

A Study into the Internal Energy
Distributions of Molecules Liberated from
an *In Vacuo* Liquid Surface

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*A thesis submitted in total fulfilment of the requirements for the
degree of Doctor of Philosophy*

July 2010

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Affidavit

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Olivia Jayne Maselli

Abstract

We use the liquid micro-jet technique coupled with laser spectroscopy to measure the rotational and vibrational energy content of benzene liberated from an *in vacuo* water-ethanol solution. A comparison is made between the internal temperatures of benzene molecules that spontaneously evaporate from the liquid surface and those that are laser desorbed by resonant IR light. In both cases it was found that rotations are cooled significantly more than the lowest vibrational modes and that the rotational energy distributions were Boltzmann. Within error, the rotational temperatures of the vibrationally excited molecules were the same as the vibration-less ground state in both systems.

Independent, collision-induced, gas phase energy transfer measurements reveal that benzene undergoes fast rotational relaxation, from which we deduce that the rotational temperature measured in the evaporation experiments (200-230 K) are an indication of the translational energy of the evaporate. Conversely, relaxation of ν_6 is found to be very inefficient, suggesting that the ν_6 temperature (260-270 K) is an indication of the surface temperature of the liquid. Modelling the relaxation of ν_{16} indicates that $>10^2$ collisions are occurring during the transition from liquid to vacuum, an order of magnitude more than have been reported to occur in the gas phase immediately above the liquid surface.

The temporal distribution of internal temperatures within the plume of laser desorbed molecules reveals that the coldest molecules are found close to the front of the expansion, and reach temperatures 60 to 100 K lower than the liquid surface temperature. Spectroscopic analysis of the mass spectra of desorbed products revealed that clusters were formed post benzene ionisation, in ion-dipole association reactions. The position of maximum cluster formation within the desorption plume was found to be a compromise between the point of maximum internal cooling and the highest translational velocities. Best estimates of the

translational temperature of the desorption plume were achieved through 3D Monte Carlo simulations of the gas expansion. The simulation revealed the plume can be described with a temperature of ~ 200 K and travelling with a bulk velocity of ~ 100 m.s⁻¹.

Acknowledgments

I would first like to thank my supervisor Professor Mark Buntine for his enthusiasm, encouragement and the advice that he has given me over the years. Mark's generous nature and strong sense of fair-mindedness have made him stand out as both a supervisor and as a person on significantly more than a handful of occasions. In particular I am grateful for the independence he has allowed me as a researcher. He has helped me to achieve all the work that I present here and more.

Dr Jason Gascooke has been a great mentor and friend throughout my PhD. He has taught me to have patience and perseverance with my research whilst at the same time advocating that life shouldn't be taken too seriously. Without his input I am sure that I would have written up this thesis years ago!

Thanks also to Professor Warren Lawrance for his help in the analysis of much of the data presented here. He curbed many a wild tangent that we often found ourselves riding.

The technical expertise of Peter Apoeffis were invaluable in building and maintaining the technical equipment for this project. I appreciate Pete's patience and enthusiasm in teaching me how to do the same.

To all the other members of the lab that I have had the pleasure of working and socialising with over the years – thanks. Special thanks to Vik Dryza who took pleasure in jumping out to scare me at any opportunity. Vik, sleep with one eye open...

Lastly I need to thank my family who have continued to support me in all facets of my life. Particularly my partner Matt, whose patience, loving and chai making skills have kept burning that light at the end of the PhD tunnel.

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Abbreviations

L μ J	Liquid Micro-Jet
UV	Ultraviolet
IR	Infrared
TOF-MS	Time-of-Flight Mass Spectrometry
MALD	Matrix Assisted Laser Desorption
MALDI	Matrix Assisted Laser Desorption/Ionisation
1+1 R2PI	One-colour Resonant Two Photon Ionisation
REMPI	Resonance Enhanced Multiphoton Ionisation
FC	Frank Condon factor
LIF	Laser Induced Fluorescence
LIDF	Laser Induced Dispersed Fluorescence
FWHM	Full Width Half Maximum
OOP	Out-of-Plane
IP	In-Plane

List of Figures

Figure 2.1: (A) Assembly drawing of the TOF-MS used for the reported experiments. (B) Isometric view of the Source Chamber of the TOF-MS. -----5

Figure 2.2: Experimental setup for performing absorption spectroscopy of molecules IR desorbed or evaporating (only UV laser employed) from a L μ J. The inline bubble filter before the HPLC pump acts to degas the solution, collecting any bubbles that may try to enter the system. -----8

Figure 2.3: (A) Photograph of a L μ J created by a solution passing through a Pico Tip Emitter at atmospheric pressure. The exit aperture of the capillary is 15 μ m in diameter. The long stable, laminar flow region of the jet is illustrated here, and continuous for over 6 cm. Shorter laminar flow distances, typically 2-3 cm, are observed under high vacuum conditions. (B) Observation of the diffraction pattern produced when the UV laser is incident upon the stable *in vacuo* liquid filament. The diffraction patterns were viewed on fluorescent card at the exit to the chamber. Observation of a stable diffraction pattern is used to align the UV onto the centre of the jet. -----10

Figure 2.4: Diffraction patterns produced when the UV laser is incident upon the *in vacuo* L μ J at increasing distance from the capillary orifice. The diffraction patterns were viewed on a fluorescent card at the exit to the Source Chamber. The black background has been removed from each image so that the diffraction bands can be clearly seen. The white dots are equally spaced marks that have been included to help in the comparison of the length and position of each diffraction band. The diameter of the L μ J dictates the distance between the diffraction bands. In this example, the diameter of the jet appears to remain constant between 0-2 mm. The diffraction pattern is absent at a distance of 2.5-3 mm from the orifice - indication that the L μ J has begun to disintegrate at this distance.-----11

Figure 2.5: Scheme for resonant photon absorption. The probability of photon absorption is high when the energy of the photon is equal to the transition energy to a resonant intermediate state. The longer lifetimes of resonant intermediate states compared with virtual intermediate states increases the probability of absorbing a second photon. If the second photon is the same colour as the first then stimulated emission from the resonant intermediate state can occur instead of absorption. In the absence of collisional deactivation or other non-radiative relaxation processes, fluorescence can also be observed starting from the original resonant intermediate state. In the low pressure conditions inside the TOF-MS collisional deactivation is minimal. Boesl has found the absorption cross-sections, σ_{α} and σ_{β} , for benzene are 2.7×10^{-17} and 3.4×10^{-18} cm², respectively [18].-----14

Figure 2.6: Intensity of benzene parent ion signal produced by R2PI via the 6^1 resonant intermediate state. The wavelength of the ionising laser was 258.93 nm and the laser collimated into a spot with FWHM of $\sim 150 \mu\text{m}$. At fluences below $9 \times 10^6 \text{ W.cm}^{-2}$ the ion signal displays a quadratic dependence on the fluence of the UV laser. Above this value the photon absorption process is saturated reducing the relationship to a direct proportionality between ion signal and UV fluence. This saturation point is consistent with $1 \times 10^7 \text{ W.cm}^{-2}$ reported by Boesl *et al* [18].-----16

Figure 2.7: (A) Assembly drawings of the electrode stack designed to be used with the $\text{L}\mu\text{J}$ injector. The different stages of the assembly have the following dimensions: (s) has a length of 18 mm, (d) a length of 70 mm and (D) a length of $\sim 1 \text{ m}$. The brass, cone-shaped cap that covers the protruding $\text{L}\mu\text{J}$ capillary has not been included in the assembly drawings. (B) Schematic of a 2 stage acceleration stack. $E_x (\text{V.mm}^{-1})$ is the electric field strength across the stage x . The ions are created in the first stage, (s), and accelerated by E_s toward the second stage, (d). Further acceleration in (d) pushes the ions into the field-free flight tube, (D). When the ions reach the end of (D) they are detected. Tuning of E_s/E_d can force the space focus to occur at the point of detection (see text for details). -----19

Figure 2.8: Demonstration of the difference between Maxwellian velocity distributions typical of a supersonic expansion (3K, 300 m.s^{-1} bulk velocity) and the thermal distribution of molecules photo-desorbed from a $\text{L}\mu\text{J}$ (350 K, no bulk velocity). It is expected that higher desorption laser fluences will increase the flux of desorbed molecules and thus increase the number of gas-phase collisions. This phenomenon would tend to narrow the molecular velocity distribution to a hybrid between that of a supersonic and of a thermal expansion. --21

Figure 2.9: Illustration of Time-lag Focusing. Two same mass positive ions are born at position S_0 . Initially they are travelling in opposite directions but once a potential is created across the electrodes at time (t), the ion travelling toward the higher potential, Repeller electrode is forced to turn around. The closer this ion gets to the repeller electrode before the potential is applied, the faster the velocity of the ion will be when it passes S_0 again. At some point later this ‘turn-around’ ion will catch-up to the other ion – eliminating the effect of the initial velocity differences on the resultant resolution. The optimal delay between ion creation and extraction is dependent upon the initial relative kinetic energies of the molecules.--24

Figure 2.10: Demonstration of the changing shape of a single mass peak (m/z 78 - benzene monomer) as a function of Time-lag Delay. The mass spectra here are produced by benzene molecules that have evaporated from the surface of an *in vacuo* $\text{L}\mu\text{J}$.-----26

Figure 3.1: Reference frames for analysis of rotational and vibrational motion of benzene. The blue axes (ξ, η, ζ) are laboratory fixed axes with origin at the centre of mass of the molecule. The magnitude of the transition dipole vector, μ_A , along these axes is used in the rovibronic transition selection rules. The Euler angles (θ, ϕ, χ) are the angles between the

laboratory fixed axis and the (x,y,z) molecule fixed axis. The magnitude of the transition dipole along the molecule's fixed axes is used when determining vibronic transition selection rules. -----34

Figure 3.2: Electronic states of neutral benzene [15]. The electronic transition of interest to this study is the Herzberg-Teller transition, ${}^1B_{2u} \leftarrow {}^1A_{1g}$. Mixing of the ${}^1B_{2u}$ state with the neighbouring ${}^3E_{1u}$ is thought to be the reason why this electronically forbidden transition is unusually intense. -----37

Figure 3.3: Assignment of rotational angular momentum quantum number, k . -----45

Figure 3.4: Allowed rovibrational transitions within the $6_0^1 16_1^1$, ${}^{ev}E_{1g} \leftarrow {}^{ev}E_{2u}$ vibronic transition. Rovibrational levels are labelled with Hougen's quantum number, g . Allowed transitions are those that involve $\Delta g = 0 \text{ mod } n$. In degenerate vibronic states such as ${}^{ev}E_{1g}$, Coriolis effects destroy the energetic degeneracy of the rovibronic state. The lower rovibronic states in this case do not display Coriolis splitting since the vibronic state is made from ν_{16} which has $\zeta_{16} = 0$. The symmetry of each rovibronic state has been assigned according to Wilson's theory [6] and summarised in Table 3.4.-----50

Figure 3.5: Allowed rovibrational transitions within the $6_0^1 16_1^1$, ${}^{ev}B_{1g} \leftarrow {}^{ev}E_{2u}$ vibronic transition. There are several important differences to note with Figure 3.4 - now that the transitions are between a degenerate and a non-degenerate vibronic state. Firstly the rovibrational levels in the non-degenerate excited electronic state are not split by Coriolis effects even though the vibronic state is the result of the product of two degenerate vibrations (ν_6 and ν_{16}). Also, note the alternating symmetries of the $k = 0$ states in ${}^{ev}B_{1g}$ as a consequence of the odd or even nature of J . Finally, symmetry restrictions prevent any transitions from the ground B_2 rovibronic state when $k = 1$, whilst allowing transitions out of the B_1 state. This is important to note when calculating the line strength of this transition.-----51

Figure 3.6: The effect of the magnitude of χ on the shape of a rovibrational contour. These examples have been calculated by changing the value of ζ'_{eff} for the 6_0^1 transition. Atkinson and Parmenter [10] established a general rule for contour shapes based on Equation 3.2.1.--57

Figure 3.7: 1+1 REMPI spectrum of benzene generated in a room temperature gas phase static cell. Band assignments are in agreement with those of Stephenson [1], Atkinson [2] and Fischer [3]. -----61

Figure 3.8: (A) ν_1 : In-plane ring stretch, (B) ν_6 : Degenerate in-Plane ring squash, (C) ν_{16} : Degenerate out-of-plane ring deformation, (D) ν_{11} : Out-of-plane C-H wagging.-----62

Figure 3.9: Zoom in of the P branch of the 6_0^1 absorption contour; experimental spectrum (black) and simulated spectrum (red). (A) The experimental absorption contour was generated by 1+1 REMPI of benzene vapour in a static cell. This technique is not mass selective so the absorption contour of $^{13}\text{C}^{12}\text{C}_5\text{H}_6$ is simultaneously generated, appearing blue shifted from the $^{12}\text{C}_6\text{H}_6$ 6_0^1 contour. However, it does appear as a small shoulder on the high energy side of the $^{12}\text{C}_6\text{H}_6$ 6_0^1 band. This is marked with an asterisk (*). The simulated contour is only the 6_0^1 band of $^{12}\text{C}_6\text{H}_6$, hence the poor fit between experimental and simulated contours at the (*) position. (B) The experimental spectrum generated from room temperature background signal in the TOF-MS. By performing 1+1 REMPI in the TOF-MS, mass selection of the ions allows the $^{12}\text{C}_6\text{H}_6$ molecules to be analysed independently of the $^{13}\text{C}^{12}\text{C}_5\text{H}_6$ isomer. Comparison with the simulated spectrum shows that the shoulder caused by the $^{13}\text{C}^{12}\text{C}_5\text{H}_6$ isomer is no longer present. The absorption contours generated after mass selection were used in the best temperature fit analyses.-----64

Figure 3.10: Simulation of 6_0^1 absorption feature. In Figure (A) the simulated contour (red) is fit to an experimental spectrum (black) generated by 1+1 REMPI in the Source of a TOF-MS. In Figure (B) the simulated contour is fit to an experimental spectrum generated in free-jet expansion of benzene and nitrogen. The best-fit temperatures were found by using the spectroscopic constants reported in Table 3.12. The reported errors are 1 standard deviation of the best-fit temperature. -----68

Figure 3.11: Illustration of the perturbation of vibrational state energies due to both anharmonic interaction and fermi resonances between vibronic states. The result is the distortion of predicted intensities of the rovibrational contours as well as displacement from their unperturbed origins. The levels in bold are those that are thought to be involved in the transitions. -----71

Figure 3.12: Figure (A) is an overlay of the simulated (red) contour with the experimentally obtained REMPI spectrum (black) of room temperature benzene vapour. The tail of the adjacent 16_0^2 and 6_0^1 bands were removed as a baseline from the experimental spectrum before fitting. The small bump on the tail on the contour has been assigned by Lyman as the $6_0^1 18_1^1$ band [33]. This band was not included in the simulations. Figure (B) identifies the three sub-bands that contribute to the overall contour. The blue and green bands are identical except that they are split by fermi resonance (see Figure 3.11). Figure (C) is an overlay of the simulated (red) contour with the experimental spectrum obtained from a free-jet expansion of benzene in nitrogen (black). The temperatures quoted are the best temperature fits to the experimental contours using the spectroscopic constants from Table 3.16.-----73

Figure 3.13: Figure (A) is an overlay of the simulated (red) contour with the experimentally obtained REMPI spectrum (black) of room temperature benzene vapour. The temperatures quoted are the best temperature fits to the experimental contours using the spectroscopic constants from Table 3.20 Table 3.20 and Table 3.21. Figure (B) identifies the sub-bands that contribute to the overall contour. Figure (C) is an overlay of the simulated (red) contour with the experimental spectrum (black) obtained from a free-jet expansion of benzene in nitrogen. The unknown feature at $\sim 38434 \text{ cm}^{-1}$ was also simulated assuming it was also a type I band. -----80

Figure 3.14: Experimental setup for recording the 2D - LIDF spectrum of room temperature benzene.-----84

Figure 3.15: Typical dispersed fluorescence spectrum generated by the imaging spectrometer. This image was collected over 10,000 laser shots with a slit size of $100 \mu\text{m}$, giving a resolution of 0.5 cm^{-1} . This image was generated by exciting warm benzene with 260.1 nm light which corresponds to the absorption transition $6_0^1 16_1^1 / 6_0^1 11_1^1$. The observed dispersed fluorescence is $1_1^0 6_0^1 16_1^1 / 1_1^0 6_0^1 11_1^1$. -----86

Figure 3.16: (A) Laser Induced Fluorescence. The energy of the excitation photon remains constant whilst the spectrum of emitted photons is collected. (B) Dispersed Fluorescence. The energy of the excitation laser is scanned whilst monitoring the intensity of the emitted photons. A single fluorescence energy can be monitored or the total summed fluorescence. The LIDF technique simultaneously records both the Laser Induced and Dispersed Fluorescence spectra. -----87

Figure 3.17: Experimental LIDF spectrum of the 6_0^1 absorbance / 6_0^1 fluorescence transition. Absorption step size 0.001 nm , Fluorescence energy/pixel 0.13 cm^{-1} (fluorescence slit width of $25 \mu\text{m}$). This spectrum has not been normalised to laser power. The intensity fluctuations of the absorption contour are due to fluctuations in laser power.-----89

Figure 3.18: Experimental LIDF spectrum of the $6_1^2 / 6_1^0 11_0^2$ absorption/ $6_1^2 / 6_1^0 11_0^2$ fluorescence transition. The spectrum has not been normalised to laser power. Absorption step size 0.001 nm , Fluorescence energy/pixel 0.13 cm^{-1} (fluorescence slit width of $25 \mu\text{m}$). The presence of the $6_0^1 18_1^1$ can clearly be seen half-way along the main diagonal feature. A more detailed schematic of the transitions involved in the absorption step of this LIDF spectrum is shown in Figure 3.11. -----90

Figure 3.19: Simulated LIDF spectrum based on the 6_0^1 absorbance/ 6_0^1 fluorescence transition. The ζ_{eff} in the excited state has been set to $+0.6$, generating absorption and fluorescence spectra both with shape of type I. The absorption points are convoluted with a

Gaussian of 0.001 nm FWHM. Whilst the fluorescence points are convoluted with a Gaussian of 0.004 nm FWHM. -----92

Figure 3.20: Simulated LIDF spectrum based on the 6_0^1 absorbance/ 6_0^1 fluorescence transition. The ζ_{eff} in the excited state has been set to 0, generating absorption and fluorescence spectra both with shape of type II.-----93

Figure 3.21: Simulated LIDF spectrum based on the 6_0^1 absorbance/ 6_0^1 fluorescence transition. The ζ_{eff} in the excited state has been set to -0.6 , generating absorption and fluorescence spectra both with shape of type III.-----94

Figure 3.22: Simulated LIDF spectrum based on the 6_0^1 absorbance/ 6_0^1 fluorescence transition. The ζ_{eff} in the excited state has been set to -1.2 , generating absorption and fluorescence spectra both with shape of type IV.-----95

Figure 3.23: Simulated image based upon absorption through a third-order transition and fluorescence through a first-order transition. The features marked with ♣, are unique features to a LIDF spectrum that involves this type of transition pathway. The complimentary process, absorption through a first-order transition and fluorescence through a third-order transition, produces an identical LIDF spectrum except it is reflected about the main diagonal.-----96

Figure 3.24: Experimental, room temperature LIDF spectrum of the $6_0^1 16_1^1 / 6_0^1 11_1^1$ absorption $1_1^0 6_0^1 16_1^1 / 1_1^0 6_0^1 11_1^1$ fluorescence transition.-----99

Figure 3.25: Experimental, room temperature LIDF spectrum of the $6_0^1 16_1^1 / 6_0^1 11_1^1$ absorption $1_1^0 6_0^1 16_1^1 / 1_1^0 6_0^1 11_1^1$ fluorescence transition. The sharp dip in signal seen in the fluorescence profile is due to a damaged pixel in the detector. See Section 3.4.4 for explanation of marker symbols.-----100

Figure 3.26: Experimental, cold LIDF spectrum of the $6_0^1 16_1^1 / 6_0^1 11_1^1$ absorption $1_1^0 6_0^1 16_1^1 / 1_1^0 6_0^1 11_1^1$ fluorescence transition generated in a free-jet expansion of benzene in helium.---101

Figure 3.27: Schematic of the transition pathways that were used to create the simulated LIDF spectrum. Absorption transitions are in blue and fluorescence transitions are in red. (A) and (B) are all the allowed pathways within the $6_0^1 16_1^1$ absorption/ $1_1^0 6_0^1 16_1^1$ fluorescence

process. The varying energy of the excited states is due to the magnitude of the Coriolis and vibrational coupling constants. The transitions marked with (*) are third-order transitions and have a much lower transition probability than the other, first-order transitions. (C) shows the allowed transitions for the $6_0^1 11_1^1$ absorption/ $1_1^0 6_0^1 11_1^1$ fluorescence process.-----104

Figure 3.28: Best-fit simulation of the room temperature $6_0^1 16_1^1 / 6_0^1 11_1^1$ absorption, $1_1^0 6_0^1 16_1^1 / 1_1^0 6_0^1 11_1^1$ fluorescence LIDF spectrum. (A) Simulated LIDF spectrum using the spectroscopic constants from Table 3.22. The labelling of the bands is explained in Section 3.4.4. (B) Difference spectrum highlighting the discrepancies between the experimental and simulated spectra. The black areas indicate that the experimental spectrum is more intense, and the white areas indicate that the simulated spectrum is more intense.-----105

Figure 3.29: (A) Best-fit simulation of the rotationally cold $6_0^1 16_1^1 / 1_1^0 6_0^1 16_1^1$ LIDF spectrum shown in Figure 3.26. The rotational temperature of the spectrum was determined to be 8 ± 1 K. The labelling of the bands is explained in Section 3.4.4. (B) Difference spectrum highlighting the discrepancies between cold experimental and simulated spectra.-----106

Figure 3.30: (A) An overlay of the simulated (red) absorption contour with the experimentally obtained REMPI spectrum (black) of room temperature benzene vapour. The spectroscopic constants used to generate the simulated contour are the result of best-fits to the LIDF spectrum presented in Table 3.22. (B) Identification of the sub-bands that contribute to the overall contour. In comparison with the results of Figure 3.13(B) the shape of the $6_0^1 l_0^{\mp 1} 11_1^1 l_0^0$ contour (blue) is now definitely of type I and sits directly under the $6_0^1 l_0^{\mp 1} 16_1^1 l_{\pm 1}^{\pm 1}$ sub-band (orange). The type III contour of the third-order transition, $6_0^1 l_0^{\pm 1} 16_1^1 l_{\pm 1}^{\mp 1}$ (pink), now appears centred between the two main absorption features.-----107

Figure 4.1: (A) Schematic of the TOF-MS with $L\mu J$ source. (B) Illustration of the relative laser position for evaporation experiments. The blue arrow represents the collimated UV laser. The laser is positioned perpendicular to both the $L\mu J$ and TOF axes and between the $L\mu J$ and detector. Only those evaporating molecules that have an initial velocity component along the TOF axis will reach the laser ionisation volume, be ionised and then detected.-----125

Figure 4.2: Example of best temperature fits to the 3 rovibrational contours of interest. Each experimental spectrum (black) is the convolution of at least 4 consecutive wavelength scans and overlaid with the best-fit simulated spectrum (red). Temperatures of simulated spectra are displayed with error bars indicating 1 standard deviation from the mean. When fitting spectrum (C) it was assumed that 16_1 and 11_1 vibrational levels were at the same rotational temperature. The justification for this assumption is provided later in this chapter. --

Figure 4.3: (A) Rotational temperatures of different vibrational modes of benzene as a function of surface residence time in the vacuum. Residence time is determined by the vertical distance of the ionising laser from the L μ J nozzle and the flow rate of the L μ J. (B) Rotational temperatures of different vibrational modes of benzene as a function of radial distance from the liquid surface. Vibrationless rotational temperatures are represented by the solid circles (\bullet), whilst rotational temperatures for ν_6 , ν_{16} (and ν_{11}) are represented by the solid squares (\blacksquare) and open circles (\circ), respectively. The error bars represent 3 times the weighted error of the mean, 3σ .-----131

Figure 4.4: Benzene 1+1 REMPI absorption spectrum produced under various experimental conditions. (A) In a room-temperature static cell. The integrated intensities of the hot bands relative the 6_0^1 are indicated under each band. (B) Evaporation of benzene from an *in vacuo* L μ J. The ionising laser was positioned 1 mm from the nozzle and 300 μ m from the jet surface. (C) Benzene seeded into a free-jet expansion of nitrogen. The expansion conditions are reported in Section 4.4.2. The intensity of all spectra at energies less than 38535 cm^{-1} have been enhanced ten-fold for display purposes.-----137

Figure 4.5: (A) Vibrational temperatures of benzene as a function of residence time in the vacuum. (B) Vibrational temperatures of the different vibrational modes as a function of distance from the liquid surface. The vibrational temperatures for ν_6 , ν_{16} and ν_{11} are represented by the solid squares (\blacksquare), open circles (\circ) and open squares (\square), respectively. The error bars represent 3 times the weighted error of the mean, 3σ .-----140

Figure 4.6: Illustration of the collisional cooling experienced in the nitrogen free-jet expansion as a function of binary collision number. The translational temperature of benzene is determined by the expansion properties of the 3D jet, including the orifice diameter and the heat capacity of the carrier gas [85]. Under the experimental conditions reported here the translational temperature asymptotes to a maximum of 360 binary collisions. The collisional cooling efficiencies of the other modes were varied until their temperature at 360 collisions was equal to that observed experimentally. The collisional cooling efficiencies required to achieve these temperatures are given in Table 4.2.-----146

Figure 4.7: General description of rates of energy transfer into and out of state ψ_i -----150

Figure 4.8: The 17 transitions included in the Master Equation (ME) kinetic model.----153

Figure 4.9: Modelling the change in temperature of the different degrees of freedom of benzene as a function of binary, hard-sphere collision number. The results of the TG model are indicated using the red lines whilst the ME results are indicated with the blue lines.----158

Figure 5.1: (A) Schematic of the TOF-MS with L μ J Source Chamber. (B) Illustration of the relative laser positions for desorption experiments. The blue arrow represents the collimated UV laser and the red arrow the focused IR laser. Both lasers are positioned perpendicular to both the L μ J and TOF axes. The IR laser is focused onto the surface of the L μ J, whilst the UV laser is positioned 300 μ m from the liquid surface between the L μ J and ion detector. Only those desorbed (or evaporating) molecules which leave the liquid surface with a velocity component along the TOF axis will reach the ionisation volume, be ionised and then detected.-----176

Figure 5.2: Comparison between mass spectra generated under different experimental conditions. IR only: Only the IR laser is incident upon the L μ J. $\lambda_{\text{IR}} = 2.85 \mu\text{m}$. UV only: The UV laser is position 300 μ m from the liquid surface, UV photon energy is 38611 cm^{-1} . The only ion signal observed is from benzene monomer that has evaporated from the liquid surface. IR + UV: The IR laser is fired and then the UV laser is fired. In this example spectrum the IR-UV delay is 10 μ s. Inset: zoom in on the baseline of the mass spectra show that the two-laser technique has greatly increased the number of fragment ions to be produced.-----178

Figure 5.3: 1+1 REMPI spectra of the fragments identified in Figure 5.2 These spectra were generated with an IR-UV delay of 1.3 μ s. Each fragment shows the same wavelength dependence - they all portray the 6_0^1 rovibronic spectrum of the benzene monomer.-----180

Figure 5.4: Dependence of ion signal on IR laser fluence. (●) Integrated intensity of benzene monomer ion signal (78 amu). (○) Integrated intensity of all benzene fragment ion signals. The UV laser is positioned 300 μ m from the liquid surface. UV photon energy is 38611 cm^{-1} , where the first absorption step is via the 6_0^1 absorption band. λ_{IR} is 2.85 μ m. The IR-UV delay is 10 μ s. The fragment intensities show an IR fluence dependence similar to that of the monomer. When the data are fitted with Equation 5.1 the monomer ion signal shows an n value of 0.8 ± 0.1 , and the fragment ion signal an n value of 1.2 ± 0.1 .-----182

Figure 5.5: Mass spectrum of benzene (m/z 78) desorbed from a 25% ethanol/water L μ J. UV photon energy is 38611 cm^{-1} and UV fluence is 0.014 J.cm^{-1} . IR wavelength is 2.85 μ m and IR fluence is 0.9 J.cm^{-2} . IR-UV delay is 0.5 μ s. Under these conditions the monomer ion signal has been enhanced by a factor of 4.3 by the introduction of the IR laser. The maximum enhancement of the monomer ion signal is seen at $\sim 3 \mu$ s delay, where the two-laser setup has enhanced the pure evaporation signal sixfold. There is no signal from the IR laser alone so it is not included in the figure. The observed clusters consist only of benzene ions clustered to solvent molecules or their fragments. Ethanol molecules are abbreviated as EtOH. No benzene dimer is seen.-----184

Figure 5.6: Changes in the observed TOF mass spectrum with time-lag delay. UV photon energy is 38611 cm^{-1} . IR wavelength is $2.85 \text{ }\mu\text{m}$. IR fluence is $0.9 \text{ J}\cdot\text{cm}^{-2}$. IR-UV delay is $2.5 \text{ }\mu\text{s}$. The time-lag delay between ionisation and ion extraction is 1.1 , 0.69 and $0.39 \text{ }\mu\text{s}$ for spectrum (A),(B) and (C), respectively. Each spectrum is shifted to shorter flight times as the extraction delay time is decreased. The increase in cluster signal with time-lag delay is evidence that the clustering process is occurring post-ionisation of the benzene. At even longer time-lag delays, distortion of the mass peak shape occurs for all masses due to spatial limitations of the electrode assembly (see Chapter 2).-----186

Figure 5.7: 1+1 REMPI spectra of selected clusters seen in the mass spectra with an IR-UV delay of $0.5 \text{ }\mu\text{s}$. Each cluster shows the same wavelength dependence - they all portray the 6_0^1 vibronic spectrum of the benzene monomer. The best-fit ground state rotational temperatures of each contour are indicated with 1 standard deviation error (1σ). Within error, all of the clusters show the same rotational temperature as the monomer.-----187

Figure 5.8: (A) The effect of changing IR-UV delay on the monomer TOF ion signal. The TOF peak displayed here belongs to the C_6H_6^+ ion. Each peak has been fitted to the sum of two Gaussians. The relative intensities of each component changes with IR-UV delay times. The identity of each component is confirmed by determining the rotational temperature of each component. (B) 6_0^1 vibronic spectrum of the benzene monomer generated with IR-UV delay of $1 \text{ }\mu\text{s}$. The green spectrum was generated by monitoring the intensity of the fast component of the mass peak. The blue spectrum was generated by monitoring the slow component.-----190

Figure 5.9: Monomer and cluster intensity as a function of IR-UV delay. (●) Benzene monomer, C_6H_6^+ , (●) two component (binary) clusters, $\text{C}_6\text{H}_6^+\bullet\text{X}$, (●) three component (tertiary) clusters, $\text{C}_6\text{H}_6^+\bullet\text{X}\bullet\text{Y}$. (A) The monomer achieves maximum desorption signal at an IR-UV delay of $\sim 3 \text{ }\mu\text{s}$, whilst the binary cluster signal is maximised at a delay of $\sim 1 \text{ }\mu\text{s}$. Data points in (A) are the average of the results from several mass spectra. Error bars represent 1σ error. (B) Zoom in on the overlay of monomer and cluster temporal profiles generated from a single mass spectrum. The tertiary clusters are now included. The plot demonstrates that stable cluster formation occurs early in the desorption plume (at short IR-UV delay). The maximum intensity of the tertiary clusters is seen at an IR-UV delay of $\sim 0.5 \text{ }\mu\text{s}$.-----192

Figure 5.10: Fit of two Maxwell-Boltzmann distributions to (A) the benzene monomer ion signal and (B) the binary cluster ion signal. Plots were produced by transforming the data of Figure 5.9(A) using Equation 5.2. The fits have been weighted by the displayed error in the data points. Both best-fits describe a velocity distribution that has zero drift velocity perpendicular to the jet axis (u_{\perp}). All distributions use a mass of 78 amu (benzene monomer). In both plots the red curve is the summation of both of the underlying components. The ionising laser energy is 38611 cm^{-1} corresponding to the maximum in the 6_0^1 absorption band of the monomer.-----194

Figure 5.11: Schematic of the conditions of the 3D Monte Carlo simulation. Different length arrows represent molecules released from the liquid surface with different initial velocities. The volume of the ionisation region runs into the page, perpendicular to the $L_{\mu J}$ axis. The different width arrows represent different initial masses emerging from the $L_{\mu J}$ – this is used in the mass-independent velocity distribution simulations.-----200

Figure 5.12: Demonstration of the effects of the diameter of the ionisation volume on the shape of the IR-UV delay distribution created by the 3D Monte Carlo simulations. The translational temperature and bulk velocity used in the simulations were 200 K and 100 $m.s^{-1}$, respectively. The diameter of the UV volume is 150 μm (blue line), diameter of the UV volume is 1.5 μm (red line). The signal/noise is worse when the UV volume is smaller since fewer molecules find themselves within the region at the time of ionisation. Larger ionisation volumes distort the maximum in the distribution to shorter delay times since molecules with a larger range of molecular velocities can reach the ionisation volume at the shorter delays. The distribution created with 1.5 μm diameter has been fitted with a function of the form of Equation 5.4 but without the pre-exponential factor, C/t^4 (black line). The best fit predicted a \bar{u} of $88 \pm 1 m.s^{-1}$ and a T_{\perp} of $19 \pm 1 K$.-----201

Figure 5.13: Simulated IR-UV delay distributions overlaid with the experimentally observed benzene monomer ion signal (\bullet) distribution. All the simulations in (A) have a bulk velocity of 200 $m.s^{-1}$ but vary in translational temperature: (red line) 300 K, (black line) 200 K, (green line) 100 K. (B) shows the effects of changing the drift velocity in the simulations with a temperature of 200 K. (red line) 300 $m.s^{-1}$, (green line) 200 $m.s^{-1}$, (black line) 100 $m.s^{-1}$.-----203

Figure 5.14: Simulated IR-UV delay distributions of different masses included in the 3D Monte Carlo simulation. (A) C_6H_6 , 78 amu (black line), $C_6H_6 \bullet 2H_2O$, 114 amu (blue line), $C_6H_6 \bullet 4H_2O$, 150 amu (green line). (B) When the distributions from each mass are summed together the resultant IR-UV delay is broader at the maximum which more closely resembles the shape of the experimentally observed distribution maximum. Only C_6H_6 (black line), C_6H_6 and $C_6H_6 \bullet 2H_2O$ (red line), C_6H_6 , $C_6H_6 \bullet 2H_2O$ and $C_6H_6 \bullet 4H_2O$ (green line). Experimental data (\bullet).-----206

Figure 5.15: Rovibrational contours of benzene molecules IR desorbed from the $L_{\mu J}$. These spectra were produced with an IR-UV delay time of 3.9 μs . Temperature fits are displayed with error indicating 1 standard deviation from the mean. The lower signal/noise and larger fitting error of (C) is due to the dramatic decrease in the intensity of the band under desorption conditions. (*) See text for a discussion of this feature.-----209

Figure 5.16: Comparison of the benzene absorption spectrum generated under different experimental conditions. See text for details. The rotational temperatures of benzene molecules are also quoted for each experimental environment. The IR-UV delay used to

generate the desorption spectrum shown here was $4 \mu\text{s}$. The intensity of all spectra has been magnified ten-fold at energies less than 38535 cm^{-1} . -----211

Figure 5.17: Temporal evolution of the internal temperatures of neutral benzene molecules laser desorbed from the surface of the $L\mu\text{J}$. (A) Rotational temperatures as a function of IR–UV delay. It is assumed that the rotational temperatures of molecules excited with vibration ν_{16} and ν_{11} are equal. Vibrationless rotational temperatures are represented by the solid circles (\bullet), whilst rotational temperatures for ν_6 , ν_{16} (and ν_{11}) are represented by the solid squares (\blacksquare) and open circles (\circ), respectively. (B) Vibrational temperatures as a function of IR-UV delay. Vibrational temperatures for ν_6 , ν_{16} and ν_{11} are represented by the solid squares (\blacksquare), open circles (\circ), and open squares (\square), respectively. The error bars on all points represent 3 times the weighted error of the mean (3σ). The temperatures at 0 IR-UV delay are the temperatures of benzene molecules that are naturally evaporating into the vacuum from the $L\mu\text{J}$.-----214

Figure 5.18: Comparison between the rates of change of ground state rotational temperatures (\bullet) and the observed intensity of the benzene monomer ion signal (\bullet) as a function of IR-UV delay. The temperature scale has been reversed to aid in the overlay. The data at 0 IR-UV delay are from benzene molecules that are naturally evaporating into the vacuum from the $L\mu\text{J}$. -----216

List of Tables

Table 3.1: Symmetries and frequencies of benzene vibrational modes. The vibrations are labelled according to the convention introduced by Wilson [3]. Descriptions of the vibrations are taken from Muller [4]. Unless otherwise indicated, frequencies are taken from Atkinson [5]. (χ) Page [6], (δ) Stephenson [7], (ϵ) Muller [4].-----39

Table 3.2: Determination of the vibronic symmetries for excitation of the vibrations ν_6 and ν_{16} in the excited electronic state ${}^1B_{2u}$ of benzene. Both ν_6 and ν_{16} have symmetry E_2 , so both θ_6 and θ_{16} equal $4\pi/6$.-----42

Table 3.3: Determination of allowed vibrational angular momentum transitions within the vibronic transition $6_1^0 11_0^2$. The only allowed transition here is shown to be $6_1 l_{\pm 1} 11_0 l_0 \leftrightarrow 6^0 l^0 11^2 l^0$ since it involves $\Delta\theta_{ev} = \mp 4\pi/6$.-----42

Table 3.4: Rovibronic symmetries of states involved in the $6_0^1 16_1^1$ transition. (\ddagger) Rotational symmetries, $\Gamma(\psi_r)$, are taken from Wilson [3]. Not all states are involved in each $\Delta k = \pm 1$ transition. -----45

Table 3.5: Determination of Hougen's Quantum number for the $6^1 16^1$ vibronic state in the ${}^1B_{2u}$ excited electronic state of benzene. (\ddagger) The symmetries were calculated in Table 3.2.--48

Table 3.6: Assignment of rovibronic symmetries using Hougen's quantum number, g . ----48

Table 3.7: $\pm l$ selection rules for rovibronic transitions. -----53

Table 3.8: Hönl-London factors for a perpendicular transition [11]. $K = |k|$. J and K values are from the initial rotational states involved in the rotational transition. The upper signs are for $\Delta K = -1$ transitions, lower signs are for $\Delta K = +1$ transitions. (*) If $K=0$ and $\Delta K = +1$, then the factor must be multiplied by 2. -----59

Table 3.9: Examples of statistical weights calculated for some of the rovibronic transitions allowed within the vibronic transition ${}^{ev}B_{1g} \leftarrow {}^{ev}E_{2u}$, and displayed in Figure 3.5. (‡) Note that although the total symmetry of ψ''_{evr} is $B_1 + B_2$ when $k = 1$, only the wavefunctions of symmetry B_1 can undergo the $\Delta k = -1$ transition due to symmetry restrictions. The statistical weight reflects only the degeneracy of states that are involved in the transition. -----59

Table 3.10: The vibronically induced transitions simulated in this study and their symmetry according to Mills' polar co-ordinate assignment. (*) These transitions were only used in the 2D simulated spectra discussed in Section 3.4. -----62

Table 3.11: Vibrational anharmonicity energy factors and effective Coriolis constant involved in the 6_0^1 transition. -----67

Table 3.12 Spectroscopic constants used in the simulation of $6_0^1 l_0^{\mp 1}$. All rotational constants and the Coriolis constant were taken from Okruss [23]. The anharmonic constants are taken from Atkinson [5].-----67

Table 3.13: Vibrational anharmonicity energy factors and effective Coriolis constant for states involved in the transition 6_1^2 . -----69

Table 3.14: Vibrational anharmonicity energy factors and effective Coriolis constant for states involved in the transition $6_1^0 11_0^2$. -----69

Table 3.15: Vibrational anharmonicity energy factors and effective Coriolis constant from states involved in the 16_0^2 transition. -----72

Table 3.16: Spectroscopic constants used in the simulation of $6_1^2/6_1^0 11_0^2$. (*)Ground state rotational constants were taken from Hollenstein [25]. (†) The value for the ground state Coriolis constant was taken from Weber [18] The anharmonic constants are taken from Atkinson [5]. The excited state rotational constants were determined by fitting of the room temperature experimental spectrum with a simulated spectrum. The standard deviation is given in parenthesis in units of the last digit. -----74

Table 3.17: Comparison of rotational defects for molecules vibrating in the ${}^1B_{2u}$ electronic state of benzene. All rotational constants are the best-fit values from fitting of the room temperature absorption spectrum. $\Delta\nu$ given in units of $\text{amu}\cdot\text{\AA}^2$. For comparison literature values of rotational constants and $\Delta\nu$ are included in the bottom half of the table. These values were taken from the following sources: (*) Riedle [19], (¥) Weber [33], (†) Sieber [37].-----76

Table 3.18: Vibrational anharmonicity energy factors and Effective Coriolis constant for states involved in the transition $6_0^1 16_1^1$.-----77

Table 3.19: Vibrational anharmonicity energy factors and effective Coriolis constant for states involved in the transition $6_0^1 11_1^1$.-----78

Table 3.20: Spectroscopic constants used in the simulation of the $6_0^1 16_1^1$ contour. (*) Ground state rotational constants were taken from Hollenstein [25]. The anharmonic constants are taken from Atkinson [5]. The excited state rotational constants were determined by fitting of the room temperature experimental spectrum with a simulated spectrum. It was assumed that the intensity of the third-order component (the $6_0^1 l_0^{\pm 1} 16_1^1 l_{\pm 1}^{\mp 1}$ transition) was negligible during the fitting process. Allowing the rotational constants of the excited states to be different did not produced any improvements in the fit. The results reported here were generated assuming that the rotational constants in the excited state were equal. The standard deviation is given in parenthesis in units of the last digit for constants determined in this study.-----79

Table 3.21: Spectroscopic constants used in the simulation of the $6_0^1 11_1^1$ contour. (*) Ground state rotational constants were taken from Hollenstein [25]. The anharmonic constants are taken from Atkinson [5]. The excited state rotational constants were determined by fitting of the room temperature experimental spectrum with a simulated spectrum. The standard deviation is given in parenthesis in units of the last digit for constants determined in this study.-----79

Table 3.22: Summary of spectroscopic constant values generated from best-fit to the LIDF spectrum in Figure 3.25. (*) Value taken from Hollenstein [25]. (†) Values calculated from the rotational defects reported by Jagod [35]. All other rotational constants are the result of best-fit simulations performed in this study. 1 standard deviation is given in parentheses in units of the last digit. $\Delta\nu$ given in units of $\text{amu}\cdot\text{\AA}^2$, all other constants have units cm^{-1} . (★) When calculated from the shape of the third-order transition, $1_1^0 l_0^0 6_0^1 l_0^{\pm 1} 16_1^1 l_{\pm 1}^{\mp 1}$, the best-fit was a $\Delta\nu$ value of -0.497 and $\zeta_{eff} = 0.484(3)$.-----103

Table 4.1: Temperatures of the different internal degrees of freedoms of benzene molecules evaporating from an in vacuo aqueous surface.-----139

Table 4.2: Mode-specific collisional energy transfer efficiencies ($k_{i\infty}$) of benzene in N₂.--
-----148

Table 4.3: Summary of possible levels to be included in the ME model of relaxation rates in S₀ benzene. †Degeneracies correlate with those quoted in Ref [98]. *Populations are relative to the vibrationless ground state at 295 K. Highlighted rows are the transitions that were included in the model. Of the 36 possible transitions only 17 are included in this model; the other transitions were discarded upon enforcement of the simplifications as stated in the text. Δ, Ω, ∞: these transitions were given equivalent rate constants, (k_{ij}), as they involve the same number of quanta change of a particular vibration. This leaves 11 independent rate constants to be calculated using the series of differential equations.-----152

Table 4.4: k_{ij} values obtained using the Master Equation model.-----155

Table of Contents

Affidavit	II
Abstract	III
Acknowledgments	V
Publications	VI
Abbreviations	VII
List of Figures	VIII
List of Tables	XX
Table of Contents	XXIV
1. Outline	1
1.1 References	3
2. Experimental Technique	4
<i>Design and Implementation of a TOF-MS with Liquid Micro-Jet Source</i>	
2.1 Introduction	4
2.2 Apparatus	4
2.3 Creating an <i>in vacuo</i> Liquid Micro-jet	9
2.4 One-colour Resonant Two Photon Ionisation (1+1 R2PI)	13
2.5 Time-of-Flight Mass Spectrometry	17
2.6 References	29
3. Spectral Simulation	32
<i>Simulation of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ Gas Phase Absorption spectrum of Benzene</i>	
3.1 Introduction	32
3.2 Theory of Optical Transitions	33
3.2.1 Selection Rules for Allowed Vibronic Transitions	35
3.2.2 Simulating Rovibronic Transitions	43

3.2.3	Energy of a Rovibronic State	54
3.2.4	Intensity of a Rovibronic Transition	58
3.3	Simulation of the Vibronic Transitions within ${}^1B_{2u} \leftarrow {}^1A_{1g}$	60
3.3.1	Simulation of the 6_0^1 Absorption Feature	66
3.3.2	Simulation of the 6_1^2 and $6_1^0 11_0^2$ Absorption Features	69
3.3.3	Simulation of the $6_0^1 16_1^1$ and $6_0^1 11_1^1$ Absorption Features	76
3.4	Laser Induced Dispersed Fluorescence (LIDF)	82
3.4.1	Experimental Technique	83
3.4.2	Interpretation of a LIDF Image	88
3.4.3	De-convolution of the $6_0^1 16_1^1 / 6_0^1 11_1^1$ absorption band	97
3.4.4	Analysis of $6_0^1 16_1^1 / 6_0^1 11_1^1$ Absorption, $1_1^0 6_0^1 16_1^1 / 1_1^0 6_0^1 11_1^1$ Fluorescence LIDF Spectrum	108
3.5	Conclusion	114
3.6	References	115
4. Molecular Evaporation		119
<i>The Dynamics of Evaporation from a Liquid Surface</i>		
4.1	Introduction	119
4.2	Experimental Method	124
4.3	Results and Discussion	127
4.3.1	Rotational Temperatures	127
4.3.2	Vibrational Temperatures	136
4.4	Determination of collision numbers upon evaporation from an <i>in vacuo</i> liquid surface	142
4.4.1	Collisional Energy Transfer	142
4.4.2	Modelling Collisional Energy Transfer Rates	144
4.4.3	Temperature Gap Model of Collisional Relaxation Rates	147
4.4.4	Master Equation Model of Collisional Relaxation Rates	148
4.4.5	Results of Master Equation Modelling	154
4.4.6	Estimate of Collisional Numbers upon Evaporation	156
4.5	Conclusion	159
4.6	References	161

5. Infrared Desorption	169
<i>Partitioning of Internal Energy within Benzene Molecules Thermally Desorbed from a Liquid Surface</i>	
5.1 Introduction	169
5.2 Experimental Method	173
5.3 Features of the Desorption Mass Spectrum	175
5.4 Translational Velocity Distributions of the Desorption Process	191
5.5 Distribution of Internal Energy by the Desorption Process	196
5.6 Conclusion	216
5.7 References	218