Synchrotron radiation studies of gas phase molecules; from hydrogen to DNA sugars

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Abstract

This thesis summarises experimental results on the molecular spectroscopy of gas phase molecules excited by synchrotron radiation in the VUV and soft X-ray regions. We have used three different detection techniques, photon induced fluorescence spectroscopy, photoionisation mass spectroscopy and near edge X-ray absorption fine structure spectroscopy to study molecular deuterium, hydrogen sulphide, ammonia, methanol, pyridine, pyridazine, pyrimidine, pyrazine, s-triazine, and 2-deoxy-D-ribose, the last one also known as the DNA sugar. Out of this variety of techniques and molecules we have shown that: (1) high resolution dispersed fluorescence allows us to identify vibrational and rotational bands in molecular deuterium, as well as to estimate the predissociation probability of the same molecule [paper I]; (2) the main species fluorescing after core excitation of methane, ammonia [paper III], hydrogen sulphide [paper II], pyridine, pyrimidine and s-triazine is H Balmer α, followed by fluorescence from ionised species, molecular bands and Balmer β,γ,δ; (3) the Rydberg enhancement seen in fluorescence measurements of water [Melero et al. PRL 96 (2006) 063003], corroborated later in H₂S [paper II], NH₃ [paper III] and CH₄ [paper III] and postulated as general behaviour for molecules formed by low-Z atoms, is also seen in larger organic cyclic molecules, e.g. azabenzenes; (4) when dissociative ionisation of pyridine, pyridazine, pyrimidine, pyrazine, s-triazine and 2-deoxy-D-ribose occurs, concerted bond rearrangement and nuclear motion takes place as opposed to stepwise dissociation [papers V and VI].
Aquesta tesi és un resum dels resultats experimentals obtinguts en espectroscopía de molecules en fase gasosa utilitzant radiació de sincrotró en la regió de raigs VUV i raigs-X. En aquest estudi hem utilitzat tres tècniques, espectroscopia de fluorescència induïda per fòtons (PIFS), espectroscopia de masses induïda per fòtons (PIMS) i NEXAFS en combinació amb deuteri molecular, sulfur d’hidrogen, metà, amonia, piridina, piridazina, pirimidina, pirazina, s-triazina i 2-dioxi-D-ribosa o altrament coneguda com el sucre de l’ADN. De tota aquesta varietat de tècniques i molecules hem extret les conclusions següents: (1) la fluorescència dispersa d’alta resolució ens permet d’identificar les bandes vibracionals i rotacionals del deuteri molecular [article I]; (2) l’espècie que emet més fluorescència després de l’excitació de les capes més internes del metà i l’amonia [article III], del sulfur d’hidrogen [article II], de la pyridina, pyrimidina i s-triazina és H Balmer α seguida de les fluorescències d’espècies ionitzades, bandes moleculars i de Balmer β, γ i δ; (3) l’increment de fluorescència vist en els estats de Rydberg per l’aigua [Me lero et al. PRL 96 (2006) 063003], corroborat en dos estudis més, H$_2$S [article II], NH$_3$ [article III] i CH$_4$ [article III] i postulat com a una tendència general per molecules formades d’àtoms amb nombre Z baix, aquest increment doncs, és observat aquí en molecules orgàniques més grans com per exemple, els azabenzens; (4) quan la dissociació de molecules aromàtiques com la piridina, piridazina, pirimidina, pirazina, s-triazina i 2-dioxi-D-ribosa és deguda al procés de ionització, aleshores, la fragmentació no té lloc en diferents passos sinó que es produeix una redistribució dels enllaços en la molècula i moviment dels nuclis atòmics prèviament concertada [articles V i VI].
List of papers


My contribution to the papers is as follows:

- Papers II, IV, V, VI: I participated in the experiments, I analysed the data and I am fully responsible for the writing. Paper I: I participated in the experiments and did part of the writing. Paper III: I did the data analysis for CH₄ and part of the discussion of NH₃ molecule.

Additionally, I have presented the following contributions to international conferences:
LIST OF PAPERS

- **ICPEAC**, International Conference on Photonic, Electronic and Atomic Collisions; Freiburg, Germany July 2007
  Poster presentation: *Photons and DNA damage—what can we learn?*

- **ECAMP**, European Conference on Atomic and Molecular Physics; Crete, Greece May 2007
  Poster presentation: *The C1s and N1s NEXAFS spectra of five azabenzenes in the gas phase.*

- **LEOPOLD-FRANZENS-UNIVERSITÄT INNSBRUCK**;
  Obergurgl, Austria June 2006
  Participant at the ESF-FWF Conference: 'Biomolecules: From gas phase to reactions relevant in living cells'. Poster presentation: *Fluorescence emission from biomolecules excited with synchrotron radiation.*

- **MAX-LAB SYNCHROTRON**, Lund, Sweden Sept 2005
  Participant at the MAX Lab User’s Meeting.
  Poster presentation: *Rotationally resolved spectroscopy of molecular deuterium.*

- **UNIVERSITY OF BERGEN**, Bergen, Norway Aug 2005
  Participant at the Nordic Network for Women in Physics.
  Poster presentation: *Rotationally resolved spectroscopy of molecular deuterium.*

- **ALS-SSRL**, Berkeley-Stanford, USA June 2005
  Participant at the Stanford-Berkeley summer school on synchrotron radiation and its applications to physical sciences.

- **MAX-LAB SYNCHROTRON**, Lund, Sweden Sept 2004
  Assistant at the MAX IV User’s Meeting organised by MAX Lab Synchrotron Radiation Facility.

Not included papers


- **PAPER IX**: *Visible-UV fluorescence studies of fragments resulting from the relaxation of molecular core hole states* M. Coreno, A. Kivimäki, M. de
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The thesis contains six chapters. In chapter 1, a general introduction of the work performed here is provided. Chapter 2 introduces the underlying physics of the experimental work we have carried out. In chapter 3 the techniques we have used in this study, as well as the methodology of the experimental work done at different synchrotron facilities are presented. Chapter 4 discusses the results we have obtained, and chapter 5 summarises the conclusions we have reached. Finally, in chapter 6, some recent additional results are presented, and a perspective for future experiments is included.
Chapter 1

Introduction

The term 'molecule', from the Latin word *molecula* meaning 'small mass', is an aggregation of atoms. The great variety of materials found in the world is the result of the infinite combinations in which molecules may be built up from the atoms in the periodic table of elements. From the chemical point of view, molecules are characterised by the atoms contained in them and their coordination number. The simplest molecules are diatomic and homonuclear, i.e., two atoms of the same kind, such as $D_2$, $H_2$, etc. The next simplest group is that of diatomic molecules containing two different atoms, e.g., $HCl$. From here on, we can continue adding atoms to form triatomic molecules, like water ($H_2O$), polyatomic molecules, like ammonia ($NH_3$), or even larger systems, such pyrimidine ($C_4N_2H_4$) or 2-deoxy-D-ribose ($C_5H_{10}O_4$). The last two are related to the DNA molecule. In this work we have studied the small diatomic molecule $D_2$, the triatomic molecule $H_2S$, the four atomic $NH_3$, the five atomic $CH_4$ and from here we have jumped to the azabenzenes family with nine atoms and to the DNA sugar, 2-deoxy-D-ribose, containing 19 atoms. A schematic of the molecules studied here is found in Figure 1.1.

As a matter of applications of the present work, $H_2$ is seen to be produced from some bacteria and algae. In humans, we find that $H_2$ is a natural component of flatus. $H_2$ is also found in interstellar molecular clouds and associated with star formation. $CH_4$ is known to be a potent greenhouse gas and found as a component of cows flatus. Furthermore, $CH_4$ is used in the chemical industry as a raw material for the manufacture of methanol, formaldehyde, or chloroform, for instance. Without leaving the track of odorous gases we encounter ammonia, $NH_3$, and hydrogen sulphide, $H_2S$. The former is used in the production of fertilisers and explosives, while the latter is found in low-oxygen environments, such as in swamps and standing waters due to the sulfate-reducing bacteria. It has a characteristic odour of rotten eggs and it is also found in the Earth’s atmosphere as a result of volcanic emissions. $H_2S$, as an additive, also gives the odour to natural gas that arrives into our houses, which is otherwise odourless, and thus dangerous. Both
ammonia and hydrogen sulphide are found as constituents of the aminoacids in cells. The azabenzenes family, pyridine, pyridazine, pyrimidine, pyrazine and s-triazine are also known to smell sour, putrid or fishy. Pyridine, s-triazine and pyridazine are starting materials in the synthesis of compounds used as intermediates in making insecticides and herbicides. Pyridazine, pyridine and pyrazine are found within the structure of several pharmaceutical drugs. Pyrimidine is the precursor of the pyrimidinic DNA bases, cytosine and thymine, and the RNA base uracil. Even though pyrimidine in itself is not found in any biological system, it provides the structural link to DNA bases. Finally, 2-deoxy-D-ribose in the five membered-ring shape is found in the DNA backbone, linking the phosphate group to the base, thus providing structural integrity to our genome.

Perturbing any of these molecules, by adding internal energy for instance, will bring them into an excited configuration. Many of these excited configurations are not stable, and therefore, after a certain time, will relax to lower energy configurations. It is in this process of relaxation that the spectroscopic properties of these molecules manifest themselves, and if recorded, will give us the characteristic fingerprint of their excited states. In this work we have used synchrotron radiation to excite our molecular systems in conjunction with detection techniques.
such as photoionisation mass spectroscopy (PIMS), photon induced fluorescence spectroscopy (PIFS), and near edge X-ray absorption fine structure (NEXAFS) spectroscopy to study relaxations from outer-shell excited $D_2$ [paper I], pyridine, pyridazine, pyrimidine, pyrazine, s-triazine [paper V] and 2-deoxy-D-ribose [paper VI] and relaxations from core excited hydrogen sulphide [paper II], methane [paper III], ammonia [paper III], pyridine, pyridazine, pyrimidine, pyrazine and s-triazine [paper IV].

The novel research on the spectroscopic properties of the molecules such as the ones studied in this work, can lead to a better understanding of the complex link between fundamental and applied physics, physical chemistry, biophysics, and even astrochemistry.
Chapter 2

Physical processes

From the physical point of view, molecules are characterised by having quantum spaced energy levels as shown in Figure 2.1 and Figure 1 in paper I. These energy levels are called electronic, vibrational and rotational energy levels, and give us a measure of the internal energy of the molecule \( E_{\text{molecule}} = E_e + E_v + E_r \). Electronic energy levels have characteristic separations of a few eV, whilst vibrational and rotational levels are characterised by separations of a few tenths of an eV. The electronic energy levels in a molecule can be further classified according to their energy. The deepest levels, most negative in energy (defining the zero of energy where the ionisation limit is) are called core levels, are the closest to the nucleus of the atoms in the molecule, and have the lowest possible principal quantum number, \( n \), e.g., \( n = 1, 2, \ldots \). Above them, we find the inner valence levels followed by the outer valence levels. The last occupied orbital in a molecule is called HOMO (highest occupied molecular orbital) and the first unoccupied molecular orbital is called LUMO (lowest unoccupied molecular orbital). Above the outer valence shell we find Rydberg levels which are usually unoccupied orbitals with high \( n \) quantum numbers. The set of Rydberg states converges to a limit, IP (ionisation potential), and after that we find a continuum of states. However, depending on the shape of the potential energy surface of the molecule, bound states embedded in the continuum can be present, and are commonly known as shape resonances.

When one or more electrons in a molecule are moved to an empty orbital below the IP, the molecule is left in an excited state. If one or more electrons are released, at least a single ionised molecule is created. In this work we have used ionising radiation to excite or ionise our molecules, see paper I for valence excitations on D2; paper II, III and IV for core-excitations of hydrogen sulphide, ammonia, methane and the azabenzene family; and paper V and VI for photoionisation of \( C_5H_5N \) (pyridine), \( C_4H_4N_2 \) (pyridazine, pyrimidine, pyrazine), \( C_3H_3N_3 \) (s-triazine) and \( C_5H_{10}O_4 \) (DNA sugar).

Ionising radiation can be found in the shape of energetic charged particles, neutrons, and VUV to gamma-ray photons. Out of this variety, we have used
high energy photons in the VUV [papers I, V and VI] and soft-X ray [papers II-
IV] regions of the electromagnetic spectrum (see Figure 2.2) to study the primary
effects of ionising radiation on our electronic systems, using photons from bending
magnet and undulator synchrotron radiation (SR) sources.

Bending magnet radiation occurs when an electron travels in a uniform magnetic
field. The radiation produced is directed tangentially to the electron path in the
forward direction in a cone resulting in a fan of radiation around the bend, like
a ‘search light’. Undulator radiation is generated when an electron traverses a
periodically alternating, relatively weak, magnetic field. The periodicity causes the
electron to experience a harmonic oscillation in the $\vec{B} \times \vec{v}$ direction resulting in a
motion characterised by small angular excursions called undulations [4, 5, 6]. SR
allows us to continuously scan over a large range of energies. Therefore, one of the
main advantages is its tunability. SR has also other useful properties, such as high
brightness ($10^{19}$ photons/s/0.1%bw/mm²/mrad² for a 3rd generation synchrotron
source [7]), high flux ( photon flux on sample: $10^{11} - 10^{13}$ ph/s in BL I411 at MAX
Lab [8]), and polarizability. In this work, we have exploited the tunability and the
high flux properties. In our fluorescence measurements a high photon flux is needed due to the low collection efficiency \[9\]. In the mass spectrometric studies high flux is also essential because the cross section for photoionisation is lower (order of \(10^{-18} \text{ cm}^2 \equiv \text{Mb} \[10\]) compared to ionisation cross sections by electron impact (order of \(10^{-16} \text{ cm}^2 \[11\]).

A photon or quantum of light is a massless particle that carries energy proportional to the radiation frequency. Contrary to other types of projectile-sample interactions, where, for example, an electron may or may not deliver all or a fraction of the energy it carries into the molecule or system of study, a photon with an energy in the VUV or soft X-ray regions, as used in this work, will undergo photoelectric effect, and will either be completely absorbed by an electronic system or not, obeying the selection rules. Thus, some photons will trigger certain processes in a particular molecule whilst the same photons will be invisible to a different one.

Because of their energy, VUV photons can interact with the outer energy layers
CHAPTER 2. PHYSICAL PROCESSES

of an atom or molecule, also called valence shells. If the energy of the photon is higher than the ionisation potential (IP) of the target molecule, an electron might be released directly, leaving behind an ion, as in the following reactions [12]:

\[
M + h\nu \rightarrow M^+ + e^- \quad (2.1)
\]

\[
M + h\nu \rightarrow M^+ + e^- \rightarrow A^+ + B + e^- \quad (2.2)
\]

\[
M + h\nu \rightarrow M^* \rightarrow M^+ + e^- \quad (2.3)
\]

\[
M + h\nu \rightarrow M^{**} + e^- \rightarrow A^+ + B + e^- \quad (2.4)
\]

All these processes are explored in papers V and VI. If the photon energy is below the IP then, in a resonant process, an electron from a valence shell might be promoted to an excited state, \( M^* \), as in reactions:

\[
M + h\nu \rightarrow M^* \rightarrow M + h\nu \quad (2.5)
\]

\[
M + h\nu \rightarrow M^* \rightarrow M^{**} + h\nu' \quad (2.6)
\]

\[
M + h\nu \rightarrow M^* \rightarrow A^+ + B^- \quad (2.7)
\]

\[
M + h\nu \rightarrow M^* \rightarrow A^+ + e^- + B \quad (2.8)
\]

\[
M + h\nu \rightarrow M^* \rightarrow A + B^* \quad (2.9)
\]

which may relax via emitting a photon of equal or lower frequency or releasing an electron among other processes. In paper I we explore the processes described by reactions (2.6) and (2.9). Note that any of these fragments, \( A, B, A^+, B^+ \) can be left in an excited state, and thus emission of a photon may occur. Using soft X-ray photons from a synchrotron source it is possible to selectively prepare neutral core electron excited states in free molecules and to monitor the electronic decay of these states. When the target electron is a core electron, depending on the excitation energy, it will be completely removed from the system, or promoted to an unoccupied molecular orbital, valence or Rydberg level. In both cases a core hole will be created (see Figure 2.3 (a)), i.e., the molecule is left in a highly excited state that will rapidly relax back to a lower energy state by different routes. A review of these electronic processes can be found in refs. [7] and [13].

In Figure 2.3 we show some of the processes of interest to us; (b.1) shows the decay of the core hole via emission of an X-ray together with the ejection of a photoelectron; (b.2) shows the emission of a second electron together with the photoelectron (Auger process). If the photoelectron is not emitted, but promoted to an unoccupied Rydberg or valence orbital, resonant Auger decay can occur (see Figure 2.3 (b.3)). In this case, we differentiate between (b.3.1) participator Auger decay, \( 1 \text{ hole} - 1 \text{ particle states} \) or, (b.3.2) spectator Auger decay, \( 2 \text{ holes} - 1 \text{ particle states} \). Paper II and III explore the decay of the core hole in hydrogen sulphide, ammonia and methane. In any of the above mentioned processes emission of soft
X-rays following core excitation competes with electron ejection. However, for molecules composed of low-Z atoms, Auger processes are dominant over X-ray fluorescence [13].

As for photon emission, different processes will lead to emission of fluorescence in different regions of the electromagnetic spectrum. Upon core excitation of a molecule X-ray fluorescence can occur when a nearby electron relaxes filling in the core hole, as seen in Figure 2.3 step (b.1). Core excitations can also lead to fluorescence in the ultraviolet (UV) or visible or near infrared (IR) regions of the electromagnetic spectrum [paper II]. The processes that lead to this fluorescence are secondary processes to the Auger decay. When relaxation via spectator Auger decay takes place, the initial core electron that was excited to a Rydberg (valence) orbital, as in the Auger sketches in Figure 2.3 (b.3), can remain at that particular Rydberg (valence) orbital of one of the neutral or ionic fragments formed after dissociation of the molecule, which then might relax emitting fluorescence. Note that UV, visible, and near IR (750-900 nm) fluorescence can also be emitted upon molecular valence excitation [14]. When the molecule absorbs a photon between 5 - 30 eV (valence excitation) any of the above reactions may occur, leaving the molecule, the molecular cation, or the neutral or ionic fragments within a manifold of electronic and ro-vibrational excited states, that may relax emitting fluorescence.
Figure 2.3: Sketch of the X-ray emission and Auger processes for core excited molecules. LUMO stands for lowest unoccupied molecular orbital. Numbers 1 and 2 in the b.2 sketch show the time sequence of the events. The kinetic energy of the photoelectron can be calculated as: \( E_{\text{kin}} = h\nu - E_K \) where \( E_K \) corresponds to the energy of the K shell, i.e., \( n = 1 \). The kinetic energy of the Auger electron can be calculated as: \( E_{\text{kin}} = E_K - 2E_L \) where \( E_L \) is the energy of the L shell, i.e., \( n = 2 \). Note that the kinetic energy of the photoelectron depends on the incoming photon energy but the kinetic energy of the Auger electron is independent on the photon energy. In both participator and spectator Auger decays, the emission of X-ray fluorescence might be a competing channel.
Chapter 3

Methodology

All the diverse processes mentioned in the previous chapter can be explored by various techniques, such as photoabsorption spectroscopy, photoionisation mass spectrometry, photon induced fluorescence spectroscopy and photoelectron spectroscopy to mention a few. In this work we have used three different techniques, namely, PIFS, PIMS and NEXAFS in combination with the different sets of molecules described in chapter II. In the following, each technique will be thoroughly discussed accompanied by a description of the experimental setup we used, and a brief description of the beam line where the experiments were performed.

3.1 Photon induced fluorescence spectroscopy, PIFS

PIFS stands for photon induced fluorescence spectroscopy and, as the name suggests, is a technique in which fluorescence emission from excited neutral/ionic species is detected. From this fluorescence emission we can identify the emitting species and trace back the dynamics of the system; e.g., if fluorescence occurs from a fragment (ionic or neutral) we can infer that the molecule has dissociated with at least one of the fragments in an excited state. If fluorescence from the neutral parent molecule or the molecular ion is detected, we can determine the energy of the excited neutral molecule since the energy of the excitation source is known. Furthermore, detection of fluorescence reveals the electronic states in molecules. PIFS does not distinguish between ions or neutrals as long as they are in an excited state prone to fluoresce. Thus this technique permits us to detect ionic and, more importantly, neutral species. One of the drawbacks of this technique is the overall low collection efficiency.

In this particular work we have detected dispersed fluorescence in the visible and near IR regions (250-900 nm), and undispersed fluorescence in the UV-near IR (121.5-900 nm) range. Other examples of dispersed fluorescence, primarily in the UV region, can be found in refs. [15, 16], and visible fluorescence experiments of $N_2$ by Marquette et al. in ref. [17].
PIFS at beam line I411, MAX laboratory, Lund, Sweden

Beam line (BL) I411 is one of the 11 operative beam lines in the MAX II ring in Lund, Sweden. This storage ring is a 3rd generation synchrotron source where electrons are stored with an energy of 1.5 GeV. The I411 synchrotron source is an undulator device that together with a modified SX-700 plane grating monochromator and a plane elliptical focusing mirror, is set up to produce SR in the range of 50 – 1500 eV [18]. The beam line is devoted to gas phase experiments and has a permanent end station with an electron analyser. In this set up we have used the removable one meter section of this beam line to mount our own fluorescence chamber. Figure 3.1 shows a top view of the beam line and the experimental set up at I411.

Figure 3.1: Beam line I411 at MAX Lab. Number 1 in the picture shows part of the beam line. In numbers 2 and 3 our experiment is set up. # 2 shows the chamber, the spectrometer and electronics, #3 shows the data acquisition computer. The beam line’s permanent end station is shown in #4. It consists of an electron analyser attached to a high vacuum chamber and the electronics.

The original experimental set up for fluorescence experiments can be found in ref. [19]. It consists of a total of five crosses (see Figure 3.2). The first two five-way DN40CF-cross chambers are used as a differential pumping stage separating
3.1. PHOTON INDUCED FLUORESCENCE SPECTROSCOPY, PIFS

Figure 3.2: Sketch of the fluorescence chamber set up used at MAX Lab (not to scale).

the ultra high vacuum region of the beam line (10^{-9} mbar) from the experimental section (10^{-4} mbar), and also to guide the synchrotron beam to the interaction region. This is accomplished with a glass capillary of 29 cm length and ca 2.5 mm diameter bore. The interaction region is in the centre of the third five-way DN63CF-cross. This chamber allocates a stainless steel cylinder with the optics necessary for the collection of dispersed and undispersed fluorescence. In the special case of using a Ly-\(\alpha\) detector, this inner cell is removed leaving this third chamber empty. In series with the fluorescence chamber is a DN40CF T-shaped chamber that contains a homemade ion detector for total ion yield measurements. Finally, a four-way DN40CF cross is added to record the photon signal with a diode, and to provide a pumping port and a window for the alignment. The gas inlet system consists of a needle valve mounted on a feedthrough that controls the flow of sample leaking inside the chamber. When the inner cell is present the needle valve is connected to this cell via a capillary. If the inner cell is not present then the gas flows from the needle valve and fills up the whole chamber.

We have recorded fluorescence in two ways: dispersed and undispersed. Dispersed fluorescence is collected perpendicular to the SR beam by a lens/mirror system allocated in the inner cell, and it is focused onto the entrance slit of an f = 0.46 m spectrometer (Jobin-Yvon spectrometer HR460). The spectrometer has two gratings, a 600 gr/mm and a 1200 gr/mm, able to disperse fluorescence in the 250-900 nm range. Fluorescence is detected with a liquid nitrogen (LN2) cooled charged coupled detector (CCD), see ref. [9] for an intensity calibration of the spec-
Due to the collection efficiency (our optic system does not collect in $4\pi$) and to the detection efficiency (quantum efficiency of the CCD), the intensity of the detected dispersed fluorescence signal is about four orders of magnitude lower than the original source \[9\]. Undispersed fluorescence is recorded perpendicular to the plane formed by the synchrotron beam and the dispersed fluorescence collection setup. To monitor the undispersed fluorescence in the visible and UV regions we have used several photomultiplier tubes (PMT’s). For the PIFS experiments at BL I411 we have used the following PMT’s: (1) Hamamatsu, R647 for the visible region (300-650 nm) (2) Hamamatsu, R1080 for the UV region (115-320 nm) and (3) solar-blind photomultiplier tube (Hamamatsu R1459) together with a Ly-\(\alpha\) filter (Acton Research Corporation) with 15 nm bandpass and 10% transmission for the detection of the Ly-\(\alpha\) fluorescence, as in papers II and III. PMT’s #1 and #2 are separated from the vacuum region by a fused silica lens (90% transmission in the 250-1000 nm range). The Ly-\(\alpha\) filter mounted on the chamber body that supports the PMT acts as a vacuum window separation. In this set up, total ion yields (TIY) can be measured simultaneously with the undispersed fluorescence by monitoring the current (with a picoammeter) of ions that are collected on one of the electrodes of the home made ion detector.

**PIFS at beam line 52, MAX laboratory, Lund, Sweden**

Beam line 52 is one of the five beam lines that were originally mounted around the MAX I (550 MeV) synchrotron ring in Lund, Sweden \[20\]. It is the oldest ring in the facility and is soon to be substituted by MAX III \[21\]. The source of VUV radiation at BL52 of the MAX I storage ring is a bending magnet, equipped with a 1 m normal incidence monochromator, to give photons in the energy range of 5 to 35 eV \[22\]. For our fluorescence experiments we used the same chamber and set up as described for BL I411.

**PIFS at the gas phase beam line, ELETTRA, Trieste, Italy**

The ELETTRA synchrotron ring is located in the area science park in Trieste, Italy. It is a third generation ring with 2.0 GeV stored electrons. Our experiments at ELETTRA are performed at the gas phase photoemission beam line, which is one of the 14 operating beam lines. This beam line is comprised of an undulator source with a 125 cm period, a spherical grating monochromator equipped with a movable planar premirror, and two refocusing mirrors. Altogether it provides high-intensity collimated radiation in the photon energy range 15-1500 eV, and a spot size of a few hundred microns at the end of the beam line \[23\].

For the dispersed fluorescence measurements, the experimental set up consists of a vacuum chamber ($10^{-4}$ mbar) in which fluorescence is collected perpendicularly to the synchrotron beam by a spherical mirror mounted inside the chamber. The collimated light is sent through a quartz window, and a lens outside the chamber focuses the light onto the entrance slit of the fluorescence spectrometer. For the
measurements in papers II and III a spectrometer (Acton Spectra Pro 500) equipped with a 1200 gr/mm and a 3600 gr/mm grating mounted on a turret, and able to cover a wavelength region of 250-900 nm, was used together with a liquid nitrogen cooled CCD detector (Princeton 10:100B). The entrance slit of the spectrograph can be adjusted to give total resolution of 0.1-2 nm, depending on the needs of a particular measurement. For the Balmer \( \alpha \) fluorescence measurements presented in chapter 4.2 a fluorescence spectrometer (CP200) with a grating of 133 lines/mm was used together with the same CCD detector. For the undispersed fluorescence measurements, several PMT’s alone or in combination with filters have been used; (1) Hamamatsu R943 PMT which covers the 300 - 900 nm range as in paper II; (2) A filter (BARR Associates) with ca 60% transmission and 10 nm bandpass was used in front of the same photo-multiplier to record the H-\( \beta \) emission from \( H_2S \); (3) For the measurement of Ly-\( \alpha \) emission we used the same PMT and filter as at BL I411. Gaseous samples are leaked into the chamber through a needle of radius 0.5 mm, which injects the sample gas at the curvature centre of the fluorescence mirror where it meets the SR. A leak valve connected to a gas reservoir controls the pressure in the chamber. The integrated ion current can be measured with a micro-sphere plate (a 1 inch diameter detector from El-Multechnologies Ltd.) mounted at the entrance of the chamber perpendicularly to the direction of the SR beam, and a diode at the back of the chamber can record the variations in the synchrotron light flux.

3.2 Photoionisation mass spectroscopy, PIMS

PIMS stands for photoionisation mass spectrometry and it is an analytical technique used to measure the mass-to-charge ratio of ions produced by photoionisation of atoms and molecules. Some of the applications of this technique are:

- to determine the structure of a molecule by observing how it fragments
- to identify unknown molecules by detecting the molecular ion itself or the fragments produced

In our case, we have used mass spectrometry to determine the photofragmentation patterns of five azabenzenes: pyridine, pyridazine, pyrimidine, pyrazine and s-triazine, as well as to study the damage produced to the DNA sugar, 2-deoxy-D-ribose upon VUV photon excitation.

PIMS at beam line 52, MAX laboratory, Lund, Sweden

The MAX I storage ring and the beam line characteristics have been described in the previous paragraphs. In Figure 3.3 is shown a top view of BL52 with the PIMS set up mounted.

The experimental set up is built around a vacuum chamber made of three crosses (see Figure 3.4). Two five-way DN40CF cross chambers are arranged such that the
CHAPTER 3. METHODOLOGY

Figure 3.3: Top view of BL52 at MAX Lab. Number 1 shows the end of the beam line, number 2 shows our experiment and number 3 shows the computer for the data acquisition.

first one is attached to the end of the beam line and connects to the second chamber via a glass capillary of 2.5 mm inner diameter in order to guide the beam to the interaction region and also to act as a differential pumping stage. The interaction region is located in the centre of the third chamber, a DN63CF six-way cross. A quadrupole mass spectrometer (VG-300SPX) is placed on the top flange and a home made repeller (see Figure 3.5, middle) kept under a constant positive voltage (4 V) at the bottom port, facing the quadrupole mass spectrometer (QMS) in order to drive the ions from the interaction region towards the QMS entrance. The QMS is used in two different modes: scanning mode, where the yield of ionic fragments is recorded as a function of the ion mass/charge ratio at a fixed photon energy, and the fixed mass mode, where the QMS is held at a constant mass and we record the ion intensity while varying the photon energy (yield of the fragment). In this cross-beam geometry, and perpendicular to the plane formed by the synchrotron photon beam and the central axis of the QMS, there is a home made molecular evaporator (see Figure 3.5, right) to evaporate the molecules, and a home made LN2 cooled plate (Figure 3.5, left) to recondense the molecular vapour outside the
3.3. NEAR-EDGE X RAY ABSORPTION FINE STRUCTURE, NEXAFS

When an X-ray photon resonantly connects a core level with a final state in an atom or molecule, identifiable characteristic peaks will appear in the ion spectrum when plotted against the incident photon energy. When these peaks are between a few
Figure 3.5: Schematic front view of the experimental set up used for the PIMS experiments. Photos of the experimental pieces are shown. Left, LN2 cooled plate; middle, the repeller (or pusher); right, the molecular evaporator.
eV below and up to 40 eV above the X-ray absorption edge of an atom, or different atoms in a molecule, then these features are called near edge X-ray absorption fine structure, or NEXAFS. Particularly below the edge, NEXAFS looks at spectator and/or participator Auger decay processes, thus NEXAFS spectroscopy has proven to be a sensitive technique for the accurate determination of the electronic structure of matter [21]. It is a technique that is atom specific and sensitive to the chemical environment of atoms in molecules. It follows from this that useful information about local bonding structure and presence of specific bonds in molecules can be obtained via NEXAFS.

It is widely used in surface science to study the properties of adsorbates [23], and has also been applied successfully for molecules in the gas phase [24]. NEXAFS spectra can be acquired with many different setups; i) recording ion currents we obtain total or partial ion yields (TIY, PIY). In this setup it is assumed that a photon is absorbed by the molecule, releasing an electron, where the ion is recorded as in refs. [27, 28] [papers II, IV]. This method is especially convenient for gas-phase studies. ii) recording the Auger electrons when the molecule is excited below the edge of one of the atoms, see ref. [29, 30]. iii) recording the photoelectron emission drain current on the sample after photon interaction (solid samples), see ref. [31].

NEXAFS at the gas phase beam line, ELETTRA, Trieste, Italy

The measurements were conducted at the undulator-based gas phase photoemission beam line at the ELETTRA synchrotron facility, Trieste, Italy (see section 3.1).

The experimental set up consists of two chambers, placed one after the other in the photon beam direction. The first chamber is a six-way DN40CF cross. It functions as a differential pumping stage and allows us to leak gaseous samples for energy calibration purposes. The second vacuum chamber contains a window-less double ionisation cell mounted in two six-way DN40CF crosses and designed to perform absolute photoionisation cross section measurements. The sketch of this
second chamber, that contains the double ionisation cell, is seen in Figure 3.6. The design is similar to the double ionisation set up used in ref. [32]; two equally long electrodes \( l \) collect the charges produced along the light path, \( i_1 \) and \( i_2 \) in Figure 3.6. Then, the Beer-Lambert law as derived by Samson [33], gives a measure of the absorption cross-section as in Equation 3.1.

\[
\sigma = \frac{1}{nl} \times \ln \left( \frac{i_1}{i_2} \right) \quad (3.1)
\]

where \( n \) is the number density of the gas in the interaction volume. If we assume an ideal gas behaviour in the calculation of the gas density, then Equation (3.1) can be written as:

\[
\sigma = \frac{k_B T}{Pl} \times \ln \left( \frac{i_1}{i_2} \right) \quad (3.2)
\]

where \( k_B \) is the Boltzmann constant, \( T \) the temperature in K and \( P \) the pressure of the gas in Pa. In order to give an approximate order of magnitude for this cross section we look at the numbers obtained for the pyrazine molecule at the N 1s edge:

\[
k_B = 1.4 \times 10^{-23} \text{ J/K}
\]

\[
T = 300 \text{ K}
\]

\[
P = 3 \text{ Pa}
\]

\[
i_1 = 9 \times 10^{-10} \text{ A}
\]

\[
i_2 = 8 \times 10^{-10} \text{ A}
\]

\[
l = 14.3 \text{ cm}
\]

Then equation (3.2) becomes:

\[
\sigma = \frac{1.4 \times 10^{-23} \text{ J/K} \times 300 \text{ K}}{3 \text{ Pa} \times 14.3 \text{ cm}} \times \ln \left( \frac{9 \times 10^{-10} \text{ A}}{8 \times 10^{-10} \text{ A}} \right)
\]

\[
\simeq 4.2 \times 10^{-21} \text{ J} \times 0.1 \simeq 9.8 \times 10^{-24} \text{ J/Pa cm}
\]

\[
\simeq 9.8 \times 10^{-24} \text{ N m}^3/\text{N cm} \simeq 9.8 \times 10^{-24} \times 10^6 \text{ cm}^3/\text{cm}
\]

\[
\sigma \simeq 9.8 \times 10^{-18} \text{ cm}^2 \simeq 10 \text{ Mb}
\]
Chapter 4

Selected results and discussion

4.1 Vibrationally and rotationally resolved fluorescence emission

Using monoenergetic synchrotron light in the range of 13.97 – 15.84 eV to excite the D 1s electron, we reached different Rydberg states (Franck-Condon allowed states) (see Figure 1 in paper 1). The relaxation of the system can take place via radiative or non-radiative emission as seen in chapter 2. The results for the recorded dispersed fluorescence (radiative emission) from $D_2$ are shown in Figure 2 of paper 1. Looking at this figure, we expect that the most intense transitions of $np\sigma, \pi – EF$ fluorescence emission terminate on the E part of the EF curve considering the Franck-Condon principle. The calculated Franck-Condon factors in ref. [34] propose as the most intense bands (0;0), (1;3), (2;6) and (3;9) \(^1\).

As seen in Figure 2 of paper 1, relaxation from the $v’=0$ vibrational state belonging to the 4$p\pi$ Rydberg state to the $v’’=0$ vibrational state in the EF curve shows a main line and the rotational components on both sides. The rotational lines are decreased in intensity in the (1;3) vibrational transition, and they have disappeared when we reach the (3;9) vibrational transition. This can be understood by looking at the potential curves shown in Figure 1 of paper 1. The vibrational states $v’=3$ and $v’=2$ in the 4$p\pi$ curve are above the dissociation limit $D(1s)+D(2l)$, therefore $D_2$ molecules with one electron in the $np\pi v’ = 2, 3$ will most likely dissociate with one atom in the ground state (1s) and the other one in an excited state (2l).

Further analysis of the intensity of the fluorescence emission in Figure 2 of paper 1 allows us to quantitatively determine the predissociation probability $X(R_x)$ for a given level $v, J$, i.e. the probability that a molecule excited to this level will predissociate. We define: $X(R_x) = 1 - \frac{R_x}{R_0}$ where $R_0$ is the ratio between

\(^1\)The numbers in (0;0), (1;3), (2;6) and (3;9) are the vibrational states of two different electronic states, the first one above the second, according to the notation $(v’; v’’)$ in Herzberg [35]. $v’$ meaning vibrational state of the upper electronic state, $v’’$ lower vibrational state of the lower electronic level.
the intensities of the rotational P(3) line relative to that of the unresolved Q-line complex for unpredissociated levels (see Figure 2 of paper I), and $R_x$ the same but for a predissociated level, i.e., the ratio between the intensities of the rotational P(3) line relative to the intensity of the Q-line complex for a predissociated level.

The maximum and minimum values in this equation are,

\[ X(R_x = R_0) = 1 - \frac{R_0}{8R_0} = 0 \]

\[ X(R_x = 0) = 1 \]

$X=0$ means no predissociation, $X=1$ totally predissociated. Then, $X(R_x \neq R_0)$ is a measure of the probability of predissociation of that particular level. From the results of table I in paper I we observe that electronic states whose vibrational states are above the D(1s)+D(2l) level have a higher probability of predissociation compared to those that lie below this dissociation limit which we observe to decay by emitting photons.

4.2 Fluorescence from core excited molecules

As discussed in the introductory part, fluorescence can occur at different regions of the electromagnetic spectrum. In the previous sections we have shown that visible fluorescence occurs after exciting the valence shell of $D_2$. In this chapter we will further discover the usefulness of visible - UV fluorescence spectroscopy when excitation of core electrons occurs. In particular, we will focus on the results of $H_2S$, $NH_3$, $CH_4$, pyridine, pyrimidine and s-triazine. The results of this work will be divided in two subsections, dispersed and undispersed fluorescence.

Dispersed fluorescence

Figure 4.1 shows the results of recorded dispersed fluorescence after excitation of 2p core electrons of $H_2S$, and 1s core electrons of $CH_4$, pyridine, pyrimidine and s-triazine. Common to all of them, we find that emission of atomic H is predominant. In particular, hydrogen Balmer $\alpha$ is the strongest species fluorescing in all the molecules studied here.

Hydrogen sulphide

For $H_2S$ [paper II] we find that in addition to atomic H, fluorescence from $S$, $S^+$, $HS$ and $HS^+$ is also emitted (see Figure 4.1 top graph). The main species fluorescing after atomic H is $S^+$; thus we concentrate on the possible pathways of producing excited $S^+$ ions and neutral hydrogen atoms. The photoabsorption spectrum of $H_2S$ shows two weak resonances at around 165 eV that correspond to excitations to unoccupied molecular orbitals followed by a manifold of transitions to valence and Rydberg states that extends to ca 171 eV, see ref. 27 and Figure 1 in paper II. According to this, we distinguish between two regions in the spectrum, excitations to the molecular resonances, and excitations to valence-Rydberg orbitals. At the molecular resonances a competition between ultrafast dissociation
4.2. FLUORESCENCE FROM CORE EXCITED MOLECULES

Figure 4.1: Top graph; fluorescence spectrum of $H_2S$ in the range of 250-900 nm obtained at a photon energy of 169.68 eV [paper II]. Note that the $H$-$\alpha$ emission is saturated in order to show the smallest contributions of $S^+, S, HS$ and $HS^+$. The calculated relative transmission curve of the spectrometer+CCD set-up is also shown [36]. Middle graph; dispersed fluorescence of methane taken at an excitation photon energy of 288 eV in the 300-500 nm region [paper III]. Bottom; main features recorded of dispersed fluorescence from pyridine, pyrimidine and s-triazine. All spectra were taken at photon excitation energies corresponding to the $\pi^*$ resonance at the $N\,1s$ edge.
and Auger decay of the parent molecule occurs. When the former takes place, the core excited molecule breaks apart into a core excited \( HS \) fragment, which we denote by \( HS^{**} \), and a hydrogen atom in the ground state, \( H(\text{g.s.}) \). The core excited \( HS \) is a very unstable configuration that will mostly decay via resonant Auger [37] to an excited configuration of the \( HS^+ \) molecular ion, which in turn may dissociate into \( S^+ \) and \( H \) [38]. The equations that describe the dissociation pathway can be written as:

\[
\begin{align*}
H_2S + h\nu &\rightarrow H_2S^{**} \\
H_2S^{**} &\rightarrow HS^{**} + H(\text{g.s.}) \\
HS^{**} &\rightarrow HS^{++} + e^- \\
HS^{++} &\rightarrow H^* + S^+ \quad \text{or} \quad H + S^{++}
\end{align*}
\]

If instead the core-excited \( H_2S \) molecule relaxes via Auger decay (process taking place at the molecular resonances, and also at Rydberg levels), then participator or spectator Auger decay takes place. The dissociation of the different Auger final states of the molecular parent ion into neutral hydrogen and sulphur ions may proceed via:

\[
\begin{align*}
H_2S + h\nu &\rightarrow H_2S^{**} \\
H_2S^{**} &\rightarrow H_2S^{++} + e^- \\
H_2S^{++} &\rightarrow H^* + HS^+ \quad \text{or} \quad H + HS^{++} \\
HS^{++} &\rightarrow H^* + S^+ \quad \text{or} \quad H + S^{++}
\end{align*}
\]

This Auger decay predominates after valence-Rydberg excitations. From the dissociation pathways shown in equations [4.4, 4.7, 4.8], we can infer that the fluorescence emission from \( H_2S \) seen in this work is mainly produced by \( H^{++}, HS^{++}, S^{++} \) and \( S^* \). Equations 4.4, 4.7 and 4.8 are the possible mechanisms that play a role in the excitations to the molecular orbitals region and Equations 4.7 and 4.8 are the possible mechanisms that lead to fluorescence when the \( S_{2p} \) electron is excited to a valence-Rydberg orbital.

**Methane**

Dispersed fluorescence from methane is characterised by a strong \( H^* \) emission (Balmer \( \alpha \) not shown in Figure 4.1) followed by less strong fluorescence from the molecular band \( CH(A-X) \). After core excitation of the \( 1s \) electron in the \( C \) atom, the methane molecules will mostly relax via Auger decay producing singly charged ions \( CH_4^+ \). Thus the possible fragmentation pathways that can lead to excited neutral \( H \) atoms after resonant Auger decay are (with dissociation limits calculated from the ground state of \( CH_4 \), written after the equation and taken from ref. [52]):

\[
CH_4^+ \rightarrow CH_3^+ + H^*; D(CH_3^+ + H^*) = 14.25eV + E(H^*)
\]
4.2. FLUORESCENCE FROM CORE EXCITED MOLECULES

\[ CH_4^+ \rightarrow CH_2^+ + H^* + H; D(CH_2^+ H^* + H) = 19.67 \text{ eV} + E(H^*) \]  
(4.10)

\[ CH_4^+ \rightarrow CH^+ + H_2 + H^*; D(CH^+ + H_2 + H^*) = 19.75 \text{eV} + E(H^*) \]  
(4.11)

\[ CH_2^{2+} \rightarrow CH_2^+ + H^+ + H; \]  
(4.12)

Expected appearance energies for Lyman \((n' \rightarrow n = 1)\) and Balmer \((n' \rightarrow n = 2)\) emission are obtained by adding the excitation energy \(E(H^*)\) of the \(H^*\) atom in different \(n\) states to the above dissociation limit energy value. As an example of \(H^*\) formation, let us look at the \(H\) Balmer \(\beta\) emission. Assuming that the photoelectron takes almost all of the incoming photon energy, what is left is stored as internal energy of the \(CH_4^+\) molecular ion. If this energy is higher than the sum of the dissociation limit and the excited hydrogen atom, then it will lead to \(H\) fluorescence. Considering the dissociation pathway via equation 4.9, Balmer-\(\beta\) emission requires at least 27.00 eV, \((12.75 \text{ eV} + 14.25 \text{ eV})\). Looking at the photoelectron spectra of \(CH_4\) we observe that the calculated energy limit of 27.0 eV is higher than the binding energies of the single hole states, thus participant decay cannot lead to Balmer-\(\beta\) emission. In the case of equations 4.10 and 4.11 the lower limits for B \(\beta\) emission are 32.42 eV and 32.5 eV, respectively. Again, looking at the Auger spectra of \(CH_4\) we observe that the maximum of the spectral intensity lies below these binding energies in the spectrum measured at the first core excitation \((C1s \rightarrow 3a_1)\), while at the higher Rydberg excitations, such as the \(C1s \rightarrow 4pt_2\), practically all the intensity in the spectrum is located at higher binding energies. Therefore, Balmer-\(\beta\) emission may follow the dissociation of the Auger final states via reactions 4.10 and 4.11 and be more effective from the higher-lying Rydberg excitations.

There is yet another channel to consider, equation 4.12 in which the Balmer emission correlates to the relaxation of the system via spectator Auger decay. Thus, when spectator Auger decay occur, the spectator electron is still bound to the dissociating system, especially if the binding energy of the Auger final state is below the dissociation limit of the reaction 4.12 and it sees a double positive core. This highly unstable situation will eventually start to dissociate into \(CH_2^+ + H^+ + H + e^-\). Thus the spectator electron can attach to an empty orbital of either of the charged species \(CH_2^+\) or \(H^+\). If it goes to the proton, an excited hydrogen is formed, and fluorescence will follow. In adiabatic dissociation, the Rydberg orbital occupied by the spectator electron after the Auger decay will determine the hydrogen orbital, to which the electron ends up after dissociation 4.11.

Azabenzenes

In Figure 4.1 bottom graph, dispersed fluorescence of pyridine, pyrimidine and s-triazine is shown in different regions after \(N1s \rightarrow \pi^*\) photon excitation energy. The strongest species fluorescing is atomic hydrogen Balmer \((-\alpha, -\beta, -\gamma, -\delta)\) followed by CN and CH bands. The same species fluoresce upon absorption of \(C1s \rightarrow \pi^*\)
photons, however, the intensity of the recorded fluorescence is lower for the same detection settings (time, slits, ring current).

As seen for the previous molecules, in order to explain the fluorescence from excited $H$ atoms we have to look at the production of atomic hydrogen. After absorption of $N_{1s} \rightarrow \pi^*$ photons the $1s$ core electron is relocated to an unoccupied valence or Rydberg state. This leaves the system in a highly excited state which most likely will relax via resonant Auger decay as seen in chapter 2. Both resonant and normal Auger spectra of thin films of pyridine, pyrazine and s-triazine were recorded by Eberhardt et al. [42] at energies of 400 and 415 eV respectively. In the resonant spectra they assign the peak at higher kinetic energy to participator Auger decay in the molecules and the rest of the spectra to spectator Auger decay, in analogy to the PES study of $N_2$ published in the same work. If we now consider the dissociation of the molecule after a charge transfer and a ring opening as seen for the azabenzences in refs. [43], [44], [45], and sketched in Figure 4.2, these molecules will break apart into at least two fragments. In the case that one of these fragments is $H$ with the electron in $n = 3, 4, 5, \ldots$, it will relax emitting a photon of a wavelength as observed in Figure 4.1.

![Figure 4.2: Possible processes leading to $H$, CH and CN fluorescence seen for the azabenzences. In this example the pyridine molecule is used but it is suggested to be the same for pyrimidine and s-triazine. The positive charge in parenthesis includes the possibility of ionised fragment formation.](image)

**Undispersed fluorescence**

We have found from dispersed fluorescence measurements that the main species fluorescing in all the molecules studied here is atomic $H$. We have also shown that from the fluorescing species we can infer some of the fragmentation pathways. In the following, we will show that undispersed fluorescence reveals another interesting result, i.e., enhancement in various fluorescence yields (Balmer $\alpha, -\beta, -\gamma, -\delta$) compared to the ionic yield upon core excitation.
Ammonia

The recorded integrated fluorescence in the visible region, as well as the total ion yield for the ammonia molecule is displayed in Figure 4.3. Specifically, this figure shows the fluorescence emission from excited atomic $H$ ($n=3$, 4, 5 and 6) and is compared to the ionic yield.

Figure 4.3: From bottom to top: intensity of the recorded ion yield, Balmer-$\alpha$, Balmer-$\beta$, Balmer-$\gamma$ and Balmer-$\delta$ emission after excitation of the $N$ 1s electron of ammonia. The energy scale is calibrated after [40].

After excitation of the $N$ 1s electron in ammonia, molecular spectator Auger decay takes place in 99% of the cases [47]. The molecule is left in a state equivalent to dicationic states, $NH_{4}^{2+}$ which most likely will dissociate into smaller fragments. Stankiewicz et al. [48] and Lindgren et al. [49] found that doubly charged $NH_{4}^{2+}$ ions dissociate into different ion pairs after direct double photoionisation via the decay of core excited states. Note that these dissociation channels include proton ejection. Therefore, when the final states of the spectator Auger decay dissociate, the proton may capture the spectator electron, leading to the production of excited hydrogen atoms that decay by fluorescence. According to Samson et al. [50] and Rabalais et al. [51] the production of $NH_{4}^{2+}$ may be associated with the 1e orbital photoionisation. Then, if after core excitation, $NH_{4} + \nu_{soft, x-ray} \rightarrow NH_{4}^{**}$, spectator Auger decay takes place, $\rightarrow NH_{4}^{*} + e_{Auger}$, the production of excited hydrogen atom together with $NH^{+}$ could be:

$\rightarrow NH^{+} + H^{+} + H + e_{spectator}$ (dissociating state)
$\rightarrow NH^{+} + H^{+} + H$ (proton captures electron)
$\rightarrow NH^{+} + H + H^{+} + h\nu$ (emission in H)

Any of these pathways that end up with an excited $H$ atom with $n=3$, 4, 5 or
6 might fluoresce in the visible region. Recording the intensity of this fluorescence across the resonances we obtain the curves as plotted in Figure 4.3. The four fluorescence yield curves show a strong peak at around 402 eV and also a second resonance closer to the N 1s ionisation threshold (405.52 eV). This second resonance becomes more intense for the higher members of the Balmer series (H-γ, H-δ) and it also shifts to higher photon energies, which corresponds to higher core-to-Rydberg excitations. This phenomenon was seen previously for water [41] and later on in H₂S [paper II, this work]. In both papers this behaviour was postulated general for molecules composed of low-Z atoms, thus ammonia [paper III, this work] corroborate once more this general behaviour for the Balmer series.

Pyridine, pyrimidine, s-triazine and benzene

In a next step, we have moved to larger aromatic molecules and we have recorded non-dispersed fluorescence of pyridine, pyridazine, pyrimidine, pyrazine and s-triazine at the N and C 1s edges and benzene at the C 1s edge. In Figure 4.4 we show the results for benzene, pyridine, pyrimidine and s-triazine molecules.

The intensity similarity between the recorded visible fluorescence (300-900 nm region) and the H Balmer α fluorescence across the resonances in pyridine, pyrimidine and s-triazine suggests that the visible fluorescence yield is mainly due to B α emission, with only small contributions from H Balmer −β, −γ, −δ and other atomic and molecular bands. The Balmer β emission recorded for pyridine suggests an enhancement in the valence - Rydberg region as previously seen for SiF₄ [52], SiCl₄ [53], H₂O [11, 54], H₂S [see paper II in this thesis], CH₄, NH₃ [see paper III in this thesis]. Thus the conclusion reached in the last paragraph for small molecules composed of atoms with low-Z number, namely that, the decay of some high-n core-to-Rydberg excited states of low-Z molecules efficiently leads to the creation of hydrogen atoms with an electron in the n > 3 shell, also seems to be true for larger aromatic molecules composed of low-Z atoms. However, the enhancement seen in these molecules is not as evident as in the smaller molecules studied here and further studies would be required.

4.3 NEXAFS - Understanding the aromatic molecules

In the previous chapter we have shown the results of visible and UV fluorescence for pyridine, pyridazine, pyrimidine, pyrazine and s-triazine, and the processes that lead to fluorescence. Additional information on the electronic structure of these aromatic molecules is achieved with NEXAFS spectroscopy [paper IV]. In this work, we have measured the near edge X-ray absorption fine structure spectrum of pyridine, pyridazine, pyrimidine, pyrazine and s-triazine. The experimental curves measured at the N 1s and C 1s edges of these molecules are shown in paper IV Figure 2.

In order to assign the features seen in the experimental NEXAFS spectra calculations using the deMon program [55] are performed to simulate the experimental
Figure 4.4: Total ion yield, TIY; UV fluorescence and Balmer α fluorescence of pyridine (N 1s and C 1s edges), benzene (C 1s), pyrimidine and s-triazine (N 1s). Total integrated visible fluorescence is also shown for pyridine, pyrimidine and s-triazine. Balmer β fluorescence is displayed for benzene and pyridine.
NEXAFS spectra, and to obtain peak assignments. For further details on the calculations the reader is referred to paper IV.

As opposed to what we have seen in the TIY for hydrogen sulphide, methane and ammonia, all of which are saturated compounds, the unsaturation of the bonds in the azabenzences is manifested in their NEXAFS spectra by a strong resonance corresponding to the transition of the 1s electron to an unoccupied $\pi^*$ molecular orbital (MO), a weaker Rydberg series in the discrete part of the spectrum and multi-electron excitations superimposed on a shape resonance structure in the near-continuum part. In Figure 4.5 a close up of the experimental and theoretical spectra below the IP of pyrimidine and s-triazine are shown.

Figure 4.5: Enlarged experimental (a) and theoretical (b) NEXAFS spectra of pyrimidine and s-triazine at the carbon 1s edge (left graphs) and at the nitrogen 1s edge (right graphs). In the top left graph C1-C3 are calculated spectra and IP’s for the three non equivalent carbon atoms in pyrimidine.
At both edges, peak number 1 corresponds to a transition of the 1s electron in the C or N atoms in the molecules to a molecular orbital with $\pi^*$ character. Below the ionisation potential, IP, the resonances are associated to $\sigma/\pi$ orbitals with mixed valence/Rydberg character. Peak number five is attributed to double excitations in agreement with the study of the $N_2$ molecule in ref. [56]. Finally, above the IP we observe two resonances (peaks 6 and 7, see Figure 2 in paper IV) assigned to transitions to $\sigma^*$ orbitals.

Further analysis on the experimental data in paper IV reveals some differences among these molecules:

1. The intensity of peak 4 when compared to the absorption continuum increases with the addition of $CH$ groups in the molecule. Let $I$ be the intensity difference between peak 4 and the far continuum (see Figure 2 in paper IV). Calculating $I$ for s-triazine, pyrazine and pyridazine we obtain the following values:
   
   \[
   I_{s\text{-triazine}} = 0.17 \text{ (arb. units)} \\
   I_{pyrazine} = 0.11 \text{ (arb. units)} \\
   I_{pyridazine} = 0.15 \text{ (arb. units)}
   \]

   We observe that pyridazine and pyrazine, both with two $N$ atoms, have lower values compared to s-triazine which contains three $N$ atoms. This result points to an enhancement of the Rydberg resonances when compared to the continuum upon $CH$ substitution. This process was observed for small molecules in different studies [57], [58], [59] and from our study we found that it is applicable to larger organic molecules.

2. We have also measured the width of the N1s $\rightarrow \pi^*$ resonances and the C1s $\rightarrow \pi^*$ splitting of all compounds (see numbers above the arrows in Figure 4.5). From the comparison of the values between edges, and when compared to values in the literature, we find that the values measured for the C 1s edge tend to be narrower than those measured at the N 1s edge. This would imply that vibrational modes are more active in the N1s $\rightarrow \pi^*$ transition than at the C 1s edge. Our results for the C1s $\rightarrow \pi^*$ peak splitting in gas phase pyridine are in agreement with the condensed phase results presented in ref. [60]. However, for the gas phase pyrazine molecule we measured a much narrower splitting than in multilayer pyridazine in ref. [60].

3. Hitchcock et al. [57] (for $H_2CO$) and Robin et al. [61] (for ethylene and its fluorinated derivatives) observed that the position of the $\pi^*$ resonance relative to the 1s IP should be rather similar at different K-edges (within 1 eV), despite the fact that absolute excitation energies are different. In our study we have calculated the $\Delta_{\pi}$ ($\Delta_{\pi} = E_{\pi}^* - IP$) and the spread of $\Delta_{\pi}$ ($\Delta_{\pi}\text{spread} = \Delta_{\pi,\text{max}} - \Delta_{\pi,\text{min}}$) for the five molecules at both edges to validate the previous observations. For the results at the C edge we have distinguished between the different environments of the C atom, i.e., C-C or C-N (see Figure 4.1), therefore the corresponding $Z$ numbers of these bonded pairs are 12 or 13, respectively. The results of $\Delta_{\pi}$, $\Delta_{\pi}\text{spread}$ are shown in Table 4.1.

From these values we observe three facts: (i) the position of the $\pi^*$ resonance with respect to the IP is indeed within 1 eV at the N edge for both theoretical and
Table 4.1: Experimental and theoretical $\Delta_\pi$, $\Delta_\pi$ spread, $\Delta_\sigma$, $\Delta_\sigma$ spread values calculated in this work.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta_\pi(N1s)$</th>
<th>$\Delta_\pi$ spread</th>
<th>$\Delta_\sigma(N1s)$</th>
<th>$\Delta_\sigma$ spread</th>
<th>$\Delta_\sigma(C1s)$</th>
<th>$\Delta_\sigma$ spread</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>-6.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyridazine</td>
<td>-5.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrimidine</td>
<td>-6.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrazine</td>
<td>-6.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-triazine</td>
<td>-6.0</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.</td>
<td>-6.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theo.</td>
<td>-6.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

experimental values. The same is true for the theoretical and experimental values at the C edge for Z=12, C-C, however, it is a little bit over 1 eV for Z=13, C-N, for the both theoretical and experimental $\Delta_\pi$ spread values; (ii) the average $\Delta_\sigma$ at the C 1s edge is 0.9 eV higher than the N 1s edge; (iii) $\Delta_\sigma$ spread decreases as Z increases, contrary to what is seen in the $\Delta_\pi$ spread. This last result was already seen for diatomic and some linear polyatomic molecules [62] and is confirmed here for some heterocyclic molecules.

4.4 Cracking patterns of ring molecules

Figure 4.6 shows the results of applying photoionisation mass spectrometry to the azabenzenes, pyridine, pyridazine, pyrimidine, pyrazine and s-triazine, and the DNA sugar, 2-deoxy-D-ribose (dR).

In common to both sets of molecules we find that (a) bond cleavage is dependent on the photon energy deposited in the molecule; (b) several of the fragmentation products, e.g. $CH_3^+$, $H_3O^+$, $C_2H_4^+$, in dR, and $C_3H_N^+$, $C_2HN^+$ in the azabenzenes involve significant bond rearrangements and nuclear motion during the dissociation time. Of all the processes that can take place when a molecule absorbs a photon (see chapter 2) the types of relaxation processes that are of interest to us are: ionisation to form the parent ion ($M + h\nu \rightarrow M^+ + e^-$ equation 2.1); dissocia-
Figure 4.6: Fragmentation patterns of pyridine, pyridazine, pyrimidine, pyrazine, s-triazine and dR at 540 Å (23.0 eV). $p^+$ stands for the parent cation. Major fragments are labelled for each molecule.
tive ionisation \((M + h\nu \rightarrow (M^+)^* \rightarrow A^+ + e^- + B)\) and autoionisation \((M + h\nu \rightarrow M^* \rightarrow M^+ + e^-)\). The first and third processes will yield the formation of parent cations, and the second process the numerous ionic fragments recorded in Figure 4.6.

**Azabenzenes**

A closer look at the mass spectra of the azabenzenes shows that three main groups of peaks are distinguished.

1. The group of ion fragments at higher masses, \(m/q=78-81\), (see Figure 4.6) is formed by the \(p^+\) and \((p-1)^+\) ion fragments of pyridine, pyridazine, pyrimidine, pyrazine and s-triazine. These fragments are also seen at two different excitation energies, 790 and 900 Å (15.7 and 13.8 eV, respectively) and their relative intensities at these three energies are given in Table 4.2. From the values in Table 4.2 we observe that the relative intensity of the parent ion is higher at lower photon energies for all five molecules. This suggests that the parent molecule is preferably left in a singly ionised state than dissociated at lower photon energies. In the case of dissociation, the production of the \((p-H)^+\) ionic fragment in the three cracking patterns recorded for pyrimidine at different energies, suggests the loss of neutral H atoms upon VUV photon absorption. As explained in chapter 3.1 the detection of neutral species is possible by fluorescence measurements. Therefore, we have gone one step further, and have studied fluorescence from gas phase pyrimidine molecules after VUV photo excitation. In Figure 4.7 we clearly show hydrogen Balmer-\(\alpha\) emission from pyrimidine after absorption of 23 eV photons, confirming the release of a neutral H atom at 23 eV, as observed in the mass spectra.

<table>
<thead>
<tr>
<th>molecule</th>
<th>fragment</th>
<th>23.0 eV</th>
<th>15.7 eV</th>
<th>13.9 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyridine</td>
<td>(p-1^+)</td>
<td>24</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>(p^+)</td>
<td>63</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>pyridazine</td>
<td>(p-1^+)</td>
<td>3</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>(p^+)</td>
<td>15</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>pyrimidine</td>
<td>(p-1^+)</td>
<td>25</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>(p^+)</td>
<td>45</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>pyrazine</td>
<td>(p-1^+)</td>
<td>10</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>(p^+)</td>
<td>12</td>
<td>35</td>
<td>100</td>
</tr>
<tr>
<td>s-triazine</td>
<td>(p-1^+)</td>
<td>15</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>(p^+)</td>
<td>25</td>
<td>70</td>
<td>100</td>
</tr>
</tbody>
</table>
(2) The group of peaks localised around m/q=50 corresponds to $C_2H_2N^+_2 (m/q = 54)$, $C_3H_3N^+ (m/q = 53)$ and $C_4H_4^+ (m/q = 52)$. The presence of these ion fragments in the spectra strongly suggests dissociation pathways via loss of HCN and HCNH molecules from their respective parent ion. As an example we take the s-triazine molecule. The strongest peak in this region for this molecule is m/q=54 and assigned here to $C_2H_2N^+_2$. The loss of an HCN molecule by the parent cation, $C_3H_3N^+_3$, leads to the formation of $C_2H_2N^+_2$. Successive losses of H atoms during the dissociation process lead to the formation of $C_2H_2N^+_2 (m/q = 53)$ and $C_2N^+_2 (m/q = 52)$ also seen in the mass spectra of s-triazine.

(3) The group of peaks around m/q=27 and common to all five molecules is mainly attributed to m/q=26-28. In all five molecules this group of peaks corresponds to $C_2H^+_2$ (assignment in agreement with ref. [63] for pyridine), HCN$^+$ and HCNH$^+$. The presence of HCN$^+$ in the spectra suggests the following dissociation pathway, $p^+ + 2HCN \rightarrow HCN^+ + 2H$; i.e., formation via loss of two HCN molecules by the respective parent cation. For pyrimidine, pyrazine, pyridazine, pyridine and s-triazine this loss of HCN molecules was already seen in refs. [43, 44, 45, 64, 65], respectively. Posterior to these studies HCNH$^+$ formation in pyrimidine is suggested to proceed via concerted H atom addition during the formation of HCN$^+$ since it is well know that H atoms migrate along the molecule [66]. Also in pyrimidine [67], HCN elimination dominates despite the fact that it requires rupture of at least two bonds. One of the reasons is the thermodynamic stability of HCN. In ref. [68] the production of HCN molecules is associated with the formation of $C_3H_4$. After absorption of 193 nm photons, the excited pyridine molecule dissociates into $C_3H_4$ and HCN. This channel competes with the formation of $C_3NH_2 + C_2H_3$. Further absorption of 118 nm photons (lower than the ionisation energy of HCN but higher than the ionisation energy of $C_2H_3$) shows the absence of $C_2H_3$, therefore suggests the formation of HCN.
Figure 4.6 shows the fragmentation pattern of 2-deoxy-D-ribose at 23 eV. Spectra at three other energies, 15.7, 14.6 and 13.8 eV are also recorded and shown in Figure 4 of paper VI. Partial ion yields were recorded in a recent independent experiment [69] and shown in Figure 4.8. From these results we observe:

(1) The fragmentation at all four energies shows a grouping pattern. The observed fragments forming the patterns are, 

- \( \text{CH}_3^+ \), \( \text{OH}^+ \), \( \text{H}_2\text{O}^+ \), \( \text{C}_2\text{H}_3^+ \), \( \text{C}_2\text{H}_4^+ \), \( \text{C}_3\text{H}_4\text{O}^+ \) (x=1,2,3), \( \text{C}_2\text{H}_2\text{O}^+ \) (x=1-5), \( \text{C}_3\text{H}_2\text{O}^+ \) (x=3-5), \( \text{C}_2\text{H}_2\text{O}_2^+ \), \( \text{C}_3\text{H}_2\text{O}_2^+ \) (x=1,2,4-6), \( \text{C}_4\text{H}_2\text{O}_2^+ \), \( \text{C}_4\text{H}_2\text{O}_3^+ \) (x=6,7), \( \text{C}_5\text{H}_2\text{O}_3^+ \), and \( \text{C}_5\text{H}_2\text{O}_3^+ \).

(2) In the study presented in paper VI, the parent cation was below the detection limit for any of the excitation energies chosen. However, in a higher transmission time-of-flight experiment performed recently [69], we detected the parent cation (m/q=134) and we estimated the threshold of formation to be at 9.3±0.1 eV (see Figure 4.8).

(3) The formation of certain fragments implies that during the process of dissociation concerted bond rearrangement and nuclear motion takes place. An interesting example is the formation of \( \text{H}_3\text{O}^+ \). \( \text{H}_3\text{O} \) as a neutral is not stable but the measured proton affinity of water is 7.3 eV [70], therefore, \( \text{H}_3\text{O}^+ \) can, in principle be formed if water and protons are present at the moment of dissociation. The formation of \( \text{H}_3\text{O}^+ \) via the breakage of three bonds, i.e. one C-OH bond and two C-H bonds calls for 20.9 eV. Assuming typical average bond energies of 3.0 eV for the C-OH bond [71], and 4.3 eV for the C-H bond [72], plus the energy necessary to ionise...
the parent molecule, 9.3 eV, we end up with a thermodynamic threshold of 20.9 eV. Instead, if the formation of $H_3O^+$ follows the breakage of one C-OH bond and one C-H bond, plus the transfer of a proton from the ionised parent molecule to the leaving water, then the thermodynamic threshold is 24.2 eV. In this case we have supposed 3.0 eV and 4.3 eV for the C-OH and C-H bonds as before, plus the average value of the proton affinity of aromatic ring molecules, 7.6 eV \cite{73} and the ionisation potential of dR. The threshold of formation measured in paper VI for this ion is $13.5 \pm 0.3$ eV instead of 20.9 or 24.2 eV, which implies that during the process of dissociation concerted bond rearrangement and nuclear motion takes place, and enough energy is regained during the concerted formation of $H_3O^+$ while the dissociation of the parent cation takes place. Then, in the first case where $H_3O^+$ is formed by $OH^+ + H + H$ the thermodynamic threshold is lowered by 10.2 eV (BDE (HO-H) = 5.1 eV, \cite{74}) that subtracted to 20.9 eV results in a thermodynamic threshold of 10.7 eV. In the second case where $H_3O^+$ is formed by $OH + H + H^+$ the thermodynamic threshold is lowered by 12.6 eV (5.1 eV \cite{74} + 7.5 eV; proton affinity of water \cite{70}) which results in a thermodynamic threshold of 11.6 eV. In both cases 10.7 and 11.6 eV are lower than the measured threshold at $13.5 \pm 0.3$ eV.

(4) The most intense ion yield at all photon energies is recorded for m/q=57 and assigned here to $C_3H_5O^+$ (see Figure 4.6 and Figure 4 in paper VI). The spectra recorded at energies lower than 23 eV show a general intensity decrease of all other fragments when compared to the m/q=57 fragment. The loss of one OH and one $C_2H_4O_2$ (m/q = 60) by the parent molecule produces m/q = 57, $C_3H_5O^+$ (see Figure 4.9).

![Figure 4.9: Formation of m/q=57. The breakage of dR along the dashed line produces two fragments, $C_3H_6O_2$ (left) and $C_2H_4O_2$ (right). If the charge localises on the right fragment, $C_2H_4O_2^+$ is formed. However, if during the dissociation time the leaving $C_3H_6O_2^+$ loses an OH group then it leads to the formation of $C_3H_5O^+$.
]
Chapter 5

Conclusions

Below we summarise the conclusions we have reached from our studies of the effects of ionising radiation on gas phase $D_2$, $H_2S$, $NH_3$, $CH_4$, pyridine, pyrimidine, pyridazine, pyrazine, s-triazine and 2-deoxy-D-ribose.

- We have demonstrated that dispersed fluorescence is a suitable technique to probe rotational and vibrational states, as well as to obtain an estimated value for the predissociation phenomena in the $D_2$ molecule.

Visible dispersed fluorescence has also been used to infer dissociation pathways upon core excitation. In all the molecules studied here, neutral hydrogen atoms are found to be the strongest emitters. In $H_2S$, $CH_4$ and $NH_3$ fluorescence from atomic hydrogen is highest at the valence-Rydberg orbitals, however $S^+$ fluorescence in $H_2S$ is highest at the antibonding molecular orbitals.

- We have demonstrated that the previously seen enhancement in various undispersed fluorescence yields ($H$ Balmer $\alpha, -\beta, -\gamma, -\delta$) compared to the ionic yield upon core excitation of water molecules $^{41, 54}$ is also present in $CH_4$, $NH_3$, the water-isoelectronic molecule $H_2S$, and in larger aromatic molecules constituted of low-$Z$ atoms such as pyridine, pyrimidine and s-triazine.

$H_2S/CH_4/NH_3$: On one hand, upon core ionisation of all three molecules, the intensity ratios of the resonances in the Lyman-$\alpha$ yield show small variations from those in the total ion yield. On the other hand, the $H$ Balmer series is more enhanced in the higher core-to-Rydberg excitation region. Balmer-$\gamma$ and -$\delta$ yields were only measured for ammonia, and they show intensity maxima shifted to even higher photon energies, i.e., even closer to the $N 1s$ threshold, when compared to the total ion yield. Based on the fact that Balmer emission has been observed in water $^{41}$, and in hydrogen sulphide, ammonia and methane, we conclude that the techniques of fluorescence measurements allows us to observe the core-to-Rydberg excitations which are unresolved in total ion yield spectra.
CHAPTER 5. CONCLUSIONS

$C_5H_5N/C_4H_4N_2/C_3H_3N_3$: For all molecules the TFY in the visible region is dominated by the fluorescence of $CN(B-X)\Delta v = +1$, $CN(B-X)\Delta v = 0$, $CH(B-X)(1,0)$, $CH(A-X)(0,0)(1,1)$, $CN(A-X)$, and Balmer $\alpha, \beta, \gamma, \delta$. The TFY in the UV region is dominated mainly by the fluorescence from $C^+, N^+$ and to a lesser degree by the fluorescence from $C^{++}, N^{++}$.

The dissociation pathways that lead to excited H atoms is proposed to be the same as seen for water, hydrogen sulphide, methane and ammonia, i.e., the high lying Auger spectator electron is captured by a proton during the dissociation time resulting in excited atomic hydrogen that will emit a photon.

We have also seen that for all the molecules the relative intensity of the resonance in the fluorescence yields obtained after excitation of the C 1s, show small variations from those in the TIY. In contrast, appreciable changes are observed in the fluorescence yields obtained after excitation of the N 1s electrons in the molecules when compared to the TIY. In view of the facts that (i) the Balmer emission has earlier been observed to be enhanced in the core excitations of water, hydrogen sulphide, ammonia and methane, (ii) Balmer emission is the strongest fluorescence in the visible TFY for the aromatic molecules studied here, and (iii) the TFY shows an enhancement in the Rydberg excitations when compared to the TIY, here, we propose that the decay mechanism of these core-to-Rydberg excitations is via spectator Auger decay with formation of an excited H atom that relaxes via fluorescence.

- We have successfully measured the near edge X-ray absorption spectra of five heteroaromatic rings, pyridine, pyridazine, pyrimidine, pyrazine and s-triazine, and have thus probed unoccupied molecular orbitals in these molecules; with the aid of theory we have assigned the main features in the spectra.

- We have recorded the cracking pattern of the DNA sugar, 2-deoxy-D-ribose, pyridine, pyridazine, pyrimidine, pyrazine and s-triazine upon VUV absorption. All six molecules dissociate yielding to numerous fragments forming a characteristic grouping pattern, also the presence of specific fragments in their respective mass spectra suggests concerted bond rearrangement with nuclear motion (atom scrambling) during dissociation.

$C_5H_5N/C_4H_4N_2/C_3H_3N_3$: The presence of $C_5H_3N_2^+$ for s-triazine, $C_5H_4N^+$ for the diazines, and $C_4H^+_3$ for pyridine in the spectra suggests dissociation pathways via losses of $HCN$ molecules. The azabenzenes studied here (six membered rings with N heteroatoms, like DNA bases) are more stable upon soft valence ionisation compared to six membered rings with O heteroatoms, like DNA sugars. Therefore, the behaviour of these planar azabenzenes upon VUV photon excitation is more likely related to the behaviour of the planar pyrimidinic bases of DNA and to other polycyclic hydrocarbons, like benzene, than to the behaviour observed for non planar ring biomolecules like 2-deoxy-D-ribose in the pyranose form when exposed to VUV ionising radiation.
$C_5H_{10}O_4$: The decreased intensity of large fragments ($m/q > 80$) in our mass spectra suggests that upon photon absorption by the DNA sugar, fragmentation clearly dominates over simple ionisation (parent cation formation) unlike the DNA bases [75] and the azabenzences [paper V]. This demonstrates that the DNA sugar is a very fragile moiety, which, after ionisation, will rapidly disintegrate into numerous radical cation and neutral radical fragments. In DNA this would result in at least a single strand break.
Chapter 6

Outlook into the future

Possible applications of the work performed here, as well as completely new experiments, modifications to our set up to improve it, and continuation of recent experiments in the condensed phase, are some of the prospects for the future:

(1) Continue and expand the recently started studies of biomolecules with synchrotron radiation, in the gas phase, in the condensed matter, or in solution, to better reproduce ‘real-life conditions’. Recent experiments we have carried out at the condensed phase beam line (I511) of MAX Lab in Lund, Sweden, offered a first step in this direction \[76\.\] The results of irradiating dry adenine (DNA base), and adenine + water on a Si surface revealed interesting preliminary results. On the one hand, the NEXAFS spectra of dried films of adenine show a dependence on the polarisation vector of the beam. As seen in figure 6.1, the relative intensity between $\pi^*$ and $\sigma^*$ resonances changes dramatically with the orientation of the sample surface relative to the polarisation vector of the beam. This suggests that the films have order with the molecules lying flat.

On the other hand, the results of irradiation of a thin film of adenine monitored with XPS at the C 1s reveal rapid damage to the sample; the shoulder on the high energy side disappears after irradiation during a few seconds. The surface plots in Figure 6.2 show the evolution of the XPS spectra as a function of number of scans. Note that the main peak shifts in energy as a function of time. This suggests efficient damage to the carbon site that contributes to this high energy peak, and means that great care must be taken when recording SR XPS or NEXAFS scans over long periods of time. In order to improve the set up of these condensed phase experiments it would be useful to mount the evaporator on a manipulator with movement in the x, y and z axis. In this manner the evaporation could take place directly on the Si surface mounted on the coolable transfer rod, and a control of the substrate temperature would be more accurately achieved. This would allow the formation of dry films of bases to study how film structures depend on temperature (different cryogenic temperatures), as well as the formation of multiple sandwich layers of base/water/base/water, etc. which would provide a better condition to
CHAPTER 6. OUTLOOK INTO THE FUTURE

study SR induced chemical reactions for instance.

(2) Another challenging direction of research would be to explore the fluorescence of vaporised powder samples of DNA bases, sugars, amino acids and the nucleoside thymidine. As seen in chapter 3 for a more efficient detection of fluorescence, the set up requires the use of optical elements. When dealing with powder samples, an evaporator would bring them to gas phase but this implies that the whole chamber has to be kept at a warmer temperature so the sample does not coat the environment. The coating of the chamber walls can be easily cleaned, but the coating of the optical elements is critical if fluorescence is to be detected. In order to avoid that, the optical elements would require heating via a heated metallic spring all around the element for instance. However this can induce change of the refractive index of a lens or outgasing of the coating on a mirror, both of which would influence the measurements.

(3) The results presented in this work could find application in radiobiology such as radiation therapy of cancer, or radiation poisoning among others. The ultimate goal of radiation therapy is the efficient damaging of the malignant tissue without harming healthy areas. At the atomic and molecular scale, the survival or death of tissue can be understood by looking at the effects of ionising radiation on single molecules. Specifically, when a molecule undergoes a core excitation and several of its electrons are pulled off from inner or outer shells, it will lose its integrity and will fragment. If these molecules are DNA components, Hieda showed that after soft X-ray absorption, such primary effects lead to single- and double-strand breaks (SSB, DSB) in DNA in addition to secondary effects caused by active radicals originating from water radiolysis or ballistic secondary electrons as seen by Boudaïffa et al. The results presented in this thesis on VUV photo ionisation mass spectroscopy of 2-deoxy-D-ribose and pyrimidine [paper VI and V] may explain in part the results found by Hieda who also showed that in photon irradiated plasmid DNA the SSB yield rises from 8 eV up to about 15 eV, after which it remains constant for photon energies up to 2000 eV. If absorption of a 15 eV photon already leads to complete disintegration of the sugar (i.e. a complex SSB) as shown here, increasing the absorbed photon energy will produce no increased damage to the sugar, and thus no increase in SSBs. However, the absorption of 14-23 eV photons in the pyrimidine molecule shows a higher survival of the parent molecule compared to the sugar, supporting the notion that DNA bases are more resistant to fragmentation and higher photon energy is needed to damage them. This could also explain the DSB yield behaviour seen in ref. 77 that rises with increasing photon energy, since it is believed to be mediated largely by base damage in the soft X-ray region. Thus, novel results like those presented here are essential to understand radiation damage at a molecular level.

(4) The effects of ionising radiation in matter are also an issue for understanding the formation of life in space. When looking for life on other planets, we may search for evidences of CO₂, H₂O, NH₃, and H₂S as these elements are constituents of cellular material. The human presence in space is delimited to ca 400000 km (or 30 times the Earth’s diameter), thus no experiments in situ can be done in order to
Figure 6.1: NEXAFS spectra of ca 15 nm thick film of dry adenine at room temperature on a Si substrate, obtained at three different angles between the surface normal and the polarisation vector of the beam.
Figure 6.2: Time evolution of XPS spectra of dry adenine films on a Si substrate at room temperature.
detect the presence of these elements. On the other hand, since so far humans can
not travel such huge distances other techniques have been developed that may allow
us to pursue the finding of evidences of life outside the Earth. In this line, observa-
tional astronomy and its branches- radio, infrared, ultraviolet, X-ray and gamma-
ray astronomy- can trace these molecules by their photon emission. Gamma and
X-rays present in space \[79, 80\] interact with matter, and the outcome of this in-
teraction can be photon emission. One way to simulate this photon emission here
on Earth is accomplished by artificially exciting the molecules with SR with which
we have control over the excitation energy. This is what we have done in papers
II and III where fluorescence of \(H_2S, NH_3\) and \(CH_4\) in the UV, visible and near
infrared is recorded.

(5) Another field of application of the experiments and results obtained here
is the chemistry (gas and condensed phase) that takes place in the interstellar
and circumstellar media. Extraterrestrial N-heterocycles might be shaped when an
\(HCN\) group replaces \(C_2H_2\) during acetylene polymerisation \[81\]. The interaction
of electromagnetic radiation with these heteroaromatic rings might cause their de-
struction; thus, in this work we have shown the survival rate of five N-heterocycles
upon VUV photoabsorption, the fluorescence emission of the same azabenzenes
upon core excitation, as well as given a deeper understanding of the electronic
configuration of the same molecules.
Bibliography


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