Ultraviolet liquid-microjet photoelectron spectroscopy of aqueous solutions

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I, Omri Tau, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
Abstract

Liquid-microjet photoelectron spectroscopy provides a direct way of measuring valence electronic structure; however, its application to solutions had been hampered by a lack of detailed understanding of the experimental parameters and procedures, and the impact of inelastic scattering of low energy electrons. A major part of the work described in this thesis is the development of rigorous experimental procedures to ensure accurate and reproducible UV photoelectron spectra of liquids, described in Chapter 2. These experimental procedures were then applied to record accurate UV photoelectron spectra of liquid water, and aqueous solutions of phenol, a common biological motif, and thymine, a DNA base. These studies aimed to elucidate the electronic structure of the liquid water (Chapter 3), aqueous phenol (Chapter 4) and aqueous thymine (Chapter 5) and how indirect ionisation processes affected their ionisation pathways.
Impact statement

Many biologically-relevant molecules and systems absorb UV light. Some have wide applicability in bioimaging and photovoltaic materials, while others are involved in fundamental biological functions. How these systems respond when interacting with UV light is dictated by intrinsic properties, such as the valence electronic structure and relaxation pathways. Studying these intrinsic properties is therefore crucial in understanding how such properties contribute to photostability and applicability of the system. Since the majority of biological processes occur within solution, an in-depth insight into the interaction between solute and solvent is critical. Liquid-microjet photoelectron spectroscopy is well-placed to study this interaction, as it can directly measure the valence electronic structure of the solute and solvent simultaneously. Much of the previous work investigating the valence electronic structure of molecules in solution has been plagued by experimental difficulties, and experimental spectra impacted by inelastic scattering of electrons. The work in this thesis contributes towards obtaining accurate UV photoelectron spectra in solution. The improvements to both the experimental procedures and the instrument itself are applicable to any liquid-microjet photoelectron spectrometer studying molecules using UV light.

The work described later in the thesis uses the new experimental procedures to investigate the valence electronic structure of liquid water, the most common solvent in biology, and two prominent molecules in biological systems, phenol, and thymine. The ability to accurately study a variety of aqueous solutions using UV light has broad applicability in designing bespoke molecules with desirable intrinsic qualities. It is also of interest to the liquid-microjet community as a whole, since the larger majority of studies focus on using EUV/X-ray light to probe the electronic structure of molecules in solution, due to the hindrances previously associated with
using UV light.
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Chapter 1

Introduction

Photoelectron spectroscopy (PES) is a well-established method to determine the electronic structure of atoms and molecules. It is used extensively to study species in the gas-phase\textsuperscript{1,27–29} and on surfaces,\textsuperscript{30} but the study of liquid species has remained difficult. Though the first major work studying liquid-phase molecules using photoelectron spectroscopy was carried out in the 1970s by Siegbahn and co-workers,\textsuperscript{31} it took roughly 15 years until progress enabled the study of higher vapour pressure liquids and aqueous solutions, with the introduction of liquid-microjets in the late 1980s. Faubel and co-workers first developed the technique, using X-rays with liquid-microjets, to record energy-resolved photoelectron spectra of liquid water and high vapour pressure liquid alcohols, providing the first absolute binding energies of the solvents studied.\textsuperscript{32,33} This was the catalyst to the development of the field of liquid-microjet photoelectron spectroscopy, which has expanded to using laser regimes ranging from visible to X-ray light and been exploited to study a varied mixture of solutions.\textsuperscript{34–36} Even with great strides being made, the field is still evolving and the collection of accurate PES of liquids is still challenging and there are many unknowns within the technique. This chapter will introduce some of the key fundamentals associated with liquid-microjet PES, and highlight some of the challenges that are encountered when undertaking liquid-microjet PES measurements.

1.1 Photoelectron Spectroscopy

Photons, the quanta of light associated with electromagnetic (EM) radiation, have discrete energy, with the amount of energy directly proportional to the EM fre-
frequency, as shown in Equation 1.1;

\[ E = h \nu \]  

(1.1)

where \( E \) is the energy of the photon, \( h \) is Planck's constant and \( \nu \) is the EM frequency of the photon. It is possible to convert the EM frequency to wavelength by using the following relationship:

\[ c = \lambda \nu \]  

(1.2)

where \( c \) is the speed of light and \( \lambda \) is the wavelength. When an atom or molecule interacts with a photon of light, the interaction is resonant if the energy of the photon is the same as the energy difference between two states in the atom or molecule. For a given resonant interaction, it is possible for the interaction to result in the promotion of an electron if the transition probability is non-zero. Spectroscopic selection rules dictate whether the transition is allowed, with optically forbidden transitions having a transition probability of zero, and optically allowed transitions having a non-zero transition probability. Valence electron transitions of neutral molecules can be induced by photons ranging from the ultraviolet (UV) region of the EM spectrum (4 – 7 eV) to the X-ray region of the EM spectrum (>100 eV), while core electron transitions from equivalent molecules are induced using X-ray photons. For gas-phase neutral molecules, ejection of an electron typically requires photon energy \( \geq 10 \) eV, which results in a process known as photoionisation.

Using the independent electron approximation (Koopmans’ theorem), it is assumed that photoionisation of an electron occurs without reorganisation of the other electrons. During photoionisation, the electron is assumed to have the total kinetic energy released during ionisation as the electron is much lighter than the parent atom/molecule. A simple example of this is comparing the relative masses of an electron and a proton, with the electron \( \sim 1/1836 \) the mass of a proton. Measuring the electron kinetic energy (eKE) distribution after photoionisation therefore allows the calculation of the electron binding energy (eBE) of the orbital from which the electron originated, using the following relation; \( eBE = h \nu - eKE \).

It is possible to build up a molecular orbital energy diagram of the occupied electronic orbitals by changing the energy regime of the photon used. In order to
1.1. Photoelectron Spectroscopy

probe the valence electronic structure or track the excited state dynamics of most photoactive molecular systems, multiphoton ionisation (MPI) of the molecule using visible (\(\sim 1.8 - 4\) eV), UV (\(\sim 4 - 7\) eV) or vacuum-UV light (VUV, \(\sim 7 - 10\) eV) is best. This is because the vast majority of excited states within photoactive molecules fall within this energy range, and therefore using specifically tuned wavelengths of light can access these states. To probe the eBEs of valence electrons, UV to X-ray photons can be used, and have been used to extensively study atoms and small molecules.\(^{37-43}\) To investigate core electron BEs, X-ray photons are specifically required.

Studying the excited states of a molecule using UV light can be achieved by tuning the wavelength of the photon to selectively photoexcite an electron to an electronic state of interest, and subsequent photoionisation from that state, in a process known as resonance-enhanced multiphoton ionisation (REMPI). REMPI has been an established technique for decades,\(^{44,45}\) after the advent of the laser allowed multiphoton excitation of atoms or molecules to be accessible due to the high light intensities generated by a laser.\(^{46}\) This has proved especially valuable when trying to access transitions that were traditionally inaccessible from single one-photon absorption processes, for example when probing centrosymmetric molecules such as hydrogen,\(^{47-49}\) oxygen,\(^{50}\) bromine,\(^{51}\) and iodine.\(^{52}\) It is also possible to induce photoionisation following photoexcitation using two photons of different energy. For most photoactive molecules, photoexcitation occurs upon absorption of one or two photons, with subsequent photoionisation requiring a further photon. This is referred to as [1+1’] REMPI for or [2+1’] REMPI, where the first number defines the number of photons required to photoexcite to an electronic excited state, and the second number defines the number of photons required to photoionise, which can have an energy that is the same or different to the excitation photons. This method of REMPI allows the excitation photon energy to be tuned over a range, which can allow information to be derived about the excited state.

REMPI is not the only technique capable of ascertaining details on the electronic structure of molecules. There are numerous techniques available to interrogate the valence electronic structure. UV/Visible transient absorption spectroscopy has been extensively used to study the electronic structure and dynamics of various
systems by measuring photoexcited state absorption energies and lifetimes.\cite{53-59} X-ray absorption spectroscopy, and the complementary technique x-ray emission spectroscopy, can provide a detailed insight into the valence and core electronic structure by measuring photoelectron or light intensity as a function of photon energy.\cite{60-67} As previously mentioned, x-ray photoelectron spectroscopy is also a capable technique for ascertaining the core and valence electronic structure of various molecular systems.\cite{68,69}

When a molecule is photoionised, there is a propensity for any vibrational energy to be conserved during the ionisation process. This is due to the timescale for ionisation being essentially instantaneous compared to the timescale for nuclear rearrangement of the generated radical. This makes it possible to separate the nuclear and electronic wavefunctions, which is the premise of the Born-Oppenheimer approximation. Typically, photoexcitation or photoionisation result in a vibronic transition, which is the simultaneous change in both the vibrational and electronic states. During a vibronic transition, the most likely vibrational state occupied in the new electronic state is determined by the degree of overlap between

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Schematic energy level diagram of a molecule, illustrating the difference in the \(\text{eKE}\) distribution when provided with the same total photon energy depending on the initial state from which photoionisation occurs, due to vibrational energy conservation. Blue: Direct photoionisation from \(S_0\) to the \(D_0\) continuum using one VUV photon to give \(\text{eKE} \approx h\nu_1 - \text{VIE}\). Red: Indirect photoionisation via UV photoexcitation to \(S_1\) with excess vibrational energy \(E_v \approx h\nu_2 - E(S_1)\) gives \(\text{eKE} \approx 2h\nu_2 - [\text{AIE} + E_v]\). Adapted from Fielding and Worth.\cite{1}}
\end{figure}
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the wavefunction of the initial vibrational state and the wavefunction of the final vibrational state. The greater the overlap between the two wavefunctions, the more intense the transition will be. This is known as the Franck-Condon overlap, and is what determines the shape of the photoionisation band generated when ionising an atom or molecule to the associated radical state. Upon photoexcitation, it is likely that the vibrational level initially occupied will be different in the excited electronic state to that in the ground electronic state, prior to any vibrational relaxation. This provides a method of differentiating direct and indirect ionisation processes, since the propensity to conserve vibrational energy is high in a system where there is not a large geometry change during the photoexcitation (or photoionisation) process. The resulting eKE distributions will therefore be different depending on whether the vibronic transitions start from the ground electronic state, or excited electronic state, due to the Franck-Condon overlap. This is shown schematically in Figure 1.1, which shows the difference in eKEs depending on the state from which ionisation occurs.

![Figure 1.2: Schematic diagram of two different ionisation energies. The adiabatic ionisation energy, or AIE, is the ionisation process from the ground vibrational level of the lower electronic state to the ground vibrational level of the upper electronic state. The vertical ionisation energy, or VIE, is the ionisation process from the ground vibrational level of the lower electronic state to a vibrational level of the upper state that has the greatest orbital overlap with the lower state, known as the Franck-Condon overlap.](image-url)
The measured eKE that corresponds to the most intense transition is known as the vertical ionisation energy (VIE), which is typically the peak maximum of an experimental PE spectral profile. Generally, the VIE corresponds to a transition that is higher in energy than the lowest vibronic transition. The eKE associated with the 0 – 0 transition, the transition between the lowest vibrational levels of the two states, is known as the adiabatic ionisation energy (AIE). Both of these transitions are illustrated in Figure 1.2.

Figure 1.3: Jablonski diagram illustrating different possible radiative and nonradiative relaxation pathways that an electron can undertake following absorption of a photon from the ground state, \( S_0 \), to an excited state, \( S_1 \). IVR corresponds to intramolecular vibrational relaxation and is represented by vertical, curly arrows, IC stands for internal conversion and ISC stands for intersystem crossing. The straight, vertical lines represent radiative transitions, and the curly, horizontal arrows represent nonradiative relaxation pathways.

Upon photoexcitation of a molecule, there are a number of relaxation pathways that can occur. Figure 1.3 illustrates some of the possible relaxation mechanisms a molecule can undertake upon photoexcitation. Excess vibrational energy of a molecule can be dissipated nonradiatively via coupling between the vibrational modes of a molecule in a process known as intramolecular vibrational energy redistribution (IVR), and has typical timescales of \( 10^{-12} - 10^{-10} \) s. An electronically excited molecule can nonradiatively decay by relaxing from the excited electronic state to a lower electronic state of the same spin via a process known as internal conversion (IC), which typically occurs on a timescale of \( 10^{-14} - 10^{-11} \) s. Alternatively, it can nonradiatively decay from an excited electronic singlet state to a lower-lying electronic triplet state via intersystem crossing (ISC). This transition is
typically only weakly allowed, since the transition is classically forbidden due to the change in spin state, but possible due to spin-orbit coupling between the states. The timescale for this transition is therefore slower, typically $10^{-10} - 10^{-6}$ s. Competing with the nonradiative decay pathways are different radiative decay pathways, depending on the state the molecule decays from and the final state. Radiative decay from an excited singlet state back to the ground singlet state is known as fluorescence, and typically has a timescale of $10^{-10} - 10^{-7}$ s, while radiative decay from an excited triplet state to the ground singlet state is known as phosphorescence, with a much longer timescale of $10^{-6} - 10^{0}$ s. Fluorescence has a much shorter timescale than phosphorescence due to the spin configuration change required to transition from an excited triplet state to a ground singlet state.

To study the molecular dynamics described above, experimental measurements are required that can measure even the shortest timescales. Femtosecond time-resolved spectroscopy offers many benefits in elucidating fast molecular dynamics, as described below.

### 1.2 Time-Resolved Photoelectron Spectroscopy

The typical vibrational period of a covalent bond within a molecule is tens of femtoseconds, so it is therefore necessary to have methods that probe on this timescale if we wish to observe the bond rearrangements during chemical reactions. The development of femtosecond time-resolved spectroscopy methods was pioneered by Zewail and co-workers in the 1980s and 1990s.\textsuperscript{70–72} Such experiments allowed excited state dynamics to be studied, and his contributions were recognised with a Nobel Prize in Chemistry in 1999.\textsuperscript{73} The aim of the studies was to spectroscopically track bond-breaking and making pathways in photoinduced chemical reactions of molecular systems. Since Zewail’s early work, there are a wide range of methods available in femtosecond time-resolved spectroscopy, such as X-ray diffraction,\textsuperscript{74} which provides structural information on macromolecular systems, and vibrational spectroscopy,\textsuperscript{75,76} which provides a non-invasive method to determining the dynamics of different functional groups. As well as the diversity in methods available, the pulse duration that is possible to generate has been steadily decreasing, with pulse durations $<10$ fs now readily accessible.\textsuperscript{77}

Femtosecond time-resolved spectroscopy employs pump-probe techniques
where a pump pulse laser initiates either a chemical reaction, or creates an excited state within a system of interest, after which a probe pulse is fired at a series of known time intervals after the pump pulse. This probe pulse is typically chosen to provide an observable parameter that provides spectroscopic information on the perturbed system. The specific parameter obtained from the probe pulse depends on the pump-probe method employed. During the past few decades, femtosecond time-resolved photoelectron spectroscopy (TR PES) has proved to be a sensitive technique for monitoring the changes in electronic structure following photoexcitation. This is because TR PES can elucidate evolving electronic structure through direct measurement of eBEs. This is possible because electron ionisation is always an allowed process due to the lack of stringent selection rules for photoionisation. In TR PES, the observable parameter is the kinetic energy of an ejected electron eKE.

![Diagram](Figure 1.4: A TRPES scheme for disentangling electronic and vibrational dynamics in an excited polyatomic molecule exhibiting Koopmans' Type I correlations, e.g. the neutral excited states, \( S_n \) and \( S_{n-m} \) in this example, correlate to different cation electronic states \( D_0 \) and \( D_1 \). Adapted from Fielding and Worth.)

from a photoionised molecule. An example of the electronic pathways within a photoexcited molecule is shown in Figure 1.4.

The choice of wavelengths used for the pump and probe pulses must be selected to probe the process of interest but minimise contributions from unwanted processes. The selected pump pulse wavelength depends on the electronic excited state to be studied, and the probe pulse wavelength is usually chosen to maximise the eKE of the electrons generated by ionising the excited state but minimising competing single or multiphoton absorption from the ground state.

1.3 Photoelectron Spectroscopy of Liquids

1.3.1 Complexity of adding a solvent

The addition of solvent adds more complexity to molecular systems. The use of polar solvents, such as water, can play a role in the stabilisation of charged species, and has an impact on all excited states in a molecular species, both energetically and also along the parts of the potential energy surface away from the Franck-Condon region. Photoionisation of a closed shell, neutral molecule generates a radical cation, and a lowering of the ground state energy of the cation relative to the neutral ground state energy is observed under the influence of a polar solvent when compared to the same process in the gas-phase. Photodetachment of an anion involves a relative lowering of the initial anion ground state rather than the generated neutral radical when compared to the gas-phase, a schematic illustration is shown in Figure 1.5.

Since the early development of liquid-microjet photoelectron spectroscopy (LJ-PES) using X-ray sources, lab-based UV and extreme UV (EUV, 10 – 50 eV) laser sources have been combined to allow a varied laser source regime for probing electronic structure of solutes. A major limitation of EUV/X-ray LJ-PES is the requirement for high solute concentrations (≥0.2 M) to obtain an adequate signal-to-noise ratio compared to the solvent, with water having a typical concentration of ∼56 M. This poses a significant problem in the study of organic molecules, which tend to have low solubilities in aqueous solution, typically on the order of µM to mM. REMPI has an advantage over direct ionisation that the resonant excitation significantly enhances the ionisation signal from the solute compared to the
non-resonant MPI of the solvent. This is because the cross-sections for two-photon ionisation for resonant and non-resonant processes are orders of magnitude different. An example of this is in Xe, where the two-photon ionisation cross-section of Xe when resonant with the 6s level at 146.9 nm was \( \sim 1 \times 10^{-45} \text{ cm}^4 \text{ s} \), whereas the cross-section for non-resonant two-photon ionisation at 150 nm was \( \sim 1 \times 10^{-49} \text{ cm}^4 \text{ s} \). This means the photon energy can be selected to be resonant with an excited state, which allows the laser power to be reduced such that the solute electron kinetic energy signal can be of a similar level, if not more enhanced compared to the solvent signal.

Line broadening can have a substantial effect on experimental spectra. For molecules in the gas-phase, there are three sources of broadening that can be observed: natural, Doppler, and pressure broadening. Natural linewidth broadening occurs because there is an uncertainty in the energy of a state due to the uncertainty in the lifetime of the state. This is derived from the Heisenberg uncertainty principle:

\[
\Delta E \Delta t \gtrsim \frac{\hbar}{2\pi}
\]

where \( \Delta E \) is the uncertainty in the energy, and \( \Delta t \) is the uncertainty in the lifetime. Doppler broadening occurs due to the thermal motion of the absorbing and/or emitting molecules, resulting in a distribution of central frequencies that depends on the

---

**Figure 1.5:** Schematic diagram illustrating the effect a polar solvent has on the relative energies of charged and neutral species during photoionisation/photodetachment in the solvent compared to the gas-phase. For closed shell, neutral molecules, photoionisation generates a radical cation, which has a greater stabilisation effect relative to the neutral molecule when compared to the gas-phase. For an anionic molecule, the ground state of the anion has a greater stabilisation effect relative to the generated neutral radical when compared to the gas-phase. Adapted from Riley 2
molecular trajectory relative to the observer. Pressure broadening occurs due to the interaction between molecular species that results in energy fluctuations.

There are even more significant broadening effects in the liquid-phase. Two of the major broadening effects in solution come from solute/solvent orientation and solute/solvent energy reorganisation. A molecule within a solution can adopt many intermolecular configurations with the solvent, and as such, each orientation can generate a molecule in its own quasi-energy state with micro changes to the energy levels of the molecule. The summation of all of these orientations generates a much broader distribution of energies compared to the gas-phase, and significantly broadens any liquid-phase photoelectron distributions. An illustration of this is shown in Figure 1.6.

Due to the vast quantity of different configurations the solvent molecules can arrange around the solute, the energy levels of the solvent can be thought of as a quasi-continuum of electronic states when compared to the electronic state of the solute. This allows almost continuous energy flow to exist between the solvent and the solute, which can further broaden the spectra since there will be a greater distribution of vibrational states occupied within an electronic energy level at any
given moment compared to if this could not happen. This energy reorganisation also influences solute and solvent relaxation in solution-phase PES. During a recent time-resolved liquid-microjet PES study of indole by Kumar et al.\textsuperscript{80}, it was noted that polar solvent relaxation can play a key role when looking at overall relaxation dynamics, appearing to accelerate pre-existing relaxation pathways.

These effects translate to different types of observed broadening effects depending on the source of the broadening. Broadening effects can be separated into homogeneous and inhomogeneous broadening. Homogeneous broadening processes include the natural linewidth and collisional broadening, and result in a Lorentzian profile. Inhomogeneous broadening typically refers to processes associated with species that are in different local environments. As such, the majority of the broadening effects in solution are a result of inhomogeneous broadening of the photoelectron signal. Inhomogeneous broadening is best modelled by a Gaussian function, \( g(E) \), an example of which is shown by Equation 1.4;

\[
g(E) = \frac{A}{w \sqrt{\pi/2}} e^{-\frac{(E-E_c)^2}{w^2}} \tag{1.4}
\]

where \( A \) is the area under the Gaussian, \( w \) is the width, which is defined as the standard deviation, and \( E_c \) is the center of the Gaussian on the energy \( (E) \) axis.

1.3.2 Considerations for liquids in vacuum

Photoelectron spectroscopy is a powerful technique to ascertain the electron binding energies of atoms and molecules, but there are a number of experimental considerations to address when using liquids in a vacuum.

The study of high vapour pressure liquids in vacuum was plagued with problems before the use of microjets as a liquid source. This was due to the rapid cooling of the liquids by evaporative cooling around the surface, resulting in near-instantaneous freezing of the liquid. The use of small diameter nozzles greatly aided in reducing the surrounding vapour pressure that the liquid sample generated, which helped reduce the cooling effects of the liquid. For liquid water at a temperature just above the freezing point, the molecular mean free path in vapour is \( \approx 10 \mu m \). By using a nozzle that produced a jet stream with a diameter comparable to the molecular mean free path, it is possible to achieve a near collision-free
zone, as defined by the Knudsen conditions. The Knudsen number is a dimensionless unit used in fluid dynamics to determine the type of flow that is occurring, and can be described using Equation 1.5:

\[ Kn = \frac{l}{D} \]  

where \( Kn \) is the Knudsen number, \( l \) is the mean free path and \( D \) is the jet stream diameter. When the Knudsen number is \( \geq 1 \), the flow is described as being in a transition regime towards free molecular flow, where the molecules collide with the walls of the container before colliding with other molecules. This greatly aids in preventing collisions between photoelectrons exiting the surface of the jet and vapour molecules surrounding the jet. The reduced jet stream size also restricts the total liquid surface, which drastically reduces the vapour flux.

The jet stream upon initial ejection using such small nozzle sizes produces a laminar flow, which can be inferred from the Reynolds number. The Reynolds number is a dimensionless quantity that is used to assess the type of flow generated under different experimental conditions and is widely used in fluid dynamics. The Reynolds number can be defined using Equation 1.6;

\[ Re = \frac{\rho \nu d}{\mu} \]  

where \( Re \) is the Reynolds number, \( \rho \) is the density of the fluid, \( \nu \) is the fluid velocity, \( d \) is the internal diameter of the nozzle, and \( \mu \) is the dynamic viscosity of the fluid. The two general types of flows that can be predicted are laminar and turbulent flows. Laminar flow is described as such due to the laminal, or plate-like, arrangement of the liquid along the propagation axis, and tends to flow without lateral mixing between the lamina and flow as if the plates were sliding over one another. The Reynolds number for laminar flow is typically \(<2000\). Turbulent flow is the opposite of this, with chaotic changes in pressures and flow velocities, and is defined by a Reynolds number of \( >4000 \). Between 2000 and 4000 is classed as a transition phase between the two flow regimes. Using a flow rate of 0.7 mL/min and a nozzle diameter of 20 \( \mu \)m, a flow velocity of \( \sim37 \) m s\(^{-1}\) was generated for the jet stream upon exiting the nozzle, which equates to a Reynolds number of \( \sim565 \),
i.e., laminar flow. Achieving such flow regime is crucial to avoid the possibility of developing surface instabilities that could perturb or destroy the quasi-stationary surface needed for reliable measurements, which for the nozzle size and jet velocity previously mentioned would cause spontaneous decay of the laminar flow from \( \sim 4 \text{ mm} \).

Fused-silica nozzles have become commonplace within the liquid-microjet community due to the relative ease of production and overall reliability over long periods of time, as the fused-silica nozzles suffer a lot less from chemical degradation compared to the metallic nozzles used in early liquid-microjet studies.\(^{84}\) However, such nozzles suffer from electrokinetic charging of the jet stream, which creates a streaming potential difference between the jet stream and the electron spectrometer, which can in turn electrostatically accelerate or retard the photoelectrons generated from the jet stream.\(^{85}\) This unwanted charging affects the photoelectron distribution recorded, resulting in an energy shift of the electrons that can skew any conclusions made.

Electrokinetic charging of the nozzle from water occurs by formation of a hydrated silica surface on the inner surface of the nozzle. At \( \text{pH} \geq 7 \), the hydroxyl groups formed on the hydrated surface generate a negative charge.\(^{86}\) This charging of the silica surface causes a diffusely bound double layer, known as a Gouy-
Chapman layer,\(^\text{87}\) which is defined as a rigid layer of ions as an inner layer, with a diffuse cloud of counterions as an outer layer. Within the silica nozzles, due to the parabolic velocity profile generated from laminar flow, part of the diffuse layer will shear from the negative surface charge. This leads to electrokinetic charging from a net separation of the charges at the nozzle surface. A schematic illustration of this is shown in Figure 1.7. To counteract this, specific concentrations of salts are added to provide enough counterions to balance this process and effectively negate the electrokinetic charging. This is discussed in more detail in Section 2.3.

A requirement of photoelectron spectroscopy has been the use of high vacuum to prevent electron-species collisions occurring between the moment of ionisation and detection of photoelectrons that would alter the initial eKEs of the photoionised electrons. Minimising scattering is therefore a key factor to ensure accurate eKE measurements. Gas-phase PES is an established method for measuring accurate eKE distributions because they typically take place at pressures \(<10^{-5}\) mbar and minimal scattering events occur between the ionisation point and detection, since the mean free path (eMFP), the distance over which collisions between the electron and another species occur, ranges from m to km with chamber pressures between \(1 \times 10^{-5} - 1 \times 10^{-8}\) mbar, determined using Equation 1.7.

\[
l = \frac{k_B T}{p \sigma}
\]  

(1.7)

where \(l\) is the mean free path, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, which for the above calculations was 300 K, \(\sigma\) is the collision cross-section of an electron and a water molecule, which for photoelectrons with 1 – 10 eV is \(120 - 21 \times 10^{-20}\) m\(^2\),\(^\text{88}\) and \(p\) is the pressure. The close proximity of molecules in solution drastically changes the mean free path. Solution-phase PES therefore poses a problem. How do we record accurate eKE distributions unperturbed from collisions between the moment of ionisation to detection?

### 1.3.3 Electron scattering

There are two general regions that scattering events that can occur. One is between the jet stream surface and the detector. Close to the surface of a solution, a photoelectron will experience scattering from the vapour around the solution. One
action taken to try to reduce these collisions is to lower the vapour pressure around
the solution in the interaction chamber by reducing the overall chamber pressure.
The reduction in jet stream size also aids in reducing the overall vapour flux at the
liquid/vapour surface.

The other scattering region is from the ionisation point in the jet stream to its
dge. Electrons are prone to inelastic and elastic scattering in the solution itself,
and careful considerations are required if the number of inelastic scattering events
are significant enough to cause eKE shifts that differ from the true initial eKE.

There have been many previous studies into understanding the inelastic mean
free path of different materials, typically as solids or on surfaces. Seah and Dench\textsuperscript{3}
i\vphantom{3}nvestigated many different surface and near-surface solid systems to generate
what has been called the "universal curve", shown in Figure 1.8. This universal
curve describes the inelastic mean free path (IMFP), the average distance between
collisions that result in a change in energy, in nanometers as a function of energy

\textbf{Figure 1.8:} Taken from Seah and Dench\textsuperscript{3}. Compilation for elements of IMFP measure-
ments in nanometers as a function of energy above the Fermi level. The full
curve is an empirical least squares fit over the complete energy range. The
dotted curves are for Penn's relation\textsuperscript{4} with (i) his mean values for \(a\) and \(b\), (ii)
values of \(a\) and \(b\) to give the least squares fit to the data above 150 eV.
above the Fermi level, which is the work required to add one electron to the system.

While this has been shown to be an accurate representation of IMFPs of electrons generated from solids, further studies have tried to quantify the IMFPs of electrons generated in liquids. Michaud et al.\textsuperscript{5} sought to aid in quantifying the IMFPs of liquid water by recording the IMFPs of amorphous ice. The inelastic-scattering cross-sections measured by Michaud et al.\textsuperscript{5} are shown in Figure 1.9. More recent studies have tried to quantify the IMFP of an electron with low eKEs in aqueous solution, assessing the significance of inelastic electron scattering in solution by measuring the PES of solvated electrons at a range of wavelengths.

Signorell and co-workers\textsuperscript{89} have used the IMFPs of amorphous ice to calculate the IMFP from monitoring electrons ejected from liquid water aerosol droplets, measuring IMFPs of 2.9 – 5.1 nm for eKEs of 1.0 – 3.0 eV respectively. These
Figure 1.10: Taken from Luckhaus et al.\textsuperscript{11} Integral scattering cross-sections for electrons in water as a function of the eKE. Shown are the total cross-section (full black line) together with their elastic (dashed black line) and total inelastic (dash-dotted black line) contributions. The individual inelastic contributions are represented colour-coded and fall into three groups: Intermolecular vibrational (L = librational, T = translational) with energy loss per collision between 0.04 and 0.1 eV, intramolecular vibrational (1,3 = stretch, 2 = bend) with energy losses per collision between 0.2 and 0.9 eV, and electronic scattering (dissociative electron detachment, electronic excitation, impact ionization) with energy losses per collision above 5 eV.

eKE ranges are of particular interest in UV LJ-PES experiments, as typical eKEs generated are between 0 – 5 eV. Suzuki and co-workers\textsuperscript{90} used UV LJ-PES to measure the eKEs of solvated electrons in water with photon energies in the range of 3.6 – 5.8 eV. They identified a profound effect on the measured eKE distributions as a function of photon energies, with significant broadening of the eKE distribution with increasing photon energy. This was attributed to a strong influence from electron-solvent inelastic scattering before emission from the solution.

These two research groups then modelled the experimental data obtained by Suzuki and co-workers.\textsuperscript{90} Signorell and co-workers performed Monte Carlo simulations of electron scattering in liquid water that took into account the energy-dependent, differential cross-sections of elastic and inelastic scattering of an electron in liquid water obtained from measurement aerosol water droplets.\textsuperscript{11,89} The
scattering cross-sections derived in Luckhaus et al.\textsuperscript{11} are shown in Figure 1.10. From this, they were able to retrieve the "true" PE spectrum of the solvated electron, with which they determined a genuine eBE for the solvated electron of 3.7 ± 0.1 eV. The spectrum itself was noted to have a double peak structure, which has since been subject to much debate, with the exact value of the escape barrier from the conduction band still inconclusive.\textsuperscript{91,92}

Following from this work, Suzuki and co-workers developed an empirical method to correct for inelastic scattering by using a UV pump laser pulse along with an EUV probe laser pulse to photoionise the solvated electron generated from aqueous NaI.\textsuperscript{93} Their use of EUV pulses was because elastic and electron-vibron inelastic scattering cross-sections in the EUV/soft X-ray region decrease, and the electron-electron inelastic scattering cross-sections increase.\textsuperscript{5} This resulted in a separation between the unscattered and scattered photoelectron distributions, allowing Nishitani et al.\textsuperscript{93} to obtain an eBE distribution from an EUV probe that was unperturbed from inelastic scattering. Using the newly measured eBE distribution, they then apply a transformation between what they call the "true" solvated electron distribution, i.e. the unperturbed EUV distribution, and the previously measured UV PE spectra of the solvated electron. This generated a set of basis functions for a single Gaussian function that had been distorted from inelastic scattering at a series of eKEs. They then applied the basis functions to a set of UV time-resolved PE spectra of NaI in water, methanol, and ethanol to attempt to retrieve a set of time-resolved spectra unperturbed by inelastic scattering.

Our group has combined these two approaches by using Monte Carlo simulations of electron scattering in water to generate linear transformations together with molecular dynamics simulations of depth profiles of different solutes in aqueous solution.\textsuperscript{12} This was done by first assuming the unscattered eKE distributions could be represented by a weighted sum of Gaussian functions, \( I_{\text{true}}(E) = \sum c_i G_i(E) \), with each Gaussian, \( G_i(E) \) having its own central eKE and full-width-half-maximum, weighted by a scaling factor, \( c_i \). The measured, scattered eKE distributions can also be represented by a linear combination of functions, \( I_{\text{meas}}(E) = \sum c_i g_i(E) \), where \( g_i(E) \) are the measured eKE distributions weighted by the same scaling factor \( c_i \). Contrary to the method used by Suzuki and co-workers, the \( G_i(E) \to g_i(E) \) trans-
The PE spectra can be fit using any number of Gaussian functions, with two different concentration depth profiles. The distribution of the $E_z$ were weighted such that there is a distance-dependency on the contribution of the $E_z \rightarrow S_z(E)$ transformation as the electron was initialised further away from the water-vacuum interface. For all the organic molecules studied in later chapters, any feature associated with the organic molecule was fit using exponential concentration depth profiles with a mean of 0.5 nm from the water-vacuum interface. For any solvent features studied in later chapters, a constant concentration depth profile was used, to represent the equal probability of forming photoelectrons as a function of laser probing depth. The choices of profiles were based on the results of molecular dynamics simulations performed by a post-doctoral research associate within the Fielding group of dilute solution-vacuum interfaces, with either no organic molecules present, a single phenolate, or single phenol molecule per unit cell. The results of these molecular dynamics simulations corroborated with previous surface tension and molecular dynamics simulations of aromatic molecules. These studies found that there was a strong surface tendency for neutral aromatic molecules, or anionic molecules with...
aromatic groups in the molecule, particularly for phenol/phenolate.

The initialised electrons underwent random walks, with step lengths determined by randomly-selected inelastic or elastic scattering channels shown in Figure 1.10, which were weighted by their relative cross-section at the current eKE. If said electron leaves the liquid with positive eKE, the final eKE value is stored and the trajectory for that electron ceased. If not, then the electron underwent another step with less energy if the previous step resulted in an inelastic collision, or was discarded if the resulting drop in energy reduced the eKE to zero.

Each Gaussian function was given initial parameters for the eKE peak center, width, and area, and the fitting of the measured PE spectrum was performed using a Levenberg-Marquardt least-squares algorithm. The output parameters were the eKE peak centers, width, and areas of the Gaussian functions used to generate the retrieved PE spectrum, which is a superposition of said Gaussian functions that represent the distribution of photoelectrons prior to inelastic scattering. This was shown to successfully transform a variety of UV eKE distributions of liquid water, aqueous phenol, and aqueous phenolate from being perturbed by inelastic scattering to being corrected for inelastic scattering as a function of the concentration profiles. The experimental data associated with this study is partly discussed in Chapters 3 and 4.
Chapter 2

Methods

This chapter describes the procedures employed to collect photoelectron spectra of organic molecules in solution using the UCL liquid-microjet photoelectron spectrometer. Section 2.1 describes the liquid-microjet and photoelectron spectrometer, detailing the components that make up various aspects of the instrument and the functional uses behind these components. Section 2.2 describes the laser systems used to collect the spectra in later chapters. This includes two different femtosecond laser systems, one used before a large-scale equipment upgrade and lab move, and one after. It also briefly details the light generation methods used to obtain the required wavelengths for the desired experiments. Section 2.3 details the changes made to the instrument in an effort to improve its performance. Section 2.4 details the procedures used to collect photoelectron spectra. This includes energy calibration of the spectrometer, solution preparations, and operation of the instrument from the beginning to the end of a collection process. Section 2.5 details the post collection procedures applied to the photoelectron spectra beyond energy calibration to ensure as accurate a conclusion can be drawn from the spectra as possible.
2.1 Liquid-microjet photoelectron spectrometer

2.1.1 The liquid-microjet

Figure 2.1: Top: Schematic diagram of the UCL liquid-microjet photoelectron spectrometer, with an inset highlighting the interaction region and the distances of different components from the ionisation point (IP).\textsuperscript{13} (1) Magnet, (2) microjet assembly, (3) skimmer, (4) recirculating catcher with CuBe tip, (5) resistive heater, (6) inner PTFE sleeve with a groove for solenoid, (7) solenoid, (8) outer PTFE tube, (9) double $\mu$-metal tube, (10) cold trap, (11) flight tube, (12) drift tube, (13) double-stack microchannel plate detector, (C1-2) CMOS cameras, (M1-3) xyz-manipulators, (T1-4) turbomolecular pumps. Bottom: Photograph of the UCL liquid-microjet photoelectron spectrometer.
Figure 2.1 shows the UCL liquid-microjet photoelectron spectrometer. The liquid-microjet assembly and interaction chamber were built by Microliquids GmbH, now Advanced Microfluidic Systems GmbH (AdMiSys), and the time-of-flight and detection chambers designed by a former postdoc and built by Scanwel. Solutions were prepared in sample holders (see Figure 2.2a) and solutions were drawn out using a polytetrafluoroethylene (PTFE) suction filter of 10 μm pore size into 1/8" PTFE tubing and into an isocratic high performance liquid chromatography (HPLC) pump (Microliquids 02, see Figure 2.2), which uses the same mobile phase under con-

Figure 2.2: Photograph of the high performance liquid chromatography (HPLC) pump. a) A schott bottle used as the sample holder with the suction filter. b) Syringe and twist connection used to remove bubbles from the pump line.
Figure 2.3: Photograph of the liquid-microjet assembly. a) The liquid-microjet assembly. b) The in-line filter with 2 \( \mu \)m frit filter inside. c) The stainless steel HPLC feedthrough.

Conventional HPLC use, by a double diaphragm pump system. From the HPLC pump, the solution was fed into 1/16 " polyetheretherketone (PEEK) tubing before passing through a stainless steel HPLC feedthrough, used to act as a contact point to apply a voltage bias to the solution if needed, and a 2 \( \mu \)m pore size in-line filter before entering the liquid-microjet assembly (see Figure 2.3). The HPLC pump had a built-in pulsation damper to reduce bubble formation in the tubing, which worked most effectively at \( \geq \)70 bar backing pressure. In some cases bubbles did form, which could typically be observed either visibly as bubbles in the clear, PTFE tubing entering the HPLC pump, or as a drop in pump backing pressure that was typically accompanied by a slight reduction in pumping stability. This was resolved using a twist connection with a syringe attached that could be used to manually draw both solution and bubbles out of the pump tubing line when the pump was not running (see Figure 2.2b). Care was needed when drawing out bubbles from the tubing, as pulling the syringe with too much force caused more bubbles to be drawn into the tubing through the suction filter.

The liquid-microjet assembly consisted of a stainless steel holder with PEEK tubing inside, feeding to a 25 mm long fused silica nozzle with an internal diameter between 20 - 50 \( \mu \)m (see Figure 2.3). The silica nozzle had a copper grounding wire coiled around the nozzle which connected to the assembly \( \sim \)15 cm away from the nozzle, which was then wrapped in copper tape with a graphite adhesive. The copper tape, grounding wire, and all stainless steel components of the
For all experiments described in this thesis, a 20 µm silica nozzle was used, and a flow rate of 0.7 mL min⁻¹ was set on the HPLC pump. This generated pump backing pressures between 70 - 90 bar, depending on the viscosity of the solution,
and the length of PEEK tubing used from the exit port of the HPLC pump to the microjet assembly.

The liquid-microjet assembly was mounted onto a motor-controlled xyz-manipulator connected to the source chamber, as shown in Figure 2.1d, for precise alignment of the microjet assembly within the chamber. The silica nozzle tip was positioned ∼2 mm above the ionisation point, as shown in Figure 2.4. The jet stream produced flowed into a recirculating catcher positioned ∼1 mm below the ionisation point, as shown in Figure 2.4. The recirculating catcher consisted of a copper beryllium (CuBe) tip with a 500 µm entrance hole. The outer casing near the CuBe tip had been graphite coated to increase its electrical conductivity and to match the work function of the other components in the interaction region. The interrogated solution was then pulled through the catcher into 1/8 " Tygon E-3603 soft tubing using a peristaltic pump (Microliquids Pump Type 1, see Figure 2.5) and then back into the sample holder. Due to charging problems from insulating components inside the recirculating catcher, the inner tubing of the catcher was replaced by AdMiSys with a titanium tube, to allow for electrical conductivity while remaining biocompatible. For efficient pumping of the catcher, it was found that the flexible tubing fed into the peristaltic pump should be positioned vertically down from the exit of the catcher to the entrance of the pump, ideally with minimal slack in the tubing. Vacuum grease also helped to ensure smooth and continuous revolutions of the pump rollers, which greatly aided in ensuring constant pumping was applied to the tubing.
2.1.2 Magnetic-bottle time-of-flight spectrometer

Once photoelectrons were generated, they were guided towards a magnetic-bottle, time-of-flight (MB ToF) photoelectron (PE) spectrometer. MB ToF PE spectrometers are advantageous compared to conventional ToF spectrometers as the addition of the magnetic-bottle greatly increases the collection efficiency, from

![Figure 2.6: Close-up photograph (top) and schematic diagram (bottom) of the magnetic-bottle time-of-flight spectrometer. All the values are given in mm.](image)
A magnet made of two cylindrical \( \text{Sm}_2\text{Co}_{17} \) pieces produced a 1 T inhomogeneous magnetic field and a soft iron cone focused the magnetic field towards the interaction region. The magnet was on a vacuum-compatible, motor-controlled, xyz-manipulator which helped align the magnet tip to be parallel with the skimmer entrance hole. The skimmer orifice allowed the ToF chamber to be differentially pumped with respect to the source chamber, and also aided in aligning the movable components such that when photoelectrons were generated, the photoelectrons would travel directly towards the detector. The skimmer was made from gold-plated copper with an entrance hole diameter of 300 \( \mu \text{m} \), and was further coated in graphite to minimise work function differences between the components around the interaction region. Photoelectrons were then directed into a differentially-pumped drift tube inside the magnetic-bottle time-of-flight spectrometer, which can be seen in Figure 2.6.

A solenoid of length 0.666 m formed of a copper wire wrapped \( \sim 393 \) turns m\(^{-1}\) with 4.00 A applied from a power supply (Aim-TTi EX355R) generated a weak, 2 mT homogeneous magnetic field. This aided in guiding the photoelectrons through the drift tube by collimating the magnetic field after the ionisation point. Electrons travelling along the magnetic field precess in a helical motion towards a double-stack microchannel plate (MCP) detector, as shown in Figure 2.7. MCP detectors act as a parallel series of electron multiplier channels arranged as a plate that emit secondary electrons from a single electron collision. The double-stack MCP detector used here had two plates arranged such that the overall shape of the stacked plates appeared as a ‘V’, to direct the electrons back to their original position upon entering the detector. An example of this is shown in Figure 2.8. The front plate had no voltage applied to it and the back plate was biased at 1800-1900 V. The cascade of electrons, or electron event, generated in the detector struck a phosphor screen, which had an applied voltage of 2000-2200 V during collection. The phosphor screen could also have 3600 V applied to it, which generated an observable flash that could be detected by a CMOS (complementary metal oxide semiconductor) camera (iDS Imaging Development Systems GmbH, UI-3250LE-M-GL). The electron event colliding with the phosphor screen generated a current signal spike...
that was then decoupled using a capacitor. The decoupled signal was amplified by a fast pre-amplifier (Ortec 9326) and the arrival time, or time-of-flight (ToF), of the electron event relative to a trigger pulse from the laser system was collected by a digitiser card. A ToF photoelectron spectrum was then collected over time from the acquisition of these electron events using a custom-built LabView software program that recorded photoelectron events as a series of 0.5 ns bins.

2.2 Femtosecond laser systems

The femtosecond laser pulses used to collect the multiphoton detachment spectra of aqueous $p$-HBDI$^-$ discussed in this chapter were generated using the older femtosecond laser system. A femtosecond oscillator (Coherent Micra-5), pumped by the second harmonic of a diode-pumped, solid state, continuous wave (CW) pump
laser (Coherent Verdi-5), generated 800 nm pulses at a 76 MHz repetition rate. A titanium:sapphire (Ti:Sapph) crystal was pumped by the 532 nm pump laser, which generated a narrow bandwidth CW laser at ∼800 nm, which was then amplified via soft aperture, Kerr-lens modelocking. Modelocking is a method used to generate ultrashort laser pulses by the constructive interference of many longitudinal modes, held in phase in a laser resonator. This can then be used to generate ultrashort pulses due to the Kerr effect, which is a nonlinear effect that causes a change in the refractive index of a material by an applied magnetic field, which has a more profound effect on the highest intensity portions. This causes an action similar to a lens, distorting the wavefronts of the pulse, and is known as Kerr-lensing. This allows the higher intensity portions of the pulse to overlap better with the pump pulse compared to the lower intensity wings, resulting in the higher intensity portion of the pulse to be more efficiently amplified. This amplified pulse left the cavity via an optocoupler. Due to the short time domain of these pulses, the bandwidth of the pulse broadened to ∼80 nm such that the time-bandwidth product for a Gaussian pulse, $\Delta\nu \Delta t \gtrsim 0.441$, was maintained.

The train of pulses from the oscillator then seeded an amplifier (Coherent Legend). The seed pulses were stretched in time to reduce the peak power of the pulses, and then amplified in a Ti:Sapph cavity by a 1 kHz pulsed pump laser (Coherent Evolution). The amplification cavity was upgraded in 2019 from a double-sided pumped cavity to a single-sided pumped cavity, similar to a newer amplifier cavity design (Coherent Legend Elite). The Nd:YLF pump laser sent high power CW light at 527 nm into the cavity, which saturated the gain medium to amplify the incoming seed pulse. The pulses were propagated a number of times to allow the greatest gain build up of the pulses without suffering losses, typically 5 – 6 times. The amplified pulse was then ejected from the cavity using a Pockels cell to change the polarisation of the pulse and a polarizer to reflect the desired pulse out of the cavity. The pulse duration was then compressed back to its original duration upon entering the amplification stage. This process is known as chirped-pulse amplification, and is shown schematically in Figure 2.10. The output of this produced 3.8 W laser pulses centred at 800 nm with 40 fs pulse duration.

A new femtosecond laser system was installed in 2020, and was used to collect
2.2. Femtosecond laser systems

Figure 2.9: Schematic diagram of the two laser systems used to collect liquid-microjet photoelectron spectra in the new UCL Ultrafast Laser Facility.

the spectra shown in chapters 3, 4 and 5. An integrated kHz femtosecond amplifier system (Coherent, Astrella) was used to produce 35 fs, 800 nm pulses. Briefly, a low power, femtosecond oscillator (Coherent, Vitara) generated a seed pulse using a Ti:Sapph cavity pumped by a high performance pump laser (Coherent, Verdi G-series) centred at 532 nm. The train of seed pulses propagated to a regenerative amplifier, which was a Ti:Sapph cavity pumped by a diode-pumped, Q-switched Nd:YLF laser with second harmonic generator (Coherent, Revolution) to generate pulses of 527 nm. An output of 9 W was generated from this system, which allowed this laser system to seed a number of different experiments. At the time of writing, the Astrella pumped three separate optical parametric amplifiers (OPAs, two Coherent, OPerA solos, and one Coherent, TOPAS-PRIME), an extreme-ultraviolet (EUV) high harmonic generation source (KMLabs, XUUS), a series of harmonic
generators (Coherent, Harmonic Generator System) to generate second, third, and fourth harmonics of the pump laser, and a commercial transient absorption spectrometer (Ultrafast Systems, Helios Fire). At the time of writing, the liquid-microjet instrument had access to one of the Coherent OPerA solos, the Light Conversion TOPAS-PRIME and output from the harmonic generators.

To generate tunable wavelengths from the ultraviolet (UV) to visible range, an OPA was used. A portion of the amplified 800 nm pulse (~1 W) was guided into the OPA, which is reflected into a beamsplitter. This splits off the amplified pulse, which will be designated the pump pulse, with between 80 - 95% being reflected to be used in the power amplification stage later, and the rest of the pulse transmitted to be used as a seed pulse. A second beamsplitter separated the low power seed pulse into two further pulses, the pre-amplifier seed pulse, which was ~80% of the incoming pulse, and the rest transmitted towards a sapphire plate which generated a white light continuum (WLC). Both the pre-amplifier seed pulse and WLC pulse were then overlapped temporally and spatially in a non-linear crystal (β-barium borate). The overlap of the seed pulse and the WLC pulse generated signal and idler pulses, whose energies sum to that of the seed pulse. The crystal angle orientation was varied depending on the desired wavelength generation, such that the phase of the pump pulse matched well with a small wavelength range of the WLC due to differing refractive index of the constituent wavelengths within the WLC through the non-linear crystal. The signal and idler pulses propagated to another non-linear crystal, where they were overlapped with the originally split pump pulse. This acted as the amplification stage with either the signal or idler pulses amplified, depending on the required wavelengths, which propagated towards mixing crystal stages. Depending on the wavelengths required, a combination of either the signal or idler
pulses, both of which have a wavelength range in the infrared region of the electromagnetic (EM) spectrum, and previously split portion of the pump pulse at 800 nm were used to generate wavelengths in the visible region of the EM spectrum. To generate UV laser light, a second mixing crystal stage was added with dichroic mirrors to separate out the required visible pulses from the pump and signal/idler pulses, and the visible pulses underwent a doubling process to generate the required UV wavelength. The use of this OPA allowed the generation of femtosecond pulses ranging from 235 nm to 2.7 \( \mu \)m. A schematic diagram showing the different non-linear processes used to generate the wavelengths of laser light in the OPA is shown in Figure 2.11.

For the work in this thesis, a total wavelength range of 235 – 305 nm was used. The laser pulse duration was measured by recording the cross-correlation between the UV laser pulse from the OPA and a second UV laser pulse from a set of two mixing boxes. The laser pulse duration for the OPA was found to be \( \sim \)200 fs. The focussed spot size was measured using a knife edge and was found to be \( \sim \)60 \( \mu \)m.

For the work in this thesis, the laser pulse energy used was 40 – 200 nJ. Using these values, the maximum focal intensity can be calculated, which for a pulse energy of 200 nJ equates to \( \sim \)20 GW cm\(^{-2}\).
2.3 Changes and improvements made to the liquid-microjet photoelectron spectrometer

2.3.1 Absolute energy collection improvements

Achieving accurate binding energies has been a major goal in the liquid-microjet community; however, only recently have there been significant strides towards reli-
2.3. Changes and improvements made to the liquid-microjet photoelectron spectrometer

ably recording absolute binding energies. Earlier work from Olivieri et al. highlighted the importance of ensuring the work function of the components around the ionisation point is the same, otherwise any photoelectrons generated experience a potential shift towards or away from the analyser, distorting the initial photoelectron kinetic energies. Nishitani et al. further highlighted the importance of ensuring the work function of different components are the same by investigating how individual components affected the photoelectron kinetic energies as a function of distance from the ionisation point. Once the work functions of all the components are the same, it is then necessary to correct for the inherent charge within the solution, known as the streaming potential, to ensure this does not alter the photoelectron kinetic energy distribution.

Olivieri et al. and Perry et al. attempted to correct for this by applying a potential bias to the solution to suppress the potential associated with the solution. Further studies by Nishitani et al. and Thürmer et al. highlighted that while it is possible to apply a potential bias to the solution to reduce the streaming potential, it is necessary to accurately recalibrate the spectrometer afterwards. Nishitani et al. used reference gases to account for the difference in the potentials after bias application, while Thürmer et al. used the low-energy photoelectron signal cutoff, which upon application of a potential bias reveals the entire low KE tail that terminates at 0 eV rather than a distribution affected by instrument cutoff (see section 2.5.1 for further discussion on the instrument cutoffs). Prior to potential bias application, streaming potential suppression was achieved by addition of electrolyte to the solution. More recently, it has been shown that fine-tuning of this electrolyte concentration can achieve similar results as potential bias application. Both methods have been used, and there is ongoing discussion within the liquid-microjet community about which method is preferential.

For all experiments detailed in later chapters, Xe was used as a reference gas to account for any differences in potentials upon addition of the solution of interest to the interaction region.

To ensure the work functions of the components around the ionisation point were equal, the skimmer, magnet tip, gas nozzle, catcher assembly, heating element rod, liquid-microjet assembly and silica nozzle were all coated with graphite.
using colloidal graphite (Aquadag). To bring the vacuum energy of the solution to the same level as graphite, a specific concentration of electrolyte was used. Figure 2.12 illustrates the effect the ionisation position has on the eBE of a reference gas when the vacuum energy level of the solution is either equal or not equal to the graphite vacuum energy level. Figure 2.13 shows the effect graphite-coating had...
on the time-of-flight of photoelectrons generated from Xe. Both sets of spectra were recorded in the magnet far position, which generated a split Xe peak; see section 2.4.1 for further clarification on why this occurs and what the magnet far position is. Crucially, upon application of the graphite-coating, the ToF of the photoelectrons are unperturbed by moving components away from the optimal position.

2.3.2 Experimental procedures changes and improvements

Previous attempts to use a recirculating catcher within the research group were plagued with problems achieving high vacuum and with ice formation at lower pressures. To achieve efficient roughing and to limit problems from the solution spilling out of the catcher, the catcher tip was heated using a 290 Ω resistor and a DC power supply (Tenma 72.2685) that allowed user control of the catcher tip temperature, as opposed to previous designs that had one fixed temperature. The current applied to the resistive heater for all measurements collected in later chapters was \( \sim 0.08 \) A. The temperature of the catcher tip at this setting under atmospheric pressure and without the jet stream was \( \sim 47 \) °C, and was found to be sufficient to enable efficient pumping down and greatly aided in preventing ice formation around the catcher tip.

2.4 Liquid-microjet procedures

2.4.1 ToF to eKE calibration

As described in section 2.1.2, the ToFs of the photoelectrons, and the time taken to travel from the ionisation point to the detector relative to a laser trigger, were recorded using custom LabView software. It was necessary to calibrate the photoelectron spectra from ToF to electron kinetic energy (eKE). This was carried out by employing multiphoton ionisation (MPI) of nitric oxide (NO) using a range of photon energies (235 - 270 nm) and Xe, such that a calibration curve could be obtained, as shown in Figure 2.14. Vibronic transitions from \( \text{NO}(X^2\Pi_{1/2}, \nu'' = 0) \rightarrow \text{NO}^+(X^1\Sigma^+, \nu^+ = 0 - 3) \) following photoionisation were recorded with the liquid-microjet assembly present but no liquid jet stream running and the eKEs corresponding to the vibronic transitions were determined using known ionisation potentials.\textsuperscript{108} Wavelengths from 235 to 250 nm were employed to collect two-photon ionisation spectra that generate photoelectrons from 0.0 to 1.3 eV, and wavelengths typically between 265 and 267 nm were used to collect three-photon ionisation
An example spectrum of a calibration curve and data obtained using the method described in section 2.4.1. Black, open circles represent MPI of NO via two-photon ionisation to the cation, the red, open triangles represent REMPI of Xe to Xe$^+$($^2P_{3/2}$) and Xe$^+$($^2P_{1/2}$) via the 5p($^2P_{3/2}$)6p[1/2]$_0$ state, the blue, open squares represent MPI of NO via three-photon ionisation to the cation, and the blue, dashed line represents the non-linear fit applied to the data points using equation 2.1. The values of the fit were $t_0 = 60.73 \pm 3.14$ ns, $s = 0.627 \pm 0.005$ m and $E_0 = 0.74 \pm 0.01$ eV.

spectra that generated photoelectrons ranging from 3.0 to 4.8 eV. Resonance-enhanced MPI (REMPI) of gaseous Xe from Xe($^1S_0$) to Xe$^+$(2$^3P_{3/2}$) and Xe$^+$(2$^3P_{1/2}$) via the 5p($^2P_{3/2}$)6p[1/2]$_0$ state was recorded using 249.7 nm to collect photoelectrons between 1.4 and 3.0 eV, as well as provide a direct reference of the time-of-flight of Xe for streaming potential collections.

To fit the calibration curve, we used the equation;

$$eKE = \frac{m_e}{2e} \left(\frac{s}{t - t_0}\right)^2 - E_0 \tag{2.1}$$

where $eKE$ is the electron kinetic energy associated with each observed vibronic transition, $t$ is the ToF of the vibronic transition, $m_e$ is the mass of an electron, $e$ is the electron charge, $s$ is the distance from the ionisation point to the detector, $t_0$ is the temporal offset that accounts for the time delay between the laser trigger and the digitiser, and $E_0$ is an energy offset that accounts for any stray electric fields in the ToF. The calibration constants $s$, $t_0$ and $E_0$ were then extracted from the calibration curve fit. These calibration constants could then be substituted back into the equation to convert any photoelectron spectra collected from ToF to eKE.
2.4. Liquid-microjet procedures

Figure 2.15: Example spectra of MPI of NO recorded at 246 nm with the magnet in the close position (top) and the far position (bottom, refer to end of section for more context). Black lines represent the first three vibronic transitions, and the red, dashed lines represent Gaussian fits to each peak. Top left: Gaussian functions are fit to the entirety of each feature. Bottom left: Gaussian functions are fit to the low ToF edge of each vibronic feature. Spectra on the right are the same spectra on the left, converted from time-of-flight to electron kinetic energy using the calibration curve shown in Figure 2.14.

When converting the photoelectron spectra from ToF to eKE, the band shape of the spectrum was distorted due to the non-linear relationship between time to energy, as shown in equation 2.1. To retain the same total integrated area during the conversion, a Jacobian factor was applied to the photoelectron counts, as shown in equation 2.2;

$$
\text{Counts}_{\text{eKE}} = \text{Counts}_{\text{ToF}} \left( \frac{\text{ToF} - t_0}{\sqrt{m_e/s^2}} \right)^3
$$

(2.2)

where \(\text{Counts}_{\text{eKE}}\) is the photoelectron counts as a function of eKE, \(\text{Counts}_{\text{ToF}}\) is the photoelectron counts as a function of ToF, ToF is the time-of-flight, and the other parameters are the same as in equation 2.1.

Calibrations were collected with the microjet assembly, without any solution present, and recirculating catcher at the positions used to collect PE spectra, which was 2 mm above the ionisation point for the microjet assembly and 1 mm below
the ionisation point for the catcher. This allowed for a reliable means of obtaining accurate energies, as the calibration accounted for not only the presence of the microjet assembly, but also accounted for any changes that occurred to the microjet assembly over time if a calibration was recorded close to the collection of a data set. Two calibration curves were generated for each data set, one in the magnet in the optimised position during normal collection, called magnet close, and the other with the magnet translated 3 mm away from the optimised position for collection of streaming potential measurements, called magnet far. An example of the band shapes generated from the two different magnet positions is shown in Figure 2.15. Due to the focusing nature of the magnetic field generated from the magnet tip, electrons detected in the optimised magnet position came from a $2\pi$ distribution with trajectories orientated towards the skimmer. When the magnet was translated into the magnet far position, the band shapes of each feature broadened as electrons generated from a $4\pi$ distribution could now be detected, with electrons that had trajectories away from the skimmer guided by magnetic field towards the skimmer after having their trajectories altered. This resulted in ToF values longer than initially expected. As such, Gaussian functions were only fit to the low ToF edge of the lower ToF peak associated with each feature generated in the magnet far position, to avoid distortions from the broadened PE features affecting peak position assignments.

The energy resolution of the spectrometer was determined using REMPI of gaseous Xe from Xe($^1S_0$) to Xe$^+$($^2P_{3/2}$) and Xe$^+$($^2P_{1/2}$), the same spectrum used in determining the ToF-to-eKE energy calibration curve. The energy resolution ($\Delta E/E$) was determined to be $\sim 0.05$ eV when the magnetic is in the magnet close position for sample measurements. This is a similar level or better compared to other UV LJ-PE spectrometers.\textsuperscript{21,101,109}

2.4.2 Solution preparation

All solutions prepared in this thesis used ultrapure water (>15 MΩ, ELGA LabWater, PURELAB Chorus 2), and solutions were made up using a high precision balance. Solutions are left in an ultrasonic bath for $\sim 15$ minutes before use to thoroughly mix and degas.
2.4.3 Instrument operation

The microjet assembly entered the vacuum chamber through a ConFlat (CF) 40 entrance port on top of the source chamber with an xyz-manipulator. A CMOS camera (iDS, UI-3250LE-M) was used to visualise the interaction region, aiding in alignment of the jet stream into the catcher, and the jet stream onto the laser. Using the camera software also allowed the user to add lines and measurements onto the computer screen, which aided in reliable realignment of the magnet and microjet to the required positions, as well as more precisely calculating the distance from the skimmer entrance to the ionisation point. This was achieved by converting pixels to distance, where 1 pixel equated to 0.027 mm. Use of a light source through the window on the vacuum-compatible door of the source chamber greatly aided in visualising the jet stream for alignment purposes and to quickly observe problems, such as slight ice formation around the ionisation point, and try to rectify them before requiring a full vent of the instrument to avoid further damage to any components. Once the jet stream was aligned into the catcher, it was beneficial to leave the system for at least 10 minutes to allow any drop in temperature of the catcher tip from jet stream alignment to return to the rest temperature, as stated in section 2.3.2.

The skimmer used in the instrument can be damaged by a pressure difference resulting from higher pressure in the ToF chamber compared to the source chamber. As such, a roughing line was kept open to the MB ToF spectrometer, which was backed by a Leybold SCROLLVAC (SC 30 D, 26.3 m³ h⁻¹ pumping speed), and kept the MB ToF spectrometer at ∼2 mbar while the source chamber was at atmospheric pressure. The source chamber achieved a pressure of ∼3 × 10⁻¹ mbar using a Leybold TRIVAC B (D 40 B, 40 m³ h⁻¹ pumping speed). When the microjet assembly was in, the force acting on the nozzle when roughing the source chamber could cause the trajectory of the jet stream to misalign with the recirculating catcher. Therefore, to effectively pump down with the jet stream flowing, a valve was used to control the load pressure applied to the pump when opening the roughing line. The load pressure initially was kept between 10 and 15 mbar to help begin the pumping process, but not misalign the jet stream with the catcher. The pressure gauges used to monitor the chamber pressures (Leybold, IONIVAC ITR
Figure 2.16: Left: Laser spot with no jet stream overlap. Right: Laser spot with jet stream overlap, displaying the diffraction pattern observed when jet stream is overlapped with the laser focal point.

90) consist of a pirani gauge, that on its own covers pressures from 1000 mbar to $\sim 1 \times 10^{-2}$ mbar, and a hot cathode Bayard-Alpert gauge, that along with the pirani gauge covered pressure ranges from $\sim 2.4 \times 10^{-2}$ mbar to $5 \times 10^{-10}$ mbar. The pressure gauge was less sensitive to changes in pressure between $\sim 200$ to 1000 mbar, therefore it was easier to monitor the changes in the MB ToF load pressure when initially pumping down, as it began to drop before the source chamber pressure appeared to drop. Once the MB ToF load pressure began to drop steadily, the load pressure of the source chamber pump was kept below 5 mbar to prevent the pulling force from the vacuum pump pulling the jet stream out of the catcher tip temporarily. Fully opening the source chamber roughing line brought the source chamber pressure to $\sim 3 \times 10^{-1}$ mbar, and the ToF chamber and detector chamber pressures to $\sim 3 \times 10^{-2}$ mbar. Once the source chamber was roughed out, it was useful to manoeuvre the jet and catcher simultaneously along the laser propagation axis, then the skimmer-magnet axis, to ensure the jet stream is well aligned into the catcher and movement of both simultaneously did not cause the jet stream to misalign from the catcher tip and sputter into the chamber, which at pressures below $\sim 1$ mbar caused water solutions to freeze.

To bring the instrument to the high vacuum regime, the roughing line to the MB ToF spectrometer was closed and a turbomolecular pump (Edwards EXT250, 250 L s$^{-1}$ pumping speed) attached to the detector chamber was used to bring the detector chamber and ToF chamber to $\sim 5 \times 10^{-5}$ and $\sim 1 \times 10^{-4}$ mbar, respectively. Two turbomolecular pumps (Leybold TURBOVAC 600c, 600 L s$^{-1}$ pumping speed)
were then used to bring both the ToF and detection chambers to $\sim 6 \times 10^{-6}$ mbar. A cold trap in the source chamber was then filled with liquid nitrogen to bring the source chamber to $\sim 1 \times 10^{-3}$ mbar. A turbomolecular pump (Leybold TURBOVAC 1000c, 1000 L s$^{-1}$ pumping speed) attached to the source chamber was then used to bring the instrument to the pressures used during photoelectron spectrum collection, which were $\sim 2 \times 10^{-5}$ mbar in the source chamber, $\sim 9 \times 10^{-7}$ mbar in the ToF chamber, and $\sim 1 \times 10^{-6}$ mbar in the detection chamber.

The laser was then aligned into the chamber using a series of irises and focused into the chamber using a 300 mm focal lens. The microjet assembly was moved using an AdMiSys-purchased program that moved the microjet assembly and recirculating catcher at the same rate onto the laser focal point. This was the ionisation point for the experiment, which is approximately 1 mm away from the skimmer entrance, and good overlap between the laser focal point and jet stream could be checked using the diffraction pattern generated when both were overlapped correctly. An example of this is shown in Figure 2.16.

2.4.4 Measuring the streaming potential

As described in section 2.3, recent studies have shown the need to flatten the streaming potential in the interaction region from the solution. Two methods have been employed to achieve this, either applying a voltage bias to the solution or adding a specific concentration of salt. For all the data presented in this thesis, a specific salt concentration that ranged from 0.8 – 2.0 mM was chosen to flatten the streaming potentials.

To record a streaming potential, the magnet was translated away from its optimal position, typically $\sim 3$ mm, to avoid collision of the microjet assembly and catcher against the magnet while recording a streaming potential measurement. The jet stream was overlapped with the ionisation point, then translated 0.2 mm away from the ionisation point in a direction perpendicular to the laser propagation axis. Xe gas was fed into the chamber via the graphite-coated continuous gas nozzle. REMPI measurements of Xe to the Xe$^+ (2P_{3/2})$ state were collected while translating the microjet assembly and catcher a series of steps away from the ionisation point, typically between 0.2 to 2.0 mm. An example of the extreme positions of the components is shown in Figure 2.17. To minimise the error associated with
the broadening of the Xe peaks from inelastic scattering from the water vapour, Gaussian functions were fit to the high energy side to obtain the peak maximum of the $^{2}\text{P}_{3/2}$ state, similar to the process described earlier in section 2.4.1.

Figure 2.18 shows an example streaming potential when the salt concentration was adjusted to reduce any streaming potential such that the kinetic energy of the

![Figure 2.17: Schematic diagram of the components around the ionisation point (IP). Left: A schematic diagram showing the component positions at the start of a streaming potential measurement. Right: A schematic diagram showing the component positions at the end of a streaming potential measurement. In both diagrams, the blue arrow dictates the direction of travel of the microjet assembly and the catcher during a streaming potential measurement.](image)

![Figure 2.18: Example of a streaming potential measurement. The black, open circles represent the data points taken at different microjet assembly/catcher positions, and the black, dashed line represents a non-linear fit to the data using equation 2.3.](image)
$^2\text{P}_{3/2}$ state of Xe was constant irrespective of liquid-microjet position.

\[
e\text{KE} = E_0 - \phi_{str} \cdot \ln \left( \frac{2Y + x}{x} \right) / \ln \left( \frac{2(Y + x) - r}{r} \right)
\]

Equation 2.3 \cite{110} was fit to the data points to obtain the streaming potential, if any, and to obtain a value for the vacuum level with the jet stream present. $E_0$ is the asymptotic value of the $^2\text{P}_{3/2}$ feature of Xe in eV, $\phi_{str}$ is the streaming potential, $Y$ is the distance from the skimmer to the interaction region, $x$ is the distance between the ionisation point and the jet stream, and $r$ is the inner radius of the capillary, which for all work in this thesis was 10 $\mu$m. This process was used in all subsequent results chapters in this thesis.

During day-to-day experimental collection, using a freshly prepared solution or using a new solution not run through the instrument before required fine-tuning the salt concentration in the solution to reduce the streaming potential to near-zero conditions. To adjust the salt concentration while the instrument was under vacuum with the microjet assembly inside the vacuum chamber, a new solution was required. Since the isocratic HPLC pump was incapable of changing solution while in operation, it was possible to change the solution by briefly stopping the HPLC pump for up to 5 seconds, which stopped solution being drawn up from the stock solution but maintained a high enough backing pressure in the pump to allow the user to reposition the suction filter in the new solution and restart the HPLC pump before the jet stream became unstable and risked freezing in the chamber. Once a zero streaming potential had been obtained after fine-tuning the salt concentration, photoelectron spectra of the system of interest were collected.

2.5 Data characterization

2.5.1 Spectral corrections

Post collection spectral corrections were required to obtain a photoelectron spectrum that represented the distribution of electrons generated immediately after ionisation of the molecule of interest. One such correction was the characterisation and correction of the instrument response function. At very low eKEs within magnetic-bottle time-of-flight spectrometers, there is a decrease in the collection efficiency of electrons as kinetic energies approaches zero as electron trajectories become
Figure 2.19: Multiphoton ionisation spectra of NO recorded to determine the instrument function shown in Figure 2.20. Purple, black, red, and blue features represent transitions to the $v^+ = 0, 1, 2,$ and 3 states of NO$^+$, respectively. The colours of the $v^+ = 1 – 3$ transitions match the data point colours of the instrument function shown in Figure 2.20.
more affected by perturbing forces. As such, it was necessary to characterise this drop in collection efficiency and correct for it in photoelectron spectra obtained. To do so, we used the MPI spectra of NO obtained when collecting a ToF-to-eKE calibration, as described in section 2.4.1, to monitor the change in peak height of select transitions as a function of wavelength. All the transitions in each spectrum were referenced to the $v^+ = 0$ transition, which for wavelengths between 235 and 250 nm has eKEs $>0.5$ eV. Figure 2.19 shows all the spectra recorded to obtain the instrument function, with the colours of the $v^+ = 1 – 3$ transitions the same as the data points shown in Figure 2.20.

Figure 2.20 shows an example of a typical instrument response function obtained. The open circles represent the relative peak heights of the $v^+ = 1-3$ transitions relative to the $v^+ = 0$ transition. An exponential decay function was fit to the data points, and the parameters obtained were used to transform photoelectron spectra recorded to recover the loss of electrons due to the spectrometer sensitivity.

The other post collection correction was correcting for any vacuum level offset due to the presence of the jet stream. While graphite coating is used to bring the work function of the components around the ionisation region without the solution, a finite concentration of salt was used to dramatically reduce the streaming potential generated from the silica nozzle. Under vacuum, the components around the ionisation point became slowly coated with water over time from evaporation around the jet stream. This may alter the vacuum level around the ionisation point slightly relative to the analyser vacuum level, and as such it was necessary to correct for any vacuum level offset generated from the presence of the solution throughout the experiment. This was done by taking multiple streaming potentials throughout data collection, then calculating the average of the asymptotic values from the streaming potential fit obtained using equation 2.3, and taking the difference between the averaged value and the $\text{Xe}^2\text{P}_{3/2}$ peak without the jet stream and shifting the photoelectron spectra collected by the difference between the two. Figure 2.21 shows an example of this, with two streaming potential measurements recorded before and after collection. In this example, the average between the two streaming potential measurements, which gave values of $2.67 \pm 0.03$ eV and $2.59 \pm 0.04$ eV, was taken as the asymptotic value to correct for any vacuum level offsets; see Figure 2.12 for
Figure 2.20: Top: An example instrument function spectrum obtained from taking the relative peak heights of the first four vibronic transitions of NO. All peak heights are scaled relative to the $v^+ = 0$ transition and the $v^+ = 1$ (black, open circles), $v^+ = 2$ (red, open squares) and $v^+ = 3$ (blue, open triangles) vibronic states are normalised to the peaks associated with energies $>0.3$ eV within the same vibronic transition set. An exponential function (black, dashed line) is fit to the data points, and the parameters obtained from the fit are used to correct for the decrease in collection efficiency. Bottom: An example of the application of the instrument function correction on the 300 nm spectrum of $\rho$-HBDI$^-$.\textsuperscript{14} Black spectrum is the PE spectrum recorded originally, and the red spectrum is post instrument function correction.
Figure 2.21: Experimentally measured eKEs associated with 2+1 REMPI of Xe to the \(^2\text{P}_{3/2}\) state of Xe\(^+\) at 249.7 nm. Data points show measurements recorded in the presence of aqueous \(p\)-HBDI\(^-\), plotted as a function of the distance between the ionisation point and the liquid-microjet before (filled circles) and after (open circles) recording the photoelectron spectra presented in Tau \textit{et al.}\(^{14}\). Solid horizontal lines represent the mean eKEs (2.67 ± 0.03 eV and 2.59 ± 0.04 eV) and shaded areas represent two standard deviations either side of each mean. The dashed line indicates the expected value of 2.766 eV.

an illustrative view of the vacuum level.
Chapter 3

Ultraviolet photoelectron spectroscopy of liquid water

A detailed insight into the electronic structure of liquid water is crucial for understanding the radiolysis pathways of water and how water molecules interact with other molecules in aqueous solution. The vertical ionisation energies (VIEs) of liquid water are also used as fundamental benchmarks in electronic structure calculations. Despite this, there has been limited study into the vertical excitation energies following two-photon absorption using ultraviolet (UV) light, and none following resonance-enhanced multiphoton ionisation. The work in this chapter used multiphoton UV liquid-microjet photoelectron spectroscopy (LJ-PES) combined with recent inelastic scattering correction method to record the electronic structure of liquid water. This chapter also discusses spectral reproducibility over different measurements and the effect the streaming potential has on the spectral distribution when the streaming potential is non-zero.

3.1 Introduction

Water is the most prevalent solvent throughout nature. The electronic structure of gas-phase water and various forms of ice have been studied for decades.\textsuperscript{38,111--113} While there has been significant interest in the electronic structure of water in the liquid-phase, the development of liquid-microjet photoelectron spectroscopy (LJ-PES) in the late 1990s made it possible to directly investigate the electronic structure of water by obtaining electron binding energies (eBEs). A number of literature studies have investigated the eBEs of the occupied valence states of liquid water using extreme-ultraviolet (EUV) and X-ray PES,\textsuperscript{18,32,114--116} shedding light on
the ground state electronic structure which underpins the chemical reactivity of liquid water.\textsuperscript{35} The eBEs of liquid water are also used as fundamental benchmarks in electronic structure calculations. However, to obtain information on the excited electronic states of liquid water, ultraviolet (UV) liquid-microjet photoelectron spectroscopy (LJ-PES) is required. Previous UV LJ-PES studies of water have concentrated on studying the structure and dynamics of the solvated electron.\textsuperscript{11,90,117–120} There has also been a lack of quantitative understanding of the effect that inelastic scattering of electrons has on the electron kinetic energy (eKE) distribution of electrons in UV LJ-PE spectra. Previous literature has attempted to quantify the inelastic scattering distortions through comparison of the eKE distributions of the solvated electron generated using different photon energy regimes,\textsuperscript{93} but only recently has a more widely applicable method become available.\textsuperscript{12} As such, there have been limited studies investigating the electronic structure of liquid water using UV laser light.

The absorption spectrum of water has previously been investigated for the isolated water molecule,\textsuperscript{15,121} and for liquid water using one-\textsuperscript{16,122} and two-photon absorption,\textsuperscript{17,123} with some of the best examples of the spectra illustrated in Figure 3.1. The gas-phase absorption spectrum of water has been used as a reference to identify the major absorption processes in liquid water. The first two absorp-
Figure 3.2: Taken from Elles et al.\textsuperscript{17} The five lowest energy transitions and associated molecular orbitals for the isolated water molecule. Each transition is labelled according to the identity of the excited state.

The five lowest energy transitions and associated molecular orbitals for the isolated water molecule. Each transition is labelled according to the identity of the excited state.

Figure 3.2: Taken from Elles et al.\textsuperscript{17} The five lowest energy transitions and associated molecular orbitals for the isolated water molecule. Each transition is labelled according to the identity of the excited state.

For the photon energies that can be generated using the laser system described in Section 2.2, at least two UV photons are required to access the electronic excited states of water. It has previously been found that there is a significant difference between the one- and two-photon absorption spectra of liquid water, with the first absorption band having an order of magnitude smaller photoabsorption cross-section in the two-photon absorption spectrum compared to the one-photon absorption spectrum, as illustrated in Fig. 3.1. Previous experimental and computational adiabatic and vertical excitation energies (AEEs/VEEs) for the electronic
excited states <10 eV following two-photon absorption, and the recent vertical ionisa-
tion energies (VIEs) of the $1b_1$ state and the lower of the two $3a_1$ states ($3a_1L$), the
splitting of which has been attributed to hydrogen-bonding, are shown in Table 3.1.

Recently, there has been significant discussion about the values of the VIEs listed in Table 3.1, even the first VIE of liquid water, ionisation from the $1b_1$ state. Two recent EUV/X-ray studies yielded 11.33 eV for the VIE of the $1b_1$ state through rigorous examination of experimental procedures involved in collection of LJ-PE spectra.

Here, the electronic structure of liquid water was investigated using UV both
resonance-enhanced multiphoton ionisation (REMPI), where ionisation occurs via
an intermediate state, and non-resonant multiphoton ionisation, where no interme-
diate state is involved. A non-resonant wavelength was chosen to provide a direct
comparison with the VIEs recorded using X-Ray LJ PES. Resonant laser wave-
lengths were chosen to probe the absorption maximum of first absorption band in
the one-photon absorption spectrum of liquid water. 290 and 272.5 nm were chosen

**Table 3.1:** Literature values for the vertical excitation energies of the first three singlet electronic states of liquid water and the vertical ionisation energies of the first two doublet states of liquid water. The literature reference and method used to obtain each value is also shown with the associated VEE/VIE.

<table>
<thead>
<tr>
<th>State</th>
<th>Energy / eV</th>
<th>Reference</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1b_1$</td>
<td>8.094 ± 0.006</td>
<td>Elles et al.</td>
<td>Two-photon absorption (TPA) spectroscopy</td>
</tr>
<tr>
<td></td>
<td>7.71/8.15</td>
<td>Cabral Do Couto and Chipman</td>
<td>Computed TPA excitation energies</td>
</tr>
<tr>
<td></td>
<td>8.16</td>
<td>Svoboda et al.</td>
<td>CCSD/d-aug-cc-pVDZ</td>
</tr>
<tr>
<td>$2^1A_1$</td>
<td>9.8</td>
<td>Elles et al.</td>
<td>TPA spectroscopy</td>
</tr>
<tr>
<td></td>
<td>9.736 ± 0.009</td>
<td>Paterson et al.</td>
<td>Computed TPA excitation energies</td>
</tr>
<tr>
<td>$3p$</td>
<td>9.2</td>
<td>Elles et al.</td>
<td>CCSD/d-aug-cc-pVDZ</td>
</tr>
<tr>
<td>$1b_1$</td>
<td>11.3 ± 0.05</td>
<td>Yamamoto et al.</td>
<td>Extreme UV (EUV, 27.5 eV)</td>
</tr>
<tr>
<td></td>
<td>11.31 ± 0.04</td>
<td>Kurahashi et al.</td>
<td>Soft X-ray (600 eV) LJ-PES</td>
</tr>
<tr>
<td></td>
<td>11.33 ± 0.02</td>
<td>Credidio et al.</td>
<td>EUV (40.814 ± 0.002 eV) LJ-PES</td>
</tr>
<tr>
<td></td>
<td>11.33 ± 0.03</td>
<td>Thürmer et al.</td>
<td>EUV/Sof X-ray (40 – 400 eV) LJ-PES</td>
</tr>
<tr>
<td></td>
<td>11.36 ± 0.07</td>
<td>Scholz et al.</td>
<td>UV (6.19 eV) LJ-PES</td>
</tr>
<tr>
<td></td>
<td>11.40 ± 0.07</td>
<td>Thürmer et al.</td>
<td>EUV (40.813 eV) LJ-PES</td>
</tr>
<tr>
<td></td>
<td>11.67 ± 0.15</td>
<td>Perry et al.</td>
<td>EUV (~17.1 – 35.6 eV) LJ-PES</td>
</tr>
<tr>
<td>$3a_1L$</td>
<td>12.93 ± 0.05</td>
<td>Yamamoto et al.</td>
<td>EUV (27.5 eV) LJ PES</td>
</tr>
<tr>
<td></td>
<td>13.06 ± 0.01</td>
<td>Nishizawa et al.</td>
<td>Soft X-ray (516 eV) LJ-PES</td>
</tr>
<tr>
<td></td>
<td>13.08 ± 0.07</td>
<td>Kurahashi et al.</td>
<td>Soft X-ray (600 eV) LJ-PES</td>
</tr>
<tr>
<td></td>
<td>13.09 ± 0.05</td>
<td>Credidio et al.</td>
<td>EUV (40.814 ± 0.002 eV) LJ-PES</td>
</tr>
</tbody>
</table>
to coincide with the longest, non-resonant wavelength used in Chapter 4 and the maximum of the first absorption band of aqueous phenol, respectively, discussed in Chapter 4. The wavelengths are shown on the UV-Vis absorption spectrum presented in Figure 3.1 as vertical arrows.

3.2 Methods

Solutions were prepared using ultrapure water and 0.8 mM NaF for the 200.2 nm PE spectrum, and 1.0 mM NaF for the 272.5, 290 and 300 nm PE spectra. The latter was added to minimise the streaming potential. The streaming potential measurements are presented and discussed in greater detail in Section 3.3.2. For the wavelengths used in this chapter, the laser power was kept at $\sim 200$ nJ.

There are a number of factors that can introduce error to the UV LJ-PES measurements: laser pulse energy width, time-of-flight to electron kinetic energy conversion, instrument function, streaming potential, and the vacuum level offset between the jet stream and the analyser (typically $\pm 0.03$ eV). Table 3.2 shows the breakdown of the different error contributions taken into account when calculating the eKE errors reported in this chapter, and in later Chapters 4 and 5. Not included in Table 3.2 is the error from the fit using the scattering code, which employed a Levenberg-Marquardt least-squares algorithm. The covariance of the parameters obtained was converted to standard deviation, and two standard deviations were included in all the eKE peak maxima values. The square root of the sum of squares of all the errors was used to calculate the total error.

Table 3.2: Error analysis associated with the eKE peak maxima values in this chapter.

<table>
<thead>
<tr>
<th>Error source</th>
<th>Error / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength</td>
<td>$\pm 0.02$</td>
</tr>
<tr>
<td>ToF-to-eKE conversion</td>
<td>$\pm 0.03$</td>
</tr>
<tr>
<td>Streaming potential</td>
<td>$\pm 0.03$</td>
</tr>
<tr>
<td>Vacuum level offset</td>
<td>$\pm 0.03$</td>
</tr>
<tr>
<td>Inelastic scattering correction method</td>
<td>$\pm 0.04$</td>
</tr>
</tbody>
</table>
Figure 3.3: Multiphoton photoelectron spectra of liquid water (black lines) together with the fits to the PE spectra using the spectral retrieval method (blue lines), the corresponding retrieved Gaussian functions (blue, green and purple Gaussians) and the retrieved PE spectra using the spectral retrieval method (red lines). The photoelectron spectrum recorded using 200.2 nm (a) is non-resonant multiphoton ionisation of liquid water, and is also in Scholz et al.\textsuperscript{12}. Photoelectron spectra recorded using 272.5 (b), 290 (c), and 300 nm (d) are resonance-enhanced multiphoton ionisation spectra of liquid water, with the two-photon absorption energies shown on Figure 3.1. Green, blue, and purple Gaussian functions represent resonance-enhanced multiphoton ionisation via the $1^1B_1$, $2^1A_1$ states and a $3p$ Rydberg state; see main text for details.
3.3 Results and Discussion

3.3.1 Assignment of liquid water features

Figure 3.3 shows the multiphoton ionisation PE spectra of liquid water using 200.2 (a), 272.5 (b), 290 (c), and 300 nm (d). All the spectra were transformed using the ToF-to-eKE transformation described in Section 2.4.1. An example of transforming the ToF spectrum to an instrument response function corrected eKE spectrum is shown in Figure 3.4. To fit each of the PE spectra, the spectra retrieval code described in Section 1.3.3 was employed. All the PE spectra in this chapter were fit using Gaussian functions with a uniform concentration depth profile under the assumption that photoelectrons generated from liquid water can be generated throughout the liquid-microjet. An example application of the spectral retrieval code is shown as a flow diagram in Figure 3.5.

Multiphoton ionisation processes exhibit different trends in the eBE depending on whether it is a non-resonant ionisation process or a resonance-enhanced ionisation process. For non-resonant ionisation, it is expected that the binding energy will be constant when calculated using the following equation;

\[
eBE = n\hbar \nu - eKE
\]

where eBE is the electron binding energy, eKE is the electron kinetic energy, and \( n\hbar \nu \) is the number of photons, \( n \), required to promote the electron above the ionisation threshold. When increasing the photon energy, this will in turn increase the electron kinetic energy. As such, the eBE will remain constant under these conditions.

Resonance-enhanced ionisation processes via an intermediate state will produce a constant one-photon eBE if the last ionisation process is one-photon. This is because any excess vibrational energy generated in the intermediate state upon photoexcitation is conserved during the photoionisation process. For wavelengths corresponding to resonance-enhanced ionisation (300, 290 and 272.5 nm), three photons are required to access the ionisation continuum, with two photons required for the photoexcitation process to the resonant intermediate. As such, the one-photon eBE for the resonance-enhanced ionisation processes will be constant, and
Figure 3.4: An example ToF-to-eKE conversion process, involving the initial ToF-to-eKE conversion, the Jacobian transformation to ensure the area under the spectrum is conserved, and the instrument response function correction. The final spectrum is the same 272.5 nm PE spectrum shown in Figure 3.3

can be explained by the following equation;

\[
eKE = 3\hbar \nu - AIE - (2\hbar \nu - AEE) \tag{3.2}
\]

where AIE is the adiabatic ionisation energy from the ground state of the parent species to the ground state of the generated radical species, and AEE is the adiabatic excitation energy from the ground state to the intermediate state of the parent species. This can be rearranged to the following equations;

\[
eKE = \hbar \nu - (AIE - AEE) \tag{3.3}
\]
3.3. Results and Discussion

Figure 3.5: Flow diagram of the application of the spectral retrieval method, using the 272.5 nm spectrum as an example. The measured PE spectrum is fed into the code alongside a set of initial parameters determined by the user. The initial parameters are then used to generate an initial set of scattering-distorted Gaussian profiles in flow (i). A Levenberg–Marquardt least-squares algorithm, (ii), is then used to fit appropriate scattering-distorted Gaussian profiles to the measured PE spectrum. The scattering-distorted Gaussian profiles are used to generate a simulated PE spectrum including electron scattering, which is then used to retrieve a PE spectrum free of electron scattering processes, alongside the parameters of the retrieved Gaussian profiles, as shown in flow (iii). The colours of the spectra are the same colours used in Figure 3.3.

Table 3.3: Maximum peak positions of the scattering-corrected Gaussian function fits to the photoelectron spectra in Fig. 3.3, full width half maximum (FWHM) values of the scattering-corrected Gaussian functions, and the vertical ionisation energies (VIEs), calculated using $nh\nu - eKE$, where $n$ is the number of photons in the ionisation process, and $eKE$ is the peak position.

<table>
<thead>
<tr>
<th>Wavelength / nm (eV)</th>
<th>Peak position / eV</th>
<th>FWHM / eV</th>
<th>$n$</th>
<th>$nh\nu - eKE$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>200.2 (6.19)</td>
<td>1.02 ± 0.08</td>
<td>0.91 ± 0.01</td>
<td>2</td>
<td>11.36 ± 0.09</td>
</tr>
<tr>
<td>272.5 (4.55)</td>
<td>1.14 ± 0.08</td>
<td>0.96 ± 0.02</td>
<td>1</td>
<td>3.41 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>2.30 ± 0.08</td>
<td>1.40 ± 0.02</td>
<td>1</td>
<td>2.25 ± 0.08</td>
</tr>
<tr>
<td>290.0 (4.28)</td>
<td>1.09 ± 0.08</td>
<td>0.86 ± 0.02</td>
<td>1</td>
<td>3.19 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>2.01 ± 0.08</td>
<td>1.30 ± 0.03</td>
<td>1</td>
<td>2.27 ± 0.08</td>
</tr>
<tr>
<td>300.0 (4.13)</td>
<td>0.99 ± 0.09</td>
<td>0.93 ± 0.03</td>
<td>1</td>
<td>3.14 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>1.79 ± 0.10</td>
<td>1.27 ± 0.05</td>
<td>1</td>
<td>2.34 ± 0.10</td>
</tr>
</tbody>
</table>

which show that there is a propensity for excess vibrational energy to be conserved upon photoionisation in a resonance-enhanced ionisation process. The propensity for vibrational energy conservation relies on there being no significant geometry change during ionisation. The lack of any significant geometry change usually holds true in the gas-phase, but recent studies have shown that this is not the case for the same molecules in solution. The breakdown in the propensity for excess vibrational energy conservation has been observed in this chapter and Chapters 4 and 5, and will be discussed in more detail later.
Figure 3.6: Resonance-enhanced multiphoton ionisation PE spectrum of liquid water using 290 nm (black line) fit with one bulk Gaussian function using the spectral retrieval method (blue line). The residual of the fit is shown below the PE spectrum.

The PE spectrum of liquid water using 200.2 nm is plotted in Figure 3.3a, which was previously presented in Scholz et al. 12. 200.2 nm is below the onset of the first absorption band of liquid water (Figure 3.1). As such, non-resonant photoionisation of liquid water is expected. The PE spectrum was fit using the inelastic scattering correction method as described by Scholz et al. 12, and was best fit to one Gaussian function. The eKE of the Gaussian function fitted using the spectral retrieval code was 1.03 ± 0.07 eV. The two-photon eBE of the feature centered around 1.03 eV is 11.36 ± 0.09 eV (Table 3.3). This is in agreement with the most accurate X-ray 18 and EUV LJ-PES measurements. 102. As such, this feature can confidently be assigned as the 1b1 VIE of liquid water.

Figure 3.3b–d shows the resonance-enhanced PE spectra of liquid water following photoexcitation using (b) 272.5, (c) 290, and (d) 300 nm laser wavelengths. All the PE spectra using resonant wavelengths were best fit using a superposition of two Gaussian functions. Figure 3.6 shows an example of a one Gaussian fit to the resonance-enhanced spectra, with the 290 nm spectrum shown. The fit poorly describes the PE spectrum, as shown by the residual of the fit.

As stated earlier, for all the wavelengths used in this chapter, the laser power was kept at ∼200 nJ. Using the two-photon photoabsorption cross-sections shown in Figure 3.1, the ionisation fraction can be estimated. The number of two-photon
excitations per molecule can be calculated using:

$$N = 0.5 \times \delta \times \phi^2 \times \tau$$

(3.5)

where $\delta$ is the two-photon photoabsorption cross-section (GM), $\phi$ is the photon flux at the center of a Gaussian beam (photon cm$^{-2}$ s$^{-1}$), and $\tau$ is the exposure time (s). Using a photon flux of $\sim 7 \times 10^{18}$ photon cm$^{-2}$ s$^{-1}$, the concentration of water molecules photoionised is $\sim 1$ nM, assuming every water molecule that is photoexcited undergoes subsequent photoionisation. This shows that under the experimental conditions in this chapter, plasma generation can be ignored.

To start, I will discuss the 300 nm PE spectrum. The eKEs of the Gaussians fitted using the spectral retrieval code were 0.99 ± 0.09 and 1.79 ± 0.10 eV, shown in Figure 3.3d as the green and purple Gaussian functions, respectively. Two photons of 300 nm give an excitation energy of 8.27 eV. As such, it is unlikely that any resonance-enhanced ionisation process will proceed via the $2^1A_1$ state, which has a vertical excitation energy of $\sim 9.8$ eV, as illustrated in Figure 3.7. The one-photon eBEs, $h\nu - $ eKE, of the Gaussian functions centered around 0.99 and 1.79 eV are 3.14 ± 0.09 and 2.34 ± 0.10 eV, respectively. The vertical excitation energies (VEEs) associated with the fitted Gaussian functions can be approximated using the following equation;

$$\text{VEE} \approx \text{VIE} - (h\nu - \text{eKE})$$

(3.6)

where VIE is the $1b_1$ VIE reported in this chapter using 200.2 nm, 11.36 eV. To make this approximation, we assume that the solvent reorganisation is negligible on the timescale of the ionisation process and that the propensity for vibrational energy conservation holds true. The fitted Gaussian functions would correspond to VEEs of 8.22 ± 0.09 and 9.02 ± 0.10 eV for the features centered around 0.99 and 1.79 eV, respectively. This suggests that the feature can be assigned to REMPI via the $1^1B_1$ state, since the approximate VEE is close to the one-photon absorption maximum of 8.2 eV,\textsuperscript{16} and in good agreement with previous experimental and computational VEEs of 8.3\textsuperscript{17} and 8.09 eV\textsuperscript{124}, respectively. The feature corresponding to a two-photon VEE of 9.02 ± 0.10 eV is close to that of the $3p$ Rydberg state of 9.2 eV.\textsuperscript{17} This difference in the two values could be due to the different $1b_1$ VIE
values used between this work, 11.36 eV, and Elles et al., 11.2 eV, as well as the different values for the $1^1B_1$ transition, resulting in differing energy ranges for the Rydberg-like states correlated to the $(1b_1)^{-1}$ hole. It could also be due to a breakdown of the assumptions described above.

Similar to the 300 nm PE spectrum, the measured resonance-enhanced 290 nm PE spectrum was best described as a superposition of two Gaussian functions, as illustrated in Fig. 3.3c. The eKEs of the Gaussians fitted using the spectral retrieval code were $1.09 \pm 0.08$ and $2.01 \pm 0.08$ eV for the green and purple Gaussian features, respectively. The one-photon eBEs for the features centered around 1.09 and 2.01 eV are $3.19 \pm 0.08$ and $2.27 \pm 0.08$ eV, respectively. Following the logic applied to the 300 nm spectrum, the $2^1A_1$ state is also unlikely to contribute to the spectrum given a total two-photon excitation energy of 8.55 eV for two photons of 290 nm. This is illustrated in Figure 3.7, showing the large gap in energy between the two-photon absorption energy and the $2^1A_1$ state. Using the same procedure as the 300 nm analysis, the one photon eBEs were used to estimate the VEEs of the resonant intermediates giving rise to the two Gaussian features in

**Figure 3.7:** Left: Energy level diagram of the four lowest energy singlet electronic states of liquid water and the two lowest energy doublet states of singly ionised liquid water involved in the recorded PE spectra. Values for the singlet electronic states were taken from Elles et al. and VIEs were taken from Thürmer et al. 
Right: Electronic configurations of the electronic states shown in the energy level diagram.
the PE spectrum. For the Gaussians centered around 1.09 and 2.01 eV, VEEs of $8.17 \pm 0.08$ and $9.09 \pm 0.08$ eV were estimated, respectively. Similar to the 300 nm PE spectrum, these values suggest resonance-enhanced ionisation processes via the $1^1B_1$ state to the $1b_1$ continuum (shaded green Gaussian in Fig. 3.3c) for the VEE of 8.17 eV, and resonance-enhanced ionisation via a $3p$ Rydberg state to the $1b_1$ continuum (shaded purple Gaussian in Fig. 3.3c) for the VEE of 9.09 eV. A comparison between the relative peak areas of the fitted Gaussian functions in the 300 nm PE spectrum with the 290 nm PE spectrum also helps confirm these assignments. A previous study using two-photon absorption spectroscopy showed that an absorption feature around $\sim 9.2$ eV had a significantly higher absorption cross-section than the $1^1B_1$ state. The increase in the relative peak area of the assigned $3p$ Rydberg state from 300 to 290 nm compared to the assigned $1^1B_1$ state is consistent with this argument.

Figure 3.3b shows the measured 272.5 nm PE spectrum. Again, the PE spectrum was best fit using a superposition of two Gaussian functions. The eKEs of the Gaussians fitted using the spectral retrieval code were $1.14 \pm 0.08$ and $2.30 \pm 0.08$ eV, shown in Figure 3.3b as the blue and purple Gaussian features, respectively. The one-photon eBE of the Gaussian feature centered around 2.30 eV is $2.25 \pm 0.08$ eV. A one-photon eBE of 2.25 eV agrees very well with the one-photons eBEs of the $3p$ Rydberg states observed in the 300 and 290 nm spectra, $2.34 \pm 0.10$ and $2.27 \pm 0.08$ eV, respectively. This Gaussian feature can therefore be assigned to the same $3p$ Rydberg state found in the 290 and 300 nm PE spectra. Using this assignment gives an estimated VEE of $9.11 \pm 0.08$ eV, which is consistent with the estimated VEEs attributed to the $3p$ Rydberg states also observed in the 290 and 300 nm spectra. It is possible that this feature centered around 2.30 eV eKE in Figure 3.3b could be associated with the $3a_1L$ ionisation continuum (VIE = $13.09 \pm 0.05$ eV) as the $3a_1L$ ionisation continuum is accessible using three photons of 272.5 nm (Figure 3.7). However, this feature with a one-photon eBE of 2.25 eV is unlikely to arise from resonance-enhanced ionisation to the $3a_1L$ ionisation continuum via a Rydberg state with $3a_1$ character as, assuming the VIE = 13.09 eV for the $3a_1L$ continuum, that would give a VEE of 10.84 eV, which is energetically inaccessible from two-photon excitation, as illustrated in Figure 3.7.
The second Gaussian feature, centered around an eKE of 1.14 eV, has a one-photon eBE of $3.41 \pm 0.08$ eV, and could be a result of ionisation of the $1b_1$ or $3a_1$ states, via the $1^1B_1$ or $2^1A_1$ states, respectively. Ionisation via the $1^1B_1$ state would give an estimated VEE of 7.95 eV, which is significantly lower than the other VEEs obtained from the 300 and 290 nm PE spectra for the same ionisation process, 8.22 and 8.17 eV, respectively. The estimated VEE is also significantly lower than the previous experimental and computational values, 8.3$^{17}$ and 8.09 eV$^{124}$ respectively. The reduction in the estimated VEE, and the increase in the one-photon eBE, could be consistent with the observations previously noted from resonance-enhanced ionisation processes of aqueous phenol, which showed a steady increase in the one-photon eBE with increasing photon energy.$^{22}$ This would mean that the feature centered around an eKE of 1.14 eV could be assigned to ionisation via the $1^1B_1$ state, under the assumption that there is a breakdown in the propensity for vibrational energy conservation. However, the peak maximum shifts from 1.09 to 1.14 eV going from the assigned resonance-enhanced ionisation process via the $1^1B_1$ state 290 nm PE spectrum to the feature with eKE of 1.14 eV in the 272.5 nm PE spectrum. This is significantly less of a shift than expected for a resonance-enhanced ionisation process involving the $1^1B_1$ state, even with the assumed breakdown in the propensity for vibrational energy conservation, given the 0.27 eV increase in photon energy. Ionisation via the $2^1A_1$ state, rather than the $1^1B_1$ state, would give an estimated VEE of $9.68 \pm 0.08$ eV, which is in good agreement with previous two-photon absorption spectroscopy, 9.8 eV.$^{17}$ Energetically, two-photon absorption using 272.5 nm would be slightly lower than the VEE for the $2^1A_1$ state, with a two-photon energy of 9.1 eV. However, the $2^1A_1$ state and the $(3a_1)^{-1}$ ionised state have full-width-half-maximum literature values of 1.3 eV$^{17}$ and 1.2 eV.$^{115}$ It is therefore possible to ionise below the VIE of the $3a_1L$ ionisation continuum via excitation to below the VEE of the $2^1A_1$ state due to the broad nature of the liquid-phase absorption and ionisation processes. All of these factors therefore suggest that the Gaussian feature centered around 1.14 eV is resonance-enhanced ionisation via the $2^1A_1$ state.

To further aid in disentangling the different REMPI processes, a laser power dependency study would be beneficial. Under the assumption that each REMPI
process would produce a different laser power dependency, this would confirm the
assignment of the resonance-enhanced ionisation via the 2^1 Λ_1 state compared to
the 1^1 B_1 state. It was not possible to perform these studies due to laboratory time
constraints, however, this would be a fruitful study for future work.

### 3.3.2 Uncertainty in measurements

During investigation of the data set presented in this chapter, a comparison was
made between data sets of liquid water PE spectra using 272.5, 290 and 300 nm on
different days of recording. Figure 3.8 shows a comparison of the different 290 nm
spectra recorded on different dates and associated streaming potential measure-
ments recorded before and after each corresponding data set. It was found that the
bandshape and overall band center of the data set used in this chapter differed from
the others presented in Figure 3.8. Upon investigation, it was found that the initial
interpretation that the streaming potential measurements in the data sets recorded
on 20^th May and 14^th June 2022 were approximately zero was false. This is shown
in Figure 3.8, where the blue and green data points were initially assumed to cor-
respond to a zero streaming potential with greater error associated with the data
set. The original streaming potential fit is shown as the dashed, horizontal lines.
It was found that there was in fact a streaming potential affecting the generated
photoelectrons in these data sets, shown as the curved fits to the blue and green
data points. As well as the streaming potential measurements and corresponding
PE spectra recorded on the 20^th May and 14^th June 2022, Figure 3.8 also shows
the other PE spectra and corresponding streaming potential measurements for the
data sets recorded on the 10^th Dec 2021 and 18^th May 2022, in black and red,
respectively. The streaming potential measurements associated with the 10^th Dec
2021 and 18^th May 2022 data sets appear to behave normally, as they are well
described by Equation 2.3, reproduced from the Methods chapter below;

\[
eKE = E_0 - \phi_{str} \cdot \ln\left(\frac{2Y + x}{x}\right) / \ln\left(\frac{2(Y + x) - r}{r}\right) \tag{3.7}
\]

where \(E_0\) is the asymptotic vacuum level value of the \(^2P_{3/2}\) feature of Xe in eV, \(\phi_{str}\) is
the streaming potential, \(Y\) is the distance from the skimmer to the interaction region,
\(x\) is the distance between the ionisation point and the jet stream, and \(r\) is the inner
radius of the capillary, which was 10 µm. The values of streaming potentials and asymptotic vacuum level values, shown as the solid, curved lines in Figure 3.8, are
summarised in Table 3.4.

The streaming potentials determined from the data sets recorded on the 10th Dec 2021 and 18th May 2022 were either near-zero or positive, which can be seen in Table 3.4. The streaming potentials for the data sets recorded on the 20th May and 14th June 2022 were negative, with the streaming potentials recorded on 14th June 2022 larger than on the 20th May 2022. Taking note of the relative magnitudes and signs of all the streaming potentials, the PE spectra show general trends depending on whether the sign of the streaming potential was negative or positive, and how large the magnitude of the potential was. It can be observed that larger, negative streaming potentials have a more profound effect on the higher eKE edge of the bandshape, seemingly shifting the PE distribution more towards the higher eKE edge when compared to PE distributions measured under near-zero or positive streaming potential conditions. Larger, positive streaming potentials have the opposite effect on the PE distribution, with an increase in the lower eKE edge of the bandshape compared to PE distributions measured under near-zero or negative streaming potential conditions. These general trends are clearly observed in the PE spectra in Figure 3.8.

Figure 3.9 shows a comparison between the two recorded data sets of 272.5 and 300 nm, with the associated streaming potential measurements recorded before and after the PE spectra. The same trends were found with the 272.5 and 300 nm spectra that were found in the 290 nm spectra. The origin of the increasing

<table>
<thead>
<tr>
<th>Date of data set</th>
<th>Wavelength / nm</th>
<th>SP₁ / eV</th>
<th>V₁ / eV</th>
<th>SP₂ / eV</th>
<th>V₂ / eV</th>
<th>Total shift / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Dec 21</td>
<td>290</td>
<td>0.04</td>
<td>2.69</td>
<td>0.04</td>
<td>2.66</td>
<td>+0.13</td>
</tr>
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Table 3.4: Streaming potentials and vacuum level offsets for the streaming potential measurements recorded by REMPI of Xe to the \(^2P_{3/2}\) state, associated with each MPI spectrum of water using Equation 3.7. SP₁ and V₁ are the values for the streaming potential and vacuum level, respectively, for the streaming potential measured before recording the associated data set. SP₂ and V₂ are the values of the streaming potential and vacuum level, respectively, for the streaming potential measured after recording the associated data set. Total shift is the linear shift applied to the associated data set, calculated by taking the sum of the average of the two streaming potential values, and the difference between the average of the two vacuum level values, V₁ and V₂, and the vacuum level without the jet stream present, 2.77 eV.
Figure 3.9: Resonance-enhanced multiphoton photoelectron spectra using 272.5 (top left) and 300 nm (top right), along with the associated streaming potential REMPI measurements of Xe to the $^{2}\text{P}_{3/2}$ state, recorded before (closed circles) and after (open circles) collection of the corresponding PE spectra. The colours of the streaming potential measurements match the PE spectra that were collected on the same day. The streaming potential measurements were either fit with Equation 3.7, shown as solid curved lines, or with a constant value under the assumption that there is no overall streaming potential, shown as horizontal dashed lines. The constant value is used to calculate the vacuum level offset under the assumption that there is no streaming potential. The streaming potential and vacuum level values are summarised in Table 3.4. The values shown in the legend of the bottom spectra were the average streaming potential values of the two streaming potential functions in the spectrum, the average vacuum level of the two streaming potential functions, and the average vacuum level when the streaming potential was initially interpreted as zero.

eKE in the streaming potential measurements at liquid-microjet distances $>1$ mm is currently unknown, but could be some low magnitude charging of a component around the ionisation point from laser scatter that is lower in magnitude than the streaming potential. As such, it would have a negligible effect on the eKEs until the liquid-microjet assembly is translated a sufficient distance away from the ionisation region. The discovery of this uncertainty in the spectra means the current data set is unpublishable, and will in the future require repeating. However, it is unexpected that the overall analysis of the spectra and subsequent interpretation of the data will change, as at the most extreme points, the deviation in eKE between the two
most differing data sets was $\leq 0.1$ eV for a given photoelectron intensity. It is therefore unlikely that the feature assignments for the spectra will change. The exact positions of the excitation energies are however likely to alter slightly, so will need further refinement in the future, but due to time limitations, I was unable to repeat these measurements myself.

The 200.2 nm spectrum does not require repeating, as the streaming potential measurements and obtained streaming potentials were described very well using Equation 3.7, as illustrated in figure 3.10, so are likely to be correctly interpreted. The obtained VIE for the $1b_1$ state also agreed very well with literature.

### 3.4 Conclusions and Outlooks

In summary, resonant and non-resonant PE spectra of liquid water were recorded using UV photons between 200–300 nm. They were recorded using the liquid-microjet photoelectron spectrometer, and the true PE spectra were retrieved from the measured data using a recently published correction code for inelastic scattering of electrons. Non-resonant ionisation of liquid water at 200.2 nm provided an eBE of 11.36 eV for the $1b_1$ state, which is in excellent agreement with accurate experimental measurements that used EUV and soft X-ray photons.\(^{18,102}\) Investigation of the one-photon eBEs allowed for the assignment of the $1^1B_1$ and $2^1A_1$ states and the $3p$ Rydberg states in liquid water. The VEEs obtained were consistent with previous experimental and computational values for these processes.

A detailed investigation into the reproducibility of the measured PE spectra
highlighted that distortions can occur to the bandshape of the recorded PE spectrum when the streaming potential is non-zero, perturbing the overall band center. It was also found that positive and negative streaming potentials distorted the bandshape more towards the lower and higher eKE edges, respectively. It is noted, however, that it was still possible to draw meaningful conclusions from the measured PE spectra.
Chapter 4

Photoelectron spectroscopy of phenol in aqueous solution

There has been limited study into the resonant photoionisation processes of aqueous phenol. Previous studies of aqueous phenol using liquid-microjet photoelectron spectroscopy (LJ-PES) have been plagued by inelastic scattering of the photoelectrons, distorting the electron kinetic energy distribution from the initially generated distribution and leading to a lack of consensus on the lowest vertical ionisation energy of aqueous phenol. The work in this chapter expands on previous studies of aqueous phenol within our group using improved experimental procedures coupled with recently developed inelastic scattering correction methods to record UV LJ-PE spectra of aqueous phenol at a range of wavelengths.

4.1 Introduction

The phenol moiety is a ubiquitous molecular motif in many biological systems. It is a building block of the chromophore in the green fluorescent protein (GFP), the most widely used in vivo fluorescent tag for monitoring biological and biochemical processes.\(^\text{129}\) The structure of phenol is highlighted in Figure 4.1.

The first absorption band in aqueous phenol is due to absorption into the \(^{1}\pi\pi^*\) state. The UV/Vis of aqueous phenol focussed on the first absorption band is shown in Figure 4.2. \(^{\pi\pi^*}\) states are known to be responsible for much of the strong UV absorption found in heteroaromatics.\(^\text{130}\) The second electronically excited state of phenol is the \(^{1}\pi\sigma^*\) state, which is dissociative along the O-H stretching mode. \(^{\pi\sigma^*}\) states typically have low absorption cross-sections. The interplay between these two states dictates much of the relaxation dynamics in phenol, with a conical in-
intersection (CI) between the $1^1\pi^*$ and $1^1\pi^*\sigma^*$ states providing an efficient electronic relaxation pathway back to the $S_0$ state as well as a nonradiative decay pathway to form the phenoxy radical.\textsuperscript{19,131–136} This is illustrated in Figure 4.3, which shows the potential energy curves for the ground state and first few excited states of gas-phase phenol taken from Dixon \textit{et al.}\textsuperscript{19} These states, therefore, play a crucial role in the photostability of biological systems containing the phenol motif.

While the role of the CI between the $1^1\pi^*\pi^*$ and $1^1\pi^*\sigma^*$ states has been well-studied in the gas-phase, there has been less experimental investigation on the en-
4.1. Introduction

Figure 4.3: Calculated potential energy surfaces for the $S_0$, $1^1\pi\pi^*(S_1)$, $1^1\pi\sigma^*(S_2)$, $2^1\pi\pi^*(S_3)$, and $2^1\pi\sigma^*(S_4)$ states of gas-phase phenol. Taken from Dixon et al.\textsuperscript{19}.

Energy of this conical intersection in aqueous solution. Oliver et al.\textsuperscript{137} used transient absorption spectroscopy to investigate the relaxation dynamics of aqueous phenol upon photoexcitation to the $1^1\pi\pi^*$ and $2^1\pi\pi^*$ states using 267 and 200 nm pump pulses, respectively. They found that the relaxation dynamics had vastly different timescales when populating the $1^1\pi\pi^*$ and $2^1\pi\pi^*$ states. Excitation into the $1^1\pi\pi^*$ state resulted in a decay on the order of nanoseconds due to populating below the $1^1\pi\pi^*/1^1\pi\sigma^*$ CI, followed by relaxation on the $1^1\pi\pi^*$ potential energy surface, and tunnelling through the energy barrier under the $1^1\pi\pi^*/1^1\pi\sigma^*$ CI to form phenoxy radicals. Excitation into the $2^1\pi\pi^*$ resulted in a femtosecond decay via autoionisation to form the phenol radical cation, followed by rapid deprotonation to form phenoxy radicals.

There has also been limited investigation into the photoionisation processes of aqueous phenol. Ghosh et al.\textsuperscript{23} used X-ray liquid-microjet photoelectron spectroscopy (LJ-PES) to record the vertical ionisation energies (VIEs) of the first two radical cation states, labelled D\textsubscript{0} and D\textsubscript{1}, of aqueous phenol, obtaining values of $7.8 \pm 0.1$ and $8.6 \pm 0.1$ eV for the D\textsubscript{0} and D\textsubscript{1} states respectively.\textsuperscript{23} Further studies of the first two ionisation states using UV resonance-enhanced multiphoton ionisation (REMPI) via the $1^1\pi\pi^*$ state obtained VIEs of $7.6 \pm 0.1$ eV\textsuperscript{20} and
Figure 4.4: a) Resonance-enhanced multiphoton ionisation PE spectra of phenol in gas-phase (black lines) and aqueous solution (blue lines) plotted as a function of $h\nu$–eKE on the bottom axis and $2h\nu$–eKE on the top axis; taken from Riley et al. Gray Gaussians represent $1\pi^\pi$–$D_0$ (I), $S_0$–$D_0$ (II), and $S_0$–$D_1$ (III) ionisation processes (I and III overlap in the 235.5 nm PE spectrum and are represented by just one Gaussian), and the blue Gaussian has been assigned to $e^-(aq) \rightarrow e^-(g)$. b) Resonance-enhanced two-photon ionisation of aqueous phenol using 267 nm; taken from Roy et al. The PE spectrum was best described using a superposition of two Gaussian functions, shown as dashed blue lines. The overall fit to the PE spectrum is shown as a red line. c) Resonance-enhanced multiphoton ionisation PE spectra of phenol in the gas-phase (black) and in aqueous solution (blue) recorded following photoexcitation at 275 nm (4.51 eV), 265.5 nm (4.67 eV), 253 nm (4.90 eV), 249.7 nm (4.97 eV) and 235.5 nm (5.26 eV), plotted as a function of one-photon eBE (lower axis); taken from Henley et al. Gaussians represent $S_1$ ($1\pi^\pi$)–$D_0$ (dark blue), $S_1$ ($1\pi^\pi$)–$D_1$ (orange), $S_0$–$D_0$ (light grey). Insets in the 265.5, 253 and 249.7 nm spectra are residuals of the fits of Gaussians to the low eBE edges of the PE spectra, corresponding to $S_0$–$D_0$. The $S_0$–$D_1$ ionisation process overlaps with the $S_1$ ($1\pi^\pi$)–$D_0$ process in the 235.5 nm PE spectrum (stripes).
4.1. Introduction

$8.0 \pm 0.1 \text{ eV}^{21,22}$ for ionisation to the $D_0$ state. The values obtained using REMPI are in relatively close agreement with the value obtained from the X-ray study, but are in relatively poor agreement with each other. As well as the poor agreement between the UV REMPI obtained VIEs, the number of Gaussian functions used to fit the PE spectra of aqueous phenol following photoexcitation to the first absorption band differed. The earlier work from our group$^{20}$ fit a single Gaussian function to the raw data from 249.7 – 275 nm, as shown in Figure 4.4a, while later work by Roy et al.$^{21}$ and within our group$^{22}$ fit the raw data to two Gaussian functions, as shown in Figure 4.4b and c, respectively.

As discussed in Section 2.3, recent literature highlighted the necessity to ensure that the work function of the instrument components around the ionisation region were the same.$^{98}$ As well as this, evidence has been published to suggest that species with enhanced surface concentration can cause a substantial shift to the observed electron kinetic energy distribution when in high concentrations.$^{97}$ Suzuki and co-workers measured the vertical binding energies (VBEs) of the $2^2P_{1/2}$ and $2^2P_{3/2}$ bands of $I^-$, and the $1b_1$ and $3a_1$ bands of liquid water using a table-top EUV laser by irradiating an aqueous solution of tetrabutylammonium iodide (TBAI). The concentration of TBAI was varied from 0 – 50 mM, and it was found that all the VBEs studied decreased by 0.6 – 1.0 eV with increasing TBAI concentration. Since aqueous phenol is known to have enhanced surface concentrations,$^{94}$ it is possible previous studies of the VIEs of aqueous phenol were affected by this eKE shift. This is due to aqueous phenol concentrations of 0.1 M being used in most previous studies. Finally, previous UV LJ-PES has been plagued by distortions to the photoelectron spectra from inelastic scattering of the generated photoelectrons. It is now possible to correct for these distortions by the development of a spectral retrieval method within our group that accounts for the inelastic scattering of photoelectrons,$^{12}$ as described in Section 1.3.3. To this end, there was a need to record previously measured aqueous phenol PES at different wavelengths to obtain accurate VIEs of aqueous phenol using improved experimental techniques.

The work in this chapter expands on previous studies of aqueous phenol within our group. Our improved experimental procedures are coupled with recently developed inelastic scattering correction methods within our group to record UV LJ-
PE spectra of aqueous phenol. A larger set of laser wavelengths than previously used was employed to investigate whether it was possible to observe solvent relaxation dynamics after photoexcitation to the $1^1\pi\pi^*$ state. Wavelengths were chosen to record PES of aqueous phenol using both resonance-enhanced multiphoton [1+1] ionisation (REMPI), where ionisation occurs via an intermediate state, and non-resonant multiphoton ionisation, where no intermediate state is involved. In principle, non-resonant ionisation using wavelengths longer than the onset of the first absorption band allows for a comparison with previous X-ray LJ-PES studies. Resonance-enhanced ionisation following photoexcitation across the first absorption band and in the dip between the first two absorption bands provides an insight into the ionisation processes and any relaxation processes involved when probing above and below the CI between the $1^1\pi\pi^*$ and $1^1\pi\sigma^*$ states. The wavelengths used in the experiments presented in this chapter are shown as arrows in Figure 4.2.

### 4.2 Methods

![Figure 4.5: Experimentally determined streaming potential measurements recorded as a function of the distance between the ionisation point and the liquid microjet. The data points (circles) are shaded such that the darker colours were collected earlier in the day, while the lighter colours were collected later in the day. The streaming potentials determined from each set of data points are shown as dashed curves. The streaming potentials obtained from the fits are between -0.01 and -0.06 eV. The vacuum level decreases from 2.78 to 2.70 eV over the course of the day.](image)

Solutions were prepared using ultrapure water, 0.1 mM of phenol and 1.75 mM of NaF. The concentration of phenol used is in the same concentration range that
Yamamoto et al. found had negligible effects on VBEs (0.1–1 mM). The latter was added to minimise the streaming potential. Figure 4.5 shows the streaming potential measurements recorded before, during and after collection of the PE spectra presented in this chapter. The data points are shaded such that the darker colours were collected earlier in the day, while the lighter colours were collected later in the day. The streaming potential measurements were recorded as follows; a streaming potential measurement was recorded, then two PE spectra of aqueous phenol using different wavelengths were collected, then another streaming potential measurement was recorded, then another two PE spectra of aqueous phenol using different wavelengths. This process continued until all the wavelengths were recorded, after which a final streaming potential measurement was recorded.

The error of the eKE values presented in this chapter was calculated the same way as described in Section 3.3.2. Briefly, the error in the eKEs is propagated by considering the errors of the laser pulse energy width ($\pm 0.02$ eV), time-of-flight to electron kinetic energy conversion (typically $\pm 0.03$ eV), streaming potential (typically $\pm 0.03$ eV), and the vacuum level offset between the jet stream and the analyser (typically $\pm 0.03$ eV). Two standard deviations of the output parameters from the spectral retrieval algorithm were also propagated in the error. The square root of the sum of squares of all the errors was used to calculate the total error of each value presented.

4.3 Results

Figure 4.6 shows the multiphoton ionisation PE spectra of aqueous phenol using 290, 285, 278.6, 272.5, 266.6, 249.7, 240 and 235 nm. To fit the PE spectra, the spectral retrieval code described in Section 1.3.3 was employed. Each PE spectrum was fit with Gaussian functions that were weighted with different concentration depth profiles, depending on whether the generated photoelectrons originated from aqueous phenol or from liquid water. Photoelectrons generated from aqueous phenol were fit using an exponential concentration depth profile, which has a mean concentration 0.5 nm below the water surface, due to the enhanced surface concentration observed with organic solutes, such as phenol, in water. Photoelectrons generated from liquid water were fit using a uniform concentration depth profile due to the assumption that photoelectrons can be generated throughout the liquid-
Figure 4.6: Multiphoton photoelectron spectra of aqueous phenol (black lines) together with the fits to the PE spectra using the spectral retrieval method (blue lines) and the corresponding retrieved Gaussian functions (solid and dashed red lines). Photoelectron spectra recorded using 290 nm and 285 nm laser wavelengths are non-resonant multiphoton ionisation spectra using wavelengths below/at the onset of the first absorption band of aqueous phenol (see Figure 4.2). Photoelectron spectra recorded using 278.6, 272.5, 266.6 and 249.7 nm are resonance-enhanced multiphoton ionisation spectra of aqueous phenol using wavelengths that probe across the first absorption band (see Figure 4.2). Photoelectron spectra recorded using 240 and 235 nm are resonance-enhanced multiphoton ionisation spectra of aqueous phenol using wavelengths in the absorption dip between the first and second absorption bands (see Figure 4.2). The fitted Gaussian functions are discussed in section 4.4. The residual of each fit is shown under the respective data set.
microjet. The choice of Gaussian functions employed to describe the PE spectra is discussed in detail in Section 4.4 below.

Figure 4.7 shows heat maps of the PE spectra presented in Figure 4.6. The PE spectra are plotted in the top plot of Figure 4.7 as eKE vs $h\nu$, with the laser wavelengths highlighted using vertical black dashed lines. The PE spectra are also plotted as a function of the one-photon (middle plot of Figure 4.7) and two-photon (bottom plot of Figure 4.7) eBEs, $h\nu$-eKE and $2h\nu$-eKE, respectively.

The one-photon eBEs were plotted as REMPI processes from the same intermediate state will produce a constant one-photon eBE. This is due to the conservation of excess vibrational energy, and can be explained using the following equation;

$$eKE = 2h\nu - D_0 - (h\nu - S_1)$$  \hspace{1cm} (4.1)

where $D_0$ is the AIE of the $D_0$ state, and $S_1$ is the adiabatic excitation energy (AEE) of the $1^1\pi\pi^*$ state. Equation 4.1 shows what the eKE is expected to be for a two-photon resonance-enhanced ionisation process, and assuming that the excess vibrational energy in $S_1$ ($h\nu - S_1$) that is generated upon photoexcitation is conserved during the ionisation process. Equation 4.1 can be simplified to;

$$eKE = h\nu - (D_0 - S_1)$$  \hspace{1cm} (4.2)

$$h\nu - eKE = D_0 - S_1$$  \hspace{1cm} (4.3)

which show that one-photon eBEs, $h\nu$-eKE, are constant when an intermediate state is involved in the photoionisation process, in this case $S_1$, if there is no relaxation of the solute or solvent during the ionisation process.

The two-photon eBEs were plotted as the non-resonant photoionisation wavelengths used in this chapter, 290 and 285 nm, can photoionise aqueous phenol using two photons. Since non-resonant ionisation processes will have limited excess vibrational energy since the molecule will be in the relaxed ground state, non-resonant ionisation processes will have a constant two-photon eBE. A comparison between non-resonant and resonant-enhanced ionisation processes with the inclusion of the excess vibrational energy in the eBE calculations is shown in Figure 4.8.
Figure 4.7: Heat maps of the multiphoton PE spectra of aqueous phenol presented in Figure 4.6. Top: eKE vs $h\nu$. Middle: $h\nu$-eKE vs $h\nu$. Bottom: $2h\nu$-eKE vs $h\nu$. Vertical black dashed lines represent the wavelengths used to record the PE spectra. Each PE spectrum in the heat map was normalised by the maximum photoelectron intensity value, with the maximum value equal to 1. The colours of the heat maps between the wavelengths were computed in OriginPro 2021 software, which uses a linear interpolation from a set of triangulated points to draw, connect, then subsequently smooth a set of contour lines. Horizontal white and grey solid lines represent the literature values for $D_0$ (7.8 eV) and $D_1$ (8.6 eV) VIEs.
Figure 4.8: Cartoon schematic energy level diagram with different types of multiphoton ionisation processes resulting in different eKE distributions. An example of non-resonant multiphoton ionisation is shown on the left energy level diagram, which involves the absorption of two photons ($h\nu_1$, black upward arrows) with no intermediate states to ionise into the $D_0$ continuum, with little to no excess vibrational energy being conserved upon photoionisation. The resulting eKE ($eKE_1$) is shown as a downward blue arrow. Examples of resonance-enhanced multiphoton ionisation are shown in the middle and right energy level diagrams, where photoexcitation of $S_1$ occurs via absorption of one photon ($h\nu_2/h\nu_3$, black upward arrows) with different excess vibrational energies (red, double-headed arrows). Upon photoionisation of $S_1$–$D_0$ using a second photon, the excess vibrational energy is conserved, resulting in eKEs ($eKE_2/eKE_3$, blue downward arrows) that are smaller in energy than if ionisation occurred to the adiabatic ionisation energy (AIE).

The eKE peak maxima, the full-width-half-maxima (FWHM) for each Gaussian function, and the $n$-photon binding energies, calculated using $n h\nu - eKE$, where $n$ is the number of photons in the ionisation process, of all the Gaussian functions in the PE spectra presented in Figure 4.6 are summarised in Table 4.1.

Individual peak assignments will be discussed as three regions of interest. First, the PE spectra recorded using wavelengths 290 and 285 nm, which are the wavelengths below/at the onset of the first absorption band of aqueous phenol, are considered. Second, the PE spectra recorded using wavelengths 278.6, 272.5, 266.6 and 249.7 nm, which are the wavelengths that photoexcite the first absorption band of aqueous phenol with increasing excess energy, are discussed. Finally, the PE spectra recorded using wavelengths 240 and 235 nm, which photoexcite into the
absorption dip between the first and second absorption bands of aqueous phenol, as well as probe near/above the $1^1\pi\pi^*/1^1\pi\sigma^*$ CI, are discussed.

**Table 4.1:** Maximum peak positions of the scattering-corrected Gaussian functions fit to the photoelectron spectra in Figures 4.9, 4.12 and 4.15, full width half maximum (FWHM) values of the scattering-corrected Gaussian functions, and the vertical ionisation energies (VIEs), calculated using $n\nu - eKE$, where $n$ is the number of photons in the ionisation process, and $eKE$ is the peak position. The method for calculating the experimental uncertainties is discussed in Section 3.3.2. FWHM values with no errors shown were found to have an error from the fit of $<0.01$ eV.

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<td>7.92 ± 0.09</td>
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### 4.4 Discussion

#### 4.4.1 Photoionisation of aqueous phenol using photon energies below/at the onset of the first absorption band

Figure 4.9 shows the photoelectron spectra of aqueous phenol recorded using 285 and 290 nm laser wavelengths. The laser wavelengths are below/at the onset of the first absorption band of aqueous phenol, as shown in Figure 4.2. As such, non-resonant photoionisation from the $S_0$ state of aqueous phenol is expected to dominate over resonance-enhanced photoionisation processes. Both plots show the PE spectra in black. For both 285 and 290 nm, the spectra were best described as a superposition of two Gaussian functions. The use of one Gaussian function...
Figure 4.9: Multiphoton photoelectron spectra of aqueous phenol following photoionisation with 285 and 290 nm. Black lines represent the PE spectra recorded and corrected for streaming potential and the vacuum level offset. Blue lines represent the fit to the PE data. Red lines represent the retrieved Gaussian functions after inelastic scattering correction from the fit to the PE data. The solid and dashed red lines represent multiphoton ionisation of aqueous phenol to the D$_0$ state and multiphoton ionisation of liquid water, respectively. The residual of each fit is shown under the respective data set.
Figure 4.10: Non-resonant multiphoton ionisation PE spectra of aqueous phenol using 285 nm (black lines) that have been described using a superposition of a) one, b) two, and c) three Gaussian functions (solid and dashed red lines). The fits to the PE spectra are shown as blue lines. For the one Gaussian fit, a surface Gaussian function (solid red line) was used. One surface Gaussian function and one/two bulk Gaussian functions (dashed red lines) were used in the two/three Gaussian function fits. The two Gaussian fit has been reproduced from Figure 4.9. The associated residuals are plotted below each PE spectrum.

poorly described the PE spectrum, while the use of three Gaussian functions resulted in two Gaussian functions with near-identical parameters, plus a Gaussian function that had eKEs >4 eV and amplitudes <0.01, which were non-physical and were a result of trying to overfit the PE spectra. An example of this is shown in Figure 4.10, which shows the 285 nm PE spectrum described using a superposition of one (Figure 4.10a), two (Figure 4.10b, reproduced from Figure 4.9), and three (Figure 4.10c) Gaussian functions using the spectral retrieval method.

For the 290 nm PE spectrum, the two Gaussian functions are fit using different concentration depth profiles. One Gaussian was fit using an exponential depth profile, designated a surface Gaussian, and the other Gaussian function was fit with a uniform concentration depth profile, designated a bulk Gaussian.

The eKEs of the Gaussians fitted using the spectral retrieval code were 0.77 ± 0.08 eV and 1.72 ± 0.10 eV for the surface and bulk Gaussians, respectively. For the surface Gaussian feature centered around 0.77 eV, the two-photon binding energy, calculated using $2\hbar\nu - \text{eKE}$, is $7.78 \pm 0.09$ eV. This is in excellent agreement with the $S_0-D_0$ VIE of aqueous phenol, determined using X-ray LJ-PES, with a value of $7.8 \pm 0.1$ eV. For the bulk Gaussian feature centered around 1.72 eV, this feature cannot be associated with non-resonant ionisation to the $D_1$ state of aqueous phenol as the total two-photon energy (8.55 eV) is just below the $S_0-D_1$ VIE at $8.6 \pm 0.1$ eV. If it were associated with the $S_0-D_1$ transition, the resulting
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The eKE distribution would have an eKE center lower than the eKE center of the surface Gaussian feature with eKE of 0.77 eV. This feature also cannot be associated with photoionisation of F\(^-\) from the NaF salt present in the solution to balance the streaming potential, as the literature vertical detachment energy of F\(^-\) obtained using X-ray LJ-PES is 11.58 eV.\(^{35}\) This is significantly higher than the three-photon eBE calculated for the feature centered around 1.72 eV, which is 11.11 ± 0.11 eV. The one-photon eBE, calculated using \(h\nu - \text{eKE}\), is 2.56 ± 0.10 eV, which is in agreement with the resonance-enhanced ionisation process of liquid water via the 3\(p\) Rydberg state discussed in Chapter 3. Therefore, it is likely the feature centered around 1.72 eV is photoionisation of liquid water.

To confirm these assignments, another experiment was performed to obtain an accurate background solvent spectrum to isolate the contributions from aqueous phenol and the solvent. Figure 4.11a shows both the 290 nm PE spectrum of aqueous phenol presented in Figure 4.9 in black, and a PE spectrum of aqueous NaF (1.75 mM) recorded at the same wavelength, shown in blue. To ensure the relative contributions from the background solution would be the same in both the background spectrum and the aqueous phenol spectrum, the laser power was kept at ∼0.19 µJ for both measurements. To isolate the aqueous phenol contribution to the overall PE spectrum, the solvent-only spectrum was subtracted from the aqueous phenol spectrum, to generate the black spectrum in Figure 4.11b. One surface Gaussian was fit to the spectrum, as the subtracted PE spectrum is expected to only contain photoelectrons generated from non-resonant ionisation from S\(_0\) to D\(_0\). The peak maximum of the retrieved fit, shown in Figure 4.11b as the red Gaussian, was 0.79 ± 0.08 eV. This gave a two-photon binding energy of 7.76 ± 0.09 eV, which is in excellent agreement with the S\(_0\)–D\(_0\) VIE for aqueous phenol without the background subtraction, 7.78 ± 0.09 eV, and with the literature value for the same VIE determined using X-ray LJ-PES, 7.8 ± 0.1 eV.\(^{23}\) From this, the lower eKE feature in the 290 nm spectrum can confidently be assigned to non-resonant two-photon ionisation of aqueous phenol from S\(_0\)–D\(_0\).

The measured 285 nm spectrum was also best described using two Gaussian functions, one with an exponential concentration depth profile and one with a uniform concentration depth profile. This is because 285 nm is at the onset of the
Figure 4.11: a) Multiphoton ionisation of aqueous phenol (black line) and liquid water (blue line) with the same salt concentration in both, and irradiated using 290 nm with the same laser power. b) Subtracted PE spectrum (black line) obtained by subtracting the two spectra in a. The dark blue line represents the fit to the PE spectrum. The red line represents the retrieved surface Gaussian function. c) Residual of the fit to the PE spectrum in b.
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first absorption band of aqueous phenol, so we expect a comparable set of non-resonant ionisation processes as observed in the 290 nm PE spectrum. The eKEs of the Gaussian functions fitted using the spectral retrieval method are 0.78 ± 0.08 and 1.94 ± 0.08 eV, for the surface and bulk Gaussian functions, respectively. For the surface Gaussian feature centered around 0.78 eV, the two photon eBE is 7.92 ± 0.09 eV, which is within error of the $S_0$–$D_0$ VIE of aqueous phenol obtained from the 290 nm PE spectrum (7.78 ± 0.09 eV) and the literature VIE determined using X-ray LJ-PES (7.8 ± 0.1 eV). The one-photon eBE for the feature centered around 1.94 eV in the 285 nm spectrum is 2.41 ± 0.08 eV, and is in agreement with the assigned liquid water feature in the 290 nm spectrum, 2.56 ± 0.10 eV, so is likely to also be photoionisation of liquid water. The relative area of the feature centered around 1.94 eV also decreases compared to the liquid water feature in the 290 nm spectrum. This corroborates the assignment that the feature centered around 1.94 eV is photoionisation of liquid water, as 285 nm is at the onset of the first absorption band of aqueous phenol. As such, aqueous phenol is likely to have a greater absorption cross-section at 285 nm than 290 nm, which would result in a relative lowering of amplitude of the liquid water feature. This further confirms that the feature centered around 1.94 eV is likely to be photoionisation of liquid water, analogous to the feature observed in the 290 nm spectrum.

4.4.2 Photoionisation of aqueous phenol using photon energies resonant with the first absorption band

Figure 4.12 shows the photoelectron spectra of aqueous phenol using 278.6, 272.5, 266.6 and 249.7 nm laser wavelengths. Laser wavelengths 278.6, 272.5 and 266.6 nm were chosen to photoexcite the three main features present across the first absorption band of aqueous phenol, while 249.7 nm was chosen as a convenient wavelength between the peak maximum of the first absorption band and the dip between the first and second absorption band that is the same wavelength used to record [2+1] REMPI of Xe for the streaming potential measurements (see Figure 4.2). All the wavelengths photoexcite aqueous phenol to the $1^1\pi\pi^*$ state ($S_1$), with increasing vibrational energy in $S_1$. As such, resonance-enhanced ionisation processes are now expected to dominate the photoelectron distributions originating from aqueous phenol over non-resonant ionisation processes.
Figure 4.12: Resonance-enhanced multiphoton PE spectra following photoionisation with (a) 278.6, (b) 272.5, (c) 266.6, and (d) 249.7 nm. Black lines represent the PE data recorded, and blue lines represent the fit to the PE data. Red lines represent the retrieved Gaussian functions obtained using the spectral retrieval method, with the solid and dashed red lines representing resonance-enhanced multiphoton ionisation of aqueous phenol to the D\(_0\) state via the \(1^1\pi\pi^* (S_1)\) state and multiphoton ionisation of liquid water, respectively. The residual of each fit is shown under the respective data set.

All the PE spectra shown in Figure 4.12 were best described as a superposition of two Gaussian functions, comparable to the 290 and 285 nm spectra. The use of one Gaussian function poorly described the overall PE spectra, but did describe the prominent feature centered between 0.5–1.0 eV found in all the PE spectra in Figure 4.12 reasonably well. An example of this is shown in Figure 4.13, which shows the 278.6 nm PE spectrum described using one surface Gaussian function, with the accompanying residual from the fit below the PE spectrum. The wavelengths used in Figure 4.12 are expected to generate photoelectrons by resonance-enhanced ionisation of aqueous phenol. It is highly likely the main feature, centered between
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Figure 4.13: Resonance-enhanced multiphoton ionisation PE spectrum of aqueous phenol using 278.6 nm (black line) described by one surface Gaussian function using the spectral retrieval method (red line). The fit to the PE spectrum is shown as a blue line. The residual of the fit is shown below the PE spectrum.

0.5–1.0 eV in all PE spectra presented in Figure 4.12, is associated with aqueous phenol for two reasons. Firstly, the total two-photon energy of all the wavelengths used in Figure 4.12 is greater than the $S_0$–$D_0$ ionisation of aqueous phenol. Secondly, the photoionisation cross-section for resonance-enhanced ionisation of aqueous phenol will be much greater than any ionisation process associated with liquid water. This is because liquid water would require three photons in either a non-resonant ionisation process or a [2+1] resonance-enhanced ionisation process for the wavelengths used in Figure 4.12, compared to the two-photon resonance-enhanced ionisation process of aqueous phenol. As such, this feature was described using a surface Gaussian function for the PE spectra using 278.6, 272.5, 266.6 and 249.7 nm.

Figure 4.12a shows the 278.6 nm PE spectrum of aqueous phenol. The eKEs of the Gaussians fitted using the spectral retrieval method were $0.73 \pm 0.08$ and $2.15 \pm 0.10$ eV, and were best fit using a surface and bulk Gaussian, respectively. The one-photon eBEs, calculated using $h\nu - eKE$, for the features were $3.72 \pm 0.08$ and $2.30 \pm 0.10$ eV, respectively. The feature centered around 0.73 eV is resonance-enhanced ionisation of aqueous phenol via $S_0$–$S_1$ photoexcitation. The two-photon eBE of the feature is $8.17 \pm 0.09$ eV, which is too low in energy to ionise to the $D_1$ state, which has a VIE of 8.6 eV. It is therefore likely that ionisation is occurring to the $D_0$ radical state. The one-photon eBE of the feature, 3.72 eV,
is higher than expected for the $S_1$–$D_0$ ionisation process, which is expected to be 3.32 eV using Equation 4.3, where $D_0$ is the $S_0$–$D_0$ ionisation energy taken from the 290 nm spectrum (7.78 eV) and $S_1$ is the AEE taken from Riley et al.20 (4.46 eV). This discrepancy will be discussed later alongside the other wavelengths presented in Figure 4.12.

The feature centered around 2.15 eV, shown as a red dashed line in Figure 4.12a, is likely to be a small contribution from liquid water, as the one-photon eBE (2.30 eV) is comparable with the one-photon eBEs for the assigned liquid water features calculated in the 285 and 290 nm spectra (Figure 4.9). The one-photon eBE, 2.30 eV, is also in excellent agreement with the values of the resonance-enhanced ionisation of liquid water via the $3p$ Rydberg state (Chapter 3 (2.25–2.34 eV)). The relative amplitudes between the two Gaussian features in the 278.6 nm spectrum also suggests that the bulk Gaussian feature centered around 2.15 eV is associated with liquid water and not aqueous phenol, as the only other ionisation process likely to occur at this wavelength is ionisation to the $D_1$ state. Using photoionisation cross-sections calculated by Riley et al.20, the peak areas for transitions to the $D_0$/D$_1$ states would be expected to have an approximate ratio of 3/1. It is clear from Figure 4.12a that the feature centered around 2.15 eV does not follow this ratio, with the relative amplitude much lower than the feature centered around 0.73 eV. Moreover, photoionisation to $D_1$ would produce a feature that has less eKE compared to the $D_0$ feature.

The 272.5 nm spectrum was found to be analogous to the 278.6 nm spectrum. Again, two Gaussian functions best described the measured 272.5 nm spectrum, shown in Figure 4.12b, with eKEs of $0.77 \pm 0.08$ and $2.32 \pm 0.13$ eV for a surface and bulk Gaussian function, respectively. The one-photon eBEs of the Gaussian functions fitted using the spectral retrieval method were $3.78 \pm 0.08$ and $2.23 \pm 0.13$ eV, respectively. Both of these features are within agreement of the features fit to the 278.6 nm, with the feature centered around 0.77 eV being consistent with the $S_1$–$D_0$ ionisation of aqueous phenol calculated using 278.6 nm (3.72 ± 0.08 eV), and the feature centered around 2.32 eV having a one-photon eBE (2.23 ± 0.13 eV) that is consistent with the one-photon eBE of the liquid water feature in the 278.6 nm (2.30 ± 0.10 eV). The relative amplitude of the feature
centered around 2.32 eV compared to the feature centered around 0.77 eV also decreases compared to the comparable features in the 278.6 nm spectrum. This would also suggest that the feature centered around 2.32 eV is ionisation of liquid water, as the photoabsorption cross-section of aqueous phenol increases going from 278.6 to 272.5 nm. As such, photoionisation features that do not originate from aqueous phenol would have a lower relative intensity in the 272.5 nm PE spectrum compared to the 278.6 nm PE spectrum, as is observed.

Figure 4.12c shows the 266.6 nm PE spectrum of aqueous phenol, and was again best described as a superposition of two Gaussian functions. Using the spectral retrieval method, the eKEs of the fitted Gaussian functions were 0.81 ± 0.08 and 2.50 ± 0.19 eV, and were fit using a surface Gaussian function and a bulk Gaussian function, respectively. The one-photon eBEs for the fitted Gaussian functions were 3.84 ± 0.08 and 2.15 ± 0.19 eV, respectively. The one-photon eBE of the feature centered around 0.81 eV is consistent with the $S_1$–$D_0$ ionisation process calculated in the 272.5 nm spectrum (3.78 ± 0.08 eV). As such, the feature centered around 0.81 eV can be assigned to the $S_1$–$D_0$ ionisation of aqueous phenol. The feature centered around 2.50 eV has a comparable one-photon eBE (2.15 ± 0.19 eV) to the one-photon eBEs of the liquid water ionisation features assigned in the 278.6 and 272.5 nm PE spectra, 2.30 ± 0.10 and 2.23 ± 0.13 eV, respectively. It is therefore likely that this feature is also resonance-enhanced ionisation of liquid water via the $3p$ Rydberg state.

The measured 249.7 nm spectrum of aqueous phenol, shown in Figure 4.12d, was also best described as a superposition of two Gaussian functions, with eKEs of the fitted Gaussian functions of 1.00 ± 0.08 and 2.76 ± 0.10 eV for a surface-fit and bulk-fit Gaussian function, respectively. The one-photon eBEs for the fitted Gaussians were 3.96 ± 0.08 and 2.21 ± 0.10 eV, respectively. The feature with a one-photon eBE of 2.21 eV is consistent with the one-photon eBEs of the assigned resonance-enhanced ionisation features of liquid water observed in the 278.6, 272.5 and 266.6 nm PE spectra. The other feature with a one-photon eBE of 3.96 eV seems to be consistent with the $S_1$–$D_0$ ionisation energy observed in the 278.6, 272.5 and 266.6 nm PE spectra of aqueous phenol, when taking into consideration the steady increase in one-photon eBE observed in the other three
Figure 4.14: Scatter plot showing the eKEs of different ionisation processes of phenol as a function of photon energy, with the equivalent wavelength plotted on the top axis. Closed black circles represent the resonant $S_1-D_0$ VIE of gas-phase phenol, taken from Riley et al.\textsuperscript{20}. Red line represents the calculated eKEs for the $S_1-D_0$ resonance-enhanced ionisation process under the assumption that excess vibrational energy is conserved upon photoionisation. This was calculated using Equation 4.2, where $S_1$ is the adiabatic excitation energy taken from Riley et al.\textsuperscript{20} (4.46 eV) and $D_0$ is the $S_0-D_0$ ionisation energy from the 290 nm PE spectrum, 7.78 eV. Open blue circles represent the measured non-resonant $S_0-D_0$ eKEs discussed earlier in this chapter. Closed blue circles represent the measured resonant $S_1-D_0$ eKEs discussed earlier in this chapter, with a linear fit to the data points with a gradient of 0.53 ± 0.04 shown as a blue line; see main text for further details. Shaded black and blue areas are the FWHM values for each measured gas-phase and aqueous phenol eKE, respectively.

resonant PE spectra. This shows that resonance-enhanced ionisation of aqueous phenol \textit{via} the $^1\pi\pi^*$ state ionises to the $D_0$ state exclusively, the same observations made by Riley et al.\textsuperscript{20} for both the gas-phase and aqueous phenol PE spectra (see Figure 4.4a). This is contrary to the observations made by Henley et al.\textsuperscript{22} and Roy \textit{et al.}\textsuperscript{21}, where resonance-enhanced ionisation of both $S_1-D_0$ and $S_1-D_1$ was identified (see Figure 4.4b and c). However, all the resonant PE spectra show a consistent rise in one-photon eBE for the $S_1-D_0$ ionisation process that is not expected for ionisation \textit{via} the same excited state. This observed increase in eBE, or reduced increase in eKE upon increasing photon energy, is shown in Figure 4.14.

Figure 4.14 shows the eKEs for the assigned $S_0-D_0$ (blue open circles) and $S_1-D_0$ (blue closed circles) eKEs of aqueous phenol as a function of photon energy (bottom axis)/wavelength (top axis). Literature values for the $S_1-D_0$ VIE of gas-
phase phenol taken from Riley et al. 20 are shown as closed black circles. As previously mentioned, the eBE of the measured aqueous phenol S1–D0 ionisation features shift with photon energy. The calculated eKE values for resonance-enhanced ionisation of aqueous phenol, S1–D0, calculated using Equation 4.2, where S1 is the adiabatic excitation energy of S0–S1 of aqueous phenol, taken from Riley et al. 20 (4.46 eV), and D0 is the S0–D0 ionisation energy obtained from the 290 nm PE spectrum, 7.78 eV, are shown in Figure 4.14 as the red line. In calculating these values, we assume that any excess vibrational energy in S1 will be conserved upon photoionisation. If this assumption were to hold true, the measured aqueous phenol data points in Figure 4.14 would produce a linear gradient of 1. This is because using Equation 4.2, which is reproduced below:

\[ eKE = h\nu - (D_0 - S_1) \]  

the eKEs can be fit to a linear fit, which using the equation for a straight line; \( y = mx + C \) where the eKE values are the y-values, and the photon energies, \( h\nu \), are the x-values. This would then equate the gradient, m, to 1 under these conditions. A gradient of 1 was observed for the resonant S1–D0 ionisation gas-phase phenol data points shown in Figure 4.14 from 4.65 to 4.97 eV, 20 but was not observed in the aqueous phenol resonant S1–D0 ionisation features from 4.45 to 4.97 eV, which produced a gradient of 0.53 ± 0.04. The fact that the measured aqueous phenol data points deviate from this trend of a gradient of 1 while the equivalent gas-phase measurements do not deviate suggests that the deviation from the expected values is associated with solvation dynamics affecting the aqueous phenol relaxation dynamics.

There has been significant investigation into the solvation dynamics of liquid water upon photoexcitation of a solute. A femtosecond fluorescence up-conversion spectroscopy study of coumarin-343 in aqueous solution found a multi-component solvation relaxation response, with a Gaussian component that was faster than 55 fs and accounted for > 50 % of the total decay, followed by two exponential components that decay with timescales of 126 and 880 fs. 138 Very preliminary work undertaken recently to record time-resolved photoelectron spectroscopy of aqueous solutions within our research group has recorded a pulse duration of >150 fs
for UV laser pulses. As such, the Gaussian component and first exponential component of liquid water solvation dynamics occur within the pulse duration of our experiment. If solute conditions alter the solvation relaxation timescales in some way in the aqueous phenol measurements, this could have a knock-on effect on the expected relaxation dynamics of the solute. This could further lead to photoexcited aqueous phenol being on a different point on the potential energy surface than expected, resulting in different Franck-Condon overlap upon photoionisation.

Literature studies on surfactant molecules have shown that the timescales of the exponential decay components of liquid water solvation can be drastically affected by surface-bound solutes.\textsuperscript{139,140} Given the surface-bound nature of phenol, it is possible that a similar scenario is occurring here, where phenol could be affecting the solvent dynamics and hindering vibrational relaxation that would occur from photoexcitation with excess energy, leading to a breakdown in the assumed VIE calculation.

More recently, there have been studies on the surface photochemical reactivity of aqueous phenol compared to that of the bulk.\textsuperscript{141,142} Kusaka \textit{et al.}\textsuperscript{141} used UV-excited time-resolved heterodyne-detected vibrational sum frequency generation to prepare electronically excited aqueous phenol using 267 nm pump pulses and broadband infrared probe pulses to investigate the OH and aromatic-CH vibrational modes of aqueous phenol and the OH vibrational modes of liquid water, all of which were measured between 2800 and 3800 cm\textsuperscript{−1}. Compared to previous photochemical reaction studies, which found that photoexcitation into the S\textsubscript{1} state below the S\textsubscript{1}/\textsubscript{1}π\textsigma\textsuperscript{*}(S\textsubscript{2}) CI decayed at a rate of \textapprox 5 ns,\textsuperscript{137} Kusaka \textit{et al.}\textsuperscript{141} found evidence of the phenoxy radical being generated within \textless 0.1 ps. This drastic increase in reaction rate could be present within the data recorded in this chapter, where either mixing between the S\textsubscript{1} and S\textsubscript{2} states is occurring, or the assigned D\textsubscript{0} ionisation via the S\textsubscript{1} state could in fact be ionisation to D\textsubscript{0} via the S\textsubscript{2} state. The measured increase in the one-photon eBEs of the S\textsubscript{1} state compared to the expected aqueous phenol eBE values would suggest that there could be some influence from the S\textsubscript{2} state, since photoionisation from the S\textsubscript{2} state would have different excess vibrational energy that would be conserved. Computational investigations of surface-bound aqueous phenol have shown that the extent of solvation, i.e. how many
water molecules are involved in the first solvation shell in total, can have a stabilisation effect on the crossing point energy of the $S_1/S_2$ CI.\textsuperscript{142} Ishiyama \textit{et al.}\textsuperscript{142} found that the fewer water molecules that were involved in the solvation of surface-bound aqueous phenol, the greater the stabilisation effect on the CI was. To disentangle the states involved in the resonance-enhanced ionisation of aqueous phenol via the first absorption band, the next step would be to exploit time-resolved photoelectron spectroscopy to track the excited state dynamics, as well as investigate computationally the extent with which aqueous phenol is solvated at the surface in LJ-PES experiments.

\section*{4.4.3 Photoionisation of aqueous phenol using wavelengths in the absorption dip between the first and second absorption bands}

Figure 4.15 shows the measured PE spectra of aqueous phenol using 240 and 235 nm, both of which photoexcite aqueous phenol between the first two absorption bands, as shown in Figure 4.2. The absorbance of aqueous phenol at 240 and 235 nm is low enough that at the experimental concentration of phenol, it is possible to have both non-resonant and resonant ionisation processes occurring.

The measured 240 nm spectrum was best described using a superposition of either two or three Gaussian functions. The 240 nm PE spectrum fit with two and three Gaussian functions is shown in Figure 4.16. However, the two Gaussian fit, as shown in Figure 4.15a, was the choice of fit for a number of reasons. The difference between the residuals of the two and three Gaussian fits is negligible, with both fits describing the measured PE spectrum extremely well. Both fits were fit using one surface Gaussian feature with an eKE of $1.22 \pm 0.08$ eV, and fit with either one or two other bulk features centered around $1.14 \pm 0.08$ eV, or $0.89 \pm 0.08$ and $2.18 \pm 0.08$ eV for the two and three Gaussian fits, respectively. All the bulk Gaussian functions shown are very broad, and in both fits there are Gaussian functions that entirely envelop other Gaussian functions, which are typically signs that the fit is bad. Since increasing the number of Gaussian functions used to fit the spectrum does not improve the overall fit, the lowest number of Gaussian functions required to adequately fit the measured PE spectrum with little residual was used.

To reiterate, the two fitted Gaussians using the spectral retrieval method had eKEs of $1.14 \pm 0.08$ and $1.22 \pm 0.08$ eV for a bulk and surface Gaussian function,
Figure 4.15: Resonance-enhanced multiphoton photoelectron spectra of aqueous phenol using a 240 and b 235 nm. Black lines represent the PE data recorded, and blue lines represent the fit to the PE data. Red lines represent the retrieved Gaussian functions from the fit to the PE data; see text for details. The residual of each fit is shown under the respective data set.
Figure 4.16: Resonance-enhanced multiphoton ionisation PE spectra of aqueous phenol using 285 nm (black lines) that have been described using a superposition a) two, and b) three Gaussian functions (solid and dashed red lines). The fits to the PE spectra are shown as blue lines. For the two Gaussian fit, one surface Gaussian function (solid red line) and one bulk Gaussian (dashed red line) was used. For the three Gaussian fit, one surface Gaussian function and two bulk Gaussian functions were used. The two Gaussian fit has been reproduced from Figure 4.15. The associated residuals are plotted below each PE spectrum.

respectively. The feature centered around $1.22 \pm 0.08$ eV has a one-photon eBE of $3.94 \pm 0.08$ eV, which is in excellent agreement with the one-photon eBE of the resonance-enhanced ionisation of aqueous phenol, $S_1-D_0$, in the 249.7 nm PE spectrum. This would suggest that the feature observed in the 240 nm spectrum is the same transition. It is also encouraging that both the two and three Gaussian fits retrieved this feature, as this allows for a more confident assignment, since irrespective of what is required to adequately describe the PE spectrum, this feature is always required.

Using 240 nm gives a total $2\nu$ energy of 10.33 eV. At this total photon energy, it is possible to populate a greater number of excited states in liquid water than discussed in Chapter 3, with at least four two-photon absorption processes possible between 9.7 and 10.6 eV.\textsuperscript{17,124} As such, the broad feature with an eKE peak maximum of $1.14 \pm 0.08$ eV is likely to be associated with multiple, overlapping resonance-enhanced multiphoton ionisation processes of liquid water, as well as possible non-resonant multiphoton ionisation of aqueous phenol. It is also possible that for the very low eKEs of $<0.5$ eV, there is some contribution to the PE spectrum from two-photon non-resonant ionisation of the $1b_1$ state of liquid water, which be-
gins to have significant photoelectron intensity in liquid water PE spectra recorded using X-ray LJ-PES when the eBE is \( \geq 10 \text{ eV} \). A more detailed investigation into the absorption processes of liquid water using this wavelength is therefore needed to disentangle the liquid water contributions. It could also be useful to use the same process of eliminating solvent contributions as used with the 290 nm PE spectrum discussed earlier to isolate photoelectrons generated from multiphoton ionisation of aqueous phenol.

The measured 235 nm PE spectrum was best described using a superposition of four Gaussian functions, presented in Figure 4.15b. The fitted Gaussians had eKEs of \( 0.25 \pm 0.08, 1.28 \pm 0.12, 2.47 \pm 0.19 \) and \( 2.92 \pm 0.25 \) eV. The feature centered around \( 1.28 \pm 0.12 \) eV was fit using a surface Gaussian function, and has a one-photon eBE of \( 4.00 \pm 0.12 \) eV. This is in very good agreement with the eBES associated with resonance-enhanced ionisation of aqueous phenol calculated in the 240 and 249.7 nm PE spectra, \( 3.96 \pm 0.08 \) and \( 3.94 \pm 0.08 \) eV, respectively.

Contrary to the eBES of the assigned \( S_1-D_0 \) ionisation processes observed when changing laser wavelength from 278.6 – 249.7 nm, the eBES of the \( S_1-D_0 \) resonance-enhanced ionisation of aqueous phenol using wavelengths \( \leq 249.7 \) nm show a trend that is more consistent with a resonance-enhanced ionisation process.

![Figure 4.17: Scatter plot showing the eKEs of resonance-enhanced ionisation of aqueous phenol (blue circles) as a function of photon energy, with the equivalent wavelength plotted on the top axis. Solid blue line represents a linear fit to the four data points with photon energy \( \leq 4.97 \) eV, with a gradient of \( 0.53 \pm 0.04 \), and the dashed, blue line represents a linear fit to the three data points with photon energy \( \geq 4.97 \) eV, with a gradient of \( 0.97 \pm 0.14 \).](image)
that conserves excess vibrational energy. This is highlighted in Figure 4.17, which shows the same measured $S_1-D_0$ eKEs of aqueous phenol from Figure 4.14 with the two extra assignments from the 235 and 240 nm spectra as blue circles. Figure 4.17 also shows two separate linear fits, one fit to the data points from $h\nu = 4.45$ up to and including 4.97 eV (solid blue line), which has a gradient of $0.53 \pm 0.04$ and a second fit to the data points from and including $h\nu = 4.97$ up to 5.28 eV with a gradient of $0.97 \pm 0.14$ (dashed blue line). The linear fit with a gradient of 0.53 represents a set of resonance-enhanced ionisation processes where excess vibrational energy is not completely conserved upon photoionisation, the same conclusion made earlier. The linear fit with a gradient of $0.97 \pm 0.14$ indicates a set of resonance-enhanced ionisation processes where excess vibrational energy is conserved. Since 249.7, 240 and 235 nm are below/at the onset of the second absorption band of aqueous phenol (see Figure 4.2), it is highly unlikely that the excited state associated with this absorption band is involved in the photoionisation process. As such, the only state that will be populated upon photoexcitation using the wavelengths $\leq 249.7$ nm used in this chapter is $S_1$. It is possible that the observed change in the behaviour of the $S_1-D_0$ ionisation processes using wavelengths $\leq 249.7$ nm could indicate the energy of the $S_1/S_2$ CI. If the dynamics on the $S_1$ potential energy surface are different when populating above/below the CI, this would likely be reflected in the measured eKEs. To investigate this further, it would be appropriate to use time-resolved PES to investigate the dynamics of photoexcited aqueous phenol using photon energies below, at, and above the crossing between the two linear fits in Figure 4.17 to see if there is a substantial difference in the excited state lifetimes. As substantial difference in the dynamics would further confirm that the CI is located at around the crossing point of the linear fits in Figure 4.17, with a relative energy of $\sim 5$ eV above $S_0$.

The feature centered around $0.25 \pm 0.08$ eV eKE in the 235 nm PE spectrum was fit using a bulk Gaussian function, and has a two-photon eBE of $10.30 \pm 0.09$ eV. Two photons of 235 nm give a total photon energy of 10.55 eV. At this total photon energy, there is significant photoelectron intensity for non-resonant ionisation of the $1\tilde{b}_1$ state of liquid water recorded using X-ray LJ-PES. The absorbance of aqueous phenol at 235 nm is very low (see Figure 4.2), which means
that it is possible that two-photon non-resonant ionisation of liquid water could be prominent in the PE spectrum. It is highly likely that the feature centered around 0.25 eV is non-resonant two-photon ionisation of the \(1b_1\) state of liquid water, ionising to a region between the AIE and VIE.

The one-photon eBE of the Gaussian feature centered around 2.92 eV eKE is \(2.36 \pm 0.25\) eV, which was also fit using a bulk Gaussian function. This is in good agreement with the eBEs of the assigned resonant-enhanced ionisation features via the \(3p\) Rydberg state calculated in all the previous aqueous phenol PE spectra, bar the 240 nm spectrum.

The feature centered around 2.47 eV eKE in the 235 nm PE spectrum, which was fit using a surface Gaussian function, is more complicated to assign. As with the 240 nm PE spectrum, there are multiple resonance-enhanced multiphoton ionisation processes of liquid water that could be accessed via two-photon absorption using a total photoexcitation energy of 10.55 eV. The feature centered around 2.47 eV has a one-photon eBE of \(2.81 \pm 0.19\) eV. Using the same logic applied in Chapter 3 to calculate the vertical excitation energy (VEE) by subtracting the one-photon eBE from the VIE, a VEE of \(10.28 \pm 0.19\) eV is obtained by subtracting the one-photon eBE of the Gaussian feature (2.81 eV) from the \(3a_1\) ionisation continuum VIE (13.09 eV). The obtained VEE is very close to absorption states identified previously, so could suggest that it is possible that photoexcitation from the \(3a_1\) state is occurring. By using the same logic to obtain the VEE and applying it to the \(D_0\) state of aqueous phenol, a VEE of \(4.97 \pm 0.19\) eV is obtained by subtracting the one-photon eBE (2.81 eV) from the \(S_0-D_0\) VIE (7.78 eV). This is in surprisingly good agreement with the crossing point of the two linear fits in Figure 4.17, which could suggest that this feature is associated with resonance-enhanced ionisation of aqueous phenol. Since a surface Gaussian function was used to obtain an eKE 2.47 eV, this might suggest that this feature should be associated with resonance-enhanced ionisation of aqueous phenol rather than liquid water. However, as previously stated, there are a number of states accessible in liquid water with two-photon absorption using 235 nm. Therefore, the use of a bulk Gaussian may also be applicable. To disentangle the liquid water photoelectron distributions from the aqueous phenol, it would be prudent to perform the same experiments
as the 290 nm PE spectrum, by taking a solvent-only background away from the 235 nm aqueous phenol PE spectrum.

One final feature of note can be observed in the residual of the 235 nm PE spectrum at \(\sim 2.7\) eV, which is present in all the 235 nm spectra recorded on the day of collection. The two-photon eBE of this feature would be \(\sim 7.85\) eV, which given that this feature is obtained prior to inelastic scattering correction, and eKE distributions originating from liquid surface species tend to shift by \(\sim 0.1\) eV after correcting for inelastic scattering,\(^{12}\) this feature would have a corrected eBE of \(\sim 7.75\) eV. This value is in excellent agreement with the \(S_0\)–\(D_0\) VIE of aqueous phenol calculated from the 290 nm aqueous phenol PE spectrum. As such, there could also be contributions from non-resonant multiphoton ionisation of aqueous phenol underpinning part of the features centered around 2.47 and 2.92 eV.\(^{143}\) As previously stated, a further study of liquid water at 235 nm would greatly aid in disentangling both the aqueous phenol and liquid water processes, as well as identifying the possible transitions in liquid water at this complex and interesting two-photon absorption region.

### 4.5 Conclusions and Outlooks

With the use of improved experimental procedures and the use of a recently developed inelastic scattering correction method, one-colour MPI PE spectra of aqueous phenol were recorded and analysed at a range of wavelengths. The \(S_0\)–\(D_0\) VIE of aqueous phenol was measured using non-resonant MPI, and was found to be \(7.78 \pm 0.09\) eV. This was in excellent agreement with the previously recorded \(S_0\)–\(D_0\) VIE of \(7.8 \pm 0.1\) eV using X-ray LJ-PES.

Contrary to some of the more recent measurements within our research group, resonance-enhanced ionisation of aqueous phenol using wavelengths resonant with the first absorption band found evidence of resonance-enhanced ionisation to the \(D_0\) state of aqueous phenol. This is contrary to some recent studies that found evidence of resonance-enhanced ionisation to both the \(D_0\) and \(D_1\) radical cation states. It is likely this discrepancy comes from the lack of inelastic scattering correction previously available, as well as the recent necessity found for PE spectra to be recorded under near-zero streaming potential conditions, as opposed to just correcting for any streaming potential present.
Alone the assignment of onl one ionisation feature in aqueous phenol, the resonan-enhanced $S_1-D_0$ ionisation energies shifted with increasing photon energy, contrary to what would be expected for a process where excess vibrational energy is conserved upon photoionisation. Due to this behaviour not being found in equivalent gas-phase PE spectra of phenol, it is likely this discrepancy comes from evidence of the reorganisation energy of the solvent affecting the relaxation dynamics of aqueous phenol. To confirm this assignment, it would be prudent to undertake time-resolved studies at a series of wavelengths as a means of checking whether it is the reorganisation energy affecting the eKE peak maximum. Further investigation on the reorganisation energy of aqueous solutions using computational studies would also greatly benefit the experimentally observed features.

For the wavelengths in the absorption dip between the first and second absorption band of aqueous phenol, the absorbance is low enough to have significant contributions from liquid water in the overall PE spectra. There was evidence found for ionisation of aqueous phenol from $S_1$ to $D_0$ as well as possible evidence for non-resonant multiphoton ionisation of aqueous phenol to $D_0$. Evidence was also found for non-resonant multiphoton ionisation into the $1b_1$ ionisation continuum of liquid water, as well as resonance-enhanced multiphoton ionisation via states not identified in the study of liquid water in Chapter 3, which only investigated liquid water using wavelengths $\geq 272.5$ nm. Further investigation into the two-photon absorption states of liquid water is therefore needed to identify exact nature of states, since the number of accessible states that overlap at two-photon absorption energies of $\geq 10$ eV are numerous and difficult to identify when not investigated in isolation. It would also be beneficial to expand on the wavelengths used in Chapter 3 to include all the wavelengths used in this chapter. This would allow the same subtraction procedure used in Figure 4.11 to be applied to all the wavelengths, which would particularly help disentangle the water features from the aqueous phenol features in wavelengths where water features also dominate.
Chapter 5

Photoelectron spectroscopy of thymine in aqueous solution

Thymine is an important molecule in biology, but there have been very few studies into the first few vertical ionisation energies. In comparison, the excited states have been studied extensively, albeit with a lack of consensus on the relaxation dynamics following photoexcitation to the first excited state of aqueous thymine. The work described in this chapter uses liquid-microjet photoelectron spectroscopy to investigate the vertical ionisation energies of aqueous thymine and the identity of the excited states involved in the early relaxation dynamics.

5.1 Introduction

Thymine is one of the four DNA nucleobases, and as such plays a vital role in biology by establishing the genetic code of all living organisms. The DNA nucleobases are known to be very stable upon irradiation, which has previously been attributed to efficient relaxation dynamics upon photoexcitation. It is also possible, however, for deleterious effects to occur upon photoexcitation of UV light, resulting in genotoxic and cytotoxic effects. Understanding the electronic structure of thymine is therefore the first step in understanding its relaxation dynamics.

There have been very few studies determining the vertical ionisation energies (VIEs) of aqueous thymine, with the only experimental study investigating the VIEs directly being in 2011, employing X-ray liquid-microjet photoelectron spectroscopy (LJ-PES). On the other hand, the VIEs of gas-phase thymine have been well-studied previously, with values of 9.14 – 9.20 and 10.03 – 10.14 eV for the $D_0$ ($\pi^{-1}$) and $D_1$ ($\eta^{-1}$) radical states, respectively. Microsolvation of thymine has also
been thoroughly investigated experimentally and computationally, with a general trend of the first VIE decreasing by 0.5 –0.9 eV upon addition of multiple water molecules.\textsuperscript{151,153–156}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_1.png}
\caption{Left: UV/Vis spectrum of 1 mM aqueous thymine and 1 mM aqueous NaF. Arrows mark the laser wavelengths used for the work described in this chapter. Right: Molecular structure of thymine with atom labelling of all atoms excluding hydrogen.}
\end{figure}

Compared to the limited study of the VIEs of aqueous thymine, the excited states of thymine have been studied extensively, both in the gas-phase and in aqueous solution. It has been shown that the two lowest electronically excited singlet states, $n\pi^*$ and $\pi\pi^*$, have vertical excitation energies in the gas-phase that are very close in energy.\textsuperscript{157,158} Upon solvation, the $\pi\pi^*$ state has been shown to stabilise by 0.2-0.3 eV relative to the gas-phase, while the $n\pi^*$ state is increased by a comparable energy shift. This sufficiently separates the two states such that the $\pi\pi^*$ state becomes the lowest-lying excited state and the $n\pi^*$ state is higher-lying at the Franck-Condon region.\textsuperscript{158,159} Previous transient absorption spectroscopy and LJ-PES investigations into the relaxation dynamics of aqueous thymine have shown that there are multiple relaxation pathways available following photoexcitation to the optically bright $\pi\pi^*$ state, which will be designated $S_1$ henceforth. There are three postulated competing reaction pathways previously described in the literature;\textsuperscript{160} relaxation from $S_1$ to $S_0$, that involves twisting along the C5-C6 double bond, relaxation from $S_1$ to $S_0$, involving an out-of-plane displacement of the C4-O8 double bond, and internal conversion from $S_1$ to the $n\pi^*$ state, referred to as $S_2$ from now on.
5.2 Methods

Figure 5.2: a: Decay associated photoelectron spectra of aqueous thymine of the three spectral contributions to the global fit of a set of time-resolved PE spectra recorded using LJ-PES with 4.66/5.2 eV pump/probe pulses; taken from Buchner et al.\textsuperscript{24} b: Select lineouts from a set of time-resolved PE spectra of aqueous thymine recorded using LJ-PES with 5.17/6.20 eV pump/probe pulses; taken from Erickson et al.\textsuperscript{25}

on, and then relaxation to the ground S\textsubscript{0} state. The atom labelling used here is shown in Figure 5.1. Previous time-resolved LJ-PES studies using 4.66/5.2 eV\textsuperscript{24} and 4.74–5.17/6.20 eV\textsuperscript{25} pump/probe laser pulses finding evidence of both relaxation pathways involving exclusively the S\textsubscript{1} state, but a lack of any evidence of internal conversion to the S\textsubscript{2} state. However, recent transient absorption spectroscopy studies using <10 fs UV probe pulses ranging from 255–290 nm found evidence of relaxation to the S\textsubscript{2} state within 100 fs.\textsuperscript{26} The involvement of the n\pi\textsuperscript{*} state is still disputed within the literature, as such, there is still debate pertaining to the identities of the excited states involved in the ultrafast relaxation dynamics of aqueous thymine.

Here, static UV LJ-PES measurements were used to investigate both the VIEs of the D\textsubscript{0} and D\textsubscript{1} states of aqueous thymine, and also identify the excited states involved in the early relaxation dynamics. Figure 5.1 shows the absorption spectrum of aqueous thymine in the UV-Vis region, with the excitation wavelengths used throughout this chapter shown as arrows above the spectrum.

5.2 Methods

Solutions were prepared using ultrapure water, 1.0 mM of thymine and 1.0 mM of NaF. The latter was added to minimise the streaming potential. Figure 5.3 shows the streaming potential measurements recorded before and after collection of the
Figure 5.3: Streaming potential measurements recorded before (closed circles) and after (open circles) the PE spectra shown in Figure 5.4. The black data set is associated with the PE spectra recorded following photoionisation using 280, 285 and 300 nm, and the blue data set is associated with the PE spectrum recorded following photoionisation using 265 nm. Streaming potential data points were fit using the Equation 2.3 described in Chapter 2.

PE spectra presented in this chapter. The closed circle data points collected before the PE spectra were recorded, while the open circle data points were collected after the PE spectra were recorded. The average streaming potentials for the black and blue data sets shown in Figure 5.3 are 0.00 ± 0.02 and 0.04 ± 0.03 eV, respectively. The average vacuum level values for the black and blue data sets shown in Figure 5.3 are 2.81 ± 0.05 and 2.87 ± 0.06 eV, respectively.

The error of the values presented in this chapter was calculated the same way as described in Section 3.3.2. Briefly, the error is propagated by taking the errors of the laser pulse energy width, time-of-flight to electron kinetic energy conversion, instrument function, streaming potential, and the vacuum level offset between the jet stream and the analyser. Two standard deviations of the output parameters from the spectral retrieval algorithm were also propagated in the error. The square root of the sum of squares of all the errors was used to calculate the total error of each value presented.

5.3 Results

Figure 5.4 shows the multiphoton ionisation PE spectra of aqueous thymine recorded using 305 (a), 285 (b), 280 (c) and 265 nm (d). Wavelengths of tuneable laser pulses were chosen to achieve photoexcitation at different energies on the $S_0 \rightarrow S_1$ transition: below the absorption onset (305 nm), on the low energy edge of the absorption band (280 and 285 nm), and at the absorption maximum (265...
5.3. Results

Figure 5.4: Multiphoton photoelectron spectra of aqueous thymine (1 mM) following multiphoton photoionisation with (a) 305, (b) 285, (c) 280 and (d) 265 nm. The PE spectrum recorded using 305 nm is a non-resonant multiphoton ionisation spectra of aqueous thymine, as 305 nm is below the onset of the first absorption band of aqueous thymine (see Figure 5.1). PE spectra recorded using 285, 280 and 265 nm laser wavelengths are resonance-enhanced ionisation spectra of aqueous thymine, photoexciting into the first absorption band of aqueous thymine with increasing vibrational energy. Black lines represent the PE data recorded. Blue lines represent the fits to the PE data. Solid, red lines represent the retrieved Gaussian functions associated with photoionisation of aqueous thymine, and dashed, red lines represent the retrieved Gaussian functions associated with photoionisation of liquid water; see main text for details.
nm) of aqueous thymine. Photoionisation using 305 nm will result in non-resonant ionisation of aqueous thymine, while resonance-enhanced ionisation of aqueous thymine will occur when using 285, 280 and 265 nm.

The differences between the electron binding energies (eBEs) associated with non-resonant and resonance-enhanced ionisation processes have been discussed in Chapters 3 and 4. However, a summary will be included here for completeness. For non-resonant multiphoton ionisation, it is expected that the binding energy will be constant when calculated using the following equation;

\[ \text{eBE} = nh\nu - \text{eKE} \] (5.1)

where eBE is the electron binding energy, eKE is the electron kinetic energy, and \( nh\nu \) is the number of photons, \( n \), required to promote the electron above the ionisation threshold. When increasing the photon energy, this will in turn increase the electron kinetic energy.

In the gas-phase, resonance-enhanced ionisation processes from the same intermediate state are expected to produce constant one-photon eBEs for liquid water and aqueous thymine. This is because there is a propensity for any excess vibrational energy generated in the intermediate state upon photoexcitation is conserved during the photoionisation process. The eKE can therefore be explained by the following equation;

\[ \text{eKE} = 2h\nu - \text{AIE} - (h\nu - \text{AEE}) \] (5.2)

where AIE is the adiabatic ionisation energy of the final state and AEE is the adiabatic excitation energy of the intermediate state. This can be rearranged to the following equations;

\[ \text{eKE} = h\nu - (\text{AIE} - \text{AEE}) \] (5.3)

\[ h\nu - \text{eKE} = \text{AIE} - \text{AEE} \] (5.4)

which show that the one photon eBE, \( h\nu - \text{eKE} \), should be constant for resonance-enhanced ionisation processes.

To extract true PE spectra from the measured PE spectra, the spectral re-
5.3. Results

Each PE spectrum was fit with Gaussian functions that were weighted with different concentration depth profiles, depending on whether the generated photoelectrons originated from aqueous thymine or from liquid water. Photoelectrons generated from aqueous thymine were fit using an exponential concentration depth profile, and are designated surface Gaussian functions. The exponential function is assumed to have a mean concentration 0.5 nm below the water surface, similar to that determined for phenol. This is due to the enhanced surface concentration observed with organic solutes in water. This was the same concentration depth profile as used for aqueous phenol in Chapter 4. Photoelectrons generated from liquid water were fit using a uniform concentration depth profile due to the assumption that photoelectrons can be generated throughout the liquid-microjet, and are designated bulk Gaussian functions. This was the same as the liquid water features assigned in Chapters 3 and 4. The choice of Gaussian functions employed to describe the PE spectra is discussed below, and the eKEs, full-width-half-maxima, and eBEs for each Gaussian function are listed in Table 5.1.

Table 5.1: Maximum peak positions of the scattering-corrected Gaussian function fits to the photoelectron spectra in Fig. 5.4, full width half maximum (FWHM) values of the scattering-corrected Gaussian functions, and the vertical ionisation energies (VIEs) corresponding to the centres of each Gaussian function, calculated using $n\nu - \text{eKE}$, where $n$ is the number of photons involved in the ionisation process, and eKE is the peak position.

<table>
<thead>
<tr>
<th>Wavelength / nm (eV)</th>
<th>Peak eKE / eV</th>
<th>FWHM / eV</th>
<th>$n$</th>
<th>$n\nu - \text{eKE} / \text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>305 (4.06)</td>
<td>0.93 ± 0.08</td>
<td>0.78 ± 0.06</td>
<td>1</td>
<td>3.13 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>1.48 ± 0.17</td>
<td>1.20 ± 0.08</td>
<td>1</td>
<td>2.58 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>3.03 ± 0.13</td>
<td>1.22 ± 0.34</td>
<td>3</td>
<td>9.17 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>3.87 ± 0.13</td>
<td>1.99 ± 0.46</td>
<td>3</td>
<td>8.32 ± 0.15</td>
</tr>
<tr>
<td>285 (4.35)</td>
<td>0.49 ± 0.08</td>
<td>0.37 ± 0.07</td>
<td>1</td>
<td>3.86 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>0.71 ± 0.08</td>
<td>0.54 ± 0.08</td>
<td>1</td>
<td>3.64 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>1.58 ± 0.21</td>
<td>2.03 ± 0.18</td>
<td>1</td>
<td>2.77 ± 0.21</td>
</tr>
<tr>
<td>280 (4.43)</td>
<td>0.55 ± 0.11</td>
<td>0.46 ± 0.10</td>
<td>1</td>
<td>3.88 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>0.77 ± 0.11</td>
<td>0.58 ± 0.11</td>
<td>1</td>
<td>3.66 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>1.74 ± 0.37</td>
<td>2.03 ± 0.33</td>
<td>1</td>
<td>2.69 ± 0.37</td>
</tr>
<tr>
<td>265 (4.68)</td>
<td>0.44 ± 0.08</td>
<td>0.24 ± 0.04</td>
<td>1</td>
<td>4.24 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>0.64 ± 0.09</td>
<td>0.39 ± 0.10</td>
<td>1</td>
<td>4.04 ± 0.09</td>
</tr>
<tr>
<td></td>
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<td>0.58 ± 0.10</td>
<td>1</td>
<td>3.80 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>1.72 ± 0.21</td>
<td>1.78 ± 0.76</td>
<td>1</td>
<td>2.96 ± 0.21</td>
</tr>
</tbody>
</table>
5.4 Discussion

Figure 5.4a shows the PE spectrum of aqueous thymine recorded using 305 nm. The PE spectrum was best described using a superposition of four Gaussian functions, two surface Gaussians (solid red Gaussians) and two bulk Gaussians (dashed red Gaussians).

Figure 5.5 shows the 305 nm PE spectrum of aqueous thymine and the fits of 1 – 4 Gaussian functions using the spectral retrieval code. Figure 5.5a shows the 305 nm PE spectrum of aqueous thymine and the fit from the spectral retrieval code using one Gaussian function, and poorly describes the prominent feature centered around 1 eV. Figure 5.5b shows the 305 nm PE spectrum of aqueous thymine and the fit from the spectral retrieval code using a superposition of two Gaussian functions. While the use of two Gaussian functions adequately describes the prominent feature centered at 1 eV, it does not describe the high energy portion of the photoelectron distribution from eKEs >2.5 eV, highlighted in the inset of Figure 5.5b. Figure 5.5c shows the 305 nm PE spectrum of aqueous thymine and the fit from the spectral retrieval code using a superposition of three Gaussian functions. As shown in the inset of Figure 5.5c, a third Gaussian function is insufficient to adequately describe the photoelectron distribution for eKEs >2.5 eV. Therefore, a superposition of four Gaussian functions is needed to adequately describe the total PE distribution of aqueous thymine using 305 nm, as shown in Figure 5.5d (the same PE spectrum as shown in Figure 5.4a) and the inset of Figure 5.5d.

The eKEs of the bulk Gaussians fitted using the spectral retrieval method were 0.93 ± 0.08 and 1.48 ± 0.17. The one-photon eBEs of the features centered around 0.93 and 1.48 eV are 3.13 ± 0.08 and 2.58 ± 0.17, respectively. These one-photon eBEs are consistent with the two bulk Gaussian features observed in Chapter 3 associated with resonance-enhanced multiphoton ionisation of liquid water via the 1\(^1\)B\(_1\) and 3\(p\) Rydberg states for the one-photon eBEs centered around 3.13 and 2.58 eV, respectively. The FWHM values are also in close agreement. Using photons of 305 nm, the total two-photon energy (8.13 eV) is only 0.03 eV above the first VIE of aqueous thymine (8.1 eV\(^{147}\)), therefore making the observation of direct two-photon ionisation of aqueous thymine highly unlikely. Given the eKEs are 0.93 and 1.48 eV for the bulk Gaussian features, these are too high in energy to be as-
5.4. Discussion

Figure 5.5: Non-resonant multiphoton ionisation spectra of aqueous thymine using 305 nm (black lines) fit with either one Gaussian function (a, blue line) or a superposition of two (b, blue lines), three (c, blue lines) or four Gaussian functions (d, blue lines) using the spectral retrieval code. The spectra shown in the inset of b, c and d highlight the high eKE tail with eKEs > 2.5 eV; see main text for details.

Associated with two-photon non-resonant ionisation of aqueous thymine, and with a one-photon energy of 4.06 eV, are too low in energy to be associated with three-photon non-resonant ionisation of aqueous thymine. Therefore, these features can be assigned to ionisation of liquid water.

Figure 5.4a also shows two surface Gaussian features, with intensities multiplied by 10 to aid in observing the assigned features. The eKEs of the surface Gaussians fitted using the spectra retrieval method were 3.03 ± 0.13 and 3.87 ± 0.13 eV. The drastic difference in relative intensity between the bulk features centered around 0.93 and 1.48 eV compared to these surface Gaussian features centered around 3.03 and 3.87 eV suggests that the surface Gaussian features are not associated with ionisation of liquid water. As such, the observed features with peak maxima of 3.03 and 3.87 eV are likely to originate from non-resonant multiphoton ionisation of aqueous thymine. As mentioned when discussing the assignment of the two bulk Gaussian features, the total energy of two 305 nm photons is 8.13 eV, which would generate a PE distribution centered around 0.03 eV.
Figure 5.6: Non-resonant time-of-flight spectra of aqueous thymine using 305 nm (a and c) and liquid water using 300 nm (b and d). c and d highlight the low ToF edge of the ToF spectra shown in a and b, respectively.

using the literature VIE of aqueous thymine (8.1 eV\textsuperscript{147}). Non-resonant ionisation of aqueous thymine is also expected using 305 nm as it is below the onset of the first absorption band (see Figure 5.1). As such, non-resonant three-photon ionisation of aqueous thymine is the most likely process, which corroborates with the observed disparity between the photoelectron intensities of the two surface Gaussian features compared to the two bulk Gaussian features for two reasons. Firstly, the ionisation cross-section of a three-photon process is significantly lower than the ionisation cross-section of the [2+1] resonance-enhanced ionisation of liquid water. Secondly, the likelihood of ionisation of aqueous thymine (1 mM) is substantially less compared to liquid water (∼56 M) due to the large concentration difference that has a more profound effect than observed with resonant wavelengths due to the lack of resonance-enhancement of aqueous thymine.

Figure 5.6 also aids in the assignment of the two surface Gaussian features. Figure 5.6a shows the PE spectrum of aqueous thymine using 305 nm as a function of time-of-flight (ToF), which is how the spectra are collected, with Figure 5.6c showing the same PE spectrum focusing on the lower ToF edge of the distribution. Due to the inverse relationship between ToF and eKE, lower ToF corresponds
to higher eKE. Figure 5.6b shows the PE spectrum of liquid water using 300 nm as a function of ToF. This ToF PE spectrum when transformed into eKE is the same 300 nm spectrum presented in Figure 3.3d in Chapter 3. Figure 5.6d shows the same PE spectrum as Figure 5.6b focusing on the same ToF and normalised intensity region as Figure 5.6c. The origin of the small shoulder in Figure 5.6d is from background electrons. When comparing Figure 5.6c to Figure 5.6d, it is clear there are extra photoelectrons generated between 450 and 550 ns. The additional photoelectrons generated were distinctive during collection of the PE spectra, and since Figure 5.6d is the PE spectrum of liquid water, this lead to the assignment that these additional photoelectrons originated from non-resonant ionisation of aqueous thymine.

The surface Gaussian features centered around 3.87 and 3.03 eV have three-photon eBEs of 8.32 ± 0.15 and 9.17 ± 0.15 eV, respectively. The three-photon eBE of 8.32 eV is in relatively close agreement with an earlier experimental value for the D\textsubscript{0} state of aqueous thymine of 8.1 ± 0.1 eV\textsuperscript{147} determined using X-ray LJ-PES with very low signal-to-noise, and is in excellent agreement with previous computed values of ∼8.3 eV\textsuperscript{155} and 8.27 ± 0.08 eV.\textsuperscript{161} The feature with a three-photon eBE of 9.17 ± 0.15 eV is likely to be ionisation to the D\textsubscript{1} state of aqueous thymine, given the comparable photoelectron intensity to the D\textsubscript{0} state and the eKE value, but is lower than previous experimental (9.6 ± 0.1 eV\textsuperscript{147}) and computational (9.5 eV\textsuperscript{155}) values. The reduction in eBE compared to the literature values may be due to slight overlap with the liquid water features, resulting in a fit that does not describe all the photoelectrons generated from aqueous thymine.

Figure 5.4b shows the resonance-enhanced PE spectrum of aqueous thymine following photoexcitation using 285 nm. The PE spectrum was best described as a superposition of three Gaussian functions, two surface Gaussian functions and one bulk Gaussian function. Figure 5.7 shows the 285 nm PE spectrum of aqueous thymine and the fits from the spectral retrieval code using either one Gaussian function (Figure 5.7a) or a superposition of two Gaussian functions (Figure 5.7b). As shown by the residuals of both fits, one and two Gaussian functions do not adequately describe the measured PE spectrum.

The eKEs of the Gaussians fitted using the spectral retrieval code were
Figure 5.7: Resonance-enhanced multiphoton ionisation spectra of aqueous thymine using 285 nm (black lines) fit with either one Gaussian function (a, blue line) or a superposition of two Gaussian functions (b, blue line) using the spectral retrieval code. The residuals of the fits are shown below the respective PE spectrum.

0.49 ± 0.08, 0.71 ± 0.08 and 1.58 ± 0.21 eV for the two surface Gaussians and bulk Gaussian, respectively. At 285 nm, the total photon energy of two 285 nm photons is 8.7 eV, and is resonant with the first absorption band of aqueous thymine (see Figure 5.1). This means that, since the total photon energy is 0.38 eV above the first VIE of aqueous thymine assigned using the 305 nm spectrum (8.32 eV), resonance-enhanced two-photon ionisation of aqueous thymine is expected to be the more likely process using 285 nm compared to non-resonant three-photon ionisation using 305 nm. The broad feature centered around 1.58 eV has a two-photon eBE of 7.12 ± 0.22 eV, which is too low to be attributed to aqueous thymine. As such, the feature is most likely to be ionisation of liquid water. The feature also has a three-photon eBE of 11.47 ± 0.22 eV, which is consistent with the VIE for the \(1b_1\) state of liquid water, and much too high in energy to be associated with non-resonant three-photon ionisation of aqueous thymine.

The surface Gaussian feature centered around 0.71 eV has a one-photon eBE of 3.64 ± 0.08 eV. Given the propensity for excess vibrational energy to be conserved upon photoionisation, and the likelihood for resonance-enhanced ionisation of aqueous thymine to dominate the PE spectrum at this wavelength compared to the three-photon ionisation of liquid water, this feature can be assigned to resonance-enhanced ionisation of \(D_0\) via photoexcitation of \(S_1\) of aqueous thymine.
The feature with a peak maximum of $0.49 \pm 0.08$ eV has a one-photon eBE of $3.86 \pm 0.08$ eV and a two-photon eBE of $8.21 \pm 0.09$ eV. Given the two-photon eBE value is in close agreement with the first VIE of $8.32$ eV, it is likely this process is a second ionisation process of aqueous thymine. It is possible that this second ionisation process could be due to a second resonant ionisation process, or could be due to the observation of both resonant and non-resonant ionisation of aqueous thymine.$^{143}$

A previous LJ-PES study of aqueous thymine by Buchner et al.$^{24}$ performed TR studies of aqueous thymine using a 266 nm pump and 238 nm probe pulse, during which they found two components contributing to the decay of the PE signal, with time constants of $70 \pm 10$ and $410 \pm 40$ fs. The average kinetic energies of the decay associated spectra linked to the time constants were 1.42 and 1.26 eV for the shorter and longer time constants, respectively, as shown in Figure 5.2a. The two decays were associated with relaxation on the $S_1$ potential energy surface towards two conical intersections (CI) that crossed with the $S_0$ potential energy surface, the shorter timescale was proposed to involve twisting along the C5-C6 double bond, and the longer timescale was proposed to involve an out-of-plane displacement of the C4-O8 double bond. The difference between the average kinetic energies was $0.16$ eV, which is a comparable difference to the peak maxima of the two assigned thymine features in the 285 nm spectrum, which has a difference of $0.22$ eV. This would suggest that the two decay channels are distinct enough to produce two separate ionisation pathways, and the second aqueous thymine feature with a one-photon eBE of $3.86$ eV is a resonant ionisation process, rather than a non-resonant ionisation process.

Xue et al.$^{26}$ describe the generation of a “deformed state” from the distortions involved with the $S_1$ decay pathways. This is a transient stable state generated after photoexcitation to the $S_1$ state that is lower in energy than the Franck-Condon region, as shown in Figure 5.8, which is reproduced from Xue et al.$^{26}$ These results suggest that the two Gaussian functions in our data (Figure 5.4b) are related to two different relaxation pathways on the $S_1$ potential energy surface that are distinct enough to generate separate PE distributions from resonance-enhanced ionisation of aqueous thymine.
Figure 5.8: Schematic potential energy diagram of the different relaxation processes involved upon photoexcitation to the $\pi\pi^*$ state of aqueous thymine; taken from Xue et al.\textsuperscript{26} Cl\textsubscript{1} and C1\textsubscript{2} are conical intersections, and $q_0$, $q_1$, $q_2$ and $q_{2d}$ are the potential curve minima of the designated $S_0$, $S_1$, $S_2$ and $S_{2d}$ states, respectively.

A comparable set of processes are found in the 280 nm spectrum, shown in Figure 5.4c. Again, the 280 nm PE spectrum was best described as a superposition of three Gaussian functions, two surface Gaussians and one bulk Gaussian, with the same arguments for three Gaussian functions as discussed with the 285 nm spectrum. The eKEs of the Gaussians fitted using the spectral retrieval code were $0.55 \pm 0.11$, $0.77 \pm 0.11$ and $1.74 \pm 0.37$ eV for the two surface Gaussians and bulk Gaussian function, respectively. The bulk Gaussian feature centered around 1.74 eV has a one-photon eBE of $2.69 \pm 0.37$ eV. This is in excellent agreement with the one-photon eBEs of the resonance-enhanced ionisation processes of liquid water measured in the 305 and 285 nm PE spectra. There is also a relative decrease in the photoelectron intensity of the feature centered around 1.74 eV relative to the other features in the PE spectra, when compared to the liquid water feature assigned in the 285 nm spectrum. This would corroborate with the liquid water assignment, as aqueous thymine has a higher absorbance at 280 nm compared to 285 nm, which in turn would reduce the relative contributions of any ionisation processes associated with liquid water, similar observations were discussed for aqueous phenol (Chapter 4). As such, the feature centered around 1.74 eV can be assigned to resonance-enhanced ionisation of liquid water.

The one-photon eBEs of the surface Gaussian features centered around 0.55
5.4. Discussion

Figure 5.9: Resonance-enhanced multiphoton ionisation spectra of aqueous thymine using 265 nm (black lines) fit with either one Gaussian function (a, blue line) or a superposition of two (b, blue lines), three (c, blue lines) or four Gaussian functions (d, blue lines) using the spectral retrieval code. The residuals of the fits are shown below the respective PE spectrum.

and 0.77 eV are $3.88 \pm 0.11$ and $3.66 \pm 0.11$ eV, respectively. Both of the one-photon eBEs are in excellent agreement with the one-photon eBEs obtained in the 285 nm spectrum for resonance-enhanced ionisation of aqueous thymine (3.86 and 3.64 eV). These features can therefore be assigned to the same resonance-enhanced ionisation processes of aqueous thymine observed in the 285 nm PE spectrum.

Figure 5.4d shows the 265 nm PE spectrum, and the measured PE spectrum was best described using a superposition of four Gaussian functions, three surface Gaussian functions and one bulk Gaussian function. Figure 5.9 shows the 265 nm PE spectrum and the fits to the PE spectrum from the spectral retrieval code using a superposition of 1 – 4 Gaussian functions, shown in Figure 5.9a–d, respectively.
As shown in the residuals of Figure 5.9a and b, one and two Gaussian functions do not adequately describe the overall PE distribution. Three Gaussian functions, as shown in Figure 5.9c, adequately describes the feature centered around 0.7 eV well, but does not describe the PE distribution with eKEs > 1.5 eV.

The eKEs of the Gaussians fitted using the spectral retrieval code were $0.44 \pm 0.08$, $0.64 \pm 0.09$, $0.88 \pm 0.09$, and $1.72 \pm 0.76$ eV for the three surface Gaussian functions and the bulk Gaussian function, respectively. The bulk Gaussian feature centered 1.72 eV is most likely to originate from liquid water due to the further reduction in the photoelectron intensity relative to the other Gaussian features in the PE spectrum when compared to features attributed to photoionisation of water in the 285 and 280 PE spectra.

The surface Gaussian features with peak maxima of 0.64 and 0.88 eV have one-photon eBEs of $4.04 \pm 0.09$ and $3.80 \pm 0.09$ eV, respectively. While the one-photon eBEs are slightly greater than measured in the 280 and 285 nm PE spectra, it is most likely that the two features are ionisation processes via the two different $S_1$ relaxation pathways, same as assigned in the 280 and 285 nm spectra, as the difference between the peak centers of the two features in the 265 nm PE spectrum is 0.24 eV, which agrees very well with the 0.22 eV difference observed between the two features in both 280 and 285 nm PE spectra. The full-width-half-maxima obtained from the fits to the 265 nm spectrum are also in good agreement with the full-width-half-maxima of the two $S_1$ photoionisation processes observed in the 285 and 280 PE spectra, as shown in Table 5.1. The slight discrepancy in the one-photon eBE possibly originates from analogous dynamics observed with aqueous phenol when photoionised with wavelengths across the first absorption band described in Chapter 4. Specifically, where increasing photon energy does not equate to an equal increase in the eKE of the features associated with the same transition.

The surface Gaussian feature centered around 0.44 eV has a one-photon eBE of $4.24 \pm 0.08$ eV and a two-photon eBE of $8.92 \pm 0.09$ eV. It seems unlikely that this feature would originate from resonance-enhanced ionisation to $D_0$ via $S_1$, as the two-photon eBE is significantly higher than measured VIE of $D_0$ in the 305 nm PE spectrum, and the one-photon eBE is higher in energy than the two assigned
features. Xue et al.\textsuperscript{26} recorded the energy of two CIs after photoexcitation of aqueous thymine to the S\textsubscript{1} state, one associated with relaxation to S\textsubscript{0} via an S\textsubscript{1}/S\textsubscript{0} CI at 4.36 eV, and a second CI associated with relaxation from S\textsubscript{1} to a point on the S\textsubscript{2} potential energy surface lower than the Franck-Condon energy, with a value of 4.45 eV. Both 285 (4.35 eV) and 280 nm (4.43 eV) would photoexcite to just below this CI, whereas 265 nm (4.68 eV) would photoexcite to above this CI. As such, it is possible that aqueous thymine does undergo internal conversion from S\textsubscript{1} to S\textsubscript{2}, and the feature with peak maximum of 0.44 eV is photoionisation of aqueous thymine to the D\textsubscript{1} state \textit{via} photoexcitation to S\textsubscript{1}, followed by internal conversion to S\textsubscript{2}, and would ionise to between the AIE and VIE of the D\textsubscript{1} state. This would agree with the assignment by Xue \textit{et al.}\textsuperscript{26} and contradict assignments made by Buchner \textit{et al.}\textsuperscript{24} and Erickson \textit{et al.}\textsuperscript{25}

5.5 Conclusions and Outlook

Here, PE spectra of aqueous thymine were recorded using wavelengths chosen to achieve photoexcitation below the onset (305 nm), on the low energy edge (280 and 285 nm) and at the maximum (265 nm) of the first absorption band. New values for the VIEs of the D\textsubscript{0} and D\textsubscript{1} state of aqueous thymine were identified as 8.32 ± 0.15 and 9.17 ± 0.15 eV, respectively. Evidence was found for three different relaxation pathways upon photoexcitation to the ππ\textsuperscript{*} (S\textsubscript{1}) state, with two relaxation pathways occurring directly from S\textsubscript{1} to S\textsubscript{0} and a third relaxing to the nπ\textsuperscript{*} (S\textsubscript{2}) state. This assignment is contrary to some recent TR LJ-PES studies, which only identified the two S\textsubscript{1}/S\textsubscript{0} relaxation pathways.

Moving forward, it would be beneficial to revisit some of these wavelengths using time-resolved LJ-PES, to track the relaxation pathways detected here. It would therefore be prudent to measure the PE spectrum of aqueous thymine with more wavelengths to further confirm the photoionisation pathway assignments made here. The greater number of measured PE spectra would also aid in confirming whether the observed discrepancy in one-photon eBEs at the absorption maximum is analogous to the observations made from measurements of aqueous phenol at/above the first absorption maximum. This could support similar observations for aqueous phenol that were attributed to solvent relaxation dynamics affecting solute dynamics.
Chapter 6

Summary and Outlook

The work in this thesis has used improved experimental procedures for liquid-microjet photoelectron spectroscopy (LJ-PES) to investigate the electronic structure of liquid water, and two important aqueous organic molecules in biology, phenol and thymine.

Chapter 3 investigated the electronic structure of liquid water using a range of resonant and non-resonant wavelengths. In this chapter, non-resonant ionisation of liquid water using 200 nm was used to record an electron binding energy of 11.36 eV, which is in excellent agreement with previous literature for the first vertical ionisation energy of liquid water.\textsuperscript{18,102,105} Resonant ionisation of liquid water provided an insight into the excited states involved in the resonance-enhanced ionisation processes of liquid water. Three resonant ionisation processes were identified, associated with photoionisation via the $1^1B_1$ and $2^1A_1$ states and the $3p$ Rydberg states in liquid water. The reproducibility of measured PE spectra was also measured, and it was found that a non-zero streaming potential distorted the PE bandshape, which altered the overall band center. It was noted, however, that it was still possible to draw meaningful conclusions from the measured PE spectra even with these distortions.

In Chapter 4, the electronic structure of aqueous phenol was studied using one-colour resonant and non-resonant ionisation at a range of wavelengths. Using non-resonant multiphoton ionisation, we were able to benchmark the first vertical ionisation energy with previous X-Ray LJ-PES studies.\textsuperscript{23} Contrary to some of the more recent measurements within our research group,\textsuperscript{22} resonance-enhanced ionisation of aqueous phenol using wavelengths resonant with the first absorption
band found evidence of resonant ionisation to the D$_0$ state of aqueous phenol only, not the D$_0$ and D$_1$ states. It was also found that the resonance-enhanced S$_1$–D$_0$ ionisation energies shifted with increasing photon energy, contrary to what would be expected for a resonant ionisation process where excess vibrational energy is conserved upon photoionisation. Since this behaviour was not observed in previous gas-phase phenol studies, solvent relaxation was assumed to be affecting the photoionisation processes. Further investigation on the reorganisation energy of aqueous solutions using time-resolved LJ-PES and complementary computational studies would help in confirming the experimentally observed trends. For the wavelengths in the absorption dip between the first and second absorption band of aqueous phenol, assignment of the ionisation processes was much more complicated. There was evidence found for resonant and non-resonant ionisation of aqueous phenol to D$_0$ as well as resonant and non-resonant ionisation of liquid water. Further investigation into the two-photon absorption states of liquid water with excitation energies $\geq 10$ eV would greatly aid in disentangling the liquid water contributions from the aqueous phenol PE spectra.

Chapter 5 examined the electronic structure of aqueous thymine by resonant and non-resonant ionisation using four different wavelengths. New values for the VIEs of the D$_0$ and D$_1$ state of aqueous thymine were identified as 8.32 ± 0.15 and 9.17 ± 0.15 eV, respectively. The former agrees well with previous literature values, while the latter is below previously recorded values.$^{147,155,161}$ Contrary to more recent LJ-PES studies,$^{24,25}$ evidence was found for three different relaxation pathways upon photoexcitation to the ππ$^*$ (S$_1$) state, with two relaxation pathways occurring directly from S$_1$ to S$_0$ and a third relaxing to the nπ$^*$ (S$_2$) state. Previous literature only identified the two relaxation pathways occurring directly from S$_1$ to S$_0$.

The next logical step in the study of the aforementioned molecular systems would be the implementation of time-resolved photoelectron spectroscopy. Not only would the ultrafast dynamics be able to be probed, but the use of time-resolved PES would greatly aid in disentangling the complicated and informative photoionisation processes possible in the UV regime, especially with the recently developed inelastic scattering correction method. The inclusion of time-resolved PES would also
allow for the direct comparison with other established techniques, such as transient absorption spectroscopy. Investigation into how the solvent relaxation dynamics affects photoionisation processes would also greatly aid further study, and would be of great interest to a broad demographic of academic and non-academic readers alike.

To further compliment the measurements recorded in this thesis, an expanded study of the REMPI of liquid water would greatly aid in disentangling the ionisation processes observed, particularly using wavelengths that have limited absorbance for the organic molecules studied in this thesis. Alongside these studies, power dependency studies at a select series of wavelengths would further aid in understanding the ionisation processes of liquid water following two-photon absorption.

With particular reference to thymine, a study expanding on the wavelengths used would assist in trying to understand the physical origin of the shifting binding energies from resonance-enhanced ionisation processes observed in this thesis.

With the study of subunits such as phenol, it would also make logical sense to expand on the measurements made by investigating more complex molecular systems that incorporate previously recorded subunits, like phenol. Example complex molecules include further study of $p$-HBDI$^-$, and the green fluorescent protein. Studying these molecules in an environment closer to the true environment, such as buffer solution, would provide a fascinating insight into the electronic structure and dynamics of complex molecules. This would bring together a wider range of scientists and even allow for designing bespoke molecules whose function can be fine-tuned from the knowledge obtained to develop photoactive molecules with favourable conditions. The study of the buffer solution itself would be prudent, to ensure that any background processes occurring are understood.

To conclude, liquid-microjet photoelectron spectroscopy is an ever-evolving area of research, with rich debate moving towards a common goal. The continued development of UV liquid-microjet photoelectron spectroscopy can only further benefit the spectroscopy community as a whole, allowing for a plethora of experimental techniques to be available for achieving a detailed understanding into the structure and dynamics of any molecular system one would choose to delve into.
Bibliography


