first stainless steel ring, providing a gas-tight seal for the tripling cell. By constructing the lens flange assembly in this modular manner, it can be easily removed from the end of the 1" dia. tube. This enables the entire tube to be removed from the XYZ translator by simply disconnecting the 70FC conflat flange which mates to the translator. This allows the same translator to be employed for sample manipulation in the ionisation chamber when the instrument is being used in the non-entrainment mode of operation.

The entire VUV cell and XYZ translator is attached to a standard 8" o.d. stainless steel flange which is mounted to the side of the ionisation chamber. The 355 nm laser radiation is steered into the cell using standard UV prisms and the beam is irised prior to being focussed with a 50 cm focal length lens.

Two different geometries can be used, either with collinear overlapping 118 nm and 355 nm beams or with the beams spatially separated. In both cases, the 118 nm and 355 nm beams are focused at different positions along the same axis, as shown schematically in Figure 7-3. The first geometry is the simplest to align. However, with this geometry it is possible for the VUV ionised molecules to further absorb the 355 nm laser radiation leading to UV induced fragmentation. In practice, this collinear method has been altered such that the exiting 355 nm beam is slightly divergent, instead of being focused as shown in the diagram. This has the advantage of lower 355 nm photon density at the 118 nm focus. The alternative method in which the 355 nm and 118 nm beams are focused at different positions along the axis is preferable, although the alignment in this case is more difficult.

The initial experiments described below were performed using a collinear beam set-up. To simplify the experiment further, the sample was directly introduced into the ionisation chamber by means of a simple flow system. This consisted of a length of flexible tubing connected to a reservoir containing a volatile sample. The flow rate into the ionisation chamber was controlled by means of a Nupro needle valve. The pressure in the ionisation chamber was monitored using a standard
Overlap of the 118 nm and 355 nm beams at the 118 nm focal point.

Separation of 118 nm and 355 nm beams at the 118 nm focal point.

Figure 7–3: Schematic diagram showing the laser beam geometries for VUV generation.
Penning gauge and controller. Later experiments were carried out using molecular beam entrainment of the volatile samples and finally CO\(_2\) laser desorption, coupled with molecular beam entrainment was used to examine a sample of poly(ethylene glycol).

### 7.4 Results and Discussion

Initially, in order to verify that VUV radiation was being generated, the test compound \(n\)-hexane was placed in the sample reservoir and the vapour allowed to slowly leak into the ionisation chamber of the mass spectrometer. The pressure in this chamber rose from the base pressure of \(1 \times 10^{-7}\) mbar to \(8 \times 10^{-6}\) mbar. The incident 355 nm laser radiation was appertured to 8 mm using an iris, and the xenon pressure in the VUV cell was 33 mbar. Under these conditions, the mass spectrum shown in Figure 7-4 was obtained following the accumulation of 100 laser shots. This soft ionisation mass spectrum shows an intense molecular ion peak at \(m/z\) 86, the \(^{13}\text{C}\) isotope peak at \(m/z\) 87 and a third peak at \(m/z\) 84, which corresponds to loss of H\(_2\). This \(m/z\) 84 peak has been observed before in the soft VUV ionisation mass spectrum of \(n\)-hexane [12]. No low mass fragment peaks are observed, which would be characteristic of further absorption of 355 nm photons. In order to be sure that the ion signals were generated exclusively from 118 nm VUV radiation, the xenon gas was pumped out of the cell and, under identical UV conditions, no signals were observed.

Characterisation of the VUV conversion efficiency was carried out to ascertain the optimum xenon cell pressure for a range of different UV laser powers (which correspond to different iris diameters). In these experiments, acetone was employed as the test compound. For a constant pressure of acetone in the ionisation chamber and constant UV laser power, the xenon pressure in the cell was varied. At each pressure, the intensity of the molecular ion peak of acetone was recorded. Figure 7-5 summarises the results obtained. The experimental data is shown by the symbols for each laser power and the solid line is a best fit curve to the experi-
Figure 7-4: VUV photoionisation mass spectrum of n-hexane. VUV conditions: iris dia. 8 mm, 33 mbar xenon.

Relative intensity / arb. units

mass / Da.

M+ n-hexane
Figure 7-5: VUV conversion curves showing the variation of generated VUV radiation with xenon pressure at constant UV laser power. The experimental points correspond to the intensity of the molecular ion peak of the test compound acetone, which was maintained at constant pressure in the ionisation region.
mental data. From Figure 7-5, it is clear that as the iris diameter is increased and more UV radiation is allowed to enter the tripling cell, then the optimum xenon pressure for that UV laser power increases and more VUV radiation is generated.

Having obtained intense VUV photoionisation mass spectra from volatile species introduced directly into the ionisation chamber, the next experiment attempted involved the generation of VUV photoionisation mass spectra from jet entrained species. The vapour from several volatile species was entrained in helium prior to supersonic expansion through the nozzle in the desorption chamber. This supersonic molecular beam was skimmed before entering the ionisation chamber where it was ionised by the VUV radiation. Using this set-up, the mass spectrum shown in Figure 7-6 was obtained.

Five different volatile compounds, namely acetone, n-hexane, toluene, aniline and n-octane were examined, with molecular weights of m/z 58, 86, 92, 93 and 114 respectively. Intense molecular ion peaks for all these compounds can be seen in Figure 7-6. In general, the relative intensity of the peaks represents the relative amount of each species present in the molecular beam, although these values would have to be corrected by the partial vapour pressure of each compound to determine the ratio of each in the reservoir.

No additional fragments are observed in the mass spectrum for any of these species. This is a particularly important point since n-octane fragments easily following the absorption of a 355 nm photon after 10.5 eV ionisation [17]. This compound can therefore be used to determine whether the alignment of the 118 nm and 355 nm beams is critical. Clearly since no fragments are observed, then, in this case at least, the collinear alignment of the two beams does not cause significant problems, i.e 355 nm fragmentation is not induced at the UV laser powers used.

The primary aim throughout this thesis has been to use the L²TOFMS technique for the identification and characterisation of polymers. The use of UV laser radiation for photoionising via multiphoton ionisation methods has restricted the field of analysis to polymers which contain a UV chromophore, i.e. those which
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Figure 7-6: VUV photoionisation mass spectrum of a series of volatile non-aromatic compounds obtained in entrainment mode. VUV conditions: iris dia. 7 mm, 25 mbar xenon.

Relative intensity / arb. units

mass / Da.

M⁺ acetone
M⁺ n-hexane
M⁺ toluene
M⁺ aniline
M⁺ n-octane
are aromatic in nature. Using VUV radiation as an ionisation source will clearly expand the number of polymer systems amenable for analysis.

As a first step towards the analysis of complex polymer systems, a low molecular weight poly(ethylene glycol) (PEG) sample was examined. This compound has the following structure

\[ H - [-O - CH_2 - CH_2 -]_n - OH \]

with oligomer masses which follow the formula \([44n + 18]\). The liquid PEG 600 sample was dropped into a slot in the stainless steel sample probe and a light dusting of alumina applied to prevent it from running out. The sample was desorbed using the Alltec CO\(_2\) laser followed by entrainment of the desorbed neutrals in a pulsed helium molecular beam. A 7 mm iris diameter and a xenon pressure of 28 mbar in the cell was employed for VUV radiation generation. Using this set-up, the mass spectrum shown in Figure 7-7 was obtained.

The most important feature in this spectrum is the series of intense peaks separated by \(m/z\) 44, the PEG repeat unit mass. These peaks begin at \(m/z\) 45 and extend to \(m/z\) 442, however, unlike the true oligomer distribution which have masses corresponding to the formula \([44n + 18]\), the peaks in this spectrum have masses corresponding to \([44n + 1]\), i.e. these are due to water loss from protonated adducts of the oligomers. This \([MH^+ - H_2O]\) series has been observed before [15]. Between this series of intense peaks lies a less prominent series of peaks with masses corresponding to the formula \([44n + 28]\). These peaks can be attributed to aluminium adducts of the primary series, the aluminium coming from the dusting of alumina applied to the sample. The most intense peak in the spectrum, at \(m/z\) 58, is due to acetone, which was present in the helium line to the pulsed valve.

The average molecular weight of this PEG sample is around \(m/z\) 600. The MALDI mass spectrum for the same sample [21] shows that oligomers are present in the sample ranging from \(n = 7\) to \(n = 22\), with the distribution peaking around \(n = 13\). Clearly the VUV ionisation spectrum does not reflect this distribution. This is thought to be due to fragmentation [15]. This fragmentation is unlikely to have been caused in the ionisation event since the VUV photon flux is so
Figure 7-7: VUV photoionisation mass spectrum of laser desorbed poly(ethylene glycol) (PEG) 600. VUV conditions: iris dia. 7 mm, 28 mbar xenon.
low. Instead it most likely arises from during desorption. Pallix et al. [15] have observed differences in the VUV ionisation mass spectra of PEG 1000 following ion beam sputtering and electron stimulated desorption. In the former case, non-specific fragmentation products were observed, whereas the electron stimulated desorption showed more specific fragmentation products. No peaks above m/z 180 were observed in either of the spectra. It is clear from the results presented here, that infrared laser desorption of PEG produces very specific fragmentation products which can be detected by VUV photoionisation. In addition, the laser desorption methodology produces larger fragment species than those produced by ion beam sputtering or electron stimulated desorption [15].

7.5 Conclusion

Coherent 118 nm VUV radiation can easily be generated by frequency tripling the third harmonic wavelength (355 nm) of an Nd:YAG laser in xenon. Radiation of this wavelength can then be employed for efficient, non-selective photoionisation of a wide variety of compounds in a time-of-flight mass spectrometer. The compounds most suited to this type of analysis are those that do not contain a UV chromophore, i.e. mostly non-aromatic species. It is also relatively easy to produce VUV generation efficiency curves which assist in the optimisation of the set-up parameters. The conversion efficiency in a single negatively dispersive gas such as xenon, is generally low, ca. 2 - 3 % max. However, higher VUV yields may be obtained by using phase-matched mixtures of xenon and argon. Due to this low conversion efficiency, VUV photon yields are generally low which facilitates soft ionisation of the species examined.

The VUV photoionisation mass spectra of a series of compounds with high vapour pressures were examined. For each species, only the molecular ion peak was seen in the mass spectrum. This is particularly significant for n-octane, where further absorption of a single 355 nm photon after 118 nm photoionisation readily induces fragmentation in the molecule. Since no fragments were observed, then it
can be concluded that the collinear alignment of the 355 nm and 118 nm radiation does not present significant problems at the laser fluences used.

VUV radiation is also a convenient photoionisation source for studying the mass spectra of laser desorbed species. One area of particular interest is the field of polymer chemistry where non-aromatic polymers can now be more easily studied. Examination of PEG 600 by this method, demonstrated that the oligomers fragmented in the desorption stage. Using UV radiation for photoionisation would not have highlighted these facts.

Clearly the use of VUV radiation for single photon ionisation in L$^2$TOFMS can only be beneficial. It not only provides an alternative ionisation method to the MPI schemes more commonly employed but, more importantly, it considerably expands the number and classes of compounds that may be studied using this novel mass spectrometric technique.
Bibliography


Appendix A

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. Mass spectrometry
2. UNIX I and UNIX II
3. Vued and Micro-emacs
4. $\text{LAT}_\text{E}X$
5. 'C' Programming Course
6. FORTRAN Programming Course

In addition, I have attended the Laser Chemistry research group meetings, departmental seminars, joint Edinburgh - Heriot-Watt and Edinburgh - Glasgow laser chemistry group meetings, and the following conferences:

1. 12$^{th}$ International Mass Spectrometry Conference (IMSC), Amsterdam, 1991.


5. 42\textsuperscript{nd} American Society for Mass Spectrometry (ASMS) conference, Chicago, USA, 1994. - poster presentation.

Appendix B

Publications


LASER PHOTOIONISATION TIME-OF-FLIGHT MASS SPECTROMETRY OF LASER DESORBED POLYCYCLIC AROMATIC HYDROCARBONS FROM CLOUD WATER AEROSOL FILTRATES

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) make up a significant fraction of the atmospheric aerosols of anthropic origin. These compounds arise from the combustion of fossil fuels (fuel-oil, coal, petrol etc.) and are abundant in aerosols derived from urban environments [1]. Aerosol materials can be translated over very long distances; they are found in a wide range of atmospheric media, such as oceanic media [2] and polar atmospheres [3]. In such zones, remote from pollution sources, they are mainly associated with particulate matter. As these compounds are mutagenic or carcinogenic their presence in such particulates represents a potential environmental health hazard [4]. The fine particulates can enter the respiratory system and be deposited in the lung. It is, therefore, of major importance to be able to assay for their polyaromatic components.

The most widely used analytical methods for the determination of PAHs are based on sample extraction and chromatographic separation followed by mass spectrometry [5]. However, due to the low volatility and the poor solubility of PAHs, the detectable mass range using GCMS is limited to around 300 amu. Furthermore, the low concentration of PAHs often requires that pre-concentration and purification steps are employed prior to analysis. The combination of all these procedures means that each analysis can take from hours to days to complete.

The technique of laser desorption laser photoionisation time-of-flight mass spectrometry (L^TOFMS) has previously been shown to circumvent many of the difficulties inherent in hydrocarbon analysis from environmental matrices [6,7]. A pulsed CO₂ laser is used to desorb the material under investigation as intact neutral species. A pulsed ultraviolet laser is then used to ionise these gas-phase species. Photoionisation is achieved via a resonance enhanced multiphoton ionisation (REMPI) process. PAHs are a class of compounds which can be efficiently ionised using REMPI and show virtually no fragmentation at low incident laser fluences.

The advantages of the technique are (i) laser desorption of the target molecules directly from their environmental matrices (in situ analysis), (ii) soft ionisation of the desorbed species leading to mass spectral simplification, (iii) semi-selective ionisation of target molecules possessing a significant absorption cross section at the chosen ionisation wavelength, and (iv) highly sensitive detection of PAHs. Therefore, it is possible to directly analyse trace quantities of target compounds, contained in complex mixtures, without recourse to time-consuming and expensive sample extraction, separation or preconcentration steps.

In the present work, we report the results of an investigation into the analysis of PAHs associated with the particulates contained in cloud water aerosols. The purpose of the investigation was to demonstrate the ability of L^TOFMS to determine the polyaromatic components of cloud water particulates directly from the bulk particulate matter.

EXPERIMENTAL

Collection and preparation of cloud water samples

The cloud water samples were provided by J NCape at the NERC Institute of Terrestrial Ecology, Pencsock, Midlothian. The cloud water collector consisted of a conical passive Harp-wire device strung with polypropylene filament (0.55 mm diameter) and draining to a polypropylene bottle [8]. A polypropylene faced lid 1200 mm in diameter was supported over the cloud collector to reduce rainfall contamination of the cloud water samples. This excluded raindrops larger than 0.5 mm in diameter at wind speeds up to approximately 5 ms⁻¹. A 100 ml sub-sample of each of the cloud water samples were filtered through a polycarbonate membrane (Nucleapore, Costar, U.K.). The membrane, loaded with solid particles, was dried to a constant weight in a vacuum desiccator over phosphorus pentoxide.

Mass spectrometric analysis of particulate material

The L^TOFMS instrument used in the experiments described here consisted of two differentially pumped vacuum chambers: the desorption/ionisation chamber and the reflectron time-of-flight mass spectrometer. A schematic of the instrument is shown in Figure 1.

The sample filters were attached to a Macor sample probe in the desorption/ionisation chamber. This probe was connected to an externally mounted XYZ vacuum-compatible manipulator to enable various locations on the sample filters to be interrogated. Sample desorption was carried out using a pulsed TEA CO₂ laser (Alltec 854MS). This was focussed to ca. 1 mm² using a 30 cm focal length NaCl lens. Typical desorption power densities were 2 MWcm⁻². The desorbed neutral molecules were photoinised directly above the surface of the sample. The sample probe ionisation laser separation was typically 5 mm. Photoionisation was performed using 193 nm laser radiation. This was generated using the ArF line of a Questek Model 2740 excimer laser. A typical ionising power density was ca. 1.3 MWcm⁻² at 193 nm. This power density was selected as it provided good detection sensitivity with minimum laser induced fragmentation of the molecular ions. The photoions were mass analysed using a reflectron time-of-flight mass spectrometer. The ions were...
detected using a tandem microchannel plate detector, the output of which was fed to a Joerger 200 MHz transient digitiser (TD).

RESULTS AND DISCUSSION

The LTOF mass spectrum obtained using 193 nm laser photoionisation is shown in Figure 2. This was obtained using a 40 ns sampling interval for the TD. This sampling frequency degrades the ultimate resolution of the mass spectrometer but enables a larger mass window to be examined in a single experiment. There are two principal regions of interest in the mass spectrum. At the low mass end, below 100 amu, there are a number of relatively intense peaks which correspond in mass to a number of metal cations. The masses 23, 27, 39 and 56 can be attributed to the presence of sodium, aluminium, potassium and iron in the sample. However, it is the higher mass region which is of more interest. Above mass 160 amu, all the notably intense mass peaks can be attributed to the molecular ions of parent PAH molecules. The signals at 202, 252, 276, 300, 326 and 350 amu can be assigned to pyrene, benzo[a]pyrene, benzo[ghi]perylene, coronene, dibenzo[a,ghi]pyrene, and benzo[a]coronene, or their isomers, respectively. The peak marked with an X is a background signal derived from the diffusion pump oil. The identities of the base peak, at 149 amu, and the relatively intense peak at 105 amu, are at present undetermined.

Figure 2 LTOF mass spectrum of PAH contaminated cloud water particulates obtained using 193 nm laser photoionisation

It is possible to achieve an improved mass resolution by changing the sampling interval on the TD to 20 ns. Doing this restricts the observable mass window but substantially increases the amount of information the mass spectrum contains. Figure 3 shows the mass spectrum obtained with improved resolution. Again background peaks are labelled with an X. Inset in this figure is an expansion of the region around mass 252. As in Figure 2, the major peaks again correspond in mass to PAH species. There are, however, a number of notable differences. In Figure 3, peaks are observed to higher mass than those in Figure 2. The highest assignable mass peak is observed at 448 amu. This can be attributed to benzo[a]pyrene and its isomers. Other assignable peaks are present at 374 and 424 amu, corresponding to dibenzo[a,abc]coronene and benzo-naphthocoronene, respectively.

A more detailed examination of the mass spectrum (see insert in Figure 3) reveals that there are other peaks present which can be related to PAHs, e.g. 252, 266 and 350 amu. It is possible that these peaks correspond to the presence of successively alkylated benzo[a]pyrene or its isomers. A similar series of peaks can be observed for other PAH parent skeletons, e.g. coronene at 314 and 328 amu.

It is clear from these mass spectra that LTOFMS has unique potential as a technique for screening aerosol particulates for their polyaromatic components. We have also demonstrated that laser desorption facilitates the analysis of the increasingly involatile and high mass components that cannot readily be examined by alternative techniques.

Figure 3 High resolution LTOF mass spectrum of PAH contaminated cloud water particulates obtained using 193 nm laser photoionisation (Insert: region from 248 to 290 amu)

REFERENCES


Determination of the structure of electropolymerized indole-5-carboxylic acid

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Abstract

The electropolymerization of indole-5-carboxylic acid leads to the deposition of a film on the electrode surface. Two different chemical species are deposited, and these can be separated by their differential solubility in dimethylformamide (DMF). These products have each been characterized by mass spectroscopy, UV—visible and fluorescence spectroscopy, IR spectroscopy and NMR spectroscopy. It is clear from these data that the DMF-soluble species is an electrodeposited trimer, whereas the species which is much less soluble in DMF or tetrahydrofuran, but is soluble in dimethylsulphoxide, appears to be a polymeric species made up of linked trimer units.

1. Introduction

Over the last 15 years, there has been considerable interest in the electropolymerization of heterocyclic molecules such as pyrroles, thiophenes and indoles to form electronically conducting polymers; these are of interest because of their wealth of potential applications [1,2]. However, to date the structural characterization of these compounds has been limited. This is chiefly because conducting polymer layers are typically inherently insoluble and intractible.

Polymer solubility is much greater if a pendant lyophilic functionality is present. A good example of this is a conducting polymer which contains pendant carboxylic acid groups. Bartlett and coworkers [3] have recently polymerized indole-5-carboxylic acid (Fig. 1). This compound is of particular interest, as they have observed a dependence of the polymer redox behaviour on the pH of the aqueous solution. Therefore they have proposed using this polymer as a fast-response pH sensor [4]. Furthermore, they have suggested that poly (indole-5-carboxylic acid) electrodes could also be used as a biological mediator for the direct oxidation and reduction of cytochrome c [5].

In this paper, we utilize this enhanced solubility to present results concerning the stuctural characterization of this polymer.

2. Experimental

All chemicals used in these experiments were of AnalAr grade or equivalent and were used as received unless otherwise stated. Electrochemical measurements were recorded using a Mininstat potentiostat (Sycopel), with a PPRI waveform generator (Hi-tek Instruments) and an x–y–t chart recorder (Bryans Instruments). The rotating-disc studies were performed using a motor controller supplied by Oxford Electrodes. A 2 cm² platinum gauze was used as a counter-electrode, with a 0.387 cm² rotating-disc electrode (Oxford Electrodes) as the working electrode. The reference electrode was constructed in house and consisted of a silver wire dipping into a solution of silver perchlorate (0.01 M) in background electrolyte solution. All potentials are reported with respect to this electrode, which has a potential of 0.437 V with respect to the saturated calomel electrode. The background electrolyte solution consisted of 0.1 M anhydrous lithium perchlorate (Aldrich) in acetonitrile (Fisons, dried distilled). Indole-5-carboxylic acid (ICA)
Fig. 1. Indole-5-carboxylic acid (ICA).

(Aldrich) was recrystallized twice from water and dried in an oven at 130°C for 2 days prior to use. N,N-di-
methylformamide (DMF) (Aldrich, 99%) and dimethyl-
sulphoxide (DMSO) (Aldrich 99 + % anhydrous) were 
used as received.

Polymerization experiments typically involved oxida-
tion of a 20 mM solution of ICA with the electrode at a 
potential of 1.46 V and rotating at 4 Hz. Steady-state 
conditions were reached within a few seconds, with a 
constant current being passed. Electropolymerization 
was generally terminated after 30 mC of charge had 
been passed in order to ensure a reproducible film 
thickness. The film was then removed from the elec-
trode and washed in background electrolyte prior to 
purification by extraction.

Thin-layer chromatography was performed on silica 
plates (Merck 60 F254 using 1:1 ethyl acetate + diethyl 
ether as the mobile phase with iodine vapour as devel-
oper.

The mass spectrometer system used in these studies 
has been described in detail elsewhere [6]. The mass 
spectra of the polymeric species were recorded using 
two-step laser desorption laser photo-ionization time-
of-flight mass spectrometry (L^2TOFMS). The sample 
was deposited onto a stainless steel rod by drop-coating 
the material in a suitable solvent followed by evap-
oration. A pulsed CO₂ laser (wavelength 10.6 μm) was 
used to vaporize the polymeric species as intact neutral 
molecules which were photo-ionized by multiphoton 
absorption using 248 nm laser radiation. In the 
L^2TOFMS technique, the desorption and entrainment 
steps are separated both spatially and temporally; this 
allows independent optimization of each process with 
respect to laser power and wavelength. The resulting 
ions were mass analyzed using a time-of-flight mass 
spectrometer [6]. The ions were detected by a mi-
crochannel plate detector and the signals were ampli-
fied then digitized with a Joerger TR200 (200 MHz) 
transient recorder. The data were processed using a 
Dell microcomputer connected to the spectrometer via 
a CAMAC interface.

UV–visible spectroscopic measurements were made 
using a Shimadzu UV-160A recording spectropho-
tometer, and fluorescence experiments were carried 
out using an LS-5 luminescence spectrometer (Perkin-
Spectra were recorded using 1 cm transmission cells with DMSO as solvent. IR spectra were collected on a Bio-Rad FT-S-7 FTIR spectrometer. NMR experiments were recorded using a 360 MHz spectrometer (Brücker) with $d_6$-DMSO as solvent.

3. Results and discussion

3.1. The solubility and purity of the electropolymerized film

Initial experiments on these electrodeposited films established their complete solubility in DMSO. Therefore we performed thin-layer chromatography (TLC) on the resulting solution. This revealed two fractions: one fraction was eluted up the TLC plate ($R_f = 0.3$) whilst there was a residual fraction which was not eluted ($R_f = 0$). However, on using DMF as solvent, incomplete dissolution of the polymer occurred; indeed, even after several washings with DMF, an insoluble fraction remained. TLC of this fraction gave a single spot with an $R_f$ value of approximately 0.3, and only the merest suspicion of a spot at $R_f = 0$. In agreement with our previous findings, the residual DMF-insoluble material was soluble in DMSO. Moreover, these two fractions also displayed similar differential solubility when THF was used as solvent.

These results indicate the presence of at least two different species in the electropolymerized film, which can be separated by their differential solubility in DMF (or THF); a DMF/THF-soluble (and DMSO-soluble) fraction, which in our TLC experiments has an $R_f$ of 0.3, and a DMF/THF-insoluble (but DMSO-soluble) fraction with an $R_f$ of zero. Neither of these can be unreacted monomer, as they are insoluble in acetonitrile. It is these fractions that we have isolated by extraction with DMF and have characterized spectroscopically.

3.2. Mass spectroscopy

A typical mass spectrum of the DMF soluble fraction is shown in Fig. 2. Multiphoton ionization of the neutral polymers ensures that the ions are singly charged; this means that the mass of the polymeric species can be measured directly. The largest peak is due to the parent ion and is observed at 477.4 atomic mass units (amu). Given that the molar mass of the monomer is 161.16 g, this is consistent with the species being a trimer. Furthermore this mass is exactly that which can be calculated for a trimer in which the indole monomers have coupled forming two new bonds and each losing two H atoms. This indicates a cyclic trimer. The other three peaks at lower mass are at 433.1 amu, 389.1 amu and 345.0 amu respectively; these correspond to fragmentation of the trimer ion by successive loss of CO$_2$ from one, two and three of the carboxyl side-groups respectively. The most likely mechanism is the dissociation of CO$_2$H followed by loss of CO$_2$ and recombination of the trimer and H* radicals. The calculated masses for these species are 433.4 amu, 389.4 amu and 345.4 amu respectively.

Therefore these results are consistent with the DMF-soluble species being a trimer consisting of three monomer units linked together in a ring. There is little evidence of fragmentation of the trimer unit in these studies or similar studies using higher-energy laser radiation (193 nm). Mass spectroscopy of the DMF-insoluble DMSO-soluble fraction gave a similar spectrum, with similar relative peak intensities, indicating the presence of a similar trimer unit in this fraction; however, the overall intensities observed are much reduced when compared with the DMF-soluble fraction.

3.3. UV–visible spectroscopy

Typical UV–visible spectra recorded for monomer and DMF-soluble and DMF-insoluble fractions of the film are shown in Fig. 3. The monomer shows a single absorption peak with a maximum at 280 nm. This peak is also present in the spectra of both the DMF-soluble and DMF-insoluble fractions; however, in both cases there are also additional peaks of comparable intensity with maxima at 305 nm and 320 nm and peaks of weaker intensity at 380 nm and 400 nm. Two conclu-
sions can be drawn from these data. First, these rich spectra with peaks at lower energy than the monomer are indicative of a greater degree of electronic delocalization in the electropolymerized species. Second, the close similarity of the spectra of the DMF-soluble and DMF-insoluble fractions indicates that the same chromophore is present in each case.

3.4. Fluorescence spectroscopy

Fluorescence spectroscopic measurements on the monomer showed a fluorescence maximum at 380 nm. The excitation wavelength for maximum fluorescence was found to be 330 nm; it is interesting that this does not correspond to the visible absorption maximum for the monomer, observed at 280 nm.

The spectra observed for the DMF-soluble and DMF-insoluble fractions were extremely similar, but markedly different from that of the monomer. Each showed very intense fluorescence, giving two peaks of roughly equal intensity with maxima at 420 nm and 435 nm. In contrast with the monomer, maximum fluorescence at these wavelengths was observed at excitation wavelengths of 280, 320, 380 and 400 nm, in close agreement with the wavelengths of maximum absorbance in the visible absorption spectra.

The essentially identical fluorescence spectra observed for both fractions indicate the presence of the same emitting chromophore in both species. Furthermore, the fluorescence excitation spectra indicate that this chromophore is excited by the same absorption transition in each case.

3.5. IR spectroscopy

Figure 4 shows IR spectra recorded in DMSO solution for the monomer and the DMF-soluble and DMF-insoluble fractions. Also shown is a reference spectrum recorded using DMSO. It is evident from these data that the spectra are rich in solvent peaks: however, the C=O stretch of the carboxylic acid side-groups at ca. 1650 cm\(^{-1}\) and a broad band at ca. 3500 cm\(^{-1}\) due to the O—H stretch of the carboxylic acid and the N—H stretch of the indole can clearly be seen. The C=O stretch of the monomer is centred at ca. 1690 cm\(^{-1}\), whereas for the DMF-soluble fraction it is at ca. 1650 cm\(^{-1}\). This indicates a greater degree of conjugation of the carbonyl into the indole π system for the DMF-soluble fraction. It is interesting that the C=O stretch observed for the DMF-insoluble fraction is at the same frequency as for the soluble fraction. This indicates that the carboxylate group is in a similar environment in the two fractions.

Turning to the bands at ca. 3500 cm\(^{-1}\), it is clear that the monomer and DMF-soluble fractions show similar absorbance intensities and peak positions. It is quite likely that some of this peak is due to the OH stretch of water in the DMSO; even so, this indicates

![Fig. 4. Typical IR spectra for (a) ICA monomer, (b) the DMF-soluble fraction and (c) the DMF-insoluble fraction of electropolymerized ICA in DMSO. Peaks due to the solvent are marked with an asterisk.](image-url)
that the carboxylic OH and indole NH groups have similar environments and concentrations in the two species. However, when we consider the DMF-insoluble fraction, we observe a band with the absorbance at and below ca. 3350 cm\(^{-1}\) much reduced in intensity. IR spectra of the monomer in Nujol gave a sharp peak at 3358 cm\(^{-1}\), which we have attributed to the N—H stretch of the indole [7]. Therefore these results are consistent with there being fewer indole N—H groups in the DMF-insoluble fraction than in the DMF-soluble fraction.

3.6. NMR spectroscopy

A typical NMR spectrum of the DMF-soluble fraction is shown in Fig. 5. A series of overlapping peaks are observed clustered around \(\delta 8.0, \delta 9.5, \delta 11.8\) and \(\delta\)

![Fig. 5. A typical NMR spectrum of the DMF-soluble fraction of electropolymerized ICA. Integrated peak areas are also shown.]

![Fig. 6. The structure of the trimer which is the DMF-soluble fraction of electropolymerized ICA. The three indole rings are labelled A, B and C, and the positions of the ring protons are numbered in accordance with the assignments of the NMR peaks in Table 1.]

**Table 1.** Chemical shifts and coupling constants for the \(^1\)H NMR spectrum of the DMF-soluble fraction and their assignment (Fig. 9)

<table>
<thead>
<tr>
<th>(\delta /\text{ppm} )</th>
<th>(J_{\text{HH}} /\text{Hz} )</th>
<th>Assignment (^b)</th>
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<tbody>
<tr>
<td>ca. 12.56</td>
<td>-</td>
<td>CO(_2)H</td>
</tr>
<tr>
<td>12.552</td>
<td>-</td>
<td>N—H (A)</td>
</tr>
<tr>
<td>11.866</td>
<td>-</td>
<td>N—H (B)</td>
</tr>
<tr>
<td>11.784</td>
<td>-</td>
<td>N—H (C)</td>
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<td>9.560</td>
<td>1.37</td>
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</tr>
<tr>
<td>9.495</td>
<td>1.60</td>
<td>H 4 (A)</td>
</tr>
<tr>
<td>9.488</td>
<td>1.60</td>
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<td>8.122</td>
<td>8.61, 1.37</td>
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<td>H 6 (C)</td>
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<td>7.904</td>
<td>8.52</td>
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</tr>
<tr>
<td>7.870</td>
<td>8.46</td>
<td>H 7 (A)</td>
</tr>
</tbody>
</table>

\(^a\) Error \(\pm 0.15\) Hz

\(^b\) Figures in bold show ring position. Letters in parentheses designate the indole unit in the trimer (see Fig. 6).
12.5. From the mass spectroscopic data, it is clear that this fraction is a trimer. The NMR data confirm this. We have integrated the peaks in these spectra to identify the number of protons which give rise to each peak, and in addition have performed nuclear Overhauser effect (NOE), correlation spectroscopy (COSY) and decoupling experiments on this sample to identify proton resonances and to probe through-space and through-bond coupling. These experiments are described in detail elsewhere [8]. The results of these experiments are explicable only if the structure of the trimer is as shown in Fig. 6. In this figure, we have labelled each indole unit (A, B, C) and the ring positions of the protons in each trimer unit. These labels have also been used in Table 1, where we attribute the observed δ values to particular protons.

NMR spectra recorded for the DMF-insoluble fraction show broad bands rather than peaks centred around the δ values observed for the trimer. This is consistent with this fraction being a polymer containing linked trimer units; these will not show narrow peaks as they will have hindered rotation and a range of chemical environments for each proton.

4. Conclusions

It is clear from the mass spectroscopy and NMR experiments reported in this paper that the DMF-soluble fraction extracted from the electropolymerized film is a trimer, with a structure as given in Fig. 6. The UV—visible and fluorescence spectroscopic spectra of this trimer show great differences from those of the monomer, with the appearance of absorption and fluorescence peaks at lower energy. These results are entirely consistent with the proposed trimer structure, as we would expect greater electronic delocalization compared with the monomer and hence smaller differences between electronic energy levels.

It is apparent that the DMF-insoluble fraction is chemically different from this free trimer. We have observed differences in solubility, in the NMR and IR spectra observed, and in our TLC studies. However, the UV—visible and fluorescence spectra indicate that a similar chromophore is present in each case, and the IR spectra indicate a similar C=O bond strength. Given that the NMR experiments indicate that this fraction is polymeric, the most likely explanation is that this polymer consists of trimer units coupled together. The IR spectra of the trimer and this polymer indicate that the polymer contains fewer indole N—H units; therefore it is plausible that, to a large extent, this linkage is via the indole ring nitrogens in the trimer.

Next we turn to the extent of delocalization in this polymer. By linking together trimer units, we can in principle gradually extend the degree of conjugation and hence the extent of electronic delocalization along the polymer chain. However, we would expect this to lead to differences between the UV—visible and fluorescence spectra of monomer and polymer as well as to differences in the observed C=O stretching frequency. As the carboxylic acid group is conjugated into the π system. This is not the case. Therefore it appears that, unlike other conducting polymers, this polymer consists of essentially localized trimer units with little delocalization between each. This could be because the trimer units are exclusively linked by N—N bonds, which would not be expected to allow significant conjugation between neighbouring trimer centres. However, our experimental evidence does not conclusively prove that linkage is exclusively N—N in character. The results may also be explained by the presence of other intertrimer bonds which could in principle allow conjugation between trimer centres. In this case, the lack of conjugation would be explicable if the trimer units were not coplanar, as this would preclude effective π bonding in the intertrimer bond.

Finally, we observe that there is little evidence for the presence of species other than trimer and polymer containing linked trimer units in the electropolymerized layer. This strongly suggests that the electropolymerization reaction involves the initial formation and deposition of this trimer species on the electrode, with coupling of the trimer to form polymer. This has been investigated electrochemically and is the subject of a further paper [9].

References