## Mass spectrometric studies of molecules using intense femtosecond laser ionisation

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

2012

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#### Abstract

University of Manchester Alessia Longobardo Doctor of Phylosophy Mass spectrometric studies of molecules using intense femtosecond laser ionisation 23/07/2012

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a sensitive technique used to analyse the molecular composition of solid samples using keV ion beam sputtering. However only a small fraction (typically  $< 10^{-3}$ ) of the desorbed material is secondary ions - the majority species (neutrals) cannot be extracted and detected by the mass spectrometer. To increase the sensitivity and efficiency of the SIMS technique, post-ionisation above the surface can be used. Lasers have been widely employed for molecular mass spectrometry due to the available high intensity, short pulse width, high spectral purity and spatial coherence that allow them to be highly focused. For molecular samples the challenge is to achieve efficient post-ionisation without inducing extensive fragmentation, which limits the diagnostic value of the resulting mass spectrum. An investigation was performed into the ionisation and dissociation characteristics of a series of organic molecules under the action of intense laser fields. This study is directed towards the analysis of biomolecules using laser post-ionisation. Here is reported progress towards the calibration of the experimental set-up and mass spectral data from representative biomolecules in the gas phase. In this work a Ti:Sapphire laser was used with fundamental wavelength of 800 nm and non-linear optical methods (OPAs) are used to extend the wavelength into the mid-IR region. System calibration is achieved using the ionisation of xenon atoms and comparing the results to established atomic tunnelling theory. This was followed by the analysis of representative organic and biological molecules to study ionisation-dissociation characteristics. The molecules chosen were toluene, acetone, nitroaniline and histamine. A clear transition in behaviour is observed favouring molecular ion production. This behaviour is discussed in the context of the underlying mechanisms, and the implications for molecular post-ionisation analysis using focused ion beams.

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## Acknowledgements

I want to thank all the persons who made this PhD work possible.

My supervisor Dr. Nicholas P. Lockyer, for transmitting me the passion for science and mass spectrometry, with patience and kindness.

Furthermore I am grateful to the SARC group, in particular Prof. John Vickerman, Dr. Alex Henderson, Dr. John Fletcher and the old and new PhD students, for the support and the amazing atmosphere created inside the group.

I would like to thank Dr. Alisdair Macpherson for supporting me with the work in the Photon Science Institute and also the EPSRC, Engineering and Physical Science Research Council for founding my PhD project.

Finally, my family, my husband and all my friends for always encourage me during my stay in Manchester and during my work.

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# Chapter 1

## Introduction

Bio-molecular imaging studies using mass spectrometry demand extreme sensitivity, high lateral resolution and depth resolution. Secondary ion mass spectrometry (SIMS) is an emerging technique for the analysis of single biological cell and whole tissues (1; 2). The limit of this technique lies in the low efficiency of ionisation and on the fragmentation which reduces sensitivity and prohibits the identification or the localisation of intact molecule with the highest possible spatial resolution. Postionisation methods offer a potential solution to this problem as discussed below.

### 1.1 Secondary ion mass spectrometry (SIMS)

Most of the surface analysis techniques involve the detection of radiation as a way to study the sample composition. Many techniques are used, including: ion scattering spectrometry (the bombardment of the sample surface by the ions produces the scattering of the secondary particles into the vacuum: the masses of the backscattered particles are identified by measuring their energy), electron/X-ray spectroscopy for chemical analysis (the sample is irradiated by electrons or X-rays, and its surface is analysed by the measure of the energy of the emitted photoelectrons). In the methods just explained, the sample surface is analysed by the detection of the backscattered particles. The secondary ion mass spectrometry (SIMS) technique, also uses the bombardment of the sample with an energetic ion beam, however the analysis of the sample surface depends on the secondary ions sputtered away from the sample.

Secondary ion mass spectrometry (SIMS) is an analytical technique for the analysis of the chemical composition of a solid sample (1; 3). This involves a beam of energetic ions (10-30 keV) that impact on a target producing secondary particles (3) (positive or negative ions and neutrals) by a process called sputtering (figure 1.1). The ion beam transfers energy and momentum on the target stripping off the uppermost atomic layers which, depending on the energetics of the process, breaks the chemical bonds of sputtered molecules (4; 5; 6).

In secondary ion mass spectrometry analysis are distinguished two methodologies: dynamic and static SIMS. These two modes are differentiated by the erosion rate of the surface, which depends on the ratio between the secondary ions yield over the damage cross section. Dynamic and static SIMS give different information about the structures of the sample (90) according to the different ion dose. The first method produces chemical destruction of the samples, since the high flux (mA) of primary ion current causes rapid erosion of the consecutive layers of the sample; the bombardment of the sample surface is done with a 10-30 keV energy primary ion beam and a high flux ( $\geq 10^{13}$  primary ions/cm<sup>2</sup>). To minimise the amount of material removed from the surface and to ensure that only the uppermost molecules or atomic layers are represented in the SIMS spectrum, Benninghoven (1970), at the University of Munster, developed the *static* SIMS method. The ion current densities are reduced down to  $10^{12}$ - $10^{13}$  ion/cm<sup>2</sup> as is also the ion flux (10 pA - 5 nA). In this case the sample analysed is subjected to minimal damage and each ion impacts a previously undisturbed region of the surface. The low primary ion dose required for static SIMS means that the high transmission ToF-MS is a good choice compared with other scanning mass spectrometers. The pulsed nature of the desorption in ToF-SIMS means that it is ideally suited to pulsed methods of post-ionisation e.g. laser SNMS. Other SNMS variants e.g. electron beam or electron gas are continuous methods, better suited to scanning MS (SIMS) instruments e.g. Quad SIMS. However, the sensitivity of these electron post-ionisation methods is rather low and they are not well-suited to molecular analysis.

#### **1.1.1** Secondary ion current equation

The electronic state of the sample surface (7, matrix effect) influences the emission of the secondary particles. This means that the secondary ion current of a given



FIGURE 1.1. Schematic diagram of the sputtering process.

species varies according to different target matrices. The secondary ion current (8) is quantified in the equation 1.1.

$$I_s^m = I_f \ y_m \ \alpha^+ \ \theta_m \ \eta \tag{1.1}$$

Considering a species m, the amount of the secondary ion current  $(I_s^m)$  depends on the primary flux  $(I_f)$ , the sputtering yield  $(y_m)$ , the ionisation probability  $(\alpha^+, \text{ which}$ for organic molecules is  $\approx 10^{-3}$ ), the fractional concentration of the species m in the surface layer  $(\theta_m)$  and the transmission of the analysis system  $(\eta)$ . The matrix effect acts through the variation in the ionisation probability of a given species.

### 1.1.2 Mass analyser in mass spectrometry: quadrupole and Time of Flight mass spectrometry

Mass spectrometry techniques uses a mass analyser to detect ions which are separated depending on the m/z values; following are described two mass spectrometry

methods: the quadrupole and the Time of Flight mass analyser.

The quadrupole analyser is made by four parallel electrode rods which are connected to a direct current (DC) and an alternating radio-frequency (RF) potential: opposing rod pairs are connected together electronically, while the RF potential allows the ions created to oscillate through the rods of the quadrupole. Most ions that travel along the trajectory collide with the rods and do not reach the detector; scanning the applied voltages enable ions of the selected m/z to have the "right" trajectory and pass to the detector. The advantages in using the quadrupole analysers are the low cost, small size and robustness, but importantly for surface analysis and imaging applications they are limited by the low transmission due to it's scanning nature and the detection of a limited mass range (13). To overcome the disadvantages of the quadrupole technique for molecular analysis, in this work is used the Time of flight mass analyser. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has proved to be a very effective technique for surface chemical characterisation of many different types of materials, in fact it improves the secondary ion mass spectrometry technique (8) by enhancing the efficiency of  $\sim 10^4 - 10^5$  signal and increasing the mass resolution  $m/\delta m > 4000$  (1). This comes from transmitting all ions to the detector regardless of their m/z up to a certain high mass value determined by the maximum acceptable flight time.

ToF-SIMS is a technique that involves the bombardment of a solid sample with a short pulse (in ns range  $\delta t_p$ ) of 'primary' ions (with energy of 5-25 keV); this produces the ejection of secondary particles including atomic/molecular ions/neutrals. An electrostatic field ( $U_{ac}$ ) accelerates the secondary ions into a flight tube where the ions are separated in time according to their different mass to charge ratio (velocity) before reaching the detector. The secondary ions (positive or negative) are extracted between two consecutive primary ion pulses and then accelerated into a field free drift region; their kinetic energy K is defined from the equation 1.2.

$$K = zU_{\rm ac} = \frac{1}{2}mv^2 \tag{1.2}$$

where:

- z is the ion charge ([z]=C);
- $U_{\rm ac}$  is the accelerating potential ( $[U_{\rm ac}] = V$ );
- m is the ion mass ([m] = kg);



FIGURE 1.2. Schematic representation of the time-of-flight mass spectrometer: a pulsed primary ion beam hits the target; the secondary ions ejected by the sputtering travel trough the time of flight analyser and then are acquired by the detector (111, Copyright ION-TOF GmbH).

• v is the flight velocity of ion ( $[v] = m s^{-1}$ ).

Lower m/z ions reach the detector before ones with higher m/z, because the latter have lower velocities. The mass of the secondary ions is determined by the flight time, as expressed in equation 1.3.

$$t = \frac{L}{\left(\frac{2eU_{\rm ac}}{m}\right)^{1/2}}\tag{1.3}$$

where L is the effective length of the flight tube ([L]=m).

The high transmission of Time of flight SIMS has the ability to produce high sensitivity chemical images and the analysis of samples in a depth profile.

For example, Nygren *et al.* (2007) (9; 10) analysed the fatty acid and phospholipids headgroups in the mouse intestine: the images are acquired by collecting the mass spectrum pixel by pixel by the focused primary ion beam that rasters across the sample surface (figure 1.3).

High mass resolution, high mass range, high spatial resolution and an excellent depth resolution of ToF-SIMS has enabled its application to many demanding analytical problems. In high resolution imaging experiment using liquid metal ion guns (LMIGs), the use of this technique was essential to produce a good analysis with the suppression of the background noise. The most inconvenient aspect of this technique regards the detection of the secondary ions subjected moreover to the matrix effect. In order to avoid this problem, the post-ionising (PI) of the neutrals offers potentially a very large increase of signal detected and also avoids the matrix effect and the ionisation is separated from the desorption mechanism, enabling some control over the molecular fragmentation.

#### 1.1.3 Objective of the research

The aim of the project presented here is the study of the improvements that the post ionisation laser could provide over the Time of Flight SIMS technique. An introduction of SIMS and ToF-SIMS technique is given in this chapter, where the reason for in using the PI ToF-SIMS technique over the ToF-SIMS is discussed. A wide explanation of the laser post-ionisation technique and theory is given is chapters 2 and 3.

The laser used in this work is a 50 fs Ti:Sapphire laser. The fundamental wavelength is 800 nm and non-linear optical methods (OPAs) are used to extend the



FIGURE 1.3. ToF-SIMS spectrum (a) and image (b) of the fatty acid and phospholipids headgroups in the mouse intestine. The spectrum is of the intestinal crypt region, and there is an high signal for the m/z 241, the phosphoryl inositol (PI) head group; Nygren *et al.* (9, Copyright 2007 Elsevier Ltd).

wavelength into the mid-IR region (the instrumentation is described in chapter 4). A detailed explanation of the laser system and the Ti: Sapphire characteristics, such as laser power equation and the laser spot size measurements, is then given in chapter 5.

The system has been calibrated by the analysis of xenon in the gas phase (as described in chapter 6) because its ionisation gives atomic charge states that have been described well by theory and in previous published work. The samples analysed in this work consisted of a range of small and relatively big molecules (toluene, acetone, histamine and nitroaniline molecules) which were chosen for the capability to be ionised in gas phase and to include both relatively simple organics that have been studied previously under MPI conditions, and small biomolecules typical of SIMS imaging studies (as explained in chapter 7). The data were processed by comparing signal levels of molecular and fragment ions over a range of laser conditions and attempting where possible to interpret observations in the context of existing theories of molecular ionisation (explained in chapter 8).

## Chapter 2

# Laser post-ionisation mass spectrometry

Post-ionisation (PI) is a very powerful technique in the ionisation of desorbed neutrals capable of producing an increase of the ionisation efficiency compared to the SIMS technique. In this chapter are described the advantages and methods of the PI technique.

### 2.1 Secondary neutral mass spectrometry

Over the last few decades *static* SIMS has been considered a powerful technique to study complex materials. In particular the use of the ToF SIMS gave an increase in detection efficiency of about  $10^4 - 10^5$  which comes from transmitting all ions to the detector regardless of their m/z up to a certain high mass value determined by the maximum acceptable flight time. Increasing the spatial resolution has been difficult to obtain due to the need of keeping the *static* SIMS conditions. The resolution can be enhanced by increasing the secondary ion yield or the instrumental transmission efficiency. In the ToF-SIMS the transmission is in the range of 50%, therefore the only way to significantly enhance the resolution is to act on the secondary ion current.

Only a small fraction of the material desorbed in SIMS are ions. Typically

neutral particles constitute more than 95% of material removed from the surface under analysis but these are not detected because they are not ionised. The need for enhancing the ion signal current and also the independence of the signal to the matrix effect is addressed by the use of lasers in mass spectrometry (11; 12).

Among the methods implemented in post-ionisation of sputtered neutrals there is the electron gas post-ionisation. This uses an electron beam crossing the flux of sputtered particles; however, due to the short travelling time of the sputtered neutrals and the low energy of the electron beam (10-15 eV), the amount of signal gained is very low. An extension of this approach employed a dense electron gas at high temperature obtained by ionising noble gas atoms (i.e. argon) at very low pressures. Therefore the electron charge is compensated by the positive noble gas ions in the generated low pressure high density plasma. The low pressure and the nature of the gas make the atomic interactions between the gas and the sputtered particles negligible (92; 89; 86; 87).

Another technique used is plasma desorption mass spectrometry (PDMS) used to analyse biomolecules. The range of masses is up to a molecular weight of 100,000 Daltons (Da). The solid sample is bombarded by heavy particles formed by nuclear fission of a nuclide (usually californium isotope). The disadvantage in using this method is that it only applies to non-volatile samples. These techniques have been recognised as soft ionisation since the energy deposited into the sample is minimised.

Another soft ionisation technique is the matrix-assisted laser desorption ionisation (MALDI), mostly used for biomolecules analysis. The sample is embedded in a chemical matrix (13; 14; 15) (an organic component) and they are both mixed in a solution with a solvent and co-crystallised. The matrix used depends on the kind of sample under analysis; however each matrix must absorb the UV light from the laser. When the target is subjected to the laser beam (after the vaporisation of the solvent), the matrix absorbs the majority of the laser energy and is desorbed, taking analytes molecules with it into the gas phase. Charge transfer process from matrix to analyses then result in charged analytes ions. Although the MALDI technique is commonly used, there are some disadvantages, such as the loss of spatial resolution compared to ToF-SIMS.

The motivation in using the laser post-ionisation mass spectrometry in this work regards the advantages in having high sensitivity and quantification, since the ionisation of the neutral species and their detection is not subjected to a matrix effect; in fact the chemical matrix has generally much less influence on the neutrals than it has on the emission of the charged particles.



FIGURE 2.1. Application of the post-ionisation in the ToF-SIMS technique: the neutrals sputtered away from the target surface are post-ionised, typically by a parallel laser beam; Zenobi *et al.* (14, Copyright 1999 by John Wiley & Sons, Inc).

#### 2.1.1 Laser post-ionisation sputtered neutral mass spectrometry (LP-SNMS)

The development of lasers in 1960 allowed the progress of research on samples subjected to a strong electromagnetic field. The photo-ionisation occurs when an atom absorbs a number k of photons whose combined energy is higher or equal than the atomic ionisation potential  $(I_p)$  (explained in more detail in the ionisation theory chapter 3). Ionisation theories including single-, multiphoton and tunnelling ionisation were developed first for atoms, including noble gases, and then more recently for molecular species, starting with sample di- and tri-atomics.

To enhance the products of sputtering, in particular to increase the sensitivity and efficiency of the mass spectrometry technique, lasers have been used more and more frequently in surface science and in mass spectrometry studies, thanks to their high power intensity, short pulse width - to achieve the high intensity needed for multiphoton processes including MPI -, high spectral purity and spatial coherence that allow them to be focused onto very small spots (16; 17; 18).

In figure 2.1 the post-ionisation technique is shown: the sputtered product is



FIGURE 2.2. Spectrum of indium post-ionised: (a) SIMS spectrum; (b) laser postionisation spectrum; Winograd *et al.* (20, Copyright 1982 Published by Elsevier B.V.).

then ionised by the laser beam. Winograd *et al.* (1998) (20) show the improvement that the laser post-ionisation technique has on the mass spectrometry in terms of signal detected. The indium sample is bombarded by a pulsed primary beam of argon ( $Ar^+$ ) and post-ionised by a 410.1 nm laser wavelength (figure 2.2).

In SIMS spectra (figure 2.2a), impurity peaks present, such as sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>) are completely absent in the post-ionisation spectrum (figure 2.2b); also the ion molecular peak signal of  $In^+$  and  $In_2^+$  is enhanced by the laser post-ionisation.

Vorsa *et al.* (1999) (21), compared the SIMS with the post-ionisation (laser wavelength 266 nm) spectra of phenylanine (I= $10^{11}$  W/ $cm^2$ ), tyrosine (I= $2 \times 10^{11}$  W/ $cm^2$ ) and tryptophan(I= $2 \times 10^{11}$  W/ $cm^2$ ), shown in figure 2.3. The spectra obtained in SIMS are more fragmented than the post-ionised spectra. Tyrosine ion signal in SIMS is 1100 counts and in laser post-ionisation is 37400 counts; this

means that the laser post-ionisation signal is enhanced by 34 times compared to the SIMS signal (figure 2.4).

Brummel *et al.* (1995) (12) analysed the improvement in the signal detection over the indium sample that the laser post-ionisation technique has on the ToF-SIMS (figure 2.5). A pulsed 25 keV  $Ga^+$  ion beam from a LIMG was used along with a Ti:sapphire laser providing 50 fs pulses at 100 MHz with an output of 4 nJ pulse. The two spectra were obtained at similar conditions apart from the stage voltage which for the post-ionisation experiment was increased up to 120 V in order to eliminate the SIMS ions. The comparison of the two spectra shows that using 266 nm the indium clusters appear to be ionised without extensive fragmentation, and also the  $In^+$  signal is 120 times higher than the SIMS spectrum.

Kelly O. *et al.* (2012) (93) analysed 1.3-butadiene and 1-butene samples by the electrostatic ion trap and the ionisation was obtained by irradiating the samples with the Ti:Sapphire laser at 800 nm which is extended up to 1400 nm by the OperA module. Figure 2.6a shows the signal obtained on the pickup ring at the geometric centre where the periodic impulses appears because of the molecular radical cation oscillations; also smaller fragments are observed at higher oscillation frequencies. The mass spectrum is shown in figure 2.6b, obtained at 800 nm and 100 fs pulse length at peak intensity of  $I = 4 \times 10^{14}$  W cm<sup>-2</sup> where the dominant peak is due to intact butadiene cations.

The 1-butene mass spectrum (figure 2.7) recorded at 800 nm, 100 fs at laser intensity  $I = 4 \times 10^{14}$  W cm<sup>-2</sup>,  $1 \times 10^{14}$  W cm<sup>-2</sup> and  $6.6 \times 10^{13}$  W cm<sup>-2</sup>, instead shows that the molecular ion peak signal is not very strong and the fragment signal is enhanced. Butene signal is explained by the fact that by increasing the dehydrogenation, the valence electrons become localised along the molecular backbone due to double bonds, hence the ionisation potential increases (figure 2.8); also the fragmentation pattern is unchanged which means that the IP value is close to the dissociation energy.

In the strong-field ionisation regime (explained in chapter 3) Willingham *et al.* (2009) (62), analysed coronene ( $C_{24}H_{12}$ ), guanine ( $C_5H_5N_5O$ ) and histamine ( $C_5H_9N_3$ ), sputtered with  $C_{60}^+$  confirming that by increasing the laser wavelength, the spectrum shows lower fragmentation and an enhancement of the molecular ions peak signal. If the electron oscillates with a frequency lower than the laser frequency, the ionisation occurs by tunnelling; vice versa the ionisation occurs by multiphoton mechanism.

The laser post-ionisation spectra of coronene (figure 2.9 a & b) and guanine (figure 2.9 c & d) at different laser wavelength show similar behaviour: if the molecules



FIGURE 2.3. Analysis of phenylanine, tyrosine and tryptophan: comparison between the SIMS spectra (a) and the post-ionised at laser wavelength of 266 nm at intensities of  $10^{11}$  W/cm<sup>2</sup> for the phenylanine sample and I=2×10<sup>11</sup> W cm<sup>-2</sup> for both tyrosine and tryptophan samples (b); Vorsa *et al.* (21, Copyright 1999 American Chemical Society).
amino acid	SIMS	260 nm	195 nm
Gly	8500	72600 (8.5)	41900 (4.9)
Ala	13900	72900 (5.2)	63800 (4.6)
Val	23200	40700 (1.8)	86100 (3.7)
Leu	12000	28500 (2.4)	31300 (2.6)
Ile	13900	17900 (1.3)	29600 (2.1)
Phe	6600	35500 (5.4)	24300 (3.7)
Tvr	1100	37400 (34)	45400 (41)
Trp	6600	42300 (6.4)	29000 (4.4)

FIGURE 2.4. Ion yield for several amino acids obtained by SIMS and laser postionisation, included the phenylanine, tyrosine and tryptophan; Vorsa *et al.* (21, Copyright 1999 American Chemical Society).

are ionised by the highest laser wavelength, the signal of the molecular ions peak increases. In particular coronene post-ionised by 800 nm (a) and 1450 nm (b) wavelength, shows that even though the fragmentation is a quite similar, the molecular ion peak signal increase at 1450 nm. A similar situation is found for the guanine post ionisation spectrum: at 800 nm the spectrum lacks of the molecular ion peak and the only peaks presents are the m/z 43 and m/z 27 probably associated with the fragments  $CH_3N_2^+$  and  $CHN^+$ . In contrast the spectrum obtained at 1450 nm laser wavelength shows the fragmentation signal but also the presence of the molecular ion peak. This confirms the hypothesis that a molecule subjected to a longer laser wavelength, is more likely to be ionised by tunnelling rather than the multiphoton ionisation (theories explained in details in chapter 3), as predicted by the Keldysh parameter.

Figure 2.10 shows that by increasing the laser wavelength (61) the probability of enhancing the parent ion signal exists relative to the fragmentation; this might be related to the presence of resonant levels in the wavelength range.

Post-ionisation is used also in the depth profile analysis, which produces information on the sample composition dependence on the primary ions fluency, therefore giving 3D information of the sample. Willingham *et al.* (2010) (37) analysed the guanine sample, irradiated with the 1450 nm laser wavelength. The sample was prepared as vapor-deposited onto a silver (Ag) substrate and placed on the silicon



FIGURE 2.5. Mass spectrum of indium foil (A) ToF-SIMS and (B) laser postionisation. The sample was bombarded by  $Ga^+$  ions and for the post-ionisation was used 266 nm at intensity of  $5 \times 10^{11} \text{W}/cm^2$ ; Brummel *et al.* (12, Copyright 1995 Elsevier Science B.V.).



FIGURE 2.6. Analysis of 1,3-butadiene sample at 800 nm, 100 fs and laser intensity  $I=4\times10^{14}$  W cm<sup>-2</sup>. a)pickup ring at the geometric centre, b) mass spectrum; Kelly O. *et al.* (93, Copyright The royal society of chemistry, 2012).



FIGURE 2.7. 1-butene mass spectrum at 800 nm, 100 fs and at at  $I=4\times10^{14}$  W cm<sup>-2</sup> and  $1\times10^{14}$  W cm<sup>-2</sup> and  $6.6\times10^{13}$  W cm<sup>-2</sup> laser intensity; Kelly O. *et al.* (93, Copyright The royal society of chemistry, 2012).

1st Ionisation Energy (eV)	1,3-butadiene 9.07	1-butene 9.55	n-butane 10.53
Appearance Energy (eV)			
-H loss	11.4	11.3	11.7
-CH <sub>3</sub>	11.3	11.8	11.2
$-CH_4$			11.2
-CH <sub>5</sub>	12.4	13.8	13.4
$-C_2H_4$	15.4	11.7	
$-C_2H_5$		13.6	12.6
$-\tilde{C_2H_6}$			11.7

 Table 1
 Ion appearance energies

FIGURE 2.8. 1-butene ionisation energies (108, Copyright 2000 ChemGlobe).

wafer. Figure 2.11 shows this results.

The spectra obtained in depth profile, shows a change in the amount of signal detected. At the beginning the signal decreases and at greater depth reaches a plateau. In figure 2.11 is shown this behaviour: (a) during the first 10 nm, the molecular neutral peak signal M decreases; afterwards it is steady until it drop again around 25 nm in depth. This behaviour is explained by the proton-enhanced ionisation theory: the ionisation probability changes are dependent on the depth because of the enhanced production of protons caused by the molecular fragmentation.

In figure 2.12a is shown the comparison between the  $M^0$  signal and the protonated  $[M+H]^+$ . As suggested by the proton-enhanced ionisation, the signal intensity of  $M^0$  is constantly lower than  $[M+H]^+$ , in fact while the first is  $\sim 1 \times 10^6$ , the second reaches  $1.7 \times 10^6$ . This theory should be verified for every protonated species, in fact figure 2.12 c & d shows the comparison between the [M+H] signal and the protonated fragments, m/z 125  $[M+H-HCN]^+$ , m/z 97  $[M+H-HNCOC]^+$  and m/z 28  $[HCN+H]^+$ . The damage accumulation strongly depends on the fragment masses: lower masses show signal than the higher masses. The proton-enhanced ionisation, is also verified in the spectra 2.12 e & f, where comparing the  $M^0$  with the [M-OH] signal, the two trends are similar.



FIGURE 2.9. Laser post-ionisation mass spectra of coronene at 800 nm (a) and 1450 nm (b) and guanine at 800 nm (c) and 1450 nm (d); Willingham *et al.* (62, 2009, Copyright 2008 Elsevier B.V.).



FIGURE 2.10. Multiphoton ionisation of the 3-Methylcyclopetanone (M=98 amu); the spectrum is normalised at the maximum intensity. By increasing the laser wavelength, up to 324 nm, the intensity of the M<sup>+</sup> peak increases over the fragments (the fragment 69 amu has the highest peak intensity for 300 nm); Boesl *et al.* (61, Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).



FIGURE 2.11. Depth profile of the laser post-ionisation of the guanine sample: the graphs show the signal intensity as a function of the depth: a) molecular ion peak, M, (black) and the silver, Ag, (red); b) ion [M+H]<sup>+</sup> in black and the Ag in red; c) signal of ion [M+H]<sup>+</sup>/M and d) ion Ag<sup>+</sup>/Ag; Willingham *et al.* (37, Copyright 2008 Elsevier B.V.).



FIGURE 2.12. Signal of the guanine depth profile as a function of the depth. (a) Trend of the protonated molecular ion [M+H]<sup>+</sup> (red) and photo-ionised molecular neutral peak (black); (b) photo-fragmentation ion trend; (c) secondary ion [M+H]<sup>+</sup>; (d) secondary ions M+H-HCN]<sup>+</sup> (black), [M+H-HNCOC]<sup>+</sup> (blue) and [HCN+H]<sup>+</sup> (red); (e) photo-ionised neutral M<sup>0</sup>; (f) [M-OH]<sup>+</sup> signal; Willingham *et al.* (37, Copyright 2008 Elsevier B.V.).

# Chapter 3

# **Ionisation Theory**

In this chapter is discussed the theory of the laser ionisation in mass spectrometry. In particular it focuses on the physical explanation of the most influential theories, such as the Keldysh parameter, the ADK and the Landau-Dykhne theory.

### 3.1 History of ionisation theory

Before 1930, the ionisation mechanism was considered as a process in which only one photon can be absorbed in order to ionise the atom. Maria Göppert-Mayer, in her doctoral thesis, introduced the theory of two-photon quantum transition in atoms (38). This was the prelude of the multiphoton ionisation theory.

The advent of the laser in the early 1960's introduced the study of the interaction between powerful laser radiation and matter (39; 40). In 1964, Meyerand and Haught (41) observed that a ruby laser pulse generates a spark in contact with the air and the hypothesis of the strong field ionisation of molecules was formulated. This process is explained in figure 3.1. Firstly the atom is ionised by multiphoton ionisation; hence free electrons are created into the laser beam volume. Secondly those electrons are able to absorb photons and also collide with other particles, a process called inverse bremsstrahlung. At this stage, since the electrons have acquired a kinetic energy higher than the molecular ionisation potential, a cascade process is generated to let



FIGURE 3.1. Interaction of the ruby laser with the air. This is the schematic representation of the laser that induces the break down in air; Wittmaack *et al.* (4, Copyright 1979 Published by Elsevier B.V.).

the electron to escape from the potential well.

### **3.2** Introduction to strong laser field

When the laser field reaches very high energy  $(\geq 10^{12} \text{ W/cm}^2)$ , comparable or stronger than the atomic Coulomb field  $(10^9 \text{ V/cm})$  it is classified as "strong laser field". If polyatomic molecules are subjected to the strong laser field, the ionisation occurs by breaking the atomic bond (96; 102)(figure 3.2).

When an atom is subjected to an external field, the electronic wave function has



FIGURE 3.2. Interaction of a diatomic molecule with a strong laser field; Levis *et al.* (95, Copyright 2002 by the American Chemical Society).

a drift with the laser wave amplitude  $(E/\omega^2)$  always lower than R, the radius of the focusing region. A free electron is subjected to acceleration dependent on the interaction with a short laser pulse, the electron is not shifted. In the case of long laser pulse, instead, the electron is subjected to acceleration dependent on the laser field strength, which is perpendicular to the laser field velocity (classical mechanics). The average energy acquired by the electron is called the ponderomotive potential (22; 44; 45, U<sub>p</sub>). The kinetic energy for free electrons (in atomic units) is:

$$E_{\rm c} = \frac{E^2(r_0, t_0)}{4\omega^2} \tag{3.1}$$

 $t_0$  and  $r_0$  are the time vector and the radius vector inside the laser volume. In this case, the total kinetic energy of the electron is due to the sum of the ponderomotive energy and the energy obtained during the ionisation process. The formulation of the ponderomotive potential is simplified by the equation 3.2.

$$U_{\rm p} = \left< \frac{e^2 E_{\rm l}^2}{4m\omega_{\rm l}^2} \right> = 9.31 \times 10^{-14} I \lambda^2 \tag{3.2}$$

The ponderomotive energy  $(U_{\rm p}, \, {\rm eV})$  of the electron depends on the time average

over a laser optical cycle ( $\langle \rangle$ ) of the ratio between the laser electromagnetic field and frequency. The factor  $9.31 \times 10^{-14}$  is just a scaling factor, while *I* and  $\lambda$  are the laser intensity (W/cm<sup>2</sup>) and wavelength ( $\mu$ m), respectively.

#### 3.2.1 Ionisation mechanisms

The ionisation mechanisms, relevant in this work, regards the case when an atom (or molecule) with binding energy  $I_{\rm p}$ , is irradiated by a photon with energy (E<sub>k</sub>), such that:

$$E_{\rm k} < I_{\rm p} \tag{3.3}$$

Multi-photon ionisation (MPI) occurs when the photon energy is lower than the  $I_{\rm p}$ , therefore a k number of photons are absorbed in order to overcome the  $I_{\rm p}$  and achieve ionisation (22; 8).

#### Single active electron ionisation (SAE)

When an atom is subjected to a strong laser field, if the ionisation occurs only by one electron (of binding energy  $I_{\rm p}$ ) tunnelling through the barrier created by the Coulomb electric field and the laser field, the single active electron approximation (SAE) is achieved. In general the tunnelling electron is the weakest bound valence electron that interacts with the laser field. Usually the SAE is valid for a noble gas; as previously discussed in chapter 2, xenon gas is ionised by stepwise process and this is described by SAE approximation. The SAE approximation fails when the ionisation occurs by multiple electrons which can also interact with each other producing multiple charges and re-scattering (96; 103).

#### Multiphoton ionisation

The multiphoton ionisation procedure is described by one of two mechanisms: (i) non resonant multiphoton ionisation (NRMPI), (ii) resonant multiphoton ionisation (REMPI). While the first goes through a virtual intermediate level, for the second the intermediate level is a real electronic state (figure 3.3)(47).

In particular, *NRMPI* requires a very high photon flux to permit transitions among short lifetimes determined by the uncertainty principle. For this reason, to favour the ionisation transition, ultra short laser pulses (power densities  $\geq 10^9 \text{ W cm}^{-2}$ )



FIGURE 3.3. Ionisation mechanisms: a) SPI process: the molecule is ionised if the photon energy exceeds its ionisation potential; b & c) if the energy of the photons is lower than the ionisation potential of the molecule two processes may occur: b) the ionisation utilise either virtual level which are not eingestate of the molecule and the lifetime is  $\sim 10^{-15}$  s and virtual states, this process is a combination of NREMPI and REMPI; c) the ionisation process goes through only real states (REMPI).

are often used. The non resonant multiphoton is explained by the quantum mechanics theory,  $\Delta E \Delta t > 1$ . This means that the ionisation between the ground state and a first energetic level occurs for the energy  $\Delta E$ , but since the event occurs in a time  $\Delta t$ , lower than the laser pulse, the electron transits through virtual states. *REMPI* ionisation mechanism occurs when a photon excites a molecule from the ground state to the first excited level and a second photon moves it to another advanced excited level. The laser (usually at power density  $\geq 10^5$  W cm<sup>-2</sup>) is tuned, to excite an electron to a real intermediate electronic level where the lifetime is  $> 10^{-9}$  s. Only if the energy of the two photons is more than the ionisation potential of the molecule under analysis, the molecule is ionised, otherwise this process needs more photons. The formalisation of the ionisation theory is due to Voron, Delone and Agostini (45), and it regards the dependence of the photo-ionisation rate (W) on the laser intensity by the following relationship:

$$W(I) = \sigma_{\rm K} I^{\rm K} \tag{3.4}$$

By plotting the log W versus the log I, the slope of the trend is the number of photons



FIGURE 3.4. Log(relative ion yield)-log(laser intensity) plot of the multiphoton ionisation process. The slope a, b and c represents the number of photons required to ionise benzene, naphthalene and anthracene respectively. The ionisation is done with the 799 nm laser wavelength; Delone *et al.* (45, Copyright Springer 1994).

(k) absorbed during the ionisation. In the case of the REMPI, it is an indication of the number of photons required to reach an intermediate rate-determining state.

Delone *et al.* (1994) (figure 3.4) show that the slope of the benzene, naphthalene and anthracene trend is in the range 8-8.5; since only 6 photons are required, the additional 2-3 may be involved in the ionisation (this is due to the above threshold ionisation, discussed later on).

#### Above threshold ionisation

Above threshold ionisation (53; 54, ATI) is the mechanism in which the atom absorbs higher number of photons than the minimum required to be ionised by MPI. Mainfray and Manus (1991)(22) treated the MPI as a simple scattering problem, where the photons, that irradiate the atom, collide with the electron being ionised producing the photoelectron spectrum with many peaks corresponding to the energy gained by photon absorption (figure 3.5). They discovered the above threshold ionisation through the analysis of the photoelectron spectrum. It was noticed that by irradiating the atom with a strong laser field, the spectrum did not contain only a peak centred at  $E = E_0 + k(h/2\pi)\omega$ , where  $E_0$  is the energy of the ground state and  $(h/2\pi)\omega$  is the photon energy, but also others with  $E = E_0 + (k+s)(h/2\pi)\omega$ , due to further *s* photons absorption. The ATI ionisation was explained as the process that occurs if the electrons are half bonded. When electrons escape from the potential well and are still subjected to the electrical field of the surrounding atoms, they can absorb photons (inverse bremsstrahlung).

The photoelectron spectrum differs if the interaction is with a long or a short laser pulse. If the atom is subjected to a long laser pulse, the electron of the outmost shell interacts at focal spot of the laser field (point where the laser has the maximum intensity) for a ns pulse the electron leaves the focus so gains additional ponderomotive energy  $U_p$ . For fs pulses the electron does not have sufficient time to leave the laser focus before the pulse ends. Levis *et al.* (1999) (88) observed the transition from MPI/ATI to tunnelling ionisation photoelectron spectrum of benzene, naphthalene and anthracene (figure 3.6). The laser parameters used for the ionisation were the wavelength of 780 nm, pulse duration 170 fs and laser intensity  $I = 3.8 \times 10^{13} \text{ W cm}^{-2}$ .

At low photon energy (from 0.3 to 0.9 eV) the photo-electron spectrum of benzene (figure 3.6a) shows a series of ATI peaks which correspond to a MPI process from 2.5 to 15 eV, while the broad electron distribution ranging from 0 to 15 eV is due to the tunnelling ionisation. The photo-electron spectrum of nephthalene (figure 3.6b) shows discrete peaks observed at low photon energy that are due to the ATI process (which represents only the 14 % of the entire ionisation process). The photo-electron spectrum of anthracene (figure 3.6c) does not show any ATI or MPI peaks, therefore the ionisation is mainly due to tunnelling ionisation.



FIGURE 3.5. Top panel: schematic representation of the above threshold ionisation; Vorsa *et al.* (21, Copyright 1999 American Chemical Society). Bottom panel: electron energy spectra of xenon ionised with 1064 nm laser wavelength at I = 7.5  $\times 10^{12}$  W cm<sup>-2</sup>, at two laser pulse, 136 ps and 50 ps; L'Huillier *et al.* (25, Copyright 1983 American Chemical Society).



FIGURE 3.6. Photo-electron spectra of benzene (a) where the inserted panel shows the spectrum at low energy, nephthalene (b) and anthracene (c) at I = 3.8  $\times 10^{13}$  W cm<sup>-2</sup>;  $\alpha$  is the scaling factor and  $\Sigma$  is the photo-electron intensity; Levis *et al.* (88, Copyright 1999 The American Chemical Society).

## 3.3 Tunnelling and barrier suppression ionisation

Field ionisation by tunnelling (TI) or barrier suppression occurs only in the case of a strong laser field. The electric field associated with the laser is strong enough to deform the ionisation potential and the electron is free to escape from the atom.

In the case of strong laser fields  $(> 10^{12} \text{ W cm}^{-2})$ , the molecule is ionised by tunnelling. In this case the laser electric field distorts the molecular binding energy (coulomb potential) and favours the escape of the electron. In the case of the barrier suppression ionisation (BSI), the atomic potential barrier (considering Z the charge of the atomic core) is reduced by the laser field to below the level of the electrons, so it goes over the top (45; 55; 106).

$$F_{\rm BSI} = \frac{E_{\rm i}^2}{4Z} \tag{3.5}$$

In the tunnelling case, the weakly bound electron tunnels, by a quantum mechanical mechanism, through the coulomb barrier which is reduced by the laser field strength. Before the laser field is reversed, favoured at low frequency (e.g. infrared, IR) irradiation, the electron must escape by the potential well; if this does not occur, the electron will be reflected back by the barrier (22)(figure 3.7&3.8).

An atom, irradiated by a strong laser field (56; 57; 58) is described by the perturbed Hamiltonian, which is written as:

$$\widehat{H} = \widehat{H_0} + \widehat{V} \tag{3.6}$$

where the  $\hat{H}$  is the field free Hamiltonian, that describes an atom in the ground state, not subjected to the laser flux;  $\hat{V}$  is the interaction with the laser. By other approximations, the final Hamiltonian equation is written as:

$$\Psi(v,t) = -i \int_0^t dt' e^{-i(1/2) \int_{t'}^t [v + A(t'') - A(t)]^2} \langle v + A(t') - A(t) | V_{\rm L}(t') | g \rangle e^{+iI_{\rm P}t'} \quad (3.7)$$



FIGURE 3.7. Schematic representation of an atom irradiated by a strong laser field; Ivanov *et al.* (97, Copyright 2005 Taylor & Francis Ltd).



FIGURE 3.8. Schematic representation of tunnelling ionisation: the green trend is the potential well distorted by the strong laser field, the red dot line is the external field, and the black dot line is the potential well not distorted; Chin S.L. (41, Copyright 2011 World Scientific).

Where the factors A(t) and A(t') represents the vector-potential of the electric field (97). This equation can be more easily explained by figure 3.7.

The ionisation occurs in two steps:

- $t \leq t'$ : the electron is in the ground state  $(g\rangle e^{+iI_{\rm P}t'})$  where g represents the ground state and the exponential is the phase accumulated during the time range [t, t'];
- t': the electron is introduced into the continuum and it gains velocity v'=v + A(t')-A(t), energy E(t''). In the continuum, the electron oscillates according to the laser wave amplitude and also it is subjected to the scattering with the parent ion.

## 3.4 Tunnelling theory: Ammosov, Delone & Krainov theory

The ADK theory was formulated by Ammosov, Delone & Krainov as a way to explain the tunnelling ionisation for the atomic system. The tunnelling theory is based on the adiabatic (quasi-static) description of the electron dynamics (63; 64). This theory can be used for atoms or small molecules but for the polyatomic it is inadequate due to greater time-scale of the electron motion throughout the molecule.

Ammosov, Delone & Krainov in the 1985 analysed xenon gas irradiated by  $CO_2$  laser, which resulted in a tunnelling ionisation. The mathematical formalisation was done for the hydrogen atom since it the simplest atomic system because it has only one electron and one proton and then it was extended for other atomic systems (46). Using the quasi-static theory, the rate of the tunnelling ionisation for an excited state of the hydrogen atom is described by the following equation (65; 66).

$$w = \sqrt{\frac{3n^3E}{\pi}} \frac{(2l+1)(l+|m|)!2^{4n-2|m|-2n-6n+3|m|}}{(n+l)!(n-l-1)!(|m|)!(l-|m|)!} \times \frac{e^{\left[\frac{2}{(3n^3E)}\right]}}{E^{2n-|m|-1}}$$
(3.8)

Where *n* is the principal quantum number, *l* is the orbital quantum number and *m* is the magnetic quantum number and this expression is used for a linear polarised laser field; in case of the circular polarisation, the equation is similar apart from the elimination of the  $\sqrt{\frac{3n^3E}{\pi}}$  factor.

For a complex atomic system and also in a linear or circular polarised laser field, the simplest equation for the the ADK theory is:

$$w = \sqrt{\frac{3n^{*3}E}{nZ^3}} \times \frac{ED^2}{8\pi Z} \times e^{(-\frac{2Z^3}{(3n^{*3}E)})} \qquad \text{with} \quad D = \frac{4eZ^3}{n^{*4}E}$$
(3.9)

where the quantum number n becomes  $n^*$  since the correction of the quantum defect, obtained by applying the Stirling formula at the first equation (46).

## 3.5 Tunnelling theory: Landau-Dykhne formalism

The non adiabatic multi electron process is explained by the Landau Dykhne formalism and it is widely used to describe transitions in two states systems and transitions to the continuum (69; 70; 71). To make a clear explanation, this theory is firstly explained through the classical theory, considering two parameters: the electron oscillation amplitude ( $a_{osc} = E/\omega_L^2$ ) and the length (L) of the delocalised electron path inside the molecule/atom.

- 1.  $a_{\rm osc} > L$ : the electron oscillates for the whole L and also is scattered by the atom/molecule; for every scattering event the energy absorbed is  $E_{\rm scat}$  and if it is higher than the atomic  $I_{\rm p}$ , the electron reaches the higher energetic states;
- 2.  $a_{\rm osc} < L$ : the E<sub>scat</sub> ~  $U_{\rm P}$ , the electron oscillates fast with low amplitude of oscillation. It can reach the atomic  $I_{\rm p}$  and the atom can still absorb a small quantity of energy per scatter therefore if the electron gains enough energy, after a large number of collisions, it is able to escape from the ionisation potential barrier.

In quantum mechanics terms, the explanation of the Landau-Dykhne parameter is similar. Basically, there are two distinctions to make: the laser frequency ( $\omega$ ) is lower (adiabatic approximation) or higher (non adiabatic approximation) than the field free level spacing,  $\Delta_0$  and also the atomic energetic levels subjected to a laser field are shifted by the Stark effect. For  $\omega < \Delta_0$ , the levels shift according to the Stark effect. This is the adiabatic case, where, because of the low laser frequency, the electron remains in its energetic levels without being ionised. By increasing the laser frequency or the Stark shift, the atom oscillates faster (with the increase of the ponderomotive potential), allowing the electron to gain enough energy to move to the high energetic levels. The formalisation of the Landau-Dykhne theory was done by Landau- Zener probability of the non adiabatic transitions during the half laser cycle (equation 3.10).

$$P_{\rm LZ} \sim e^{\left(\frac{-\pi\Delta_0^2}{4\omega_{\rm L}E\mu}\right)} \tag{3.10}$$

where  $\Delta_0$  is the field-free level spacing,  $\omega$  is the laser frequency, E is the laser electric field and  $\mu$  is the dipole matrix-element. Since  $\mu$  depends linearly on L, when  $\omega_{\rm L} \text{EL} \sim \Delta_0^2$ , the electronic transitions to the high excited levels reaches the saturation.

### 3.6 Keldysh parameter

The multiphoton, tunnelling and barrier suppression mechanisms have been described by Leonid Keldysh in 1965 through the theoretical formalisation of an atomic system subjected to an intense laser field (26; 28; 29). He assumed the adiabatic approximation, considering that the non linear ionisation of an atom occurs when the tunnelling frequency ( $\omega_t$ ) of the electron into the potential well is lower than the half period of the laser cycle ( $\omega_0$ ). This is formalised in the following expression:

$$\gamma = \frac{2\omega_0}{\omega_t} \tag{3.11}$$

From the quantum mechanics theory, the length of the potential barrier is defined as (equation 3.12):

$$l_{\rm ZR} = \frac{I_{\rm P}}{eE_0} \tag{3.12}$$

The value of the average velocity of the electron (with mass  $m_e$ ) that travels inside the potential is defined from the ionisation potential, as (equation 3.13):

$$\langle v \rangle = \sqrt{\frac{2I_{\rm P}}{m_{\rm e}}} \tag{3.13}$$

From the equations 3.12 and 3.13 the tunnelling time and frequency is calculated (equation 3.14):

$$t_{\rm ZR} = \frac{l}{\langle v \rangle} = \frac{I_{\rm P}}{eE_0} \times \sqrt{\frac{m_{\rm e}}{2I_{\rm P}}} = \frac{1}{eE_0} \times \sqrt{\frac{I_{\rm P}m_{\rm e}}{2}}$$
(3.14)

$$\omega_{\rm ZR} = \frac{2\pi}{t_{\rm ZR}} \tag{3.15}$$

The expression of the electron tunnelling frequency is substituted in the equation 3.15, obtaining the formalisation of the Keldysh parameter (equation 3.16):

$$\gamma = \frac{2\omega_0}{\omega_{\rm ZR}} = \omega_0 \frac{\sqrt{2I_{\rm P}m_{\rm e}}}{eE_0} = \omega_0 \frac{\sqrt{2I_{\rm P}}}{E_0} \tag{3.16}$$

The equation 3.16 considers that both e and  $\hat{m_e}$  in atomic units are set to 1. As previously explained, the Keldysh parameter represents two cases:

- $\gamma >> 1$ : when  $I_{\rm p} > (\frac{E_0}{\omega_0})^2$ . In this case, the ionisation occurs by multiphoton ionisation because the field strength is not high enough to allow the electron to escape from the potential well;
- $\gamma \ll 1$ : when  $I_{\rm p} \ll (\frac{E_0}{\omega_0})^2$ . In this case the ionisation occurs by tunnelling because the laser field strength is higher than the ionisation potential.

Those two cases are represented in figure 3.9, where is shown the dependence of the ionisation probability on the Keldysh parameter, in logarithmic scale.

In particular, the graph in figure 3.9 (top panel), shows that for  $\gamma > 1$ , the multiphoton ionisation is represented by a linear trend (since the molecule sequentially absorbs photons) while for  $\gamma < 1$ , the tunnelling ionisation is represented by an exponential trend (the laser field strength is high enough to induce a fast absorption of the photons by the molecule), shown by the knee structure.



FIGURE 3.9. Top panel: non linear ionisation process, where a: multiphoton ionisation; b: tunnelling ionisation, the external laser field strength is so high to deform the atomic potential and let the electron escape (112, Copyright 2012 HASYLAB). Bottom panel: dependence of the log W on the Keldysh parameter ( $\gamma$ ): for  $\gamma > 1$  the trend is linear, while for  $\gamma < 1$  it is exponential; Delone & Krainov (46, Copyright 1998 Uspekhi Fizicheskikh Nauk, Russian Academy of Science).

For simplicity, in this thesis a rearranged formula of the Keldysh parameter is used that is obtained by substituting the oscillation energy (equation 3.16) into the Keldysh parameter (100) (equation 3.17).

$$\gamma = \sqrt{\frac{I_{\rm P}}{1.87 \times 10^{-13} I \lambda^2}} \tag{3.17}$$

The equation 3.17 considers the ratio between the atomic ionisation potential  $(I_{\rm p}, \text{ in eV})$  and the laser intensity I (W cm<sup>-2</sup>) and the wavelength  $\lambda$  ( $\mu$ m); the coefficient 1.87 ×10<sup>-13</sup> represent a conversion factor. In this case, it is considered that the  $\gamma > 5$  for multiphoton ionisation and  $\gamma < 0.5$  tunnelling ionisation.

The ADK and Keldysh theories are experimentally applied in the case of xenon gas phase: if the atomic potential barrier is higher than the laser field, the ionisation process is explained by quantum mechanics, by the Keldysh parameter and the ADK theory (38). In order to demonstrate this, high power lasers have been used (54) on the gas phase laser ionisation of xenon and helium atoms. The laser intensity is from  $10^{16}$  to  $10^{18}$  W cm<sup>-2</sup> with short a pulse duration of 40 fs.

In figure 3.10 top panel, is shown the signal of multiple charge state of xenon versus the laser intensity. The trends of Xe<sup>+</sup> and Xe<sup>2+</sup> ionisation, not shown in the graph, follow the known Keldysh theory and behave as a mixture of multiphoton and tunnelling ionisation. Most probably for low laser intensity the ionisation occurs by multiphoton process since the atomic  $I_p$  is higher than the ponderomotive potential. Increasing the laser power, instead, the ionisation process occurs by tunnelling because the ionisation potential of the atom is lower or equal to the ponderomotive potential.

Yamakawa *et al.* (2004) (55) analysed the dependence of the xenon's atomic structure by ionising it by a strong laser field using the 800 nm laser wavelength with 20 fs pulse duration and a power range  $10^{13} - 10^{18}$  W cm<sup>-2</sup>. Figure 3.11 shows how the multiply charge state of xenon change by increasing the laser power and also this behaviour is compared with the ADK theory.

The experimental trend of  $Xe^{2+}$  until the  $Xe^{9+}$  signal diverges from the ADK theory from which a shift factor was calculated (figure 3.11). While  $Xe^{2+}$  signal is shifted from the theoretical trend by 15%, the  $Xe^{3+}$  signal completely disagrees with the theory and the  $Xe^{9+}$  matches again the theory. L'Huillier *et al.* (1983) (25) suggested that the potential of the outmost shell screens the electron of the inner shell from the external field and also the screening effect changes by changing



FIGURE 3.10. Top panel: dependence of the xenon ions on the laser power, the dashed lines represent the sequential tunnelling ionisation and the straight lines represent the atomic re-scattering. Bottom panel table of the xenon ionisation potential  $(I_{\rm P})$ , laser intensity (I), Keldysh parameter  $(\gamma)$  and Kepler orbit time  $(\tau k)$  for ionisation rate of  $10^{13} \ s^{-1}$ ; Becker *et al.* (54, Copyright 2002 Elsevier Inc.).



FIGURE 3.11. Dependence of the xenon ion signal on the laser peak intensity, the line shows the ADK theory; Yamakawa *et al.* (55, Copyright 2004 The American Physical Society).

the laser strength. For this reason by changing the laser field the chemical atomic structure changes, hence the agreement with the theory has to be accorded by shifts parameters.

To explain the ionisation mechanism of the xenon gas and the motivation that the Xe<sup>3+</sup> does not agree with the theory, helium gas phase was used since the  $I_p$  is similar to the Xe<sup>3+</sup>. According to the Keldysh parameter if the helium gas ionises by tunnelling ionisation Xe<sup>3+</sup> does also, producing the multiply charged state Xe<sup>4+</sup> (stepwise process). L'Huillier demonstrated that the Xe<sup>3+</sup> does not produce any charge state, because the Kepler orbit time for the n=5 shell (outmost shell) is longer than the optical cycle of the laser ( $2.6 \times 10^{-15}$  s). The agreement with the theory instead comes back when the Kepler orbit time reduces for Xe<sup>5+</sup> where the ionisation mechanism again resemble helium ionisation. Kepler orbit time values are shown in figure 3.11.

## 3.7 Multiple ionisation: sequential and nonsequential ionisation

Multiple ionisation occurs when the laser field interacts directly with many electrons in the atoms or when the ionisation occurs by laser-electron interaction and then electron-electron scattering. The electrons can be ejected by sequential or nonsequential process (104; 105).

The sequential ionisation mechanism results from the successive removal of electrons; it is the process that leads to the direct ionisation in xenon.

A re-scattering process can occur when an atom is subjected to an intense laser field and the electrons' trajectory depend on the laser parameters. The electrons can be driven back towards in the atomic core, causing a recollision with the parent ion - this can lead to non-sequential ionisation, excitation of the parent ion or recombination) high-harmonic generation.

The trajectory of an electron is plotted in figure 3.12.

- If the electron is born at  $\varphi = 0$  ( $\varphi$  initial phase, figure 3.12a), it is firstly accelerated away from the nucleus by the field strength. When it is decelerated, the electron changes direction and as the field strength oscillates back to negative values leads the electron to move away from the nucleus.
- If the electron is born at  $\varphi = \pi/2$  ( $\varphi$  initial phase, figure 3.12b) it moves away from the nucleus for half of the field strength; this means that when the electron is accelerated, it oscillates to and from the ion core.
- If the electron is born at  $\varphi = 1.9$  radians ( $\varphi$  initial phase, figure 3.12c) it is firstly accelerated away from the nucleus but then it will be directed towards the other side and can re-collide with the core.

If the electronic re-collision occurs at  $0.5\pi < \varphi < 0.57\pi$  ( $0.6\pi = 1.9$  radians) the maximum return kinetic energy,  $3.17 U_p$  is obtained.

One of the first experiments of this type on helium and xenon gas was done by Mainfray and Manus (22). Figure 3.13 shows the ionisation of the xenon gas at laser wavelength 532 nm comparing the different laser pulse duration: 5, 30 and 200 ps.

Irradiating the Xe atom by 5 ps laser pulse duration (figure 3.13a), the signal of  $Xe^+$  and  $Xe^{2+}$  reaches saturation at the same laser intensity value: this means that the ionisation occurs by a direct process. Both charge states are formed by the contemporaneous removal of one and two electrons. At laser pulse of 30 ps



FIGURE 3.12. Electronic trajectory obtained when an atom is subjected to an external laser field. The blue path represents the electron motion and the dashed red line is the starting position; Posthumus (98, Copyright 2004 IOP publishing Ltd).

(figure 3.13b), the ionisation process drastically changes. The Xe<sup>+</sup> and Xe<sup>2+</sup> signal saturation does not occur at the same intensity and the production of the latter charge state is strongly reduced. When the xenon is irradiated by longer laser pulse duration, 200 ps (figure 3.13c), the ionisation occurs by a stepwise process: only after the saturation of the Xe<sup>+</sup> signal are the Xe<sup>2+</sup> ions created. This means that the ionisation uses xenon atoms to generate Xe<sup>+</sup> ions which, at saturation intensity, produce Xe<sup>2+</sup> ions. This study shows that the change of the laser pulse affects the removal of the electrons, i.e. simultaneously- direct ionisation- or sequentially- stepwise ionisation. By increasing the laser power and using 40 ps laser pulse duration, it was possible to reach higher multiple charges state. By ionising the xenon gas at 532 nm multiple charge states (up to the fifth level) are obtained via a stepwise process (figure 3.14). Each charge state is produced from the previous one; for example Xe<sup>3+</sup> is produced from the Xe<sup>2+</sup> ions and the Xe<sup>4+</sup> is produced from Xe<sup>3+</sup> ions and so on.

The helium laser ionisation spectrum is shown in figure 3.15. He<sup>+</sup> ions are achieved at I  $\sim 10^{13}$  W cm<sup>-2</sup>; when the signal is saturated at I  $\sim 10^{14}$  W cm<sup>-2</sup>, He<sup>2+</sup> are formed. This is stepwise ionisation: the laser interacts only with the He<sup>+</sup>



FIGURE 3.13. Xenon gas phase ion signal as a function of laser intensity; a) laser pulse of 5 ps ; b) laser pulse 30 ps and c) laser pulse 200 ps; Mainfray *et al.* (22, Copyright 1991 IOP Publishing Ltd).



FIGURE 3.14. Dependence of the xenon multiple-charge state ions signal on the laser intensity. The laser wavelength is 532 nm and the pulse duration is 40 ps; Mainfray *et al.* (22, Copyright 1991 IOP Publishing Ltd).



FIGURE 3.15. Laser ionisation on helium: (a) dependence of the ion signal on the laser intensity (in logarithmic scale); (b) schematic representation of the ionisation potential  $(I_p)$  for helium and its multiple charged states; Mainfray *et al.* (22, Copyright 1991 IOP Publishing Ltd).

to produce the  $He^{2+}$ . Moreover, the scheme in figure 3.15b shows that helium needs to be ionised by absorbing 11 photons to create  $He^+$  state and 24 photons to reach the  $He^{2+}$  state.

Kaminski *et al.* (2006) (23), explained how the ejection of the first electron influences the probability of the emission of the following electrons using the re-scattering model. When the first electron is ejected from the atom, it is accelerated by the laser field strength and returns to the parent ion and, by inelastic scattering, creates the subsequent electrons.

Figure 3.16 shows the dependence of the ratio  $Xe^{2+}/Xe^{+}$  on the laser wavelength



FIGURE 3.16. Xenon ionisation trend: dependence of the ratio Xe<sup>2+</sup>/Xe<sup>+</sup> on laser wavelength in the range 700-1600 nm; Kaminski *et al.* (23, Copyright 2006 The American Physical Society).

in the range 700-1600 nm. At 800 nm the ratio decreases rapidly then increases at higher laser wavelength. The highest signal is found at 1185 nm and 1475 nm, but then, in the range of 1160 and 1525 nm the ratio decreases again. This is explained from the calculation of the number of photons  $(N_k)$  needed to ionise the xenon.

$$N_{\mathbf{k}} = \frac{I_{\mathbf{P}}}{E_k} \quad ; \quad E_k = \frac{hc}{\lambda} \tag{3.18}$$

where  $I_{\rm p}$  is the ionisation potential,  $E_k$  is the photon energy,  $\lambda$  is the laser wavelength, h and c are the Planck's constant and light velocity, respectively.

The equation 3.18 shows that by increasing the laser wavelength ( $\lambda$ ), the number of the photons ( $N_{\rm k}$ ) required to ionise increases. Hence for example between 1155 nm and 1565 nm, the number of photon required to produce Xe<sup>+</sup> goes from 14 to 22 and from 23 to 32 to produce Xe<sup>2+</sup>. Charalambidis *et al.* (1994) (24), L'Huillier *et al.* (1983) (25) and Walker *et al.* (1993) (26) interpreted the xenon ionisation as produced by a mixture of direct and stepwise ionisation.

At intensities  $I < 10^{12} \text{ W cm}^{-2}$ , (figure 3.17) Xe<sup>+</sup> and Xe<sup>2+</sup> charge states are produced by non-sequential ionisation. At  $I > 10^{12} \text{ W cm}^{-2}$  this is no longer valid: Xe<sup>2+</sup> is produced by a stepwise process, i.e from the ionisation of the first charge state Xe<sup>+</sup>. This is explained by the fact that in this region the xenon singly charged state is saturated, hence all the neutrals have been used to produce it and in order to obtain Xe<sup>2+</sup>, Xe<sup>+</sup> needs to absorb other photons.

Delone and Krainov (1998) (46) (figure 3.18) have found multiple charge production in helium ionisation experiments, in the case of  $\gamma < 1$  (TI) and laser field strength is lower than that required for barrier suppression ionisation. These charge states are formed by the stepwise ionisation; hence He<sup>+</sup> is obtained by the absorption of photons from the neutral state while the He<sup>2+</sup> is obtained by the absorption of photons by the first charge state.

As shown in figure 3.18 the ADK theory agrees well with the experimental trend. This theory, disagrees (for low laser intensity) with the multiple charge states obtained by direct ionisation, as shown in figure 3.18 bottom panel. In particular, the latter charge states are produced by the shake off model or re-scattering. In the shake off model, the second electron is created by the fact that the first leaves very quickly and the potential well creates a distortion in the atomic energy.



FIGURE 3.17. Dependence of the xenon charge state signal on the laser intensity and schematic representation of the xenon ionisation energies. The Xe<sup>+</sup> signal reaches saturation at I <  $10^{12}$  W cm<sup>-2</sup>; L'Huillier *et al.* (25, Copyright 1983 The American Physical Society).


FIGURE 3.18. Top panel: dependence of the yield of singly charged and doublycharged states of helium gas on the laser intensity. The solid trend is the ADK theory. Bottom panel: dependence of the double charge state yield of He and Ne on the laser intensity; the solid trend is the ADK theory; Delone *et al.* (46, Original Text Copyright 1993 by Astro, Ltd. Copyright 1993 by Interperiodica).



FIGURE 3.19. Schematic representation of the ionisation-dissociation mechanisms in molecule. a): nanosecond laser pulse; b) femtosecond laser pulse; Weinkauf *et al.* (50, Copyright 1994 American Chemical Society).

## 3.8 Dissociation mechanisms

Figure 3.19 shows the different molecular ionisation/dissociation mechanisms using a nanosecond laser pulse (panel a) and the femtosecond laser pulse (panel b). The irradiation with the nanosecond laser typically produces more fragmentation than the femtosecond. The dissociation time of a molecule is typically shorter than a nanosecond, thus when the molecule is irradiated it will fragment from an excited neutral state before absorbing further photons to produce fragment ions (know as ladder switching). Ladder climbing occurs when the photon absorption rate is much higher than the rate of dissociation (i.e. femtosecond pulses) from the neutral excited states. In this way, many dissociation pathways are bypassed meaning that any fragmentation occurs from the cation.

### 3.8.1 Coulomb explosion

The study of the ionisation in diatomic and polyatomic (28; 29; 100; 31) molecules is quite complex considering the structure. One of the systems mostly analysed is the

benzene molecule because of the symmetric ring. Shimizu *et al.* (2000) (32) analysed the coulomb repulsion and explosion of the benzene molecule (figure 3.20). The coulomb explosion is a dissociative ionisation process which results from repulsion of a highly charged positive ion formed by removal of multiple electrons (107). The laser used in S. Shimizu *et al.* (2000) (32) work was a Ti: sapphire with short pulse (120 fs) and high laser intensities,  $2.9 \times 10^{16}$ ,  $1.3 \times 10^{17}$ , and  $1.8 \times 10^{17}$  W cm<sup>-2</sup>.

The spectrum obtained at the highest laser intensity, shows that the broadness of the parent ion  $(C_6H_6^+)$  peak depends linearly on the increasing of the laser intensity. More interesting behaviour is related to the multiply charged states of the carbon fragments: C<sup>+</sup>, C<sup>2+</sup>, C<sup>3+</sup>, and C<sup>4+</sup> (figure 3.20 top panel). The ions C<sup>+</sup> and C<sup>2+</sup> are created from low laser intensity, while C<sup>4+</sup> is created from the intensity of  $10^{17}$  W cm<sup>-2</sup> (figure 3.20 bottom panel).

As benzene is a symmetric ring, all the carbon atoms have the same probability to be ionised in the same way. In this work, Shimizu *et al.* (2000) (32) calculated the value of the coulomb repulsion energy (equation 2.18) for each possible combination of carbon atoms (figure 3.21a): comparing the results with the expected coulomb repulsion energy it is possible to calculate the ionisation probability for each carbon bond

$$E_{\rm coul} = 14.4 \times \frac{q_1 q_2}{R} \quad [eV]$$
 (3.19)

where 14.4 is a conversion factor and R is the separation distance of the point charges  $q_1$  and  $q_2$ .

The expected kinetic energy of Coulomb explosion has to be smaller than the Coulomb repulsion energy at the equilibrium. The typical values of  $E_{exp}/E_{coul}$  ( $E_{exp}$  values are listed in 3.21a) are between 45 and 65%. In the case of benzene, comparing the ratio  $E_{exp}/E_{coul}$  with the values found for the channels (see figure 3.21a) the best approximation is found for the channels (1, 4) of and (2, 4), whose ratio is between 47 and 66%, respectively. This means that the distance between the carbon atoms - in C<sup>+</sup> and C<sup>2+</sup> - approximates the coulomb repulsion and explosion theory perfectly. However in the C<sup>3+</sup> and C<sup>4+</sup> the favourite channels are (3,3), (3,4), (4,3) and (4,4), and the theoretical ratio  $E_{exp}/E_{coul}$  is 73/97%. In this case, the benzene is exposed for a very short time to the laser power, therefore the time to elongate the carbon bond is very short and the coulomb explosion may occur before it.

Similarly Cornaggia *et al.* (1995) (33) analysed the coulomb explosion of the  $C_3H_4^+$  and  $C_3H_8^+$ , depending on the laser characteristics (in figure 3.22). Laser



FIGURE 3.20. Benzene molecule ionised by Ti: Sapphire laser. Top panel: benzene spectra at different laser power values; bottom panel: dependence of the carbon multiply charged state on the laser intensity; Shimizu *et al.* (32, Copyright 2000 Published by Elsevier Science B.V).

Carbon	$E_{\rm exp}$	Channel	$E_{\rm coul}$	$E_{\rm exp}$ /
ion	(eV)	$(A^+, B^+)$	(eV)	$E_{\rm coul}(\%)$
C <sup>+</sup>	40	(1,1)	24	167
	-	(1,2)	44	91
	_	(1,3)	65	62
	-	(1,4)	85	47
C <sup>2+</sup>	120	(2,1)	58	207
	-	(2,2)	99	121
	-	(2,3)	140	86
	-	(2,4)	181	66
C <sup>3+</sup>	210	(3,1)	102	206
	. <del></del>	(3,2)	164	128
		(3,3)	226	93
	_	(3,4)	287	73
C <sup>4+</sup>	330	(4,1)	157	216
	10-00	(4,2)	239	138
	-	(4,3)	321	97
	-	(4,4)	404	82
<u>t.</u>				
		$H^+_{\setminus}$	H+	
		$\langle \rangle$		
		С <sup>В+</sup>	C <sup>B+</sup>	
		9		
			$\backslash$ .	
	$H^{+}$ $C^{A+}$ $G^{A+}$ $H^{+}$			
		$\backslash$		
		С <sup>В+</sup>	~B+	
		7	$\sim$	
			$\backslash$	
		H <sup>∔</sup>	Ĥ⁺	
	h			

FIGURE 3.21. a) Values of energy expected and calculated for the coulomb repulsion; b) diagram of the benzene molecular structure; Shimizu *et al.* (32, Copyright 2000 Published by Elsevier Science B.V).

coulomb explosion has become possible with the use of the femtosecond (fs) and picoseconds (ps) laser at  $I \sim 10^{15} - 10^{16}$  W cm<sup>-2</sup>. The ionisation releases multicharged atomic ions and energy. The aim of this work was to determine the geometry of the carbon chain. This was done by using the Ti:Sapphire at 130 fs,  $\lambda$ =790 nm and I=2 ×10<sup>16</sup> W cm<sup>-2</sup>. The single ionisation occurs at the beginning of the laser pulse, and then for higher laser intensity the ionisation occurs by multiphoton ionisation (MPI).

The table (in figure 3.22b) shows the calculated values of the coulomb explosion energy: the coulomb explosion occurs for inter-nuclear distance ( $R_c$ ) larger than the equilibrium distance ( $R_e$ ) due to the stretching of the bonds followings 1<sup>st</sup> ionisation.

#### 3.8.2 Re-scattering

When molecules or bio-molecules are subjected to a strong laser field, as discussed in previous sections, multiphoton or tunneling ionisation are high probable processes in atoms, hence dissociation and re-scattering phenomena become dominant.

Tasker *et al.* (2002) (35) analysed aromatic (34) and nitro-aromatic molecules in order to understand the impact that the ionisation has on the presence (or absence) of the nitrogen monoxide (NO) and dioxide (NO<sub>2</sub>) groups. The molecule examined were benzene (C<sub>6</sub>H<sub>6</sub>), nitrobenzene (C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>), toluene (C<sub>7</sub>H<sub>8</sub>) and 3-nitrotoluene (C<sub>7</sub>H<sub>7</sub>NO<sub>2</sub>); the laser wavelength is 800 nm and the laser intensity is in the range  $8.5 \times 10^{14}$  and  $1.6 \times 10^{16}$  W cm<sup>-2</sup>. Figure 3.23 shows the behaviour of benzene and nitrobenzene.

In figure 3.23 (top panel) the benzene molecule ionised by femtosecond (80 fs) laser intensity of I =  $3.5 \times 10^{15}$  W cm<sup>-2</sup> is shown, where the parent ion peak [C<sub>6</sub>H<sub>6</sub>]<sup>+</sup> and the multiply charged fragments as [C<sub>3</sub>H<sub>3</sub>]<sup>2+</sup>, [C<sub>4</sub>H<sub>3</sub>]<sup>2+</sup> and [C<sub>5</sub>H<sub>3</sub>]<sup>2+</sup> are visible. In figure 3.23 a & b it is shown the nitrobenzene ionised by a femtosecond (80 fs) laser intensity  $1.1 \times 10^{15}$  and  $3 \times 10^{15}$  W cm<sup>-2</sup> laser intensity. Although the two spectra show the presence of the M-NO<sub>2</sub> peak, there is an enormous difference in the presence of the low mass fragments. While the lower laser intensity spectrum shows no ions with a mass-to-charge ratio less than 12 and in the range [CH<sub>n</sub><sup>+</sup>] (n=1-4), the high laser intensity spectrum has ions in both ranges. This is explained by the authors by the coulomb explosion theory: the electric field at  $3 \times 10^{15}$  W cm<sup>-2</sup> is comparable to the electrostatic atomic field of the valence electron. When those are irradiated by the laser, are ejected from the outmost shell and through re-scattering they return to the atoms producing multiply charged ions.

The comparison between the benzene and the nitrobenzene mass spectra shows



FIGURE 3.22. Mass spectrum of  $C_3H_4$  and  $C_3H_8$  at  $I = 2.5 \times 10^{15}$  W cm<sup>-2</sup> and  $\lambda$ =799 nm and table with the coulomb energy calculated and expected; Cornaggia *et al.* (33, Copyright 1995 The American Physical Society).



FIGURE 3.23. Top panel the benzene photoionisation mass spectrum at laser intensity I =  $3.5 \times 10^{15}$  W cm<sup>-2</sup> is shown. In the central and bottom panel the nitrotoluene spectrum is shown: (a) ionisation spectrum laser intensity I =  $1.1 \times 10^{15}$  W cm<sup>-2</sup>, (b) laser intensity I =  $3 \times 10^{15}$  W cm<sup>-2</sup>; Tasker *et al.* (35, Copyright 2002 American Chemical Society).

an important result. While the benzene spectrum shows the presence of a doubly charged parent peak this does not happen for the nitrobenzene molecule. This could be attributed to the strong coulomb repulsion between the aromatic and the nitro group. In fact the nitrotoluene spectrum shows the presence of  $[NO_2]^+$  and  $[C_6H_5]^+$ , which is assumed to be produced by the dissociation of  $[C_6H_5NO_2]^{2+}$ . Secondly, while the benzene spectrum has multiply charged ions, this is absent in the case of the nitrotoluene spectra. Therefore, it is possible to conclude that the coupling laser-benzene ring is stronger than laser-nitrobenzene.

#### 3.8.3 Resonant excitation of cation

Nakashima *et al.* (2000) (99) studied the ionisation mechanisms of molecules subjected to femtosecond laser pulse in terms of intact molecular and fragments created by analysing the molecule at similar laser intensity and different laser wavelength. 2,3-dimethyl-1,3- butadiene sample is analysed by the ToF mass spectrometry ionised by a Ti: Sapphire laser at 130 fs pulse length, intensity  $1.6 \times 10^{14}$  W cm<sup>-2</sup> and laser wavelengths 1.4  $\mu$ m and 0.8  $\mu$ m. Figure 3.24 showing the mass spectra of a 2,3-dimethyl-1,3- butadiene sample obtained at the longer (figure 3.24b) and shorter (figure 3.24c) laser wavelength and the cation absorption spectrum (figure 3.24b).

The spectrum at 1.4  $\mu$ m does not show any strong fragmentation but the molecular ion peak, while in the spectrum at 0.8  $\mu$ m the fragmentation signal is enhanced. This is explained clearly by the cation absorption spectrum which shows that at the shorter laser wavelength (0.8  $\mu$ m) the absorption is resonant with the molecular cation, while at 1.4  $\mu$ m there is no resonant absorption by the cation. The results of a similar experiment using the laser at pulse length of 130 fs, similar laser intensity and 1.4  $\mu$ m and 0.8  $\mu$ m laser wavelength are shown in figure 3.25.

The fragmentation signal of 2,3-dimethyl-1,3- butadiene sample is reduced when the laser wavelength is non resonant with the molecular cation, while at smaller laser wavelength (0.8  $\mu$ m) the ionisation favours fragment production. The conclusions drawn by Nakashima *et al.*(2000) (99) were that in the femtosecond regime the fragmentation signal is favoured when the laser wavelength is resonant with the electronic absorption of the parent cations

Anthracene, pyrene, tetracene and chrysene samples were analysed by Robson  $et \ al. (2002) (100)$  by ionising at 800 nm and 400 nm laser wavelengths. Both spectra contain similar fragmentation and molecular ion peak signals; this is due to the fact that the absorption strength at the 800 nm and at 400 nm laser wavelengths. These



FIGURE 3.24. Mass spectra of 2,3-dimethyl-1,3- butadiene sample ionised by a Ti: Sapphire laser at 130 fs pulse length, intensity  $1.6 \times 10^{14}$  W cm<sup>-2</sup> and laser wavelength 1.4  $\mu$ m (a) and 0.8  $\mu$ m (b). The molecular ions are indicated by M<sup>+</sup> and the asterisk (\*) represents the H<sub>2</sub>O<sup>+</sup> signal. The absorption spectrum of 2,3-dimethyl-1,3- butadiene cation radical is shown in (c), where the two Gaussian shapes are the spectra of the excitation pulses; Nakashima *et al.* (99, Copyright 2000 Japanese Photochemistry Association).



FIGURE 3.25. Mass spectra of anthracene at  $1.4\mu m$  (a) and  $0.8\mu m$  (a) at  $1.6 \times 10^{14} \text{ W cm}^{-2}$ ; the cation absorption spectrum in a low-temperature matrix with two spectra of the excitation pulses is shown in b; Nakashima *et al.* (99, Copyright 2000 Japanese Photochemistry Association).



FIGURE 3.26. Mass spectra of anthracene, pyrene, tetracene and chrysene samples and the degree of fragmentation at 400 nm at intensity of about  $8 \times 10^{14}$  W cm<sup>-2</sup>; Robson *et al.* (100, Copyright 2002 Elsevier science B.V.).

two laser wavelength are resonant with the electronic absorption of the parent cation. Figure 3.26 shows the spectra of the four molecules and their cation absorption spectrum at 400 nm laser wavelengths at  $5 \times 10^{14}$  W cm<sup>-2</sup> and  $9 \times 10^{14}$  W cm<sup>-2</sup>.

The conclusion reached by Robson *et al.* (2002) (100) is quite different from the conclusions of Nakashima *et al.* (2000) (99), in fact his work shows that for these polycyclic aromatic hydrocarbons the fragmentation is quite low even when the cation has a resonance. This may be because these molecules require more than one bond to break to produce a fragment. In fact they are quite stable even to ns laser ionisation. In Itakura *et al.* (2001) (101) benzene neutral and benzene cations were analysed by a ToF spectrometer and exposed to an intense laser field  $(2.5 \times 10^{16} \text{ W cm}^{-2})$ at 395 and 790 nm laser wavelength (figure 3.27) and pulse duration 50 fs. In both figures it is shown that the major fragments obtained from benzene neutral and cations are similar therefore the ionisation and dissociation dynamics of the benzene neutrals and cations are the same apart from the formation of the benzene cations.

Figure 3.27 c&d shows the different ionisation signal produced by REMPI on benzene and benzene cation molecule. It is shown that at the same laser intensity of 395 nm and laser pulse length of 50 fs the  $C_3H_j^+$  (j=3) ions signal is lower than the  $C_4H_i^+$  (i=3) ions signal, for both benzene and its cation. At 790 nm the small fragments are not identified, while the benzene dications are detected. The schematic diagram of the benzene neutral ionisation is shown in figure 3.28.

#### 3.8.4 Bond softening

When a molecule is subjected to a strong laser field, the multiphoton ionisation process that occurs can be explained through the bond softening (BS) and vibrational trapping (VT). The bond softening represents the high dissociation probability reached by the ground state when it becomes not bound with the increasing of the laser intensity: the molecular dissociation is favoured in the gap between the ground state when it is distorted by the strong field, reducing the potential well and bond energy. Conversely, the vibrational trapping is the low dissociation probability, which occurs when the potential well in the excited state is deepened meaning that the high excited vibrational states that were dissociative are now trapped into the laser-induced well.

These processes are seen in the analysis of the  $H_2^+$  molecular dissociation in a strong laser field, studied by Posthumus (2004) (98). The dynamics of the molecule is described by the integration of the time-dependent Schrödinger equation where the nuclear motion is restricted on the polarisation direction of the electric field of the laser. The molecule is analysed by a ToF mass spectrometer and the ionisation is enhanced by the Ti: Sapphire laser pulse width 55 fs, peak intensity  $10^{15}$  W cm<sup>-2</sup>, wavelength 750 nm and the field is linearly polarised (figure 3.29).

 $\rm H_2^+$  is dissociated to  $\rm H+H^++2e^-$  or ionised, yielding a Coulomb explosion:  $\rm H^++H^++2e^-$ . The ground state of  $\rm H_2^+$  molecule is a super strong electric field. When the polarisation is long the molecular axis, the laser field couples the  $1s\sigma_g$ (ground state) with the  $2p\sigma_u$  causing the electron to be pushed to one of the nuclei. When the molecule is subjected to a long wavelength laser field, the ionisation



FIGURE 3.27. Mass spectra of neutral benzene molecules irradiated at (a) 395 nm and (b) 790 nm laser wavelength at  $2 \times 10^{16}$  W cm<sup>-2</sup>. Mass spectra of benzene cations at (c) 395 nm and (d) 790 nm laser wavelength at  $2.5 \times 10^{16}$  W cm<sup>-2</sup>; the peaks labelled with one, two or three asterisks are fragments of C<sub>6</sub>H<sub>5</sub>; Itakura *et al.* (101, Copyright 2001 American Institute of Physics).



FIGURE 3.28. Schematic representation of the ionisation and fragmentation processes of benzene; Itakura *et al.* (101, Copyright 2001 American Institute of Physics).



FIGURE 3.29. Photo-dissociation spectrum of  $H_2^+$  obtained by Ti:Sapphire laser pulse width 55 fs, peak intensity  $10^{15}$  W cm<sup>-2</sup>, wavelength 750 nm linearly polarised; Posthumus (98, Copyright 2004 IOP publishing Ltd).



FIGURE 3.30. Energetic representation of the nuclear dynamics. a) Small internuclear (R) distance, b) large internuclear distance; Posthumus (98, Copyright 2004 IOP publishing Ltd).

depends on the internuclear distance, which is shown in figure 3.30.

For small R (figure 3.30a) the molecular polarisation changes with the changing of the laser field. For large R (figure 3.30b) the electron obtained by the  $H_2^+$  dissociation is localised, therefore it cannot tunnel from one side to the other hence the distribution of the population on the left and right is the final and it can be H+H<sup>+</sup> or H<sup>+</sup>+H.

Figure 3.31 shows the distortion of the field-free ground state and excited state potential energy diagram of  $H_2^+$  as a function of the nuclear distance (R). Molecules initially in high vibrational states are trapped in the upper potential well but can still dissociate by a ZPD mechanism. Lower vibrational states dissociate by bond softening (BS) through a curve crossing between the ground state and the excited state dressed with 1 photon.

## 3.9 Conclusion

When an atom/molecule is irradiated by the laser field, two ionisation mechanisms are possible: the multiphoton and the tunnelling ionisation. The first occurs for a laser field not stronger than the coulomb binding energy, while by for higher



FIGURE 3.31. Plot of the potential ionisation in function of the internuclear distance in  $H_2^+$  molecule; Posthumus (98, Copyright 2004 IOP publishing Ltd).

intensities, the ionisation occurs by tunnelling. The disadvantage in ionising by MPI is the high degree of fragmentation, which can be partly reduced by the use of a ultra-fast (fs) laser pulse. The two mechanisms are distinguished by the Keldysh parameter (equation 3.17) and explained by the ADK (equation 3.9) and the Landau-Dykhne theory (equation 2.16). In this work, the samples were analysed in gas phase and ionised by a femtosecond laser pulse duration. In the discussion of the data the only guide for the understanding of relevant dynamics is the Keldysh parameter since the other two theories are not simple to calculate for the molecules concerned due to the lack of accurate information on the relevant parameters.

# Chapter 4

# Instrumentation

In this chapter the instrumentation used will be presented: a combination of a time of flight mass spectrometer and femtosecond laser.

## 4.1 Time of Flight Mass Spectrometer

The mass spectrometer used is the LIMA, Laser Ionisation Mass Analyser (Cambridge Mass Spectrometry Ltd). It is equipped with a Ga primary ion gun for SIMS analysis and optics for laser desorption studies, as well as windows allowing postionisation or gas phase laser ionisation. It is a Time of Flight Mass Spectrometer that uses the time of flight to determine m/z of the ions produced in the source region.

### 4.1.1 LIMA instruments

The instrument components are shown in figure 4.1 and are described briefly bellow:

• Sample Loading & Preparation chamber: the sample is transferred transferred into the main chamber through the Load chamber and the Preparation chamber using magnetically coupled transfer arms. Both chambers are connected with



FIGURE 4.1. Laser ionisation mass spectrometer (LIMA) instrument.

a 150 L/s turbo pump (one for each) and share a common rotary pump; this pumping system will provide a vacuum of  $\sim 10^{-8}$  mbar;

- Main chamber: this is the location of the sample stage. Optically flat windows allow the ionisation laser to be directed across the face of the sample. This chamber is connected with its own 500 L/s turbo and rotary pumps; the base pressure inside the chamber is  $\sim 10^{-8}$  mbar (figure 4.2);
- Ion Gun: here, the primary ions that will bombard the sample to produce the secondary ions are generated (figure 4.2). A 25 kV Liquid Metal Ion Gun (LMIG) is available on this system, producing a current of 1.5 nA microfocused to a spot that can be rastered over the sample area with a magnification >150x. In this system a gallium liquid-metal ion gun is used. The ion source is pumped with a 50 L/s ion pump;
- Sample Stage: it is located inside the main chamber and it has a circular shape for holding up to eight samples (figure 4.2);
- Secondary ions extraction optics: these are used to extract the ions into the mass spectrometer, thanks to the potential difference that is applied between the end of the extraction optics ( $\sim 0 \text{ V}$ ) and the sample stage ( $\sim 3 \text{ kV}$ ) which

are placed 1 cm away. There are three types of lenses available on the LIMA, mounted on a rotating system inside the main chamber: *Optical Lens, Laser lens* and *SIMS lens* (figure 4.3). The Optical Lens is a low magnification glass lens that only allows the view of the sample from a camera or microscope system connected to a TV screen using a combination of mirrors; the Laser Lens (high magnification lens) and the SIMS lens will convey the ions into the Time of Flight-MS with the only difference that the SIMS lens uses only the electrostatic ion extraction lens whereas the Laser lens has additional mirrors allowing a separate laser beam to be brought to a focus at the sample for direct laser desorption/ionisation. The Laser lens system has a hole to let the ions go through to the MS (figure 4.4). The throughput of the electrostatic optics is very difficult to measure given all the uncertainties involved. Because the interest in this work regards the relative quantification and not the absolute quantification, it is assumed that over the range of focal volumes used it should be quite constant;

- Collimation lens: these are necessary to direct the extracted analytes ions into the secondary ions extraction lens of the Time of Flight (figure 4.2). These are a set of steering and focusing electrodes that collimates the secondary ions and deflect them into the optimum path through the ToF-MS onto the detector. The steering voltages is about  $\pm$  150 V and the focusing voltage is about <4 kV;
- Time of Flight Mass Spectrometer: ions accelerated by the electrostatic field above the sample enter a flight tube where they are separated according to different mass-to-charge ratio of the basis of their velocity distribution. The ToF-MS contains a dual-stage reflectron for ion kinetic energy-compensation. The total flight length is ~ 3 m. At the end of the Time of Flight SIMS the ions are detected by the micro-channel plates;
- *Micro-channel plates*: a dual MCP electron multiplier assembly is used in the LIMA instrument (35 mm diameter). It consists of very many electron multiplier channels (in glass) oriented in parallel one with respect to the other. An electrical voltage (2-3 kV) is applied between the front and rear in order to amplify the ion signal by electron cascade, resulting in an output of a 10-25 mV for each ion impact. The absolute ion production per shot is obtained from MCP signal by converting the signal area recorded by the MCP through the DA500 into ion counts using the average area of a single ion arrival. It

is not possible to calculate the absolute ion numbers produced because the transmission and detection efficiency have not been calibrated. In this work is assumed that the MCP efficiency is constant over the range of laser wave-length. Any mass dependent effects should be smaller for different analytes and not vary with laser conditions;

- *Preamplifier*: this is used to amplify the signal from the anode of the MCP assembly and to send it to the transient digitiser in the computer. The gain of this unit is x40, providing a voltage pulse of  $\sim 0.5$  V for the transient digitiser to record. The preamplifier also allows discrimination against background noise levels in the detector by setting a threshold ( $\sim 10$  mV), below which signals are not amplified;
- The transient digitiser DA500 (Signatec Ltd) has a 2 ns time resolution. It is triggered by the laser start-pulse and records ion arrival times from the signals coming out of the pre-amp;
- *Ion gauge*: it measures the gas pressure inside the main chamber. It consists of a filament, a grid and a collector. The heating of the filament generates electrons that, getting through the grid collide with the gas molecule inside it, producing ions. Only the positively charged ions are attracted by the collector since it is negatively charged.

### 4.1.2 Laser Ti:Sapphire

The laser medium in use is Ti:Sapphire (chemically  $Ti^{3+}:Al_2O_3$ ). The importance of the Sapphire monocristalline  $Al_2O_3$  is in its thermal, physical and optical proprieties; in fact the  $Ti^{3+}$  ions have a very large gain bandwidth, that favour the generation of very short pulse and wide wavelength tunability. The pulse length duration is 50 fs. with a central wavelength of 800 nm. This can be converted to a longer wavelengths by Optical Parametric Amplification (OPA). The separate components of the laser system are summarised below, followed by an outline of the operation of the complete system to generate the laser light that is used in this work.

Laser is schematised in figure 4.5:

Micra 5: it is the oscillator laser at the core of the Ti: Sapphire system. The characteristics are: between 30-100 nm bandwidth with pulses width of ~ 100 fs; power >300 mW at 80 MHz, operating between 760-850 nm using one set of optics (figure 4.6);



FIGURE 4.2. LIMA components: the Ion Gun, the Sample Stage and the Collimation lens.



FIGURE 4.3. Secondary ions extraction optics: different lens (Microscope, SIMS (right panel) or Laser) can be selected by rotating the external knob on the top of the LIMA. While the SIMS and Laser lens are used for the SIMS and post-ionisation analysis, the Microscope lens only allow the sample visualisation through the microscope.



FIGURE 4.4. Laser lens (on the left); Optical lens (on the right).



FIGURE 4.5. Sapphire laser components from coherent (72, Copyright Coherent, Inc. 2012).



FIGURE 4.6. From left to right: Micra 5, Coherent Micra-CEP and Silhouette II (72, Copyright Coherent, Inc. 2012).

- Legend-Elite Duo USP: this is a power amplifier. The characteristics are: for pulse width < 40 fs at a central wavelength of 800 nm, the high energy and high efficiency of the amplifier is designed to be greater than 6 mJ at a frequency of 1 kHz (figure 4.7);
- Evolution HE: it is a high energy pump laser, diode pumped, Q-Switched and intracavity frequency-doubled Nd:YLF laser (its medium is Nd<sup>3+</sup>: YLF, neodymium yttrium lithium fluoride). It produces more than 45 W of average power for 527 nm wavelength and more than 45 mJ pulse energy at 1 kHz (figure 4.7);
- *OPerA Solo*: Optical Parametric Amplifiers. This extends the tuning capability of the Legend Elite. The laser instrumentation contains three of them: one is configured to emit between 190-2600 nm; the second to emit between 240-2600 nm and the third to emit from 1100 nm up to 18,000 nm (figure 4.7);
- Coherent Legend HG: is an ultra-short harmonic generation, where the second harmonic generation SHG- (as shown in figure 4.5) is for a wavelength of 400 nm, whereas the third harmonic generation THG- is for a wavelength of 266 nm, and the fourth harmonic generation FHG- for a wavelength of 200 nm.

The oscillator in the Micra 5 allows the laser light to go out and through the CEP. These are modified in phase and amplitude by the Silhouette that produces in output another laser radiation. The latter goes through the power amplifier Legend, inside of which the laser beam follows two paths: the rays reach firstly the pump (Evolution HE) and then they reach the output.



FIGURE 4.7. From left to right: Legend-Elite Duo UPS, Evolution HE and OPerA Solo (72, Copyright Coherent, Inc. 2012).

After this, the laser beam goes to the output from the amplifier and goes inside the OPA, used to select different wavelengths.

The input of the mass spectrometer is a UV Grade Calcium Fluoride  $(CaF_2)$  window. It is used because it has the following properties:

- Low Absorption, High Transmission;
- Ideal for Applications Ranging from 250 nm to 7  $\mu$ m;
- Low Index of Refraction.

# Chapter 5

# Experimental

In this work a Ti:Sapphire laser with pulse duration 50 fs, repetition rate of 1KHz and fundamental wavelength 800 nm was used. An OPA system was used in order to extend the laser wavelength up to 1300, 1500, 1714 and 1900 nm. To estimate the laser characteristics, such as the beam dispersion and the laser power, it was necessary firstly to measure the beam spot size. Two different methods have been used to do this; one was applied only for the 800 nm and a second one for longer wavelengths. Due to the large laser diameter at 800 nm, the beam spot size was measured at the focal point in two ways; the first consists in a simple manual measure of the beam diameter (D) in the output of the amplifier, while the second is an experimental measure of the beam profile at focal distance (both methods will be discussed in following subsection). For longer wavelengths the laser beam diameter is smaller, therefore a CCD camera has been used in order to measure the beam profile either next to the output of the OPAs system ("near field") and also just before the focal lens ("far field"). In this way it has been also possible to measure the beam dispersion ( $\theta$ ). The camera uses the software Beam Gauge (73), a laser beam analyser. For the OPAs it was not possible to measure the beam spot size at the focal point due to the very small beam profile.

## 5.1 Laser radiation characteristics

A plane electric field is propagated in time and space as a sinusoidal wave. However, a real laser beam does not behave as an ideal monochromatic wave. When, at two different times, the ratio of the phases of two points in the wave changes, the wave has lost its temporal coherence. If, instead, the ratio of the phases is constant, the wave is temporarily coherent. The wave is also in spatial coherence when the phase difference remains constant during the time interval dt. The laser beam has high temporal and spatial coherence and the laser wave is monochromatic, since the amplitude never changes over the time t.

The laser beam has a defined direction because the active medium is placed into a resonant cavity and the output beam is forced to follow a certain path. The brightness B of the laser beam is related to the laser power E emitted per unit of surface area S and per unit of solid angle  $\Omega$  (74).

$$dE = B \cos\theta \ dS \ d\Omega \tag{5.1}$$

Considering that the laser has a circular beam diameter whose area is defined  $\pi d^2/4$ , the solid angle is equal to  $\pi \theta^2$ , where  $\theta$  is the divergence angle (explained more in details in the next section). Because  $\theta$  assumes small values such that  $\cos\theta \sim 1$ , the brightness *B* is defined as follow:

$$B = \frac{dE}{\cos\theta \ dS \ d\Omega} = \frac{E}{\left(\frac{\pi d^2}{4}\right) \times (\pi \theta^2)} = \frac{4E}{(\pi d\theta)^2}$$
(5.2)

## 5.2 Lens focusing

The focusing lens has different propriety for different laser characteristics, i.e. the laser wavelengths. For the present work, a BK-7 Plano convex lens was used, since it is adaptable for waves between 380-2100 nm wavelengths.

A characteristic parameter of a lens is the *focal point* (figure 5.1), defined as the point where the parallel rays converge after going through the lens. The distance between this point and the lens is defined as the effective focal length f. For a plano-convex lens it is calculated in the following way:



FIGURE 5.1. Schematic representation of the lens.

$$f = \frac{R}{n-1} \tag{5.3}$$

where R is the curvature radius and n is the refractive index, which is calculated:

$$n = \frac{c}{v} \quad and \quad \lambda = vT \tag{5.4}$$

where c is the speed of the light in vacuum, v is the speed of the light in a transparent medium, T is the wave frequency and  $\lambda$  is the laser wavelength. In this case, the lens has a thickness of 3.5 mm and the curvature radius is 155 mm. Typically the refractive index is about 1.5, therefore the focal length of the BK-7 Plano convex lens is f = 30 cm.

In this experiment the focal point was placed at about 1 mm away from the SIMS lens and this position was determined by a manual alignment of the laser rays inside the LIMA chamber. In order to do this, the main chamber was opened and the path of the laser rays was checked through the use of a paper (thermal sensitive



FIGURE 5.2. Schematic representation of the laser optics.

for the OPAs wavelength and a normal one for the 800 nm). For safety reasons the laser power used was the lowest possible (at 800 nm it was about 1.5 mJ, while at 1300 nm was about 180  $\mu$ J).

## 5.3 Laser optical characteristics

In figure 5.2 it is shown that:

- Green rays: laser beam before going through the focusing lens;
- Blue oval :the lens;
- *Red rays*: laser beam after have gone through the focusing lens. The dashed red lines represent the not deviated rays, while the solid lines are the deviated rays;
- θ: divergence angle; it is formed by the intersection of the divergent and not divergent rays (red rays);
- d and  $\omega$ : diameter and the radii of the beam spot size, respectively;



FIGURE 5.3. Schematic representation of the laser beam divergence.

- *f*: focal distance;
- $z_{\rm r}$ : Rayleigh range (where the beam waist is increased by a factor of the square root of 2) defined as the distance between w and  $\sqrt{2}w$ ;
- *straight black line*: optical axis.

The important parameters that need to be calculated by trigonometry are the beam divergence  $\theta$  and the laser beam diameter d.

The beam divergence is calculated with the trigonometry, considering the triangle made by w, the dashed red line (called a in figure 5.3) and the straight red line (called b in figure 5.3). For low angles ( $\theta \ll 1$ ) the latter can be approximated with f. In theory  $\omega = b \sin\theta$  and for  $\theta \ll 0$ ,  $\sin\theta \to 0$  and also  $b \to a = f$ , hence:

$$\omega = f \ \theta \tag{5.5}$$

Those equations are used for all the wavelengths taken into consideration for our

work. Considering an ideal lens, where the average power energy of the laser beam in input and in output have the same value E, the laser fluency  $\Phi$  is defined as:

$$\Phi = \frac{E}{\pi (f\theta)^2} = \frac{4E}{\pi d^2} \tag{5.6}$$

The lasers beam intensity I is defined as the ratio of the fluency and the laser pulse  $\tau$  ( = 50 fs):

$$I = \frac{\Phi}{\tau} \qquad [W \ cm^{-2}] \tag{5.7}$$

The laser beam diameter is then calculated by the following equation (78; 79):

$$d = \frac{4\lambda f}{\pi D} \times M^2 \tag{5.8}$$

where:

- *d* is the diameter of the laser beam;
- $\lambda$  is the laser wavelength;
- *f* is the focal distance;
- *D* is the diameter of the laser beam before being focused;
- $M^2$  is the quality factor, which defines how much the laser beam is approximated to a Gaussian shape. The value is 1 for a perfect beam; in this case the quality factor is ~ 1.2.

## 5.4 Laser characteristics at 800 nm wavelength

### 5.4.1 Laser beam path

The laser beam path, from the amplifier to the sample stage is schematically represented in figure 5.4.

Distances:



FIGURE 5.4. Laser beam path from the amplifier (legend elite duo) to the sample stage. The dashed lines represent the laser beam path; the dashed blue circles are the iris positions, the double blue circles are the mirrors (M) positions, the single blue circles are the mirrors before the focal lens, the green double circle is the focal lens and the transparent full circle is the CaF2 window.  $P_{0,1,2,3,4,5}$  represent the average laser power values of the laser along the beam path.

- 1. Distance between the legend-elite duo USP to M1 is 32 cm;
- 2. Distance between the M1 to M2 is 124 cm;
- 3. Distance between the M2 to M3 is 445 cm;
- 4. Distance between the M3 to focusing mirror is 10 cm;
- 5. Distance between the focusing mirror and the input window is: 16 cm.

As shown in the graph  $P_i$  (for i = 0,1,2,3,4,5) represent the position where the average laser power measurements are taken ( $P_0$  is the maximum power reached by the 800 nm laser wavelength).

- (a)  $P_0 = 6.82$  W;
- (b)  $P_1 = 6.66 W;$
- (c)  $P_2 = 6.51 \text{ W};$
- (d)  $P_3 = 6.37 W;$

(e)  $P_4=6.19$  W;

(f)  $P_{4*}=5.82$  W (power taken for the beam that pass through the CaF<sub>2</sub> window);

(g)  $P_5 = 5.42$  W.

The list below shows the percentage of the power waist at each step of the measurements:

- % power lost from  $P_0$  to  $P_1$ , is: 2.3%;
- % power lost from  $P_1$  to  $P_3$ , is: 6.6%;

 $\Rightarrow$  % power lost P<sub>0</sub> to P<sub>3</sub> is: 9%: this is due to the interaction with the air and the passage of the beam through the mirrors.

- % power lost from  $P_3$  to  $P_4$ , due to the interaction with the air is: 2.8%;
- % power lost from  $P_0$  to  $P_{4*}$ , due to the passage through the CaF<sub>2</sub> is: 8.6%;
- % power lost from  $P_3$  to  $P_5$ , due to the passage through the focal lens is: 15%;

 $\Rightarrow$  % power lost P<sub>0</sub> to P<sub>5</sub>, considering also the percentage lost through the CaF<sub>2</sub> window (approximated to the 9%), is 33%.

#### 5.4.2 Beam spot size

One way to estimate the beam spot size (d) is to hit a material, in this case normal glass, with the laser beam in the focal point; this will generate a crater, as shown in figure 5.5, in the target.

When the laser beam hits the glass, the edge of the irradiated area represents the tail of the Gaussian distribution (corresponding to  $\frac{1}{e^2}$ ). Approaching to the FWHM (full width at half maximum) the resulting crater is the melting area and the peak of the Gaussian is the ablated area (see figure 5.5). The measure of the diameter of the irradiated area is the estimation of the beam spot size in the focal point (called d). The instrumentation used for this purpose is composed of the laser and a stage where the sample is fixed. Basically, the sample has been irradiated with different laser powers, each time for a duration T = 1.5 minutes which was manually controlled. The craters on the glass were analysed with a microscope using a program called Image J (75). The software calibration was done by using the image shown in the picture below, that was acquired on a piece of metal (figure 5.6).



FIGURE 5.5. Schematic representation of the laser beam spot size also represented in relation to the Gaussian distribution.



FIGURE 5.6. Calibration image: the distance, indicated by the red arrow, is 50  $\mu$ m.

The figure 5.7 shows the dependence of the diameter spot size (now indicated with  $d_a$ , irradiated area) on the laser power.


FIGURE 5.7. Energy, crater and diameter spot size measured.

$$\Phi = \frac{2E}{\pi\omega^2} \tag{5.9}$$

$$d_{\rm a}^2 = 2\omega^2 \ln(\frac{\Phi_0}{\Phi_{th}}) \tag{5.10}$$

Where  $\Phi_{th}$ , is the threshold fluency,  $\Phi_0$  is the fluency at  $\frac{1}{e^2}$  of the Gaussian distribution. From the equation 5.9 it is clear that the fluency and the laser energies are linearly related, therefore the beam radius ( $\omega$ ) is estimated by plotting  $d_a^2$  in function of  $\ln E$ .

From the equation 5.2:

$$d_{\rm a}^2 = 2\omega^2 \ln E \tag{5.11}$$

Therefore the slope of the trend in the graph 5.8 is  $2\omega^2$ 

$$(3.8 \pm 1.6) \times 10^6 = 2\omega^2 \quad (\mu m)^2 \tag{5.12}$$

Another way used to calculate the diameter spot size (d) is to measure the diameter (to make a distinction with previous calculations it will be called D) of the beam before it goes through the focal lens by using a micro-meter. Those two quantities are related by the equation 5.8 (76; 77).

Where f is the focal distance and  $M^2$  is the quality factor. The values of f and  $M^2$  are 30 cm and 1.2, respectively. Having D = 4.8 mm, from the above equation, we find d = 64 ± 4  $\mu$ m.

The first method to measure the beam spot size was not applied since part of the required instrumentation described above (the fixed sample stage and the shutter) was not available. As result of that the images of the craters are non clear to analyse: in fact in figure 5.7 the irradiated area can be easily confused with the ablated one. For this reason this experiment was repeated few times and the pictures shown in figure 5.7 are selected among the best ones. The measurements of the beam diameter



FIGURE 5.8. Dependence of the laser diameter squared  $(d_a^2)$  on the log of the laser power density. The slope is the value of the radius of the laser beam spot size.

on the craters were taken 5 times and the plot in figure 5.8 shows the measurements with the correspondent standard deviation error, at which the parallax error, that cannot be estimated, should be added.

Also the second method used is uncertain, because the measurement of D with the micrometer is not accurate enough.

As an alternative, the focal diameter was estimated from xenon saturation data: the xenon gas is taken as a control sample because its ionisation trend is well known and it produces multiple charge states without fragments (it will be explained in details in the next chapter). Figure 5.9 shows the ionisation yields of xenon ions obtained by Larochelle *et al.* (1998).

From Larochelle *et al.* (1998) (80) the laser intensity at the saturation is  $I = 10^{14}$ 



FIGURE 5.9. Multiple ionisation of the xenon gas phase at 800 nm laser wavelength: dependence of the ion signal on the laser intensity (log-log plot) where the solid lines correspond to the ADK theory; Larochell *et al.* (1998) (80).

W cm<sup>-2</sup>, while the power density obtained in this work (shown in the chapter 5) at which the Xe<sup>+</sup> reaches saturation is 3.4 mJ. Finally, considering the equations 4.6 and 4.7, with a laser pulse duration of 50 fs, the diameter spot size is estimated to be  $d \sim 0.029$  cm.

The dispersion angle is calculated with the formula

$$d = 2 \times f \times \theta \tag{5.13}$$

therefore it is about  $4.8 \times 10^{-4}$  rad.

## 5.4.3 Effective ionisation volume

Another important characteristic of the laser is the estimation of the effective ionisation laser volume. When the sample is ionised in gas phase, a certain amount of particles will be ionised by the laser; therefore is important to define the volume of ionisation.

In figure 5.2 the effective ionisation region, is the volume included between two times the  $\sqrt{2}\omega$ , two times  $\omega$  and the Rayleigh range  $(z_{\rm R})$ , is half of the effective ionisation volume. To simplify, the volume can be approximated with a truncate cone as shown in figure 5.10.



FIGURE 5.10. Approximation to a truncate cone.

The Rayleigh range can be approximated as a straight line; however this will slightly overestimate the laser volume because the laser beam rays are not straight lines. Therefore, considering the diameter spot size calculated d = 0.29mm knowing that:

- $\omega = 0.145 \text{ mm};$
- $2\omega = 0.29$  mm;
- $2\sqrt{2}\omega = 0.38$  mm;
- $z_R = \frac{\pi \omega^2}{\lambda} = 71 \text{ mm.}$

The volume from which ions can be successfully detected is limited by the ion extraction optics. Hence, the effective ionisation volume is:

$$V_{\rm L} = \frac{1}{3}\pi (r_1^2 + r_1 r_2 + r_2^2)h = 0.33mm^3$$
(5.14)

where:  $r_1$  is  $2\omega$ ,  $r_2$  is  $2\sqrt{2}\omega$  and h is 1 mm.

# 5.5 Laser characteristics at OPAs wavelengths

The beam shape was detected from the camera in two places, outside of the OPAs system and before the focal lens; to be clear in the further discussion the first measurement is called "near field" (NF) and the second is "far field" (FF). A schematic representation of the laser beam path from the OPAs to the input of the LIMA is schematised in 5.11.



FIGURE 5.11. Laser beam path from the amplifier OPAs to the sample stage. The dashed lines represent the laser beam path; the dashed blue circles are the iris positions, the double blue circles are the mirrors positions, the single blue circles are the mirrors (M) before the focusing lens, the green double circle is the focusing lens and the transparent blue full circle is the  $CaF_2$  window.

Distances:

- From the first mirror M1 to the first iris  $P_1$ : 60 cm;
- From the first iris  $P_1$  to the second  $P_2$ : 440 cm;
- From P<sub>2</sub> to the focusing lens: 15 cm;
- From the focusing lens to the CaF<sub>2</sub> window: 3 cm.

The distances were taken considering the iris positions only to simplify the measurements. The beam power along the beam path has been measured in  $P_0$ ,  $P_1$ ,  $P_2$ , and  $P_3$  positions. The measure of the percentage of power lost from the focusing lens to the CaF<sub>2</sub> window, was taken in the  $P_4$  and  $P_5$  after moving the focusing lens on the table and using a second CaF<sub>2</sub> for the measurement. This was done because it was not possible to remove the CaF<sub>2</sub> shown in the diagram above and the space between that and the focusing lens was very small, not allowing any kind of measure.

## 5.5.1 Wavelength 1300, 1500, 1714, 1900 nm

#### Power study

In table 5.1, is shown the percentage of the power lost along the beam path .  $P_0$  is the maximum power reached at every laser wavelength and P is the output power.

Wavelengths	P <sub>0</sub>	$P_2$	P <sub>3</sub>	$P_4$	$P_{4,5}$	Р
(nm)	(mW)	(mW)	(mW)	(mW)	$(\mathrm{mW})$	(mW)
1300	370	350	280	290	274	274
1500	250	218	130	170	160	160
1714	260	250	220	190	170	170
1900	240	234	200	160	150	150

TABLE 5.1. Average power values for 1300, 1500,1714 and 1900 nm.

Considering that inside the LIMA the chamber is under vacuum, the power at about 1 cm before the focal point should be the same as the power in  $P_5$ , because there should not be further interaction laser-air. Therefore the percentage of power lost from  $P_0$  up to P is approximately 27.5% for 1300 nm, 38% for 1500 nm, 36% for 1714 nm and 36% for 1900 nm.

#### Laser beam profile at 1300 nm lase wavelength

As mentioned previously, the CCD camera and the software Beam Gauge have been used to take the two an three dimension images of the beam profile in the narrow and far field (fig. 5.12) at  $\frac{1}{e^2}$  of the Gaussian distribution.

As shown in figure 5.12, the two dimensional intensity profile (which is presented as a 20 column, 2D relief plot) of the beam profile taken at FF has a very broad shape in respect to the NF images, and so the diameter of the beam (before going through the focal lens) size measured in far field ( $D_{\rm FF}$ ) is broader by ~ 59% than the diameter of the beam size measured in narrow field ( $D_{\rm NF}$ ).

Narrow Field:  $\lambda$  = 1300 nm; f = 30 cm; M<sup>2</sup> = 1.2 and D<sub>NF</sub> = 5.536 mm, d<sub>(NF)</sub> is 0.108 mm,  $\theta_{(NF)}$  = 2  $\times10^{-4}$  rad

Far Field:  $\lambda = 1300$  nm; f = 30 cm; M<sup>2</sup> = 1.2 and D<sub>FF</sub> = 9.333 mm,



FIGURE 5.12. 2D and 3D image of the beam profile taken for the NF and FF positions for the 1300 nm wavelength.

 $d_{(FF)}$  is 0.064 mm,  $\theta_{(FF)} = 1 \times 10^{-4}$  rad

The divergence angle calculated at the narrow field is two times the ones estimated at the far field. Although d calculated at the narrow field has lower value than the far field, in this work has been used the  $d_{FF}$  to be consistent in the comparison with the 800 nm, where the laser beam diameter (D) was measured at the far field.

The study of the percentage of the power lost, beam shape and divergence angle has been done also for the 1500, 1714, 1900 nm. Because the methodology is the same, the data will be schematically represented.

### Laser beam profile

A comparison of the beam profile at the 1500 nm wavelength, corresponding to the  $\frac{1}{e^2}$  of the Gaussian distribution, is shown in figure 5.13.



FIGURE 5.13. 2D and 3D image of the beam profile taken for the NF and FF positions for the 1500 nm wavelength.

The diameter of the beam size measured in the far field ( $D_{FF}$ ) is wider by ~ 54% than the diameter of the beam size measured in the narrow field ( $D_{NF}$ ).

Narrow Field:  $\lambda$  = 1500 nm; f = 30 cm and D<sub>NF</sub> = 4.185 mm, d<sub>(NF)</sub> is 0.143 mm,  $\theta_{(NF)}$  = 2  $\times 10^{-3}$  rad

Far Field:  $\lambda = 1500$  nm; f = 30 cm and D<sub>FF</sub> = 8.964 mm,

 $d_{(FF)}$  is 0.077 mm,  $\theta_{(FF)} = 1 \times 10^{-4}$  rad

### Laser beam profile at 1714 nm

A comparison of the beam profile taken at the 1714 nm wavelength, corresponding to the  $\frac{1}{e^2}$  of the Gaussian distribution, is shown in the graph below. The D<sub>FF</sub> is wider than the D<sub>NF</sub> of about 47%.

- Narrow Field:  $\lambda = 1714$  nm; f = 30 cm and D<sub>NF</sub> = 2.991 mm, d<sub>(NF)</sub> is 0.26 mm,  $\theta_{(NF)} = 4 \times 10^{-3}$  rad
- Far Field:  $\lambda = 1714$  nm; f = 30 cm and D<sub>FF</sub> = 6.372 mm, d<sub>(FF)</sub> is 0.12 mm,  $\theta_{(FF)} = 2 \times 10^{-4}$  rad

#### Laser beam profile at 1900 nm

A comparison of the beam profile taken at the 1900 nm wavelength, corresponding to the  $\frac{1}{e^2}$  of the Gaussian distribution, is shown in the graph below. The D<sub>FF</sub> is broader than the D<sub>NF</sub> of about 41%.

Narrow Field:  $\lambda = 1900$  nm; f= 30 cm and D<sub>NF</sub> = 2.819 mm, d<sub>(NF)</sub> is 0.031 mm,  $\theta_{(NF)} = 5 \times 10^{-4}$  rad

Far Field:  $\lambda = 1900$  nm; f= 30 cm and D<sub>FF</sub> = 6.824 mm, d<sub>(FF)</sub> is 0.13 mm,  $\theta_{(FF)} = 2.1 \times 10^{-4}$  rad

# 5.6 Comparison of the laser beam characteristics

In table 5.2 is shown the characteristics of the laser beam at different laser wavelength. The percentage of the power lost, the beam spot size and the divergence angle values are similar at longer wavelengths (from 1500 to 1900 nm), while in the case of 1300 nm it has a lower percentage of power lost and divergence angle but

Laser beam profile	NF	FF
Measure (mm)	2.991	6.372
2D		
3D		

FIGURE 5.14. 2D and 3D image of the beam profile taken for the NF and FF positions for the 1714 nm wavelength.

Laser	Pulse Energy	% average	Beam	Divergence	Effective
Wavelength $\lambda$	E	power lost	spot size $d$	angle $\theta$	ionisation region
[nm]	[mJ]		[mm]	[rad]	$[\mathrm{mm}^3]$
800	6.8	33	0.29	$4.8 \times 10^{-4}$	0.33
1300	0.37	27.5	0.064	$1 \times 10^{-4}$	0.02
1500	0.25	38	0.077	$1 \times 10^{-4}$	0.03
1714	0.26	45	0.12	$2 \times 10^{-4}$	0.06
1900	0.24	36	0.13	$4.5 \times 10^{-4}$	0.07

TABLE 5.2. Laser beam characteristics along the beam path.



FIGURE 5.15. 2D and 3D image of the beam profile taken for the NF and FF positions for the 1900 nm wavelength.

also a lower value of the beam spot size. The effective ionisation volume calculation is done by using the equation 5.14.

# Chapter 6

# System calibration using xenon ionisation

Xenon analysed in gas phase is considered a control which is suitable for system calibration since it does not fragment and its ionisation gives multiple atomic charge states. This analysis is done in order to maximise the power density by producing the highest charge state, calibrating the ToF mass spectrum and estimating the intensity by comparing charge state yields to theory and previous experiments. In every experiments the starting pressure (without the xenon gas) in the main chamber is  $P_0=10^{-8}$  mbar. A series of measurements as a function of the gas pressure were taken starting from above  $P_0=10^{-8}$  mbar until reaching  $P=10^{-6}$  mbar where the spectra were showing multiple charge states of the xenon gas. In the ionisation plots (signal versus laser intensity) the laser intensity scale is corrected over the whole wavelength range, taking into account the percentage of power loss, as reported in table 5.5. In order to provide a spectra with minimum contribution from the background gas, the main chamber is pumped down and several spectra is taken before the introduction of the sample. In case of a strong presence of background signal no experiment is performed until it is strongly reduced.

# 6.1 Xenon gas ionised at 800 nm laser wavelength

In table 6.1 the xenon characteristics are summarised and a reminder of the equations used are shown below.

Xenon charge state	Ip	I <sub>BSI</sub>	N <sub>k(T)</sub>	
	eV	${\rm W~cm^{-2}}$	$(\mathbf{E}_{\mathbf{k}} = 1.5 eV)$	
Xe <sup>+</sup>	12.21	$8.89 \times 10^{13}$	7-8	
$Xe^{2+}$	33.3	$1.23 \times 10^{13}$	21	
$Xe^{3+}$	65.4	$8.13 \times 10^{15}$	42	
$Xe^{4+}$	111.0	$3.79 \times 10^{16}$	71-72	

TABLE 6.1. Xenon ionisation potential  $(I_p)$ , barrier suppression intensity  $(I_{BSI})$ and number of photons theoretically absorbed  $(N_{k(T)})$  during the MPI, considering the 800 nm laser wavelength (108).

$$I_{\rm BSI} = 4 \times 10^9 \ \frac{I_{\rm p}^4}{Z^2}$$
 (6.1)

$$N_{\mathbf{k}(\mathbf{T})} = \frac{I_{\mathbf{p}}}{E_{\mathbf{k}}} \quad ; \quad E_{\mathbf{k}} = \frac{h c}{\lambda} \tag{6.2}$$

Where in equation 6.1, z is the charge state of the remaining core, i.e. z=2 for  $2^{nd}$  ionisation; in equation 6.2,  $N_{k(T)}$  is the theoretical number of photons absorbed during the multiphoton ionisation,  $E_k$  is the photon energy. Larochelle *et al.* 1998 (80) and Hankin *et al.* 2001 (81), show the ionisation of xenon gas using the 800 nm Ti:Sapphire laser (figure 6.1).

In figure 6.1a, the trend of xenon ionisation is shown in a log-log plot of the ion signal versus the laser intensity. The laser used is the Ti:Sapphire with pulse duration of 200 fs and a wavelength of 800 nm. Xe<sup>+</sup> reaches saturation at laser intensity of  $I_{sat} \sim 1 \times 10^{14}$  W cm<sup>-2</sup> and Xe<sup>2+</sup> ions are formed by the xenon neutral state; this means that the ionisation is a direct process (the direct and step-wise processes as explained in detail in chapter 3). The plots 6.1b, 6.2 c & d (81) show



FIGURE 6.1. Multiple ionisation of xenon gas phase 800 nm: (a) dependence of the ion signal on the laser intensity (log-log plot) where the solid lines corresponds to the ADK theory, the points are the measured data and the numbers written are the charge state; in (b) is shown the dependence of the xenon signal on the laser intensity, for the multiple charge state (b); Larochelle *et al.* (80, Copyright 1998 IOP Publishing Ltd) and Hankin *et al.* (81, Copyright 2001 The American Physical Society).



FIGURE 6.2. Multiple ionisation of xenon gas phase 800 nm: (c) and (d) is shown the dependence of the xenon signal on the laser intensity for the whole signal, specifying the I<sub>sat</sub> (in c) and the ADK trend (straight line, in d); Larochelle *et al.* (80, Copyright 1998 IOP Publishing Ltd) and Hankin *et al.* (81, Copyright 2001 The American Physical Society).

the xenon multiple charge state and the Xe<sup>n</sup> signal in dependence on the laser intensity; those are obtained with the Ti:Sapphire 780 nm and laser pulse of 44 fs. In figure 6.1b it is shown that at low laser intensity, the double charge state is formed by electronic removal from the neutral state, Xe = Xe<sup>2+</sup> + 2 e<sup>-</sup>, while by increasing the laser intensity sequential ionisation dominates. In figure 6.2c, the dependence of the sum of the all charge state signal (Xe<sup>n</sup>) on the laser intensity (in logarithmic scale) is shown; the intersection of the slope with the x axis represents I<sub>sat</sub> ~  $1.02 \times 10^{14}$  W cm<sup>-2</sup>.

In figure 6.3 our results are displayed. The plots show the dependence of the xenon secondary ion signal on the laser intensity. From the figure it is clear that the saturation intensity of the  $Xe^+$  and  $Xe^{2+}$  signals agree with the theoretical expectations.

As mentioned in the previous chapter, the intensity of the 800 nm was determined by matching saturation of Xe results with those of Larochelle *et al.* (1998) and Hankin *et al.* (2001). The shape of the ion yield curves depends on the intensity variations across the focal volume. In particular the signal increases as  $I^{1.5}$  above saturation due to the expansion of the ionisation volume in a focused Gaussian beam for a given *k*-photon ionisation due to more effective ionisation in the wings of the laser beam. The laser intensity at the signal saturation ( $I_{sat}$ ) is defined in MPI theory as the intensity at which the 43% of the molecules in a region of constant intensity are ionised (81).

$$I_{\text{sat}} = (\sigma\tau)^{-\frac{1}{k}} e^{-\frac{\gamma}{k}}$$

$$(6.3)$$

In the equation 6.3, by substituting k=8 (number of photons theoretically absorbed  $N_{\rm k(T)}$ ), the k-photon cross section s  $\sigma=10^{-99}~W^{-k}~cm^{2k}~s^{-1}$ ,  $\tau=20$  fs and the Euler constant  $\gamma \sim 0.577$ , the referenced value of I<sub>sat</sub> = 1.13 ×10<sup>14</sup> W cm<sup>-2</sup>. In this work the I<sub>sat</sub> = 1.01 ×10<sup>14</sup> W cm<sup>-2</sup> since the laser pulse is 50 fs. Within experimental errors the latter agrees with the I<sub>sat</sub> found in figure 6.3f. In figure 6.3e, the top x axis (in green) shows the values of the Keldysh parameter as a function of the laser intensity and the ionisation potential. In this analysis the transition between the two ionisation mechanisms is not well defined. As shown in figure 6.3e the values of the Keldysh parameter are always in between the theoretical values for the MPI and the TI, suggesting that both ionisation mechanisms are occurring.



FIGURE 6.3. Dependence of the xenon gas phase 800 nm with the laser intensity (e); dependence of the  $Xe^{n+}$  on the laser intensity, where the intersection of the slope with the x axis is the  $I_{sat}$  (f), and the solid line is the ADK theory (g).

# 6.2 Xenon gas ionised at 1300 nm laser wavelength

The physical and chemical characteristics of the xenon gas ionised by the 1300 nm laser wavelength are shown in table below.

Xenon charge state	Ip	I <sub>BSI</sub>	N <sub>k(T)</sub>	
	eV	$W cm^{-2}$	$(\mathbf{E_k} = 0.95 eV)$	
Xe <sup>+</sup>	12.21	$8.89 \times 10^{13}$	12-13	
$Xe^{2+}$	33.3	$1.23 \times 10^{15}$	35	
$Xe^{3+}$	65.4	$8.13 \times 10^{15}$	68-69	
$Xe^{4+}$	111	$3.79 \times 10^{16}$	116-117	

TABLE 6.2. Xenon ionisation potential  $(I_p)$ , barrier suppression intensity  $(I_{BSI})$ and number of photons theoretically absorbed  $(N_{k(T)})$ , considering the 1300 nm laser wavelength (108).

The ionisation behaviour of xenon gas is shown in figure 6.4, where the photoions signal in function of the laser intensity is plotted on a logarithmic scale. In figure 6.4 the ionisation of xenon gas subjected to 1300 nm laser wavelength is shown: direct ionisation is visible, in fact the multiple charges state ( $Xe^+$ ,  $Xe^{2+}$  and  $Xe^{3+}$ ) are formed from the neutral state. The overall trend is complex and it is not straight forward to understand, and probably the fluctuations are due to the OPAs instability. The plot does not show any saturation so cannot be used to calibrate the intensity. Instead we use the analysis in Chapter 5 to determine the intensity.

# 6.3 Xenon ionisation efficiency

The ionisation efficiency is calculated by normalising the  $\Sigma X^n$  (total multicharge states signal) at the highest signal reached among 800 nm, 1300 nm, 1500 nm laser wavelength.

 $efficiency = \frac{No. of ions detected}{(detector efficiency)(number density)(effective ionisation volume)} (6.4)$ 



FIGURE 6.4. Direct ionisation of xenon gas phase at 1300 nm wavelength.



FIGURE 6.5. Xenon relative ionisation efficiency: comparison among the 800 nm (blue dots), 1300 nm (orange dots), 1500 nm (violet dots).

Relatively to the signal obtained from each laser wavelength the highest value is reached by the 800 nm (figure 6.5). From the plot, it is evident that at low laser intensity  $6 \times 10^{12} < I < 2.3 \times 10^{13}$  W cm<sup>-2</sup> the ionisation efficiency achieved by the 1300 nm ionisation is higher than the one reached by the 1500 nm. At higher laser intensity range,  $3.5 \times 10^{13} < I < 1.5 \times 10^{14}$  W cm<sup>-2</sup>, only the ionisation by 800 nm laser wavelengths produces signal.

# 6.3.1 Xenon ionisation efficiency at 800 nm laser wavelength

The xenon ionisation efficiency plot at 800 nm is compared with the work done by Hankin *et al.* (2001)(81).

The plots (figure 6.6) show the dependence of the xenon relative ionisation efficiency on the laser intensity obtained. The two studies have been carried out at different laser intensity ranges; the plot on the top panel in figure 6.6 is obtained at  $1.3 \times 10^{13} < I < 1.5 \times 10^{14}$  W cm<sup>-2</sup> laser intensity range and shows a linear increase of the ionisation efficiency, until I = I<sub>sat</sub>~ 10<sup>14</sup> where the signal reaches a plateau. The bottom panel of figure 6.6, instead shows the behaviour of the ion signal at a factor of 2 higher laser intensity.



FIGURE 6.6.  $Xe^{n+}$  production at 800 nm, normalised at the saturation value. Top panel: experimental data for this work. Bottom panel from Hankin *et al.*(81, Copyright 2001 The American Physical Society).

# Chapter 7

# Femtosecond Laser Ionisation-Dissociation Characteristics of Organics Molecules

# 7.1 Introduction

The following chapter covers the analysis of a selected range of organic molecules to determine their ionisation-dissociation behaviour under intense femtosecond (fs) irradiation at various wavelengths. The range of samples chosen goes from relatively simply organic, toluene and acetone, up to small biomolecules representative of the type of species that might be the target of future SIMS imaging experiments nitroaniline and histamine.

All compounds were analysed in gas phase directly from volatilisation of the sample. The starting pressure was  $P_0 = 10^{-8}$  mbar while the pressure rose to  $P=10^{-6}$  mbar when the target gas was admitted. Samples were introduced into the main chamber by two means:

- from the liquid phase: the compounds that belong to this category are toluene and acetone. The advantage of this method is the ease with which a high number of molecules can be introduced into the main chamber. This process was possible using a glass vial directly connected to the main chamber through two valves. The first valve allows the liquid or gas vapour to leak out from the glass vial; then the vapour goes into a tube that, through a fine-leak valve, is inserted inside the main chamber. The gas line is also connected to the "backing line"' which is directly connected with the rotary pump of the prep chamber. This connection is used to pump out the residual gas in this part of the system before sample introduction. In order to further reduce the amount of the background contamination admitted into the main chamber, the liquid sample were frozen with liquid nitrogen and degassed;
- from the solid phase: the samples that belong to the second category were nitroaniline and histamine. The sample was prepared by pressing it into indium placed on the sample stub and introducing it in the main chamber. The samples were of sufficient volatility that no sample heating was required to establish a gas phase concentration suitable for laser ionisation. By regulating the distance between the sample and the laser path, it was possible to ensure thermal desorption rather than laser ablation of the sample.

The aim of this study was to demonstrate how the molecular ion signal and molecular fragmentation changes by increasing the laser wavelength (concept widely discussed in the laser theory chapter 3). The laser wavelengths used were 800, 1300, 1500, 1714 and 1900 nm and for the laser power was corrected for transmission losses and detailed in table 5.5. The optimal alignment of the laser beam was achieved when the area of ion peaks in the mass spectrum were maximised. Saturation effects were closely monitored by observing the photoion peak shape and absolute intensity. Where saturation was observed the analyte pressure was reduced or the detector gain was turned down

# 7.2 Toluene

## 7.2.1 Toluene molecule ionised at 800 nm

Toluene is an aromatic molecule, and its characteristics are shown in table 7.1.Io

Tasker *et al.* (2001) (82) analysed a toluene sample in the gas phase by a Ti: Sapphire laser at 800 nm and pulse duration of 20 fs.



FIGURE 7.1. Toluene molecule ionised at 800 nm laser wavelength. The spectrum is recorded at 3.8  $\times 10^{15}$  W cm<sup>-2</sup> laser intensity Tasker *et al.* (82, Copyright 2002) American Chemical Society).

#### 7.2 Toluene

Toluene $M^+$	Ip	I <sub>BSI</sub>	N <sub>k(T)</sub>
m/z	eV	${\rm W~cm^{-2}}$	$(E_k=1.5~{\rm eV})$
92.14	8.82	$2.4 \times 10^{13}$	5-6

TABLE 7.1. Characteristics of the toluene molecule: ionisation potential  $(I_p)$ , barrier suppression intensity  $(I_{BSI})$  and number of photons theoretically absorbed  $(N_{k(T)})$  during the MPI, considering the 800 nm laser wavelength, Tasker *et al.* (82, Copyright 2002 American Chemical Society).

In figure 7.1 the highest intensity peak of the mass spectrum is the molecular ion peak,  $M^+$  (m/z 92.14); however the spectrum includes a lot of fragments in the range of  $[C_3H_n, C_4H_n]$ . This region is highlighted by the five boxes inside figure 7.1. In particular in the biggest box, it is emphasised that the removal of two hydrogen atoms is favoured compared to the removal of only a single hydrogen atom. In fact:  $[M-2H]^{2+}$  (m/z 45) >  $[M-H]^+$  (m/z 45.5) and also  $[M-4H]^{2+}$  (m/z 44) >  $[M-3H]^+$ (m/z 44.5).

In comparison with the study of Tasker *et al.* (2001), the experiment done in this work, for  $I = 1.6 \times 10^{14} \text{ W cm}^{-2}$  is displayed in figure 7.2; although the two spectra are recorded at different laser intensity, the comparison is useful to give an indication on the toluene ionisation behaviour.

In figure 7.2 the presence of doubly ionised toluene fragments is highlighted . Those are preferably formed by the removal of two hydrogen atoms rather than only one. To be more precise the signal of  $[M-2H]^{2+}$ , that is  $[C_7H_6]^{2+}$ , is about seven times higher than the signal of  $[M-H]^{2+}$ , that is  $[C_7H_7]^{2+}$ . A similar situation is observed for the signal of  $[M-4H]^{2+}$ , that is  $[C_7H_4]^{2+}$ , higher than the signal of  $[M-3H]^{2+}$ , that is  $[C_7H_5]^{2+}$ , by a factor of 25. In this spectrum the signal due to  $C^+$  is (~ 9 × 10<sup>5</sup> counts),  $C^{2+}$ (~ 6 × 10<sup>5</sup> counts) and  $C^{3+}$ (~ 1 × 10<sup>4</sup> counts). The toluene gas phase mass spectrum at lower laser intensity (in figure 7.3) shows that by reducing the laser power, the fragments in the range of m/z 42-48 disappear and also the  $C^+$  and  $C^{2+}$  charges states slowly decrease in counts while the  $C^{3+}$  is completely absent. With the spectrum obtained at I =1.6 × 10<sup>14</sup> W cm<sup>-2</sup>, the ratio  $C^{2+}/C^+ \sim 6\%$ , while at I =1.3 × 10<sup>14</sup> W cm<sup>-2</sup>,  $C^{2+}/C^+ \sim 60\%$ .

Figure 7.4 shows the trend of ion intensity versus the laser intensity, where the fragments with significant signal intensity were chosen.

In the two plots, in figure 7.4, the toluene molecular peak and its photo-fragmentation



FIGURE 7.2. Toluene molecule gas phase spectrum with 800 nm laser wavelength at laser intensity of  $1.6 \times 10^{14} \text{ W cm}^{-2}$ .



FIGURE 7.3. Toluene mass spectra at 800 nm at laser intensity  $1.3 \times 10^{14}$  W cm<sup>-2</sup>(a) and  $8 \times 10^{13}$  W cm<sup>-2</sup> (b).



FIGURE 7.4. Toluene gas phase graphs at 800 nm: dependence of the absolute ion yield (a) and proportion of molecular ions produced (b) on the laser intensity.

#### 7.2 Toluene

ratio  $(M^+/F_{tot})$  that is the ratio of the  $M^+$  counts over the sum of the molecular fragments counts) have a behaviour that can be summarised in three steps as follows: a) at I <  $1.1 \times 10^{14}$  W cm<sup>-2</sup> the trend is linear; the photo-fragmentation signal trend decreases, relative to the molecular ion signal; b) at laser intensities between  $1.1 \times 10^{14}$  W cm<sup>-2</sup> and  $1.4 \times 10^{14}$  W cm<sup>-2</sup> the absolute M<sup>+</sup> signal reaches a plateau, while the M<sup>+</sup>/F<sub>tot</sub> reaches a minimum of 0.4 at I =  $1.3 \times 10^{14}$  W cm<sup>-2</sup>; c) for laser intensities higher than the 1.4  $\times 10^{14}~{\rm W~cm^{-2}}$  the molecular and photofragmentation signals increase exponentially. All these measurements were taken at laser intensity in excess of the predicted threshold for BSI (see table 7.1). Hence over barrier ionisation is likely to be attained for some portion of the ionisation volume. As the peak laser intensity increases this BSI region will increase in volume until it dominates the overall ionisation of extracted photoions. The reversal in the trend of  $M^+/F_{tot}$  is particularly interesting. Detector saturation effects can be ruled out as the cause of this behaviour as M<sup>+</sup> is still the dominant signal intensity and therefore would be the first signal to show saturation effects which would therefore decrease the observed  $M^+/F_{tot}$  ratio. The conclusion is therefore that a change in the dominant ionisation mechanism is responsible for this observation.

Muller *et al.* (2000)(109) analysed the dependence of the toluene ion yield in function of the peak intensity at 800 nm. In figure 7.5 is shown that the molecular ion peak has a linear trend (at low laser intensity) and the linear fit gives  $5.94 \pm$ 0.10, which means that 6 photons are used to ionise the toluene molecule, while by increasing the laser intensity the behaviour is linear which suggest, saturation of the ionisation process. The behaviour of the ionisation probability per unit of time during the temporal evolution of the pulse is shown in figure 7.5: by increasing the laser intensity, the 6 photon ionisation becomes an 7 photon-ionisation and then an 8 photon-ionisation. This can be explained by a channel-closing mechanism due to the ac Stark shift between the ground state and the ionisation energy, equal to the ponderomotive energy Up. Since at high laser intensity the signal does not behave as a straight line (MPI ionisation) anymore, tunnelling ionisation is expected. The intensity range used is lower than what was used in this thesis, in fact the slope of the linear trend for M (figure 7.5) is 7.2±0.6 suggesting that the ionisation occurs by the absorption of over 7 photons.

In order to estimate the value of the ionisation saturation of the toluene ion signal, figure 7.6 (top panel) shows the dependence of the total ion signal on the log of the laser intensity and also a comparison with the MPI theory. In figure 7.6 bottom panel is shown the dependence of the saturation intensity on the ionisation



FIGURE 7.5. Top panel: toluene mass spectrum at 800 nm, 80 fs and linearly polarised laser pulse. Bottom panel: ionisation probability per unit of time of toluene at 800 nm, 80 fs and linearly polarised laser pulses. The order of the process (i.e. MPI Theory) is indicated in the strip at the bottom of each graph; Muller *et al.* (109, Copyright 2000 American institute of physics).



FIGURE 7.6. Top panel: dependence of the  $\sum (M^+ + F_{tot})$  ions on the laser intensity in logarithmic scale obtained in this work (toluene molecule is ionised at 800 nm). Bottom panel: dependence of the I<sub>sat</sub> on the ionisation potential of many molecules, including toluene (green arrow); Hankin *et al.* (2000) (83, Copyright 2000 American Chemical Society).

### Femtosecond Laser Ionisation-Dissociation Characteristics of Organics Molecules

potential (83). The estimation is done for 23 volatile organic molecules, such as ethane, ethane, propane, benzene, toluene and many others. The interest for this work is on toluene, which has an ionisation potential of 8.82 eV, and  $I_{sat} \sim 60 \times 10^{12} \text{ W cm}^{-2}$ , calculated using the equation 3.4. In this work the  $I_{sat}$ , is obtained by the intersection of the  $\sum (M^+ + F_{tot})$  with the laser intensity axis, which is  $\sim 1.4 \times 10^{14} \text{ W cm}^{-2}$ . The two estimations do not agree completely being a factor  $\sim 2$  different; this is due to the fact that the ADK theory is not in perfect agreement with the experimental results especially for molecule.

The ADK parameter is the estimation of the rate of the tunnelling ionisation for an atom (chapter 3), and the formulation is based on the adiabatic (quasi-static) description of the electron dynamics; in fact electronic motion is negligible compared to the atomic motion. ADK theory can be used for atoms or small molecules, but for polyatomics it is inadequate due to the timescale of the electron motion throughout the molecule. Hankin *et al.* (2000) found a good agreement with the ADK theory for He, Ne and Xe; in this way they provided a lower and upper limit for the ionisation rate. As already explained the ADK theory for molecules does not approach the experimental trend: it was found that  $I_{sat}$  is greater than the predicted by the ADK theory of ~ 5 times.

Therefore, the fact that the saturation intensity was found to be a factor of 2 greater than that predicted by ADK is in line with previous studies with large molecules.

### 7.2.2 Toluene molecule ionised at 1300 nm

Figure 7.8 shows the comparison between the toluene spectra obtained by irradiating the molecule with the 800 nm wavelength at the highest laser power (4.5 mJ, I= 1.6  $\times 10^{14}$  W cm<sup>-2</sup>) and with the 1300 nm wavelength, also for the highest laser power (0.3 mJ, I= 2.8  $\times 10^{13}$  W cm<sup>-2</sup>).

The M<sup>+</sup> signal obtained by the 1300 nm wavelength at the highest laser intensity (figure 7.8b) is higher by a 2.5 factor than in the 800 nm gas phase spectrum, and also the total fragmentation signal is strongly reduced. This comparison illustrates that the use of the longer laser wavelength has the advantage in reducing the fragmentation signal, leaving the molecule almost intact. The fragmentation pattern created with the 800 nm wavelengths, favours removal of 2 hydrogen atoms is also present for the 1300 nm case. In fact  $[H-4H]^{2+} > [M-3H]^{2+}$  by a factor of 3.4 (peak height  $2 \times 10^5$  and  $6 \times 10^4$  counts respectively),  $[M-2H]^{2+} > [M-H]^{2+}$  by a factor of 3 (peak height  $3 \times 10^4$  and  $1 \times 10^4$  counts respectively). Figure 7.9 shows the toluene

	Ionization potential <sup>a</sup> (eV)	$I_{sat}$ (10 <sup>12</sup> W cm <sup>-2</sup> )	$I_{CE}$ (10 <sup>12</sup> W cm <sup>-2</sup> )	I <sub>CE</sub> /I <sub>sat</sub>	$I_{ADK}$ (10 <sup>12</sup> W cm <sup>-2</sup> )	Isat/IADR
1,3-cyclo-hexadiene	8.25	66	158	2.4	25	2.64
1,3,5-hexatriene	8.42	89	213	2.4	32	2.78
1,3-hexadiene	8.51	81	165	2.04	32	2.53
n-propylbenzene	8.72	59	144	2.45	30	1.97
i-propylbenzene	8.73	51	156	3.03	30	1.7
ethyl benzene	8.77	48	144	3	30	1.6
1,4-cyclo-hexadiene	8.82	81	161	1.99	25	3.24
toluene	8.82	56	154	2.75	32	1.75
cyclo-hexene	8.94	117	194	1.66	33	3.54
benzene	9.24	71	201	2.83	38	1.86
1-hexene	9.4	71	156	2.19	40	1.77
propene	9.73	95	208	2.19	46	2.06
cyclo-propane	9.86	110	296	2.69	48	2.29
cyclo-hexane	9.88	85	204	2.41	48	1.77
dimethylether	10.03	95	268	2.82	51	1.86
hexane	10.13	63	135	2.14	53	1.19
2-methoxyethanol	10.13	71	163	2.29	53	1.34
propyne	10.36	98	210	2.14	57	1.72
ethene	10.50	110	373	3.39	60	1.83
methanol	10.85	158	397	2.51	67	2.36
propane	10.95	112	293	2.62	69	1.62
ethane	11.52	182	400	2.20	83	2.19
xenon	12.13	112			100	1.12
neon	21.56	750			740	1.01
helium	24.58	1158			1160	1

FIGURE 7.7. Saturation intensity ( $I_{sat}$ ), coulomb explosion intensity ( $I_{CE}$ ), saturation intensity for tunnelling ionisation ( $I_{ADK}$ ) calculated for organic molecule and atoms; Hankin *et al.* (2000) (83, Copyright 2000 American Chemical Society).



FIGURE 7.8. Comparison of toluene gas phase spectra detected at: (a) 800 nm wavelength at I=  $1.6 \times 10^{14}$  W cm<sup>-2</sup> and (b) 1300 nm wavelength at I=  $2.8 \times 10^{13}$  W cm<sup>-2</sup>. In the 800 nm spectrum the ion signal axis is adapted to the 1300 nm signal.


FIGURE 7.9. Toluene gas phase spectra: ionisation done with the 1300 nm at 1.9  $\times 10^{13}$  W cm<sup>-2</sup> and 7.7  $\times 10^{12}$  W cm<sup>-2</sup> laser intensity.

gas phase spectrum for laser intensity  $1.9 \times 10^{13}$  W cm<sup>-2</sup> and  $7.7 \times 10^{12}$  W cm<sup>-2</sup>.

Figure 7.10a shows the overall behaviour of toluene molecule as a function of the laser intensity; it is linear for the laser intensity I  $< \times 10^{13}$  W cm<sup>-2</sup>; then it reaches a plateau. The photo-fragmentation trend (figure 7.10b) shows that for I



FIGURE 7.10. Toluene gas phase ionised at 1300 nm: a) Overall trend; b) photofragmentation trend obtained by including m/z 63, 54 and 90 ions.



FIGURE 7.11. Toluene gas phase ionised at 1300 nm ion signal versus log of the laser intensity. The red line is a best-fit allowing an estimation of the saturation intensity.

 $< 1 \times 10^{13} \ {\rm W \ cm^{-2}}$  the molecular ion peak signal is greater than the fragmentation, while for higher intensity values the combined fragments signal increase. This can be explained by the fact that the BSI threshold is reached, hence the extent of fragmentation might be expected to remain more constant once the BSI mechanism dominates.

#### 7.2.3 Toluene molecule ionised at 1500 nm

In figure 7.12 the differences of the toluene spectra irradiated by the 1500 nm and 1300 nm laser wavelength at similar laser intensities is shown.

Figure 7.12 shows that the spectrum obtained with the 1500 nm wavelength has fewer fragments than the one obtained with the 1300 nm wavelength; moreover the  $C^+$ ,  $C^{2+}$  and  $C^{3+}$  signals are completely absents as are the  $[M-4H]^{2+}$  and  $[M-3H]^{2+}$ signals. The fragment  $[M-2H]^{2+}$ , that corresponds to  $[C_7H_6]^{2+}$  is approximately double peak area of  $[M-H]^{2+}$ , which is  $[C_7H_7]^{2+}$ . The plot of the peak area (counts) as a function of the laser intensity, on a logarithmic scale, is shown in figure 7.13.



FIGURE 7.12. Spectrum of toluene gas phase with 1500 nm laser wavelength at I=  $1.3 \times 10^{13}$  W cm<sup>-2</sup>(a) and with 1300 nm wavelength at I=  $1.5 \times 10^{13}$  W cm<sup>-2</sup>(b). For the comparison has been chosen similar laser intensity.



FIGURE 7.13. Toluene gas phase ionisation at 1500 nm: a) Plot of the M<sup>+</sup> and fragments ion peak area; b) photo-fragmentation dependence on the laser intensity.



FIGURE 7.14. Toluene gas phase at 1500 nm: ion signal versus log of the laser intensity. The red line shows a linear fit allowing an estimation the value of the saturation intensity from the intercept with the x-axis.

## 7.2.4 Toluene molecule ionised at 1714 nm

The spectrum obtained by irradiating the toluene with the 1714 nm laser wavelength, for the highest laser intensity (considering the 45% of power lost) is shown in figure 7.15.

Due to the low laser intensity and to the longer laser wavelength, the signal is not very strong, but the spectrum shows only the molecular ion peak area of about  $3.4 \times 10^3$  counts.

The figure 7.16 shows only the  $M^+$  and the  $[M+H]^+$  ions, but because of the low signal the uncertainly of the signal is high (probably the presence of H is due to contamination of the sample). These data are not reliable enough to make any conclusions on the ionisation mechanisms that occurs by ionising toluene with 1714 nm laser wavelength.

## 7.2.5 Summary: toluene

In this section the behaviour of toluene ionisation in the gas phase using the 800, 1300, 1500 and 1714 nm wavelengths has been shown. By increasing the wavelength

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FIGURE 7.15. Toluene molecule ionised with the 1714 nm wavelength at the highest laser intensity  $6.6 \times 10^{12}$  W cm<sup>-2</sup>.

the molecular fragmentation signal decreases, in fact at 1714 nm, the spectrum contains only  $M^+$  and  $[M+H]^+$  ions. Due to the conversion efficiency of the OPA, higher pulse energies were achievable for the shorter wavelengths, therefore although the 1714 nm spectrum shown only the molecular ion peak, the total signal is very low. The best ionisation condition was obtained by analysing the toluene molecule by 1300 nm laser photons as this gives the highest ion yield while still generating high parent ion fraction. The lowest fragmentation signal is found by ionising the molecule with the 1714 nm laser wavelength, but also the overall signal is low.

#### Toluene ionisation and fragmentation efficiency

The analysis of the relative ionisation and fragmentation efficiency is done by comparing the normalised signal of  $M^+$  and  $M^+/F_{tot}$  obtained by ionising the sample at 800 nm, 1300 nm, 1500 nm and 1714 nm.

The relative ionisation efficiency plots are made by plotting the relative ionisation efficiency as a function of the laser power density (W cm<sup>-2</sup>). The signal levels had been adjusted to account for the number of neutrals in the ionisation volume, therefore the number of counts obtained for  $M^+$  is normalised by the ionisation



FIGURE 7.16. Plot of the toluene gas phase for 1714 nm laser wavelength with the increasing of the laser intensity, done in logarithmic scale.



FIGURE 7.17. Dependence of the ionisation efficiency of toluene for the  $M^+$  and  $M^+/F_{tot}$  signal for the whole laser wavelength range.

volume and number density (see table 5.2).

In figure 7.17 (top panel) is shown the relative ionisation efficiency for M<sup>+</sup> signal. The highest value is reached by the 1300 nm laser wavelength; while there is relatively low ionisation efficiency at 800 nm, even though it has the highest laser intensity.

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The  $M^+/F_{tot}$  signal is also compared for the whole laser wavelength, as it is shown in figure 7.17 (bottom panel);

The highest  $M^+/F_{tot}$  ratios are reached with 1300 nm and 1500 nm photoionisation. Under conditions of the same laser intensity these wavelengths produce very comparable  $M^+/F_{tot}$  ratios.

# 7.3 Acetone

### 7.3.1 Acetone molecule ionised at 800 nm

The acetone ionisation potential is 9.7 eV and the intensity of the barrier suppression is  $I_{BSI} = 3.5 \times 10^{13}$  W cm<sup>-2</sup>. The theoretical number of photons that the molecule should absorb during the multiphoton ionisation process is between 6-7 knowing that  $E_k=1.5$  eV. Tang *et al.* (2007) (84) analysed the acetone in the gas phase (figure 7.18), with a Ti: Sapphire laser at 800 nm wavelength, 160 fs pulse, at I =  $0.4 \times 10^{14}$  W cm<sup>-2</sup>, I =  $0.72 \times 10^{14}$  W cm<sup>-2</sup>, I =  $0.96 \times 10^{14}$  W cm<sup>-2</sup> and I =  $1.1 \times 10^{14}$  W cm<sup>-2</sup>.

The first plot (figure 7.18a) shows the complete absence of fragments and only the  $M^+$  ions  $CH_3COCH_3^+$ . By increasing the laser intensity, up to  $0.72 \times 10^{14}$  W cm<sup>-2</sup> (figure 7.18b) two additional ions are created,  $CH_3^+$  and  $CH_3CO^+$ , meaning that the first bond to break is C-C. Then, by a further increase of the laser intensity to  $0.96 \times 10^{14}$  W cm<sup>-2</sup> (figure 7.18c), the double bond CO is broken generating the  $CH_3CCH_3^+$  and  $O^+$  peaks. For laser intensity of  $1.1 \times 10^{14}$  W cm<sup>-2</sup> (figure 7.18d), the molecular ion peak is even more saturated and the fragment signal increases. Other bonds are broken, yielding  $CH_3C^+, CH^{2+}$  and  $H^+$  fragments. The figure 7.19 shows the acetone spectrum obtained in this work, at the laser intensity  $1.4 \times 10^{14}$  W cm<sup>-2</sup>

The literature explanation of the acetone molecule dissociation matches completely with the results found in this work; in fact the gas phase spectrum (figure 7.19) shows the fragments  $CH_3CO^+$ , and  $CH_3CCH_3^+$  and the ions  $C^+$  and  $C^{2+}$  which depends on fragments of acetone or on the ionisation of the residual gas present in the spectrometer. In figure 7.20 the molecular and fragments ions as a function of the laser intensity are displayed.

The top panel in figure 7.20, shows that for  $I < 8 \times 10^{13} \text{ W cm}^{-2}$  the trend is linear and the fragment created is m/z 43; at higher laser intensity, the molecular ion peak signal reaches saturation with creation of the m/z 42 and m/z 44 fragments. On



FIGURE 7.18. Acetone gas phase mass spectrum: a) Laser intensity,  $I = 0.4 \times 10^{14} \text{ W cm}^{-2}$ ; b)  $I = 0.72 \times 10^{14} \text{ W cm}^{-2}$ ; c)  $I = 0.96 \times 10^{14} \text{ W cm}^{-2}$ ; d)  $I = 1.1 \times 10^{14} \text{ W cm}^{-2}$ ; Tang *et al.* (84, Copyright 2003 American Chemical Society).



FIGURE 7.19. Acetone gas phase spectrum for 800 nm laser wavelength. The pulse energy is 6 mJ and the laser intensity is  $1.4 \times 10^{14} \text{ W cm}^{-2}$ .



FIGURE 7.20. Dependence of the acetone molecular ion peak and fragments signal (top panel); dependence of the photo-fragmentation signal on the laser intensity at 800 nm (bottom panel).



FIGURE 7.21. Acetone saturation intensity plot at 800 nm: ion signal versus log of the laser intensity. The red line shows a linear fit allowing an estimation of the saturation intensity, given by extrapolating back the fit to the x-axis.

the bottom panel of figure 7.20, the photo-fragmentation  $(M^+/F_{tot})$  has a similar behaviour, but then for  $I > 8 \times 10^{13}$  W cm<sup>-2</sup> while the M<sup>+</sup> signal increases the M<sup>+</sup>/F<sub>tot</sub> decreases hence the fragments signal is higher than the acetone molecular signal. The Keldysh parameter is in the range [0.7-1.4], therefore the ionisation is not occurring purely for by a tunnelling process, and neither by purely multiphoton ionisation. Moreover the fact that the laser intensity is higher than the I<sub>BSI</sub> = 3.5  $\times 10^{13}$  W cm<sup>-2</sup>, suggests that the threshold for barrier suppression ionisation maybe have been reached. According to Hankin *et al.*(2000)(83) the intensity saturation value has been estimated by plotting the acetone signal (M<sup>+</sup>/F<sub>tot</sub>) as a function of the log of the laser intensity; I<sub>sat</sub> = 7  $\times 10^{13}$  W cm<sup>-2</sup> (figure 7.21).

Field ionisation of aliphatic ketones, including acetone, butatone and 3-pentanone in an intense laser field was achieved by a Ti: Sapphire laser operating at 800 nm and pulse width 50 fs. This experiment was performed by Chengyin *et al.* (2000)(110) who demonstrate how the field ionisation depends on the molecular structure. These three aliphatic ketone molecules were analysed over an intensity range of  $3.5 \times 10^{13}$ up to  $1.2 \times 10^{14}$  W cm<sup>-2</sup>. The spectra in figure 7.22 are recorded at intensity 9.2  $\times 10^{13}$  W cm<sup>-2</sup>. While at low laser intensity the parent ion dominated the spec-

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FIGURE 7.22. Mass spectra of (a) acetone, (b) butatone, (c) 3-pentanone with 800 nm laser wavelength at I=9.2  $\times 10^{13}$  W cm<sup>-2</sup>; Chengyin *et al.*(110, Copyrigh 2001 American Chemical Society).

tra. By increasing the laser intensity the contribution of the fragments becomes important with the increasing molecular size.

To estimate the probability of field ionisation of the acetone, butatone and 3pentanone, the experimental results were compared with the theoretical approximation, considering that the external electron in HOMO is responsible for the ionisation and it is orientated towards the external electric field.

The method used to calculate the ionisation probabilities of the molecules at different laser intensity is called the transfer matrix method. Figure 7.23 shows that the ionisation starts at  $I=3 \times 10^{13}$  W cm<sup>-2</sup> and increases with the laser intensity; the BSI threshold intensity is calculated for the molecule analysed and it is  $6.2 \times 10^{13}$ ,

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FIGURE 7.23. Trend of the ionisation probability in function of the laser intensity for a) acetone, (b) butatone, (c) 3-pentanone Chengyin *et al.* (110, Copyrigh 2001 American Chemical Society).

 $5.1 \times 10^{13}$  and  $6.0 \times 10^{13}$  W cm<sup>-2</sup> for acetone, but atome and 3-pentanone, respectively. This agrees well with the present measurements of the saturation intensity for acetone.



FIGURE 7.24. Acetone gas phase mass spectrum at 1300 nm at the highest laser intensity  $2.8 \times 10^{13}$  W cm<sup>-2</sup>.

### 7.3.2 Acetone molecule ionised at 1300 nm

The acetone molecular ion peak signal ( $M^+ \sim 1.15 \times 10^6$  counts) obtained at 1300 nm laser wavelength at the highest laser intensity (figure 7.24) is 5 times higher than the signal at 800 nm ( $M^+ \sim 2.2 \times 10^5$  counts, figure 7.18), despite the 800 nm laser intensity ( $1.4 \times 10^{14} \text{ W cm}^{-2}$ ) being 5 times higher than the 1300 nm ( $2.8 \times 10^{13} \text{ W cm}^{-2}$ ) laser intensity. Figure 7.25 shows the dependence of the molecular ion peak and its fragments on the laser intensity at 1300 nm. The fragments considered are the same as for the 800 nm wavelength, with the only addition of the fragment m/z 54, since it is a quite strong peak in the spectrum.

The plot in figure 7.25 shows that the trend of the molecular ion is almost linear up to I = 2 ×10<sup>13</sup> W cm<sup>-2</sup>. In theory, based on atomic behaviour, the barrier suppression ionisation occurs for  $I_{BSI} = 3.5 \times 10^{13}$  W cm<sup>-2</sup>.

### 7.3.3 Acetone molecule ionised at 1500 nm

Figure 7.27 shows the acetone gas phase spectrum at 1500 nm laser wavelength. The acetone molecular ion peak signal at 1500 nm (figure 7.27) is  $\geq 2$  times lower than obtained at 1300 nm (figure 7.24) considering also that the laser intensity is  $\geq$ 



FIGURE 7.25. Top panel: Ions signal as a function of the laser intensity (at 1300 nm); bottom panel: molecular ion peak and photo-fragmentation signal as a function

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FIGURE 7.26. Dependence of the  $M^++F_{tot}$  signal on the laser intensity at 1300 nm laser wavelength: the red trend represents the best fit allowing the estimation of the acetone saturation intensity.

2 times lower.

Figure 7.28 shows that the trend of M<sup>+</sup> and its fragments increases linearly with the laser intensity; this is also evident from the photo-fragmentation trend, where the ratio M<sup>+</sup>/F<sub>tot</sub> decreases linearly, meaning that by increasing the laser intensity the F<sub>tot</sub> signal increases. The Keldysh parameter does not distinguish between the multiphoton and the tunnelling ionisation (1.3 <  $\gamma$  < 2.5), but since the trend is almost linear this does not suggest any barrier suppression ionisation. In fact its theoretical estimation is I<sub>BSI</sub> =  $3.5 \times 10^{13}$  W cm<sup>-2</sup> which is not reached for the 1500 nm wavelength.

### 7.3.4 Acetone molecule ionised at 1714 nm

The acetone mass spectrum gas phase ionised at 1714 nm wavelength at the highest laser intensity is shown in figure 7.29. In this case there is no comparison with the 1500 nm gas phase spectrum because the overall signal is low,  $\sim 8 \times 10^2$  counts, there is only the molecular ion peak [(CH<sub>3</sub>)<sub>2</sub>CO]<sup>+</sup> and the fragments signal is very low.



FIGURE 7.27. Acetone gas phase spectrum at 1500 nm laser wavelength at I = 1.3  $\times 10^{13}$  W cm<sup>-2</sup> (pulse energy is 200  $\mu$ J).



FIGURE 7.28. Acetone gas phase 1500 nm, dependence of the  $M^+$ , fragments and photo-fragmentation  $(M^+/F_{tot})$  on the laser intensity.



FIGURE 7.29. Top panel: acetone gas phase spectrum at 1714 nm laser wavelength and at the highest laser intensity I= $3.8 \times 10^{12}$  W cm<sup>-2</sup> (pulse energy 160 µJ). Bottom panel: dependence of the molecular signal on the laser intensity (at 1714 nm). The red line represents the linear fit to estimate the ionisation saturation value.

### 7.3.5 Summary: acetone

In this section it has been shown how the acetone molecule ionises and dissociates at 800, 1300, 1500 and 1714 nm laser wavelength. The main difference among the various cases is that by increasing the wavelength the molecular fragmentation signal decreases following the laser intensity. At 1714 nm a very low signal has been obtained. In terms of the overall ionisation signal, the best spectrum is obtained at 1300 laser wavelength; in fact the M<sup>+</sup> signal (M<sup>+</sup> ~  $1.15 \times 10^6$  counts) is the highest compared with 800 nm (M<sup>+</sup> ~  $2.2 \times 10^5$  counts) 1500 nm (M<sup>+</sup> ~  $5 \times 10^5$  counts) and 1714 nm (M<sup>+</sup> ~  $8 \times 10^2$  counts).

#### Acetone ionisation efficiency

The analysis of the acetone ionisation efficiency is done by comparing the signal obtained and  $M^+/F_{tot}$  detected by ionising the sample at 800 nm, 1300 nm, 1500 nm and 1714 nm.

The signal levels had been adjusted to account for the number of neutrals in the ionisation volume, therefore the number of counts obtained for  $M^+$  is normalised by the ionisation volume (see table 5.2). The largest ionisation efficiency is reached for each laser wavelength at different laser power and the signal have been normalised to the highest single value of the peak area among the whole wavelength range.

The ionisation efficiency plots of  $M^+$  signal is shown in figure 7.30. The maximum  $M^+$  signal is reached for each laser wavelength at different laser wavelength and it have been normalised on the ionisation volume (see table 5.2). The comparison among the whole laser wavelength range is obtained by normalising each signal on the largest ionisation efficiency.

The highest value is reached by the 1300 nm laser wavelength; hence it has the highest efficiency of ionisation.

The  $M^+/F_{tot}$  signal is also compared for the whole laser wavelength, as it is shown in figure 7.30; the largest signal is obtained by ionising the molecule at 1300 nm laser wavelength.

# 7.4 Histamine

#### 7.4.1 Histamine molecule ionised at 800 nm

Histamine is a bigger molecule ( $M = C_5H_9N_3$ , m/z 111) than the ones previously analysed and the ionisation potential ( $I_p$ ) value is not found in the literature; there-



FIGURE 7.30. Dependence of the ionisation efficiency of acetone for the M<sup>+</sup> (top panel)  $M^+/F_{tot}$  (bottom panel) signal for the whole laser wavelength range.



FIGURE 7.31. Mass spectrum of histamine thermally desorbed and ionised using 800 nm (a) and 1450 nm (b) wavelengths. The authors does not specify the intensity at which the spectra have been recorded; Willingham *et al.* (62, Cpyright 2008 Elsevier B.V.).

fore the value of the intensity required for barrier suppression and also the number of photons that the molecule should absorbed to be ionised by MPI have not estimated. In Willingham *et al.* (2009) (62) the histamine sample was analysed following thermal desorption using a Ti: sapphire laser at 800 nm (1 kHz and laser pulse 125 fs) that reaches 1.5 mJ laser pulse energy. A system of TOPAs was used to extend the wavelength range from 1150 nm to 2650 nm (1 kHz at laser pulse 125 fs, 400  $\mu$ J) which works in an intensity range of  $10^{12}$ - $10^{13}$  W cm<sup>-2</sup>.

Figure 7.31 shows that the spectra obtained by Willingham *et al.* (2009) (62) at the laser wavelengths of 800 nm (a) and 1450 nm (b) are quite similar, apart from the fragment peak at m/z 30 which is absent at the higher laser wavelength. The m/z 30 fragment is  $CH_2NH_2^+$  and the fragment at m/z 81 is [M-  $CH_2NH_2$ ]<sup>+</sup>.

Figure 7.32a shows the dependence of the thermally desorbed histamine signal on the laser wavelength. The photo-fragmentation signal has a non linear increase with the laser wavelength, meaning that the fragments signal has a relative decrease compared to the molecular ion signal. This plot indicates the advantage in using the longer laser wavelength. The other plots represents the analysis of the histamine with the 1450 nm laser wavelength; in particular in figure 7.32b and 7.32c is shown



FIGURE 7.32. Thermally desorbed histamine: (a) dependence of the M<sup>+</sup>/F<sub>tot</sub> on the laser wavelength. Thermally desorbed histamine at 1450 nm: (b) dependence of the photo-fragmentation signal on the laser intensity; (c) dependence of the relative ion signal on the laser intensity; (d) linear fit of the total signal as a function of the laser intensity; Willingham *et al.* (2009) (62, Cpyright 2008 Elsevier B.V.).

that with its increase, the  $M^+$  and the  $M^+/F_{tot}$  signal also increases.

The analysis of the thermally desorbed histamine using the Ti: sapphire laser at 800 nm performed in this work is shown in figure 7.33. The spectrum (figure 7.33) includes the M<sup>+</sup> (m/z 111), [M<sup>+</sup>H]<sup>+</sup> and fragments at m/z 83, 82, 81, 54 and M<sup>2+</sup>. Previous work (figure 7.31) shows that the fragment at m/z 81 [C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>]<sup>+</sup> correspondends to the presence of m/z 30 [CH<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>, also the m/z 82 [C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>]<sup>+</sup> corresponds to the m/z 29 [CH<sub>2</sub>NH]<sup>+</sup> and m/z 83 [C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>]<sup>+</sup> corresponds to the m/z 28 [CH<sub>2</sub>N]<sup>+</sup>.

The trend has a non linear behaviour, decreasing with the increasing of the laser intensity.

#### 7.4.2 Histamine molecule ionised at 1300 nm

Figure 7.35 shows the trend of histamine mass spectrum obtained for 1300 nm at the highest laser intensity (I =  $2.8 \times 10^{13}$  W cm<sup>-2</sup>).

By comparing it with the previous work in figure 7.34b, it is noted that the ionisation reached at 1450 nm laser wavelength (pulse energy ~ 400  $\mu$ J) results in lower fragmentation signal than our work at the histamine ionised at 1300 nm (pulse energy ~ 370  $\mu$ J); however the laser pulse in the first case (125 fs) is higher than the one used in this work (50 fs) which may explain the increase in the fragment signal.

In figure 7.36 is shown the dependence of a thermally desorbed histamine signal and the photo-fragmentation  $(M^+/F_{tot})$  decreases with increasing laser intensity. The molecular ion peak increases exponentially with the laser intensity and at I =  $1.7 \times 10^{13}$  W cm<sup>-2</sup> the signal reaches the saturation.

At the lowest laser intensity  $(I = 5.7 \times 10^{12} \text{ W cm}^{-2})$  the M<sup>+</sup>/F<sub>tot</sub> has the highest value, but then it decreases almost exponentially. Also in this case it is necessary to consider that the M<sup>+</sup>/F<sub>tot</sub> ratio decreases by a factor ~ 2, while the M<sup>+</sup> increases almost 2 order of magnitudes.

### 7.4.3 Histamine molecule ionised at 1500 nm

The spectrum obtained by ionising the histamine with 1500 nm laser photons at the highest laser intensity, shows similar fragmentation to the 1300 nm spectrum, with the reduction of the carbon's charge state. The base peak, m/z 82, signal is reduced by only 25%, while the M<sup>+</sup> is 2 times lower than the signal obtained at 1300 nm. The figure 7.38 shows the dependence of the signal on the laser intensity.

While the histamine signal increases with the laser intensity; the photo-fragmentation



FIGURE 7.33. Spectra of the histamine molecule ionised at 800 nm laser wavelength, at I =1 ×10<sup>14</sup> W cm<sup>-2</sup> (pulse energy 4.4 mJ), 6.8 ×10<sup>13</sup> W cm<sup>-2</sup> (pulse energy 2.9 mJ) and 3.06 ×10<sup>13</sup> W cm<sup>-2</sup> (pulse energy 1.33 mJ) laser intensity.



FIGURE 7.34. Histamine ionised at 800 nm: dependence of the signal ( $M^+$  and fragments) as a function of the laser intensity.

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FIGURE 7.35. Mass spectrum histamine ionised at 1300 nm laser wavelength; the pulse energy is 370  $\mu$ J and laser intensity I = 2.8 ×10<sup>13</sup> W cm<sup>-2</sup>).

is >1 for only one data point. Although the trend in  $M^+/F_{tot}$  is similar to 1300 nm, the absolute values are bigger, reflecting a reduction in the amount of fragmentation that is consistent with Willingham *et al.* (2009) (62).

### 7.4.4 Histamine molecule ionised at 1714 nm

Figure 7.39 shows the comparison of the histamine ionised with the 1714 nm and 1500 nm at similar laser intensity: the spectrum obtained for the higher laser wavelength has the  $M^+$  signal 3 times higher than the lower laser wavelength.

The trend of the molecular ion signal and the fragments is almost linear with the laser intensity. Also the photo-fragmentation signal behaves linearly, and it should be noted that it changes by a factor of  $\sim 2$ , while for the M<sup>+</sup> the change is about one order of magnitude. The absolute values of M<sup>+</sup>/F<sub>tot</sub> are increased compared to 1500 nm.

#### 7.4.5 Histamine molecule ionised at 1900 nm

The spectrum obtained with the 1900 nm wavelength is shown in figure 7.41.



FIGURE 7.36. Histamine ionised at 1300 nm wavelength: top panel total total signal; bottom panel: photo-fragmentation signal.



FIGURE 7.37. Histamine mass spectrum at 1500 nm at the highest laser intensity (laser pulse energy is 230  $\mu$ J and laser intensity 2.8 ×10<sup>13</sup> W cm<sup>-2</sup>).

The laser power used is the lowest  $(4.6 \times 10^{12} \text{ W cm}^{-2})$  and the wavelength is the highest (1900 nm), the figure 7.41 shows a spectrum where the highest peak is at the threshold for detection. It appears that the molecular ion is the base peak. The low signal to noise ratio precludes further interpretation of this data.

#### 7.4.6 Summary: histamine

Histamine molecule has been ionised at 800 nm, 1300 nm, 1500 nm, 1714 nm and 1900 nm photoionisation wavelength. The figure 7.42 is obtained by plotting the  $M^+/F_{tot}$  signal ratio as a function of the laser wavelength, for the same pulse energy 157 mW. The 800 nm analyses is not included due to the higher power, while the 1900 nm data are not reliable due to the low signal obtained.

In figure 7.42, by increasing the laser wavelength that the  $M^+/F_{tot}$  ratio signal increases. At 1900 nm the signal is too low to be detected, hence no estimation can be done to strengthen our argument.

In Willingham *et al.* (2009) (62), the dependence of the laser wavelength on the photo-fragmentation (figure 7.32a) follows a similar behaviour to that obtained in this work (figure 7.42); however we note that in the range 1200 nm to 2000 nm laser



FIGURE 7.38. Histamine ionised at 1500 nm wavelength. Top panel: plot of the total signal versus the laser intensity. Bottom panel: photo-fragmentation signal.



FIGURE 7.39. Comparison of histamine ionised at 1714 nm (laser pulse energy 187  $\mu$ J and laser intensity 4.4 ×10<sup>12</sup> W cm<sup>-2</sup>) and 1500 nm at similar laser intensity.



FIGURE 7.40. Histamine ionised at 1714 nm, dependence of the M<sup>+</sup> and fragments signal (top panel) and of the photo-fragmentation (bottom panel) on the laser intensity.



FIGURE 7.41. Histamine ionised at 1900 nm laser wavelength, at laser pulse energy is 180  $\mu$ J and laser intensity is 4.6  $\times 10^{12}$  W cm<sup>-2</sup>.

wavelength the photo-fragmentation signal is on average 0.05, while in this work it is higher by a factor ~ 10. This could be due to the different laser pulse duration involved. In Willingham *et al.* (2009) use a 125 fs pulse whilst in this work a 50 fs pulse was used. Although pulse duration is not expected to be a significant factor in tunnelling ionisation behaviour, it is well-known to affect the fragmentation under MPI conditions. Even if MPI is only dominating in the wings of the laser ionisation volume, the relatively large field of view of the instrument used by Willingham *et al.* (2009) will result in a greater contribution of MPI background under given conditions than in the experiments performed in this work. In figure 7.43 is shown the spectrum obtained at each wavelength at the highest laser intensity.

#### Ionisation efficiency

The  $M^+$  signal have been normalised with the volume and the highest value of the peak area among the whole wavelengths (in figure 7.44 top panel) at 1300 nm laser wavelength, which has the highest efficiency of ionisation.

Also the  $M^+/F_{tot}$  has also been obtained by normalising the photo-fragmentation signal at 1, with the maximum achieved at 1500 nm (figure 7.44 bottom panel).


FIGURE 7.42. Dependence of the histamine molecular ion peak signal and the photo-fragmentation on the laser wavelengths. The plot is obtained at 157 mW pulse energy.



FIGURE 7.43. Histamine spectra at 800, 1300, 1500, 1714 and 1900 nm.



FIGURE 7.44. Ionisation efficiency of histamine:  $M^+$  (top panel) and  $M^+/F_{tot}$  (bottom panel) signals compared among the 800, 1300, 1500, 1714 and 1900 nm.



FIGURE 7.45. Nitroaniline mass spectrum analysed at 800 nm wavelength at I=9.4  $\times 10^{13}$  W cm<sup>-2</sup>.

### 7.5 Nitroaniline

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### 7.5.1 Nitroaniline molecule ionised at 800 nm

Nitroaniline, C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> (138.12 g/mol), is a relatively complex molecule (the benzene ring is bonded with NO<sub>2</sub> and NH<sub>2</sub>) and the ionisation potential (I<sub>p</sub>) is 8.31 eV. The barrier suppression intensity is I<sub>BSI</sub> =3.32 ×10<sup>13</sup> W cm<sup>-2</sup> and the number of photons absorbed by MPI at 800 nm is N<sub>K(T)</sub> = 5-6. In figure 7.45 is shown the spectrum obtained by irradiating the sample with the laser wavelength 800 nm and pulse energy 4 mJ at I=9.4 ×10<sup>13</sup> W cm<sup>-2</sup>.

The fragmentation pattern is dominated by complete fragmentation of the molecule with groups of hydrocarbon peaks  $(C_nH_n)$  although there is still a substantial parent peak and peaks corresponding to the removal of amino and nitro groups (NO<sub>2</sub> e NH<sub>2</sub>). Figure 7.46 shows the plot of the molecular and fragment ion signals versus the laser intensity.



FIGURE 7.46. Nitroaniline ionised at 800 nm laser wavelength: dependence of the total signal and photo-fragmentation on the laser intensity.

Nitroaniline thermally desorbed 1300 nm

M 2.5x10° Ions signal (counts) 2.0x10<sup>6</sup> 1.5x10<sup>6</sup> [M-NO\_] 1.0x10<sup>6</sup> 5.0x10<sup>5</sup> [M-NH\_] 0.0 20 40 60 80 100 120 140 0 m/z

FIGURE 7.47. Nitroaniline thermally desorbed at 1300 nm laser wavelength. The pulse energy is 300  $\mu$ J and the laser intensity is I=2.8 ×10<sup>13</sup> W cm<sup>-2</sup>.

The range of small fragments, m/z 45, m/z 52, m/z 62 which have the highest peak area are hydrocarbons (m/z 45 and m/z 52) and m/z 62, created by the removal of the amino and nitro groups and the hydrogen ions. The higher mass fragments are at m/z 122 ( $C_6H_4N_2O_2$ ) obtained by the removal of the H<sub>2</sub>, m/z 108 ( $C_6H_4O_2$ ) removal of N<sub>2</sub>H<sub>2</sub> due to the breaking of the NO<sub>2</sub> and NH<sub>2</sub> bonds to the benzene ring and also at m/z 92 that is  $C_6H_6N$  (removal NO<sub>2</sub> from the benzene ring) (see the chemical structure shown in figure 7.46).

The nitroaniline M<sup>+</sup> signal increases linearly at I < 6 ×10<sup>13</sup> W cm<sup>-2</sup>, and then reaches a plateau at higher intensities. The photo-fragmentation plot (figure 7.46) shows that the relative parent yield decreases with the increase of the laser intensity. At higher values of the laser intensity (I > 9 ×10<sup>13</sup> W cm<sup>-2</sup>), the sum of the fragment signal increases over the molecular ion peak.

#### 7.5.2 Nitroaniline molecule ionised at 1300 nm

Figure 7.47 displays the nitroaniline mass spectrum obtained at 1300 nm wavelength at the highest laser intensity (I= $2.8 \times 10^{13}$  W cm<sup>-2</sup>).

Figure 7.48 shows the dependence of the signal and the photo-fragmentation on

the laser intensity.

The 800 nm and 1300 nm data show an approach to a plateau which would also suggest the ionisation is becoming saturated at the highest laser powers for these wavelengths. However, this is unlikely at these low intensities. A possible reason why the signal might then increase again at higher power is if a new mechanism became favourable over a greater ionisation volume, thereby accessing a greater number of neutrals for ionisation. The  $M^+/F_{tot}$  signal, on the other hand, decreases by a factor of  $\sim 6$ .

#### 7.5.3 Nitroaniline molecule ionised at 1500 nm

Figure 7.49 shows the mass spectrum from thermally desorbed nitroaniline with the 1500 nm laser wavelength at the highest laser intensity.

The nitroaniline spectrum obtained at 1500 nm, I =1.4  $\times 10^{13}$  W cm<sup>-2</sup>, is compared with the one at 1300 nm at similar laser intensity. In this case the M<sup>+</sup> signal obtained at the longest laser wavelength is more than 2 times lower than the one obtained for the same laser intensity at 1300 nm.

The trend of the total signal, fragments and  $M^+$ , shows a linear increase with the laser intensity; the photo-fragmentation, on the other hand, shows a decreasing trend. The  $M^+/F_{tot}$  ratio decreases by a factor ~ 4, while the  $M^+$  increases over 3 orders of magnitude.

Since the M<sup>+</sup> signal has a linear trend, equation 6.2 can be used to estimate the number of photons absorbed. Since  $E_k$  ( $\lambda$ =1500 nm) = 0.83 eV, the number of photons needed for ionisation is ~ 8-9. The slope of the molecular ion peak is  $5.7 \pm 0.2$  which is lower, suggesting that there is resonant enhancement of the MPI process or that tunnelling is occurring.

#### 7.5.4 Nitroaniline molecule ionised at 1714 nm

In figure 7.52 is shown the spectrum obtained with the 1714 nm laser wavelength.

The spectrum contains only the molecular ion peak  $M^+$ ,  $[M+H]^+$  and the fragment at m/z 108. The dependence of the signal on the laser intensity is shown in figure 7.53. Although the signal rates are too low to draw definite conclusions.





FIGURE 7.48. Nitroaniline thermally desorbed at 1300 nm, trend of the total signal and photo-fragmentation with the laser intensity.

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FIGURE 7.49. Nitroaniline thermally desorbed at 1500 nm laser wavelength at the highest laser intensity  $1.4 \times 10^{13}$  W cm<sup>-2</sup> (pulse energy 220  $\mu$ J) and comparison with the spectrum obtained with the 1300 nm at similar laser intensity (1.3  $\times 10^{13}$  W cm<sup>-2</sup>).



FIGURE 7.50. Nitroaniline thermally desorbed at 1500 nm: total signal and photofragmentation dependence on the laser intensity.



FIGURE 7.51. Linear fit of the molecular ion peak trend for the thermally desorbed nitroaniline at 1500 nm: .



FIGURE 7.52. Nitroaniline spectrum obtained at 1714 nm wavelength at pulse energy of 187  $\mu$ J and I=4.4 ×10<sup>12</sup> W cm<sup>-2</sup>.

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FIGURE 7.53. Dependence of the nitroaniline thermally desorbed: signal on the laser intensity at 1714 nm laser wavelength.

### 7.5.5 Summary: nitroaniline

In conclusion the nitroaniline sample as been analysed with 800 nm, 1300 nm, 1500 nm and 1714 nm. The wavelength dependence on the photoionisation signal at a fixed intensity shown in figure 7.54 and 800 nm is not included as it was acquired at higher intensities.

The photo-fragmentation signal ratio increases with the increase of the laser wavelength, meaning that the signal  $M^+$  signal increases over the  $F_{tot}$ . The figure 7.55 shows the spectra obtained for each wavelength at the highest laser intensity.

#### **Ionisation efficiency**

The  $M^+$  signal has been normalised, taking into consideration the ionisation volume (see table 5.5) and then normalised to the highest value of the peak area for all wavelengths (in figure 7.56).

The highest ionisation efficiency is reached by the 1300 nm laser wavelength. The relatively high level of fragmentation seen for this molecule at 800 nm is  $\approx x10$  that seen under any other molecule/wavelength conditions. This could imply that the cation M<sup>+</sup> has a resonant absorption at 800 nm and this leads to significant

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FIGURE 7.54. Dependence of the nitroaniline molecular ion peak and photofragmentation on the laser wavelength at laser pulse energy  $E=190 \ \mu J$ .

additional photon absorption and fragmentation of this species as seen in the data (99).



FIGURE 7.55. Nitroaniline spectra obtained with 800 nm, 1300 nm, 1500 nm and 1714 nm wavelength.



FIGURE 7.56. Ionisation efficiency of nitroaniline thermally desorbed: M<sup>+</sup> (top panel) and M<sup>+</sup>/F<sub>tot</sub> (bottom panel) signals compared among the 800, 1300, 1500, 1714 and 1900 nm.

# Chapter 8

## **Conclusions and Future Work**

In this work, the photo-ionisation spectra for several organic molecules is reported. Utilising strong-field photo-ionisation, the extension of the laser wavelength from 800 nm to 1900 nm has led to a substantial reduction in the amount of photo-fragmentation compared to shorter wavelength. Xenon was used as a calibration standard since it does not fragment and its ionisation gives multiple charge states. Xenon was analysed at the whole range of laser wavelengths available and the signal was obtained at 800 nm, 1300 nm and 1500 nm; while lack of sufficient power meant that there was insufficient signal at 1714 and 1900 nm.

At 800 nm xenon ionisation behaviour agrees well with ADK theory (figure 6.1 and 6.2). The ionisation shows behaviour that is a mixture of the stepwise and the direct processes for both 800 and 1300 nm; while, for the 1500 nm, only the ionisation of the single charge state takes place. However it can be concluded that in most of the cases the ionisation tends towards a stepwise process.

For toluene and acetone, the best spectra was obtained at 1300 nm laser wavelength, in terms of the signal of  $M^+$  being the highest and the total fragmentation being minimised. It was noted that the fragment ions present in the spectrum was dependent on the wavelength used. This could be due to the different excitation mechanisms operating for each wavelength. Depending on the internal energy of the ion produced, its fragmentation pathway may be different, or different excited states in the cation are being resonantly excited. For histamine and nitroaniline, by increasing the laser wavelength, the fragment signal decreases compared to the molecular ion peak.

The Keldysh parameter calculated for toluene, acetone, histamine and nitroaniline does not agree with the experimental trend. It is concluded that this parameter cannot be used to accurately predict the onset of tunnelling ionisation in the case of molecules but only in the atomic system. In general the ionisation is considered to be in between the MPI and the TI mechanisms for the experiments reported in this work. The results presented here are sufficient to suggest that this approach may considerably expand the utility of lasers as molecular ionisation tools for small organic molecules. The data presented, along with advancement in the theory, suggest that experiments performed at even longer wavelengths and higher power using polarised light may further improve the quality of the spectra. A future extension of this work would be the analysis of larger, non-volatile molecules by also using the post-ionisation technique, sputtering the target with the ion beam. This would provide a more precise analysis of the ionisation/dissociation study, and would confirm the work done by Winograd et al. (1998) (20) and Vorsa et al. (1999) (21) of increasing ion yield with laser ionisation compared to SIMS spectra. The postionised spectra could also be compared with the gas phase spectra, in order to have an understanding on the effect of the internal energy deposited during the sputtering. Further optimisation of the laser characteristics such as the pulse duration, the wavelength, the laser power and the laser polarisation (81; 49) could be investigated which could further improve post-ionisation. Finally, how these properties change as the molecular size increases will clearly be important in the application of this technique for surface analysis of biological molecules.

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