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The Determination of Molecular Parameters of Ices Relevant to Astrochemistry

James William Stubbing

A thesis presented for the degree of PhD in chemistry University of Sussex

September 2019

I hereby declare that this thesis has not been, and will not be, submitted in whole or in part to any other university for the award of a degree. I confirm that the work presented in this thesis is my own, and where information has been derived from other sources, it is indicated in the thesis.

> James William Stubbing September 2019

Abstract

Dust grains in the interstellar medium (ISM) provide a surface onto which molecules can accrete and form icy mantles. This thesis describes laboratory investigations of interstellar ice analogues. In particular, the design, installation and testing of a novel, newly developed, ultraviolet/visible (UV/vis) reflection spectrometer is presented. This apparatus allows simultaneous measurement of the ice thickness and refractive index at cryogenic temperatures (≈ 25 K) for the first time. These data are essential for modelling the spectra and radiative transfer of energy in the ISM. The key feature of the apparatus is an ultra-high vacuum (UHV) compatible variable angle lens assembly. A Python program has been written to analyse the spectra in order to determine the wavelength dependent complex refractive index of ices. The advantages that the apparatus has over previous methods of measuring the refractive index and ice thickness are discussed. Prior to the measurement of the refractive index, temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) were used to characterise the ices.

Several molecules were studied in this thesis, and the carbonaceous dust grain analogue surface used was highly oriented pyrolytic graphite. Benzene was used as a test system due to its well defined UV/vis spectrum and the fact that is has been detected in space. Toluene offers a good comparison to benzene, to examine the effect of a small molecular modification on surface behaviour. Finally, methyl formate is an example of an interstellar complex organic molecule (COM, molecules containing > 6 atoms), and has been shown in previous work to interact with water in a mixed ice. Previously, it has been assumed that the refractive index of a mixed ice can be taken to be the weighted average of the ice constituents. This work challenges that assumption.

List of Publications

Published articles:

Peeling the astronomical onion, A. Rosu-Finsen, D. Marchione, T. L. Salter, J. W. Stubbing, W. A. Brown and M. R. S. McCoustra, *Phys. Chem. Chem. Phys.*, 2016, **18**, 31930–31935.

A fibre-coupled UHV-compatible variable angle reflection-absorption UV/visible spectrometer, J. W. Stubbing, T. L. Salter, W. A. Brown, S. Taj and M. R. S. McCoustra, *Rev. Sci. Instrum.*, 2018, **89**, 054102.

A TPD and RAIRS comparison of the low temperature surface behaviour of benzene, toluene, and xylene on graphite, T. L. Salter, J. W. Stubbing, L. Brigham and W. A. Brown, *J. Chem. Phys.*, 2018, **149**, 164705.

Articles in preparation:

Thermal processing of small aromatic ices: laboratory investigations and astrophysical implications, T. L. Salter, J. W. Stubbing, L. Brigham and W. A. Brown, to be submitted to *Monthly Notices of the Royal Astronomical Society*.

A new technique for determining the refractive index of ices at cryogenic temperatures using amorphous and crystalline benzene ice, J. W. Stubbing, M. R. S. McCoustra and W. A. Brown.

Dedicated to Jennifer Jones 1940 – 2019 Grandma

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List of Abbreviations

| AGB | Asymptotic Giant Branch |
|----------------|--|
| ASW | Amorphous Solid Water |
| CI | Crystalline Ice |
| CNT | Carbon Nanotube |
| СОМ | Complex Organic Molecule |
| DFT | Density Functional Theory |
| DPRF | Differentially Pumped Rotary Feedthrough |
| EELS | Electron Energy Loss Spectroscopy |
| EPD | Electron-Promoted Desorption |
| FTIR | Fourier Transform Infrared |
| FWHM | Full Width at Half Maximum |
| GC × GC-TOF-MS | Two-Dimensional Gas Chromatography Coupled to Time-of- |
| | Flight Mass Spectrometry |
| H-bond | Hydrogen Bond |
| HOPG | Highly Oriented Pyrolytic Graphite |
| HREELS | High Resolution Electron Energy Loss Spectroscopy |
| HW | Heriot-Watt University |
| IP | Ion Pump |
| IR | Infrared |
| ISM | Interstellar Medium |
| JWST | James Webb Space Telescope |
| MCT | Mercury Cadmium Telluride |
| MIES | Metastable Impact Electron Spectroscopy |
| ML | Monolayer |
| NEXAFS | Near Edge X-ray Absorption Fine Structure |
| OFHC Cu | Oxygen Free High Conductivity Copper |
| РАН | Polycyclic Aromatic Hydrocarbon |
| PPN | Protoplanetary Nebula |
| QCM | Quartz Crystal Microbalance |
| | |

| QMS | Quadrupole Mass Spectrometer |
|----------|--|
| RAIRS | Reflection Absorption Infrared Spectroscopy |
| RGA | Residual Gas Analysis |
| RNA | Ribonucleic Acid |
| Sgr B2 | Sagittarius B2 |
| TMP | Turbomolecular Pump |
| TOF-SIMS | Time-of-Flight Secondary Ion Mass Spectrometry |
| TPD | Temperature Programmed Desorption |
| TSP | Titanium Sublimation Pump |
| UHV | Ultra-High Vacuum |
| UV | Ultraviolet |
| UV/vis | Ultraviolet/visible |
| VUV | Vacuum Ultraviolet |
| WIM | Warm Ionised Medium |
| WNM | Warm Neutral Medium |
| YSO | Young Stellar Object |

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1 Introduction

This thesis describes the design, installation and testing of a novel ultraviolet/visible (UV/vis) spectroscopy apparatus. The apparatus has been used to directly measure the refractive index and thickness of astrophysically relevant ices at cryogenic temperatures. The ices were also characterised by temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). The results described in this thesis are relevant to ices which form on dust grains in the interstellar medium (ISM) and other astrophysical environments. This is because the molecules examined, benzene, toluene, methyl formate and water, are all astronomically important. Equally, the conditions under which the experiments are performed, under ultra-high vacuum (UHV) and at cryogenic temperatures, simulate those in regions of space.

1.1 The Refractive Index

1.1.1 Definition of the Refractive Index

The refractive index of a material describes how light interacts with it. Specifically, refractive index, *n*, refers to the change in velocity of light upon moving from a vacuum into a material. It is defined by equation (1.1),¹ in which *c* is the speed of light in a vacuum and *v* is the speed in the medium.

$$n = \frac{c}{v}$$
(1.1)

The change in velocity of light passing between two media causes the angle at which the light impinges to change upon crossing the interface between them, a phenomenon called refraction. As a consequence of this, the refractive index of a medium can be determined using Snell's law (equation (1.2)). Snell's law states that the ratio of the velocities of light in two homogenous media is equal to the ratio of their refractive indices and to the sines of the angle of incidence, θ_1 , and refraction, θ_2 .¹ These angles are shown in Figure 1.1 for light travelling from one medium to another, labelled 1 and 2, with different refractive indices, n_1 and n_2 .

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{v_1}{v_2} = \frac{n_1}{n_2}$$
(1.2)



Figure 1.1 Schematic representation of the refraction of light from one medium (1) to another (2) with different refractive indices. θ_1 is the angle of incidence. θ_2 is the angle of refraction. The surface normal is indicated by the dotted line.

Whilst *n* describes the behaviour of light propagating in non-absorbing media, it does not take into account the absorption or attenuation of light upon entering a material. In order to take this into account, the complex refractive index, *N*, must be used, which is given by equation (1.3).¹

$$N = n + ik$$
 (1.3)

Here, n is the part of the refractive index concerning refraction, known as the real part, and k is the extinction coefficient which describes absorption. Whilst k is part of the imaginary part of N, k itself is a real parameter. As absorption of light is known to be strongly dependent on wavelength, N (and hence n and k) must be a wavelength dependent parameter. Indeed this is shown to be the case in the phenomenon known as dispersion. Dispersion leads to the splitting of white light into its constituent wavelengths, upon passing through a prism, as different wavelengths of light are refracted at different angles.

As well as describing refraction and extinction of light within a medium, the refractive index is also used to describe the ratio of reflected and transmitted light when propagating light encounters an interface such as the one shown in Figure 1.1. The reflection and transmission coefficients for s- and p-polarised light, r_s and r_p , and t_s and

 t_p respectively, are determined by the Fresnel equations,^{1,2} equations (1.4) – (1.7) below. s-polarised light is that which is polarised perpendicular to the plane of incidence of the propagating light wave, and p-polarised light is parallel to this plane.

$$r_{s} = \frac{n_{1}\cos\theta_{1} \cdot n_{2}\cos\theta_{2}}{n_{1}\cos\theta_{1} + n_{2}\cos\theta_{2}}$$
(1.4)

$$r_{p} = \frac{n_{2}\cos\theta_{1} - n_{1}\cos\theta_{2}}{n_{2}\cos\theta_{1} + n_{1}\cos\theta_{2}}$$
(1.5)

$$t_{s} = \frac{2n_{1}\cos\theta_{1}}{n_{1}\cos\theta_{1} + n_{2}\cos\theta_{2}}$$
(1.6)

$$t_{p} = \frac{2n_{1}\cos\theta_{1}}{n_{2}\cos\theta_{1} + n_{1}\cos\theta_{2}}$$
(1.7)

Given the above, it is clear that the refractive index of a material is an important parameter, and determination or knowledge of it has been used in a range of fields and applications. For example, volcanic glasses can be identified and dated using their refractive indices.³ Additionally, by making use of differing refractive indices within a layered system, anti-reflective coatings can be produced.^{4,5} Measurement of the refractive index has also been used as a compositional analysis tool in the food industry⁶ and recent work has demonstrated the importance of a detailed knowledge of the refractive index in the design of holographic devices.⁷ Additionally, because it is wavelength dependent, the refractive index of a material can be used to predict its spectral behaviour.^{8,9}

<u>1.1.2 The Refractive Index of Ices</u>

This thesis examines films of molecules adsorbed on a surface at low temperature, which are referred to as ices. The importance of these ice systems to astrochemistry is outlined in Section 1.2. In order to determine *N* for ices, the Kramers-Kronig relation is one method that has been used.^{9–19} The Kramers-Kronig relation allows the determination of the real part of a complex function from its imaginary part, or vice versa.^{13,20,21} In this work, this means the real and imaginary parts of the wavelength dependent complex refractive index. The Kramers-Kronig relation has typically been used to determine *N* for ices in the infrared (IR) spectral range,^{9,10,12–17,22} however it is not limited to this range. Indeed it was first developed to examine the dispersion of X-rays.^{21,23}

In order to determine *N* for an ice using the Kramers-Kronig relation, experimental absorption spectra are required. First, it is necessary to define the ice system and how spectra are collected. Figure 1.2 shows the interaction of an incoming ray of light of intensity I_0 with an ice (1) of thickness *d* and refractive index N_1 deposited on a transparent substrate (2) of refractive index N_2 . The vacuum phase (0) has n = 1.



Figure 1.2 Schematic of the interaction of an incoming ray of light with an ice adsorbed onto a transparent substrate. Dashed lines are reflected rays and solid lines are transmitted rays. The Fresnel coefficients of each ray are shown. Adapted from Rocha and Pilling.¹³

In Figure 1.2, the reflected (dashed) and transmitted rays of light are labelled with their respective Fresnel coefficients and the fully transmitted ray has intensity *I*. The absorbance, *A*, is given by the Beer-Lambert law, equation (1.8), which can be expressed as transmission, *T*, by equation (1.9).²⁴

$$A = \ln \left(\frac{l_0}{l}\right) \quad (1.8)$$
$$T = \frac{1}{c^A} \quad (1.9)$$

The experimental spectrum is compared to a simulated spectrum which is produced using the following procedure. The theoretical transmittance, T_{th} , is given by equation (1.10) which makes use of the Fresnel coefficients and the ice thickness.^{13,14,17}

$$T_{th} = e^{-\alpha d} \left| \frac{t_{01} t_{12} / t_{02}}{1 + r_{01} r_{12} e^{2ix}} \right|^2$$
(1.10)

In equation (1.10), x is a dimensionless parameter given by equation (1.11) and α is the Lambert absorption coefficient given by equation (1.12).^{9,13,14,18,19,22}

$$x = \frac{2\pi dN_1}{\lambda}$$
(1.11)
$$\alpha = \frac{4\pi k}{\lambda} = \frac{1}{d} \left[A_{\lambda} + \ln \left| \frac{t_{01} t_{12} / t_{02}}{1 + r_{01} r_{12} e^{2ix}} \right|^2 \right]$$
(1.12)

Equation (1.12) shows that α can be used to determine k, which is used to determine n using the Kramers-Kronig relation, equation (1.13).

$$n(\overline{\nu}) = n_0 + \frac{2}{\pi} \mathscr{D} \int_{\overline{\nu}_1}^{\overline{\nu}_2} \frac{\overline{\nu}' k(\overline{\nu}')}{\overline{\nu}'^2 - \overline{\nu}^2} d\overline{\nu}' \quad (1.13)$$

In equation (1.13), n_0 is the refractive index in the visible region and \bar{v}_1 and \bar{v}_2 are the wavelength range limits in wavenumber (where $\bar{v} = 1/\lambda$). It should be noted that n at a given wavelength is affected by the value of k at all other wavelengths, hence $n(\bar{v})$ is dependent on $k(\bar{v}')$ in equation (1.13).²¹ This leads to the need to include \wp , the Cauchy principle value,¹³ in equation (1.13) which avoids the integral becoming infinite when $\bar{v} = \bar{v}'$.

When using the Kramers-Kronig relation in practice, a starting guess of k is used to determine n which subsequently allows Fresnel coefficients to be calculated and a T_{th} spectrum to be produced. This spectrum is compared to the experimental spectrum and the procedure can be iterated until a good match is found. This indicates that the determined n and k values are correct.^{13–15,17,18,22}

Whilst the Kramers-Kronig relation is a powerful tool to determine N for ices, there are some considerations that must be addressed. Firstly, because transmission data are required, as shown by equations (1.10) – (1.12), it cannot be applied to reflection spectra. The implications of this are outlined below and in later chapters. Secondly, an accurate value of the ice thickness is required to calculate k correctly, shown in equations (1.11) and (1.12).

Measuring the ice thickness is non-trivial and has previously been attempted in several ways. The most accurate way to determine the ice thickness is by using a quartz crystal micro-balance (QCM).^{25,26} The QCM exploits the piezo-electric nature of quartz. By applying a current to the crystal, oscillations at a resonant frequency, *f*, are induced.²⁶ The adsorption of molecules on the surface of the crystal, or more accurately a surface in contact with the surface of the crystal, causes a change in the resonant frequency, Δf . This change in frequency can be related to the change in mass, Δm , *via* the Sauerbrey equation, equation (1.14).^{26,27} In order to determine the ice thickness, the area of the surface, *A*, must be known, as well as the density of the ice.^{26,28,29} In equation (1.14), μ and ρ are the shear modulus and density of quartz respectively.^{26,27}

$$\Delta f = -\frac{2f^2}{A\sqrt{\mu\rho}}\Delta m \qquad (1.14)$$

An alternative method to measure the ice thickness uses interference fringes produced by reflecting a He-Ne laser off the substrate during the deposition of the ice. The fringes are used to determine the ice thickness, *d*, using equation (1.15), in which $m(\lambda)$ is the number of complete fringes and θ is the angle of reflection from the surface normal.

$$d = \frac{m(\lambda)}{2\sqrt{n^2 - \sin\theta}}$$
(1.15)

In equation (1.15), *n* is the real part of the refractive index of the ice. In some cases for ices, this has been taken as equal to the refractive index of the ice component under ambient conditions.^{10,14} Surface science experiments on ices are typically performed under high-vacuum^{30,31} ($p \approx 10^{-7}$ mbar) or ultra-high vacuum (UHV, $p \approx 10^{-10}$ mbar)^{32,33} and employ cryogenic cooling of the order 10 K – 30 K.³⁴ Therefore it is questionable to assume that an ice made of a material will have the same optical parameters as the material under ambient conditions. Another assumption that has been made is that, when a mixed ice is being examined, a weighted average of the individual *n* values of each component is used to give the overall value of *n* for the ice.¹⁵ However, this has been shown not to be appropriate in all cases, due to interactions between the ice constituents.^{35,36} A final limitation of using equation (1.15) to determine the ice

thickness is that only the thickness of the as-dosed ice can be determined. As discussed below, if the ice undergoes any processing which may affect its thickness, this cannot be measured.³⁴

In order to overcome the need to use an assumed value of *n*, and to allow the ice thickness to be measured independently of ice deposition, the integrated infrared band strength, A_s , and density, ρ , can be used to determine the ice thickness.^{15,37–40} The column density in molecues cm⁻², N_c is initially determined using equation (1.16), where A is the absorbance as shown in equation (1.8) in a given wavelength, v, range.^{37,38}

$$N_{c} = \frac{1}{A_{s}} \int A \, dv \qquad (1.16)$$

Once N_c is known, it can be used with a value of ρ for the ice to estimate the ice thickness. This method of determining the ice thickness relies on the band strength and density of the ice being known accurately. However, band strengths are not always measured directly, instead they are taken from the literature or assumed.³⁸ This is problematic if, for example, values are taken from a pure ice when a mixed ice is being examined.¹⁰ Similarly, care must be taken with the value of ρ used. Often, even in mixed ices, ρ is assumed to be equal to that of water ice (taken as 1 g cm⁻³).^{14,37,38} Alternatively, a weighted average of densities of each component is used, which has also been shown to be inappropriate as densities do not follow this behaviour.³⁵ Ice densities of various compositions are in fact shown to be sensitive to deposition conditions.⁴¹⁻⁴⁶

The method of using band strengths to determine thickness is not thought to be as accurate as using interference fringes. Indeed errors on the thickness value can be up to 50% using the former method.¹⁵ Overall, variations in the values of the ice thickness have consequences for the Kramers-Kronig analysis, where they lead to conflicting results for the same ice system.¹⁶

Because an accurate value of the ice thickness is required in the Kramers-Kronig analysis, as well as a value of *n* in the visible region, methods have been developed to measure *n* for an ice. This removes the need to assume *n*. One such method involves reflecting two laser beams off the substrate during ice deposition at two angles of incidence, θ_1 and θ_2 .^{35,41,47} The periods of the resulting interference fringes, τ_1 and τ_2 , are used to determine *n* using equation (1.17).^{47–49}

$$n = \sqrt{\frac{\sin^2 \theta_2 - (\tau_1 / \tau_2)^2 \sin^2 \theta_1}{1 - (\tau_1 / \tau_2)^2}} \qquad (1.17)$$

Similarly, Berland *et al.*⁵⁰ used the ratio of the maximum and minimum of interference fringes of a single laser, along with n of the substrate, to determine the n value of the ice. These methods require no assumptions, nor knowledge of the ice thickness, however they still only measure n for the ice as it is grown. Therefore, any post-deposition change in the ice which may affect its optical parameters cannot be measured.

An alternative method to measure the ice thickness directly without knowledge of its refractive index is given by Ishikawa *et al.*⁵¹ where three angles of incidence are required. This method overcomes the issue of measuring *d* only during deposition, however *n* cannot be determined.

The methods used in the literature to determine the refractive index of ices as outlined here have several issues. The methods described above all require separate experimental procedures. A reference film is grown to determine *n*, and a subsequent deposition is then required to find *d*.³⁴ Additionally, assumptions are made which are not always appropriate for ices, such as using an assumed density to determine the thickness. Similarly, an overall refractive index of an ice may be assumed based on its constituents' refractive indices, which is not necessarily the case. Finally, the widely used Kramers-Kronig analysis is only applicable to transmission experiments. In this thesis, a novel ultraviolet/visible (UV/vis) spectroscopy apparatus is presented which has been used to address these concerns. The design, installation and testing of this apparatus is described in detail. The apparatus is then used to determine the refractive index and thickness of astronomically relevant ices using a single experimental procedure, without the need for assumptions. The adsorption and desorption behaviour of the ices examined are characterised using TPD and RAIRS. These data are related to the determined refractive indices and thicknesses.

1.2 Ices in Space

Section 1.1 outlined the importance of the refractive index, and how it has been determined for ices previously. This section gives context to the ices themselves and explains why examining their properties is of interest.

1.2.1 The Interstellar Medium and Astrophysical Environments

The interstellar medium (ISM) is the area of space between the stars. It makes up the majority of the volume of space, but is not empty, in fact it has a diverse composition. It is made up of a mix of gaseous and solid material. This gas is in the form of atoms, molecules and ions, whilst the solid material is in the form of small (\leq micron size)^{52,53} dust grains.⁵⁴ The ISM consists of a range of environments, which vary in composition, density and temperature. These environments have unique properties and behaviours, in particular their dynamics lead to the ISM being referred to as the birthplace of stars.^{20,38}

By volume, most of the ISM consists of hot ionised regions, HIRs. These are so named because they consist of ionised gas, and experience temperatures of 10⁵ K.^{20,54} The conditions in these regions are so extreme that species such as O⁶⁺ and N⁴⁺ can be used as chemical markers, as their ionisation potentials are sufficiently high that they can only form in HIRs. These regions form in the vicinity of young massive stars, which emit large amounts of high energy photons. They can additionally be formed by the high energy ejections of supernovae.⁵⁴ HIRs are not densely populated, with densities of 10⁻³ cm⁻³.⁵⁴

The next hottest region of the ISM is known as HII regions, named because they mostly consist of ionised hydrogen. As with the hot ionised regions, they are formed by energetic radiation from stars. Eventually an equilibrium between ionisation and recombination is reached in these regions.⁵⁴ Some HII regions are bright enough that they can be observed from Earth by the naked eye. An example of this are those HII regions found in the Orion nebula, Figure 1.3. Temperatures in these regions are of the order of 8000 K, and their densities are high, approximately 10⁴ cm⁻³.^{20,54}

The intermediate regions in the ISM, in terms of their temperatures, are known as the warm ionised medium (WIM) and the warm neutral medium (WNM). These regions are

both characterised by temperatures of several thousand Kelvin, and densities of 0.2 cm⁻³ - 0.5 cm⁻³.^{20,54} They contain a mixture of atomic neutral and ionised gases, primarily hydrogen atoms.



Figure 1.3 The Orion nebula, containing star forming regions and dust grains. Image credit: ESO/G. Beccari.

The coldest regions of the ISM are the interstellar molecular clouds. These clouds fall into two categories, diffuse molecular clouds and dense molecular clouds. Molecular clouds form from the collapse under gravity of other regions of the ISM, which is accompanied by cooling as radiation no longer penetrates as deeply into the cloud.⁵⁵ Because of this lack of penetrating radiation, molecular species are present, as opposed to the solely ionised species found in warmer regions. Diffuse clouds are characterised by temperatures of around 100 K and densities of 10 cm⁻³ – 100 cm⁻³.^{20,54} Dense clouds (also known as dark clouds), as the name suggests, have higher densities than diffuse clouds, of 10^2 cm⁻³ – 10^6 cm⁻³. This also leads to lower temperatures, as low as 10 K. The lower temperatures and shielding of stellar radiation by dust grains allow species to exist in molecular form rather than only ionised or atomic forms as in the warmer regions of the ISM. These molecules show a large amount of chemical diversity. Table 1.1 shows the more than 200 molecules that have been conclusively identified in the ISM.⁵⁶ The range of molecules detected is noteworthy, from simple diatomics such as H₂^{57,58} to fullerene species.^{59–61}

| Number of stores | | | | | | | |
|---|--------------------------------|--|-------------------------------------|------------------------------------|------------------------------------|----------------------------------|--|
| 2 | | Λ | F | | 7 | 0 | |
| | <u> </u> | 4 | 5 | | | | |
| | C-H | | C.U | LH-C. | | | |
| | | | | | | | |
| AICI | C20 | | | | | | |
| | | C30 | | | | | |
| | | | | | | | |
| CH | HCN | | H2CCN | | | | |
| | | | | | | | |
| CO | HCO+ | HCCN | HC3N | | | | |
| <u> </u> | HCS+ | HUNH | HC2NC | | | | |
| <u><u></u> <u></u> <u></u> <u></u> <u></u> <u></u> <u></u> <u></u> <u></u> <u></u> <u></u> <u></u> <u></u> </u> | HUC | HNCO | HCOOH | NH2CHO | CH3NCO | H2NCH2CN | |
| SIC | H ₂ O | HNCS | H ₂ CNH | C5N | HC50 | CH3CHNH | |
| HCI | H ₂ S | HOCO | H ₂ C ₂ O | I-HC4H | HOCH ₂ CN | CH ₃ SIH ₃ | |
| KCI | HNC | H ₂ CO | H ₂ NCN | I-HC4N | | | |
| NH | HNO | H ₂ CN | HNC ₃ | c-H ₂ C ₃ O | | | |
| NO | MgCN | H₂CS | SiH ₄ | H ₂ CCNH (?) | | | |
| NS | MgNC | H₃O⁺ | H₂COH⁺ | C₅N⁻ | | | |
| NaCl | N₂H⁺ | c-SiC₃ | C₄H [−] | HNCHCN | | | |
| OH | N ₂ O | CH₃ | HC(O)CN | SiH₃CN | | | |
| PN | NaCN | C₃N⁻ | HNCNH | C₅S (?) | | | |
| SO | OCS | PH₃ | CH₃O | | | | |
| SO+ | SO ₂ | HCNO | NH4 ⁺ | | | | |
| SiN | c-SiC ₂ | HOCN | H ₂ NCO ⁺ | | | | |
| SiO | CO ₂ | HSCN | NCCNH ⁺ | | | | |
| SiS | NH ₂ | H ₂ O ₂ | CH₃Cl | | | | |
| CS | H ₃ ⁺ | C₃H⁺ | | | | | |
| HF | SiCN | HMgNC | | | | | |
| HD | AINC | HCCO | | | | | |
| FeO ? | SiNC | CNCN | | | | | |
| 02 | HCP | | | | | | |
| CF⁺ | CCP | | | Number of atom | าร | | |
| SiH ? | AIOH | 9 | 10 | 11 | 12 | >12 | |
| PO | H_2O^+ | CH₃C₄H | CH₃C₅N | HC₃N | c-C ₆ H ₆ | C60 | |
| AlO | H ₂ Cl ⁺ | CH ₃ CH ₂ CN | (CH ₃) ₂ CO | CH₃C ₆ H | n-C₃H ₇ CN | C ₇₀ | |
| OH⁺ | KCN | (CH ₃) ₂ O | (CH ₂ OH) ₂ | C ₂ H ₅ OCHO | i-C ₃ H ₇ CN | C_{60}^+ | |
| CN⁻ | FeCN | CH ₃ CH ₂ OH | CH ₃ CH ₂ CHO | CH₃OC(O)CH₃ | $C_2H_5OCH_3$? | c-C₀H₅CN | |
| SH⁺ | HO ₂ | HC ₇ N | CH ₃ CHCH ₂ O | | | | |
| SH | TiO ₂ | C ₈ H | CH ₃ OCH ₂ OH | | | | |
| HCl⁺ | C_2N | CH ₃ C(O)NH ₂ | | | | | |
| TiO | Si ₂ C | C ₈ H [−] | | | | | |
| ArH ⁺ | HS ₂ | C₃H ₆ | | | | | |
| N ₂ | HCS | CH ₃ CH ₂ SH (?) | | | | | |
| NO ⁺ ? | HSC | CH ₃ NHCHO ? | | | | | |
| NS ⁺ | NCO | HC7O | | | | | |

Table 1.1 List of molecules detected in the ISM up to January 2019.⁵⁶ ? indicates that the detection is tentative but has a reasonable chance of being correct. (?) indicates that partial line overlap cannot be ruled out or the line list is small.

It is not only pre-stellar environments in space which are of relevance to this thesis. An additional environment is the protoplanetary nebula (PPN). This is a late stage in the life cycle of a medium sized star, of mass 0.8 M_{\odot} - 9 M_{\odot}^{62–64} where M_{\odot} is one solar mass, approximately equal to 1.99 × 10³⁰ kg. A PPN consists of a late asymptotic giant branch (AGB) stage star (commonly known as a red giant) which ejects material as its outer shell burns away. This ejection of material causes a stellar wind which shocks and perturbs the surrounding gas and dust.^{62,63} This causes a range of temperatures and velocities within the PPN, from hot regions (up to 10⁴ K)⁶³ near to the star, to shielded dense clumps with temperatures as low as 100 K.^{65,66} These regions are so named because they are the precursors to planetary nebulae which are themselves named because they resembled gas giants in early observations. These regions should not be confused with protoplanetary disks, a distinct type of astronomical object named due to their potential to form planetary bodies.

1.2.2 Dust Grains

In all the environments discussed above, as well as gaseous species, dust grains are present.⁵³ The most likely first observation of dust in the interstellar medium was by William Herschel in around 1784, although it was not interpreted as such at the time. Herschel observed that regions of the night sky were completely devoid of stars.⁶⁷ An example of one of these regions is shown in Figure 1.4. What was thought to be an absence of stars was in fact the presence of interstellar dust grains which obscured the radiation from stars behind them. These solid particles form in the outflows of dying stars.⁶⁷ The first link between observed reddening of the light from stars and the extinction of radiation from the ISM being due to dust grains was drawn by Trumpler in 1930.⁶⁸ It is this extinction that gives clues about the composition and size of dust grains. Figure 1.5 shows an average extinction curve for the Milky Way as a function of wavelength. Fitting of this curve yields a size distribution of grains from 0.001 μ m – 1 μ m in size.^{52–54,67,69}


Figure 1.4 An apparent "hole in the sky" as observed by Herschel. In fact this image shows the dense molecular cloud B68. Image credit: ESO.



Figure 1.5 Extinction curve of the Milky Way as a function of wavelength. Adapted from Fitzpatrick.⁷⁰

This curve also yields information about the composition of dust grains in space. The bump in the curve at 2175 Å has been attributed to carbonaceous grains.⁵² Stecher and Donn⁷¹ showed that small graphitic grains would reproduce the bump in the extinction curve well. However graphite grains alone cannot reproduce the observed variation in

the full width at half maximum (FWHM) of the feature.⁷² As a result, carbonaceous grain candidate materials include graphite,⁷¹ diamond,^{52,73} amorphous carbon^{52,74} and polycyclic aromatic hydrocarbons.^{52,67,75}

Silicaceous material is also thought to make up a large fraction of dust grains. The evidence for this is spectroscopic, as shown in Figure 1.6, which shows a spectrum of the young stellar object (YSO) W33A.⁷⁶ The spectrum shows strong absorptions at around 10 μ m and 18 μ m, which correspond to the Si-O stretching mode and O-Si-O bending mode respectively.⁵² By comparison with spectra of silicates produced in the laboratory, it is thought that the majority of silicaceous material in dust grains is amorphous.⁵²

Figure 1.6 also exhibits features which are not due to silicates, as shown on the figure. These are not due to dust grains made of other material, but due to solid material adsorbed onto the dust grains themselves.



Figure 1.6 Spectrum of W33A showing silicate grain spectral features. Additional features are due to ices on the dust grain. Reproduced from Gibb et al.⁷⁶

1.2.3 Icy Mantles

Whilst dust grains account for only 1% of the mass of the ISM,^{25,52,54,67} they play a pivotal role in its chemistry. This is because of the presence of icy mantles, made up of molecules which accrete onto the dust grains at low temperature. Evidence for ices is

shown in Figure 1.6, where several molecules are shown spectroscopically to be present on silicaceous dust grains around W33A.⁷⁶ Spectra around other objects also show the presence of ices and dust in their IR spectra.⁷⁷

These mantles undergo energetic processing which leads to the formation, and subsequent evaporation, of more complex molecular species.²⁵ Forms of ice processing are summarised in Figure 1.7. Evidence of this grain surface chemistry is shown by the fact that ice compositions and abundances do not match the local gas environment.⁷⁸ Additionally, observed gas phase abundances of some species such as H₂⁷⁹ and H₂O⁸⁰ cannot be recreated in models of the ISM using gas phase processes alone. For other species such as H₂O₂⁸¹ and HO₂,⁸² only surface chemistry can explain their presence, and observed gaseous abundances agree well with those predicted by surface reactions.^{80,83,84}



Figure 1.7 Schematic showing the processing routes which ices undergo in astrophysical environments. The main constituents of ices are shown in the inner layer. Reproduced from Burke and Brown.²⁵

The composition of interstellar ices varies according to their environment.^{25,77} Regions of high abundances of H give rise to largely water dominated ices, known as polar ices,⁸⁵ whereas less H rich regions tend to favour the accretion of apolar ices containing molecules such as CO and CO₂.⁹ Nevertheless, water is thought to be the dominant species in ices.^{25,54,67,86} Other species that are commonly found in ices are CH₃OH, CH₄ and NH₃, these and others are shown in Figure 1.7. The relative abundances in ices of

several species compared to water are shown in Table 1.2, as measured by their IR spectra.

Table 1.2 The ice abundance of several species around different stellar sources with respect to water. –

 indicates no detection was made. * indicates that a detection was made but an abundance was not

 determined. afrom references^{77,87–92}, bfrom references^{77,93–95}, cfrom references^{77,87,88}, dfrom

 references^{77,90,96–98}.

| Ice Species | Source | | | | |
|-----------------|-----------------------|----------------------|-----------------------|--------------------------|--|
| | W3 IRS 5 ^a | Elias 1 ^b | Orion BN ^c | R CrA IRS 2 ^d | |
| H₂O | 100 | 100 | 100 | 100 | |
| CH₃OH | <12.5 | n | <27 | 46 | |
| СО | 3.1 | 8.7 | * | 53 | |
| CO ₂ | 13.9 | 52 | 11.6 | 36 | |
| CH ₄ | <1.3 | - | <1.7 | - | |
| NH ₃ | <5.7 | * | <10 | - | |
| РАН | - | * | * | - | |

1.2.4 Icy Planetary Bodies

As well as icy mantles on dust grains, ice is present in the universe on planetary bodies. The term planetary body refers to any body which orbits a larger body, be that a star or other planetary body. They are defined, by Stern and Levison, as being within a certain mass range as follows:⁹⁹

"1. Be low enough in mass that at no time (past or present) can it generate energy in its interior due to any self-sustaining nuclear fusion chain reaction (else it would be a brown dwarf or a star). And also,

2. Be large enough that its shape becomes determined primarily by gravity rather than mechanical strength or other factors (e.g., surface tension, rotation rate) [...]"⁹⁹

A representative example of an icy planetary body in the solar system is Europa, the sixth moon of Jupiter in terms of distance from the planet. Europa is primarily made up of silicaceous rock, with an outer layer of water around 100 km thick, which is partly frozen and partly liquid.^{100,101} Both the underlying liquid ocean, and its ice layer are thought to contain large amounts of salt species including carbonates, sulfates and chlorides of magnesium, sodium, calcium and potassium.¹⁰² This has been suggested

from laboratory experiments and through magnetic field measurements by NASA's *Galileo* mission.¹⁰³

Water is not the only species that can cover an icy planetary body. For example, the surface of Pluto is dominated by N₂ ice, with the next most abundant species being CH₄, CO_2 and water at approximately 50 times lower abundance.¹⁰⁴ More recent observations of Pluto by NASA's *New Horizons* craft revealed that, across the surface, the ice composition changes and contains species such as CH₃OH, C₂H₆, C₂H₄ and C₃H₈.¹⁰⁵

1.3 Experimental Astrochemistry

Laboratory experiments have been used to gain a greater understanding of the chemical processes that occur in the ISM. Both gas phase and surface processes have been the focus of laboratory studies. This thesis is focussed on ices, therefore gas phase experiments are not summarised here, however they have been examined in detail in a review by Smith.¹⁰⁶

<u>1.3.1 Laboratory Ice Experiments</u>

In order to gain a better understanding of the chemistry that occurs in ices in space several experimental techniques have been used. Typically these experiments employ high vacuum or UHV chambers which contain a cold substrate on which molecules are deposited. Once molecules are deposited, they can be subjected to processing analogous to interstellar ices. This allows their spectra, adsorption and desorption parameters, chemical reactivity and interaction with radiation to be determined.

A range of substrates have been used in ice experiments. Metal surfaces such as gold,^{28,35,41} stainless steel^{107,108} and gold plated copper¹⁰⁹ have been used. Additionally semiconductor materials such as silicon^{110,111} and germanium⁴⁹ and IR transparent materials such as CsI,^{13,14,112} KBr,^{18,22,39} CaF₂¹¹³ and thallium bromoiodide¹⁷ have been employed. These substrates are useful as they can be easily characterised structurally, and allow high signal to noise transmission experiments to be performed. However, they are not representative of dust grains. In order to examine the behaviour of molecules on more representative surfaces, amorphous silica (a-SiO₂)^{33,114,115} and highly oriented pyrolytic graphite (HOPG)^{32,116–119} surfaces have been used in astrochemical ice

experiments. These surfaces are used as silicaceous and carbonaceous dust grain analogues respectively. Other carbonaceous surfaces have been used such as graphite^{119–121} and graphene.^{122,123} Recently nanostructured HOPG¹²⁴ has been used as a substrate in order to replicate a dust grain even more accurately, since real grains are unlikely to be smooth but will be rough, with a range of adsorption sites.^{52,67}

Once the molecules of interest are deposited on the chosen substrate, a range of experimental techniques have been used to gain different information relevant to interstellar ices. The most basic information that can be obtained from ices is their spectra. Whilst relatively simple to obtain, spectra in a range of regions of the electromagnetic spectrum are useful in order to compare to observations of the ISM and aid the identification of molecules.¹²⁵ For example laboratory IR spectra of NH₃ ices were used to provide the first detection of NH₃ around a low mass YSO.¹²⁶

Spectroscopy of ices is also used to examine the effect of processing of the ice. One such processing method is ion bombardment. This is used as a simulation of cosmic ray irradiation¹¹⁰ of interstellar ices and interstellar ion bombardment.¹²⁷ Irradiation of CH₃OH and mixed CH₃OH/CO ices by H⁺ ions has shown by its IR signature that the important interstellar molecule methyl formate (HC(O)OCH₃) can be formed in ices, in abundances consistent with those observed in the ISM.¹¹⁰ An alternative energetic processing method is UV photon irradiation. This is analogous to the UV light of stars processing ices and leads to both photodissociation and photodesorption of ice species,¹²⁸ explaining both the formation and presence in the gas phase of species. Photon irradiation of ices made up of H₂O, CH₃OH and NH₃ (all shown to be present in interstellar ices in Table 1.2) led to a variety of photochemical products.¹²⁹ Most notably, the sugar ribose (C₅H₁₀O₅), which is the backbone of ribonucleic acid (RNA), was found in the irradiated ice.¹²⁹ The ice was analysed using two-dimensional gas chromatography¹³⁰ coupled with time-of-flight mass spectrometry (GC × GC-TOF-MS).¹³¹ This is an example of another powerful laboratory technique which can be applied to surface astrochemistry.

As well as the formation of molecules in ices, their return to the gas phase is of interest to the astrochemical community. In addition to photodesorption described above, electron stimulated desorption is an astronomically relevant desorption process, as low energy secondary electrons are thought to exist as a result of cosmic ray ionisation events.¹³² Thermally induced desorption of ices also occurs in the ISM, which is examined in this thesis. Examining the thermal desorption of ices is useful to astronomers; if the temperature of desorption of a species is known, it can be used to show the temperature of an astrophysical object. More accurately, the desorption parameters of a molecule, that is the desorption order, desorption energy and preexponential factor, can be used to predict if a species will be gaseous or in an ice.²⁵ These parameters, determined by TPD experiments, can be used in models of the ISM.^{133,134} The details of TPD and how it is used to determine desorption parameters are given in Chapter 2.

1.3.2 Water Ice

As the most abundant species in ices, the surface behaviour of water has received considerable attention in the laboratory.^{14,28,33,45,86,111,124,135–143} Understanding the adsorption and desorption of water ice is vital to understanding the chemistry of the ISM. Due to its importance in space, several water containing ices are examined in this thesis. It is therefore relevant to discuss the behaviour of water ices, as examined previously in the literature.

Water has been shown to adsorb on surfaces at low temperature (\leq 30 K) in a porous amorphous form, characterised by a rough surface morphology, known as amorphous solid water (ASW).²⁵ As the temperature of the ice is increased, between 30 K and 70 K it compacts and molecules can become trapped in the pore system. Subsequently, water undergoes a phase change from ASW to crystalline ice (CI) at which point trapped molecules rapidly desorb in what is known as volcano desorption.^{25,28,139} Furthermore, some species remain trapped within the water ice until the complete desorption of CI and desorb concurrently with the water, known as co-desorption.²⁵ In this work, the ASW-CI phase change occurs at 147 K, and the CI desorption temperature is 156 K. The desorption behaviour of water ice is shown in Figure 1.8.



Figure 1.8 Cartoon illustrating the trapping and desorption of a volatile adsorbate (orange) by water (blue) under laboratory conditions.

The exact morphology of water ice is dependent on several factors, including deposition temperature, deposition angle and thermal history of the ice and subtrate.^{42–44,140} Direct deposition and temperatures > 50 K favour the formation of less porous compact ASW, whereas lower deposition temperatures and deposition angles far from the surface normal favour the formation of more porous ASW.^{42,43,137} Alternatively, CI can be grown directly by depositing water at even higher temperatures, around 130 K.¹⁴²

In this thesis, pure water ices and two component, water containing ices are examined. Multi-component ices containing water are relevant to space, due to the high abundance and relatively low volatility of water.

1.4 Polycyclic Aromatic Hydrocarbons

Two of the molecules examined in this thesis are benzene and toluene. They are both of interest to the astrochemical community as building blocks of polycyclic aromatic hydrocarbons (PAHs).^{144,145} A PAH is an aromatic molecule made up of more than one aromatic ring. The simplest example is naphthalene, made up of two fused benzene rings. Some example PAHs are shown in Figure 1.9.

Identification of interstellar PAHs is done through their distinct IR emission signatures, which are made up of characteristic aromatic C-C and C-H stretching modes, alongside combination modes of C-C stretches and C-H bending and wagging modes.⁷⁵ Spectra of PAHs in the ISM also led researchers to the conclusion that there is little aliphatic substitution on PAH edges,^{145,146} and that PAH species in space are likely to be relatively unsubstituted. The intensity of PAH spectral features has also been used to estimate

their abundance. Whilst this varies in different astronomical environments, with lower abundances in HII regions and higher abundances in cooler regions such as diffuse clouds,¹⁴⁵ overall it is estimated that PAHs account for 5 – 20% of elemental interstellar carbon.^{20,75,145–147} The observed PAH IR emission is due to PAH molecules being excited by UV photons and subsequently fluorescing in the IR spectral range.^{145–148}



Figure 1.9 Examples of PAH molecules. A: naphthalene. B: anthracene. C: coronene. D: ovalene.

The formation of PAH species in space is thought to occur in the AGB stage of carbon rich stars, where material is ejected from the dying star.^{145–147} However direct observation of PAHs around AGB stars is lacking. This is a consequence of the fact that AGB stars are not highly emissive in the UV and therefore PAH excitation occurs to a lesser degree.¹⁴⁵ However PAH emission around an AGB star has been observed from a binary system where one star is more emissive in the UV.¹⁴⁹ Additional evidence for PAH formation in AGB stars is that PAHs are observed in protoplanetary nebulae and planetary nebulae, which form in the aftermath of an AGB star.¹⁴⁵ One suggested chemical mechanism for the production of PAHs is from small C and H containing building blocks,¹⁵⁰ *i.e.* benzene is formed initially and is subsequently built up to form PAH species. This mechanism is based upon the formation of aromatic species in flame soot, however more recent experimental work also suggests that benzene formation in the ISM proceeds *via* the reaction between C₂H radicals and butadiene.^{151,152} Further

evidence that benzene may be an important species for PAH formation is that its first detection was in a protoplanetary nebula, where PAHs are also found.¹⁵³ The related species toluene may also play a role in PAH formation, as part of the pathway between benzene and larger aromatics. Indeed, toluene is thought to be formed in the gas phase in a similar manner to benzene,¹⁵⁴ and is predicted to be present in the same environments.¹⁵⁵ PAHs are a candidate material for carbonaceous dust grains.^{52,67,75} Hence laboratory studies on these two potential building blocks are of clear importance.

1.5 Complex Organic Molecules

Another molecule which is examined in this thesis is methyl formate, $HC(O)OCH_3$. This is the simplest ester and was first detected in 1974 in the giant molecular cloud Sagittarius B2 (Sgr B2).¹⁵⁶ Methyl formate is an example of an interstellar complex organic molecule (COM), which is defined as a carbon containing molecule which is made up of ≥ 6 atoms.¹⁵⁷ As shown in Table 1.1, every molecule detected in space which contains more than 6 atoms is in fact a COM, and they are detected in nearly all astronomical environments.¹⁵⁷ Detection and identification is usually a result of gas-phase COMs, as spectral signals in ices are often overlapping and extremely weak.¹⁵⁷ However, as shown in Figure 1.6, COMs in ices are shown to be present, CH₃OH in this case. With the upcoming launch of the James Webb Space Telescope (JWST), more condensed COMs are likely to be detected as increased spectral resolution and sensitivity becomes possible.¹⁵⁸

Because of their ubiquity and variety, COMs can be used as chemical tracers in the ISM. An example of this is the cyanopolyynes which are molecules with the general formula $H-CC_nC\equiv N$ where *n* is an odd integer and the bond orders alternate between 1 and 3.¹⁵⁹ The determined abundance of these molecules for different *n* values has been used to show local variations in temperature within the Taurus molecular cloud.¹⁶⁰ Equally they have been used to age the binary star system IRAS 16293–2422.¹⁶¹

An additional reason for the interest in COMs is because they encompass the class of molecules known as pre-biotic molecules. Typically these are COMs containing atoms or structural motifs in common with molecules in living organisms.¹⁵⁷ Examples of pre-biotic molecules that have been detected are glycolaldehyde, CH₂OHCHO, considered to

be the first interstellar sugar, and amino acetonitrile, H₂NCH2CN, a direct precursor to the amino acid glycine (H₂NCH₂COOH).^{162,163}

As is the case for PAHs, above, due to their importance and ubiquity in the ISM, COMs are an ideal class of molecule to examine in the laboratory. In this thesis, ices containing the COM methyl formate are examined and discussed.

1.6 Thesis Overview

In light of the discussion presented in this introduction, a novel UV/vis spectrometer has been developed which is used to determine refractive indices and thickness of interstellar ice analogues. The design, testing and installation of the apparatus is described in detail in Chapter 3. The analysis method is also described in detail. The issues with previous methods to measure the refractive index and thickness of ices, outlined in section 1.1.2, are addressed by the apparatus.

Benzene is used a test system due to its relevance to the ISM and because it has well defined UV/vis absorptions. This apparatus is also used to determine the refractive indices of toluene, methyl formate and water ices. The importance of these determined parameters is discussed. The refractive indices of mixed ices of methyl formate and water in varying proportions are also examined. The refractive indices of pure water and methyl formate ices are used to examine the assumption that the refractive index of a mixed ice can be determined from the weighted average of its constituents.

The ices examined in this thesis are characterised in terms of their structure, adsorption and desorption using TPD and RAIRS. In the case of benzene and toluene, both as pure ices and in the presence of water, the desorption parameters which are determined are applied to simple model of desorption on astronomical timescales.

Overall, this thesis shows the importance of accurate and comprehensive laboratory data to the wider field of astrochemistry.

2 Equipment and Experimental Techniques

In order for the experiments described in this thesis to be relevant to the interstellar medium (ISM), the pressures and temperatures described in Chapter 1 (up to 10^6 hydrogen molecules cm⁻³ and 10 - 100 K)^{20,25} must be simulated. Whilst current vacuum technology is insufficient to obtain the pressures of the ISM (approximately 1.4×10^{-13} mbar using a gas density of 10^4 H₂ cm⁻³ and a temperature of 100 K), the pressures achieved ($\approx 10^{-10}$ mbar in this work) are low enough to ensure sample cleanliness during a typical experimental timescale of several hours. This level of vacuum is known as Ultra High Vacuum (UHV). Temperatures of approximately 25 K are routinely obtained in this laboratory.

This chapter will describe the general equipment required to simulate these conditions, the analytical instruments used in this work and the principles of the experiments performed.

2.1 Ultra High Vacuum Chamber

The stainless steel UHV chamber used in this work is shown in Figure 2.1. In order to obtain UHV, a series of procedures and various pumps are employed. When pumping the chamber down from atmospheric pressure, and periodically to maintain UHV in general use, a bake out is required. Pumping down from atmospheric pressure is initially done using a rotary pump (Leybold D8B) until a pressure of approximately 5×10^{-3} mbar is achieved. A turbomolecular pump (TMP) (Leybold Turbovac 151), backed by the rotary pump, is then employed to reduce the pressure to between 1×10^{-8} mbar and 1×10^{-7} mbar. At this pressure, the chamber is enclosed inside insulated metal covers and heated to 380 K. This heating causes species which are adsorbed on the chamber walls, in particular water, to desorb and also reduces outgassing of any newly installed components. The temperature is maintained for at least 24 hours, until the pressure inside the chamber, as measured by an ion gauge (ITL Vacuum), stabilises indicating that desorption is complete. Simultaneously, the ion pump (IP) (Physical Electronics) is baked to remove adsorbed material from its electrodes. Once the bake out is complete, the IP is switched on to achieve UHV. The IP works by ionising incoming gas molecules via collisions with electrons which are trapped in a strong magnetic field. Once the molecule

is ionised it is trapped on an electrically charged metal plate. Further pumping is achieved with a titanium sublimation pump (TSP). This pump uses high currents of approximately 50 A to vaporise titanium (Ti) which coats the walls around the TSP with a clean layer of Ti onto which reactive gas molecules adsorb, reducing the chamber pressure. With this setup, base pressures of 1×10^{-10} mbar inside the chamber are routinely achieved.



Figure 2.1 Photograph of the UHV chamber used in this work. The expander is part of the closed cycle helium refrigerator. All labelled parts are discussed in detail in the text.

External to the chamber, there is a vacuum line which is pumped by a TMP (Leybold Turbovac 50) backed by a rotary pump (Leybold D4B). Pressures of 1×10^{-3} mbar, as measured by a Pirani gauge, are routinely achieved. Attached to this line are glass chemical reservoirs which contain the molecules of interest. It is also possible to attach gas cylinders or lecture bottles when these are gaseous. These molecules are used to

grow ices by admitting them into the chamber *via* one of two high precision leak valves. This is known as dosing and is described in section 2.3.

Gate valves allow the chamber TMP and the ion pump to be isolated and kept under vacuum. This is useful to protect the pumps if the chamber needs to be vented to atmospheric pressure, such as when new equipment is installed or maintenance is required. The system of pumps and valves for the chamber is shown schematically in Figure 2.2.



Figure 2.2 Schematic of the pump and valve setup of the chamber which allows UHV to be obtained and ices to be grown.

In order to maintain UHV and avoid a pressure gradient between atmospheric pressure and UHV, for example at the infrared (IR) windows (see below), differential pumping is employed. Using the same rotary pump which backs the chamber TMP, the IR windows and rotary feedthrough (differentially pumped rotary feedthrough, DPRF) of the sample manipulator are differentially pumped. Differential regions are typically held at 5×10^{-4} mbar as measured by a Pirani gauge. The surface used in this work is highly oriented pyrolytic graphite (HOPG), mounted on the end of a cold finger to obtain a surface temperature of approximately 25 K. The sample and mounting are described in detail in section 2.2. The cold finger is mounted on a manipulator which allow movement in the x, y and z directions. The x and y movement allows 5 micron control, and millimetre control is given in the z direction. Additionally, the sample can be rotated *via* a DPRF. This setup allows the sample to be moved depending on experimental requirements, additionally it is essential to obtain the best signal possible in infrared experiments.

The chamber is equipped with several pieces of analytical equipment which are shown schematically in Figure 2.3. In order to carry out temperature programmed desorption (TPD) experiments and record residual gas analyses (RGA), the chamber is equipped with a quadrupole mass spectrometer (QMS) (Hiden Analytical HAL 201 PIC) which faces the centre of the chamber. The QMS is controlled *via* a PC which runs MASsoft software.¹⁶⁴



Figure 2.3 Labelled schematic of the analytical equipment installed on the UHV chamber, including the RAIRS optical path. All the ports are at the same level, allowing UV and RAIRS experiments to be performed simultaneously.

Reflection absorption infrared spectroscopy (RAIRS) experiments employ a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700) coupled to an external, liquid nitrogen cooled mercury cadmium telluride (MCT) detector (Thermo Fisher Scientific). Infrared light (IR) is directed into the chamber through a potassium bromide (KBr) window by a pair of directing mirrors, where it reflects off the surface. The light passes through a second KBr window and is collected in the MCT detector *via* two more directing mirrors. The IR path is shown in Figure 2.3. KBr is chosen as the window material as it is highly transmitting in the spectral range from 40000 cm⁻¹ – 400 cm⁻¹ (0.25 μ m – 25 μ m), which corresponds to the near ultraviolet (UV) to far IR range.

A second reflection absorption technique described in this work is ultraviolet/visible (UV/vis) reflection absorption spectroscopy, which has been developed during the course of this research. Figure 2.3 shows the variable-angle lens arrangement which is fibre optically coupled to a UV/vis light source (Ocean Optics DH-2000-S-DUV-TTL) and spectrometer (Ocean Optics QE Pro). The design and installation of this apparatus is described in detail in Chapter 3. Briefly, the setup allows simultaneous recording of UV and RAIR spectra, along with heating.

2.2 Cold Finger and Sample

The sample and mounting were designed by Dr D. Burke, former member of the Brown group. Several considerations were taken into account when designing the sample mount. Namely, the sample must be in good thermal contact with the cold finger to ensure that temperatures of around 25 K (applicable to the ISM) are reached and that controlled, linear, heating of the sample is possible.

2.2.1 Temperature Control

The cold finger, on which the sample is mounted, is connected to a closed cycle helium refrigerator (SHI Cryogenics) which allows base temperatures of 25 K to be achieved. The temperature is measured by an N-type (Nicrosil-Nisil) thermocouple, attached to the back of the sample.

The entire cold finger and sample mount is housed in a gold plated radiation shield with a section cut out around the sample, which protects the sample from heating *via*

radiation from the chamber walls. Additionally, the thermocouple wire and wires which connect to the heating circuit are wrapped tightly around the length of the cold finger. This is necessary to avoid conductively heating the sample, as one end of the wires are at room temperature and the other at base temperature. The wires which connect to the heating circuit are made of Kapton-coated copper and attach to the sample mount. Details of the heating circuit are given in section 2.2.2.

Heating of the sample is achieved *via* resistive heating controlled by a Eurotherm temperature controller and iTools software. This allows the sample to be heated linearly, which is vital for the experiments described below. An example of the linear heating that can be achieved is shown in Figure 2.4, where the sample is heated from 25 K to 250 K at a heating rate of 0.5 K s⁻¹, held for one minute, and then allowed to cool.



Figure 2.4 An example heating ramp and subsequent cool to base temperature, 25 K, of the sample.

2.2.2 Sample Mount

The sample mount is composed of an oxygen-free high conductivity copper (OFHC Cu) plate, which is mounted on the end of the cold finger with a piece of sapphire between the two. Several layers of silver (Ag) foil are sandwiched between the mount and cold finger, and both sides of the sapphire, to ensure good thermal conductivity. The

sapphire piece serves two purposes. Firstly, it electrically isolates the cold finger from the mount, and secondly it protects the cold finger from heating when the sample is heated. This is due to the thermal properties of sapphire; it has high thermal conductivity at low temperatures, but poor thermal conductivity at high temperatures.¹⁶⁵ It is therefore an ideal material for this application.

The sample mount is shown schematically in Figure 2.5. Components of the heating circuit are mounted onto the back of the OFHC Cu plate. The Kapton coated wires, which are wrapped around the cold finger, feed into two OFHC Cu blocks, which are mounted onto a sapphire plate on the main OFHC Cu mount. These blocks are isolated from one another by a ceramic spacer to avoid a short circuit. In the bottom of each OFHC Cu block is a hole, into which a tungsten (W) stud is placed and held in place by a molybdenum screw. In the W stud, a piece of 0.5 mm diameter W/Rhenium (W/Re) wire is attached by silver solder. These wires are then attached to the sample to complete the resistive heating circuit.



Figure 2.5 Schematic of the sample mount and tension mechanism which is mounted on the end of the cold finger. Adapted from J. L. Edridge.¹⁶⁶

On the OFHC Cu plate there is a piece of sapphire, which is in thermal contact with the plate *via* Ag foil. This sapphire piece is blackened with the flame of a wax candle in order to avoid IR reflections from the sapphire interfering with RAIRS experiments. This sapphire piece electronically isolates the sample from the mount and, as mentioned above, has favourable thermal properties which protect the cold finger during sample heating. The next layer is a piece of tantalum (Ta) foil which is the same size as the HOPG sample. Onto this foil the N-type thermocouple wire is spot welded. In direct contact with the Ta is the HOPG sample (Goodfellows Ltd). The HOPG dimensions are 20 mm × 10 mm × 2 mm and the sample is cleaned using the "Scotch tape method"¹⁶⁷ before mounting. In the back of the HOPG there are grooves to house the W/Re heating wires and the thermocouple wire which are sandwiched between the HOPG and Ta foil.

The HOPG mounting is held together by a tension mechanism, shown in Figure 2.5. Wires are passed over the HOPG and through the sapphire and OFHC Cu plate to a tension mechanism. The tension wires are electrically isolated from the OFHC Cu plate by ceramic sleeves. The tension mechanism consists of an OFHC Cu cross into which four holes are drilled which the tension wires enter. The wires are held in place by stainless steel screws. The cross piece has a screw in the centre which is tightened against the OFHC Cu plate of the mount to increase the tension on the tension wires and hold the sample in place. On the end of the central screw is an OFHC Cu cap which ensures that there is an even distribution of force across the sample. The tension mechanism is electrically isolated from the rest of the mount by a ceramic disc.

HOPG is a form of graphite characterised by its highly ordered structure. It is defined as graphite with an angular spread between layers of < 1° .¹⁶⁸ Individual carbon atoms are separated by 0.142 nm and the interlayer distance is 0.335 nm.¹⁶⁹ The structure of HOPG is shown in Figure 2.6. It is used in this work as it can be considered a dust grain analogue.^{52,145}



Figure 2.6 Structure of graphite with the interatomic and interlayer distances shown. Dotted lines show the offset between the layers.

Additionally, HOPG possesses favourable experimental properties. It is thermally stable in the temperature range used, from 25 K – 500 K. It is also relatively chemically inert. Both of these mean that it is resistant to degradation and therefore will have a long experimental lifetime. The highly ordered structure of HOPG means that it is also well suited to theoretical studies which can be complementary to experiments, and it has been examined by both classical^{170,171} and quantum^{172–175} calculation methods.

2.2.3 Sample Cleanliness

At the start of each day, all pressures were recorded and a residual gas analysis (RGA) was performed. This involves using the QMS to scan across a mass range of 1 - 100 amu to ensure that the chamber is free of contaminants. Typically, the major species present were H₂ (mass 2) and H₂O (mass 18). Some other minor species were also present in small amounts compared to H₂ and H₂O. An example RGA is shown in Figure 2.7.

After a bake out, the sample is heated from room temperature to 500 K for approximately 3 minutes and the TSP is fired in order to remove adsorbed species and reactive gaseous species in the chamber. During normal operation, when the sample is kept at 25 K, each morning and after each experiment any adsorbates were removed from the surface by heating to 250 K for 3 mins. When 250 K is reached, the TSP is fired to remove reactive species from the chamber. This relatively low temperature is sufficient thanks to HOPG's low chemical reactivity. Additionally, the TSP is set to fire whenever the chamber pressure > 1×10^{-9} mbar, with the exception of during experiments. Sample cleanness was confirmed by the lack of desorption products (as measured by the QMS) during a simple heating cycle (as shown in Figure 2.4).



Figure 2.7 An example RGA for the UHV chamber.

2.3 Experimental Techniques

The data in this work are the result of three experimental techniques, the principles of which are described below. The details of the ice systems examined will be given in detail in later chapters. In all cases, doses are presented in Langmuir, L_m , where $1 L_m = 1 \times 10^{-6}$ mbar s. All chemicals were purified prior to use by repeated freeze-pump-thaw cycles to remove any dissolved gases. All chemicals used in this work, with their suppliers and purities, are shown in Table 2.1.

In order to grow an ice, the sample must be dosed with the desired molecules. The external vacuum lines are closed to the TMP by closing the Nupro valves shown in Figure 2.2, leaving them under static vacuum. The Young's tap or Nupro valve (depending on which chemical reservoir is being used) is then opened to fill the line with the gaseous

molecule. In this work the pressure in the line typically reaches 0.5 mbar – 12 mbar, which is sufficiently high for all doses. The maximum pressure used is 4×10^{-7} mbar. The relevant leak value is then opened to introduce the gaseous molecules into the chamber up to the desired pressure, as monitored by the ion gauge, for the appropriate time to give the dose in L_m. For example, a pressure of 5×10^{-8} mbar for 500 s would correspond to a dose of 25 L_m (as 0.05×10^{-6} mbar $\times 500$ s = 25 mbar s).

| Chemical | Supplier | Purity | |
|--|---------------|----------------|--|
| Benzene, C ₆ H ₆ | Sigma Aldrich | 99.9% | |
| Methyl Formate, HC(O)OCH ₃ | Sigma Aldrich | Anhydrous, 99% | |
| Toluene, C ₇ H ₈ | Sigma Aldrich | 99.9% | |
| Water, H ₂ O | N/A | Deionised | |

Table 2.1 Chemicals used in this work, with their suppliers and purities.

During a dose, the QMS is used to monitor the gas composition in the chamber. An example dose curve is shown in Figure 2.8, for a dose of 50 L_m of methyl formate. For clarity only the most intense mass fragment, m/z 31, is shown in the figure. However, other less intense methyl formate fragments are monitored simultaneously. Other fragments which are monitored include m/z 18, 28 and 44, corresponding to H₂O, N₂/CO and CO₂ respectively to check for atmospheric contaminants in the dose line. Over the course of a dose, the amount of adsorbate molecule in the chamber is kept constant by monitoring both the chamber pressure and QMS intensity, with the leak valve being adjusted if necessary.

It is important to note that the Langmuir is a non SI unit, and is not comparable between different experimental setups. That is, a dose of 10 L_m in the chamber used in this work will not give the same number of molecules on the surface as a 10 L_m dose in a different chamber. Differences in chamber volume, pumping efficiency, sample position and ambient gas temperature will all affect the dose. However, in any one chamber, when all factors are controlled, the same dose gives reproducible ices. This is shown in Figure 2.9, where the area under the dose curve for 3 separate 50 L_m doses of methyl formate are compared. In the case of the doses shown in Figure 2.9, deviations from the mean of the three areas are < 3%.



Figure 2.8 An example dose curve recorded by the QMS for 50 L_m methyl formate. The dose pressure and time were 2×10^{-7} mbar and 250 s respectively and the fragment shown is m/z 31.



Figure 2.9 Comparison of the area under the dose curve for three separate 50 L_m doses of methyl formate. The dose pressure and time were 4×10^{-7} mbar and 125 s respectively.

The areas of the dose curves shown in Figure 2.9 show that the same amount of methyl formate is admitted into the chamber during each dose. Whilst this is not a direct measure of the amount of adsorbate on the surface, all other factors are controlled and

therefore the sticking probability remains constant. Hence a reproducible dose curve means a consistent surface coverage is achieved. The position of the sample relative to the leak valve outlet will also affect the number of molecules on the surface. Dosing can be performed *via* backfilling, whereby the sample is positioned facing away from the leak valve and the adsorbate molecule is allowed to fill the chamber, or directionally where the sample faces the outlet. In this work both methods are employed. Backfilling is experimentally simpler, since the sample position need not be altered during an experiment. For example in a RAIRS experiment, if the sample is not moved between recording the background and dosing (see below), the risk of the optical alignment changing is reduced. However, it does mean that adsorbate molecules are more likely to freeze out on all cold surfaces of the chamber.²⁵ Directional dosing avoids this issue and allows thicker ices to be grown for the same dose when compared to backfilling, reducing gas load in the chamber.

Tests were performed to determine the difference between backfilling and directional dosing. The sample was dosed with $5 L_m - 15 L_m$ both by backfilling and directionally and TPD experiments were performed (see below section 2.3.2). The area under a TPD trace is directly proportional to the amount of adsorbate, therefore a plot of TPD area as a function of dose is linear. An example is shown in Figure 2.10 for benzene TPD areas as a function of dose in L_m.

It is clear that more molecules are deposited for the same dose *via* directional dosing than backfilling, evidenced by the larger TPD areas. In both cases a linear relationship is observed between dose and TPD area. The ratio of the gradients can be used to determine how much more adsorbate is deposited *via* direct dosing compared to backfilling. The ratio from the above figure is 18.56, meaning that approximately 19 times as many molecules are deposited for the same dose performed directionally compared to *via* backfilling.



Figure 2.10 Area under the benzene TPD curve as a function of dose in L_m for different dosing positions. Purple circles: dosed directionally. Black squares: dosed via backfilling. The lines represent a linear line of best fit to the data.

2.3.1 RAIRS

RAIRS is an established surface science technique which is used to examine vibrational transitions of adsorbates. Indeed it has been the subject of several recent reviews.^{176–179} RAIRS can be used to determine molecular orientations of adsorbates, due to the metal surface selection rule. The rule states that only modes with a component of their transition dipole moment parallel to the surface normal will be present in the spectrum. This can be explained with reference to the electric field vectors of the incident and reflected light, which can be split into p- and s- polarised which are parallel and perpendicular to the plane of incidence respectively. Figure 2.11 shows the effect on the p- and s- electric fields upon reflection from a metal surface. The s-polarised light undergoes a 180° phase shift, which cancels out the incident beam *via* destructive interference. The phase shift upon reflection of p-polarised light is found to vary with angle of incidence.¹⁸⁰ For metal surfaces, it was found that at an angle of incidence of around 88° with respect to the surface normal, the largest amplification of the p-polarised light occurs,¹⁸⁰ depending on the optical parameters of the specific metal.



Figure 2.11 The effect of reflection on the s- and p-polarised electric field vectors of the impinging light at a metal surface. I and R are the incident and reflected light paths respectively. The red arrows show the direction of the p-polarised electric field vector of the incident and reflected beam. Green arrows show the direction of the s-polarised electric field vector of the incident and reflected beam. Note that the spolarised light is cancelled out at a metal surface.

HOPG has been found to follow the metal surface selection rule.^{181,182} This is due to its semi-metallic nature, with a delocalised π electron cloud analogous to a metal's sea of electrons. The optimum reflection angle is 73°, shown in Figure 2.12, where the surface intensity factor as a function of angle of incidence is plotted. The intensity factor is shown for the s- and p-polarised electric fields. The surface intensity factor, $(E/E_0)^2/\cos\theta$, is obtained by combining the square of the ratio of the oscillating electric field vector at the surface, *E*, and the field vector in the incident beam, *E*₀, with the change in the area of the surface which is illuminated with angle of incidence, θ , which is given by $1/\cos\theta$. In the setup described above, the reflection angle used is 75°, however this slight difference does not significantly hinder the RAIRS experiments.



Figure 2.12 Surface intensity factor for s- (E_s) and p-polarised (E_p) IR light as a function of angle of incidence on a graphite surface. Reproduced from Heidberg and Warskulat.¹⁸¹

The entire external IR path is enclosed within metal boxes which are purged with dry, CO_2 free air. This is to minimise the absorption of IR light by gaseous atmospheric H₂O and CO_2 . The boxes are shown around the mirrors and detector in Figure 2.3.

To produce a RAIR spectrum, an initial background spectrum of the clean HOPG surface is recorded, then after the sample is dosed a second spectrum is recorded. This allows the spectra in this work to be plotted as $\Delta R/R$ as a function of wavenumber, as shown in equation (2.1) where R_0 and R represent the background and sample spectra respectively.

$$\frac{\Delta R}{R} = \frac{R - R_0}{R_0} \qquad (2.1)$$

Plotting spectra in this way corrects for the fact that the output from the IR source is not of a constant intensity across the spectral range recorded (4000 cm⁻¹ – 800 cm⁻¹ or 2.5 μ m – 12.5 μ m). An example RAIR spectrum of 100 L_m benzene deposited at 25 K on HOPG is shown Figure 2.13. The region between 2500 cm⁻¹ – 2000 cm⁻¹ is omitted as it contains a large CO₂ asymmetric stretch centred around 2360 cm⁻¹, which is a contribution from atmospheric CO₂, which is not removed by the purge. In all experiments, after the background is recorded, a spectrum of the clean sample is recorded to give a $\Delta R/R$ spectrum. This allows a clean spectrum to be subtracted from a sample spectrum if necessary to remove residual water peaks which are not removed by the purge.



Figure 2.13 RAIR spectrum of 100 Lm benzene deposited on HOPG at 25 K. The vibrational modes leading to the bands at 3090 cm⁻¹, 3034 cm⁻¹, 1479 cm⁻¹ and 1036 cm⁻¹ are illustrated on the spectrum. The region between 2500 cm⁻¹ – 2000 cm⁻¹ is omitted to remove contributions from atmospheric CO₂.

In this work, two types of RAIRS experiments are performed. Adsorption experiments monitor the evolution of RAIR spectra with increasing dose. A spectrum is recorded of the clean surface, and subsequently a dose is performed and another spectrum taken. This process is then repeated until a total dose of up to 200 L_m is reached. The endpoint is chosen to match the maximum TPD dose, however higher doses can be performed. Dosing *via* backfilling is employed so the RAIRS alignment need not be altered in these experiments. Adsorption experiments can be used to obtain information about molecular orientation on the HOPG surface using the metal surface selection rule. However, care must be taken not to assume that a band is not present because the transition responsible for it is parallel to the surface, when in fact its intensity may just be too low to distinguish from the noise of the baseline.

The second method is an annealing experiment. A single dose is performed and a spectrum recorded. The sample is then heated to a fixed temperature for 3 minutes and allowed to cool, then another spectrum is recorded. This continues until all of the RAIRS bands are no longer visible, indicating that desorption of the ice has occurred. Typically, temperature intervals of 10 K are used, however this is sometimes reduced in order to examine any temperature induced changes in more detail. Finally, the sample is heated to 250 K for 3 minutes and a spectrum is recorded of the clean surface. Annealing experiments are used to examine temperature induced changes in the ice structure, as well as complementing TPD experiments by showing desorption of the ice at a given temperature.

In all cases in this work, the RAIR spectra presented are the co-addition of 256 scans, with a resolution of 4 cm⁻¹. These parameters are chosen to give the best signal to noise ratio, whilst allowing spectra to be recorded over a short timescale, approximately 3 minutes in total.

<u>2.3.2 TPD</u>

TPD is a mass spectrometry technique that, whilst conceptually simple, is an extremely useful tool. Once an ice has been grown, the sample is positioned to face the QMS to give the greatest QMS signal and heated at a constant rate. In all cases in this work, the heating rate is 0.50 ± 0.01 K s⁻¹. The thermally induced desorption of the ice as a function of temperature is monitored by the QMS. Dependent on the system examined, several mass fragments, including the parent ion, are simultaneously monitored which are shown in Table 2.2. The subsequent trace of QMS intensity as a function of temperature can be used to determine desorption parameters, such as desorption energy, of a given adsorbate. It can also be used to examine physical desorption behaviour of the ice such as intermolecular interactions and trapping behaviour, *i.e.* where a molecule is held on the surface beyond its natural desorption temperature by the presence of another adsorbate. Example TPD traces for multilayer exposures of toluene are shown in Figure 2.14A.

| Malagula | Parent ion / m/z | Most intense | Other fragments |
|----------------|------------------|--|--|
| Wolecule | | fragment / m/z | monitored / m/z |
| Benzene | 78 | 78 (C ₆ H ₆) | 77 (C ₆ H ₅), 51 (C ₄ H ₃) |
| Methyl Formate | 60 | 31 (OCH₃) | 29 (CHO) |
| Toluene | 92 | 91 (C ₆ H₅CH ₂) | 39 (C ₃ H ₃) |
| Water | 18 | 18 | none |

 Table 2.2 Fragments monitored for each of the molecules used in this work.

The starting point of TPD analysis is the Polanyi-Wigner equation^{25,183} (equation (2.2)), below,

$$r_{des} = -\frac{d\theta}{dt} = v\theta^n \exp\left(\frac{-E_{des}}{RT}\right)$$
 (2.2)

where r_{des} is the rate of desorption, θ is the coverage, t is time, v is the pre-exponential factor, n is order of desorption, E_{des} is desorption energy, R is the gas constant (taken as 8.314 J K⁻¹ mol⁻¹) and T is the surface temperature.

Because a linear heating rate is used, the rate of change of coverage with time, $d\theta/dt$, is linked to the rate of change of coverage with temperature, $d\theta/dT$, as shown in equation (2.3).

$$-\frac{d\theta}{dt} = -\frac{d\theta}{dT} \times \frac{dT}{dt}$$
(2.3)

The rate of change of coverage with time is directly proportional to the QMS intensity, I(T). Therefore equation (2.2) becomes equation (2.4):

$$I(T) \propto v \theta^{n} \exp\left(\frac{-E_{des}}{RT}\right)$$
 (2.4)

This equation can be subsequently manipulated to determine n, E_{des} and v. By rearranging equation (2.4) and taking natural logarithms, equation (2.5) is given.

$$\ln[I(T)] \propto \ln(v) + n\ln(\theta_{rel}) - \left(\frac{E_{des}}{RT}\right)$$
 (2.5)

Using equation (2.5), a plot of In[I(T)] as a function of $In(\theta_{rel})$ at a fixed temperature for a number of TPD traces of different exposures will have a gradient of n. This is shown in

Figure 2.14B for toluene. Only points for multilayer exposures are shown for clarity. The temperature selected must be on the leading edge of all of the traces used. In Figure 2.14B, the temperature selected is 133 K and is shown by the dotted line on Figure 2.14A. It is also important to note that only the relative coverage, θ_{rel} , is known (taken as the area under the TPD trace from the temperature selected, shown as the red shaded area for a 70 L_m exposure on Figure 2.14A) as the QMS signal is proportional to the number of molecules desorbing.



Figure 2.14 Plots showing how desorption order, n, and desorption energy, E_{des} , are found for a series of toluene TPD traces shown in A. B: a plot on ln[I(T)] against $ln(\theta_{rel})$ for a fixed temperature of 133 K on the leading edge of traces from 40 L_m – 200 L_m of toluene. The red circles are individual data points, the red line is a linear fit to the data. C: a plot of $ln[I(T)] - nln(\theta_{rel})$ against 1/T for a 70 L_m exposure of toluene on HOPG. Blue squares are data points and the red line is the linear fit to the data.

Once *n* is known from equation (2.5), further rearrangement yields equation (2.6):

$$\ln[I(T)] - nln(\theta_{rel}) \propto ln(v) - \left(\frac{E_{des}}{RT}\right)$$
 (2.6)

Plotting $ln[I(T)] - nln(\theta_{rel})$ against 1/T for the leading edge of the TPD trace, shown in Figure 2.14C for a 70 L_m dose of toluene, allows E_{des} to be determined from the gradient, which is equal to $-E_{des}/R$.

Using the determined values for *n* and E_{des} , the value of v can be calculated. However, because the absolute coverage is not known, an estimation of the number of molecules deposited onto the surface must be made. This is done by considering the impingement rate of molecules onto the surface, which is the collision rate of molecules on the surface, *Z*, in molecules m⁻² s⁻¹ given by equation (2.7),

$$Z = \frac{p}{\sqrt{2\pi m k_B T}} \quad (2.7)$$

where *p* is the pressure in Pa, *m* is the mass of a single adsorbate molecule in kg, k_B is the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹) and *T* is the gas temperature (assumed to be 300 K in this work). It can be assumed that, when deposited at base temperature, the sticking probability is unity.^{33,125,132,184} As such, the number of molecules on the surface, N_m , is given by the product of *Z*, the dose time in seconds, *t*, and the sample area in m², *A*, shown by equation (2.8):

$$N_m = ZtA$$
 (2.8)

Given that a dose is measured in L_m , pressure multiplied by time, equation (2.8) can be re-written as equation (2.9),

$$N_{\rm m} = \frac{10^{-4} LA}{\sqrt{2\pi m k_{\rm B} T}}$$
 (2.9)

where *L* is the dose in L_m . The 10⁻⁴ term converts the pressure in mbar to Pa, as 10⁻⁶ mbar = 10⁻⁴ Pa. An additional consideration is the ion gauge sensitivity factor, this is given in later chapters where used.

The number of molecules on the surface is then plotted as a function of area under the TPD trace, and the gradient is taken as a scaling factor. This factor is used to relate the measured QMS intensity, I(T), and TPD trace area, θ_{rel} , to absolute intensity and coverage, $I_s(T)$ and θ_s respectively. Rearrangement of equation (2.2), gives equation (2.10), which is used to determine v.

$$v = \frac{I_s(T)}{\theta_s^n \exp(\frac{E_{des}}{RT})}$$
(2.10)

Once the desorption parameters of a given adsorbate are known, they can be used to simulate desorption on timescales more relevant to the ISM, such as 1 K century⁻¹. Additionally, non-linear heating rates can be simulated which are also more realistic than a linear rate.

3 Design, Installation and Testing of a Novel Ultraviolet/visible Reflection Absorption Spectroscopy Apparatus

This chapter describes the design, installation and testing of a novel UV/visible (UV/vis) reflection-absorption spectrometer. The apparatus is used to determine the optical parameters and thickness of interstellar ice analogues. These values are of interest as they can be used to model radiative transfer and spectra of various regions of space. Therefore it is important to be able to measure them accurately under conditions relevant to space. The key design feature, a variable angle lens assembly, is discussed. Additionally, modifications were required after the initial build which are detailed below. An analysis method which was originally applied to infrared spectra under ambient conditions has been adapted to the system used in this work. An analysis program to determine the complex refractive index, *N*, has been written in the Python language and tested using data from the literature. The application of this analysis to the experimental data presented in this chapter is discussed. The data are a proof of concept of the new apparatus and are used as a benchmark for later chapters.

3.1 Introduction

Determining refractive indices is of particular interest to the astrochemical community, specifically those of thin ice films. This is because dust grains present in the interstellar medium (ISM) provide a surface onto which molecules can accrete to form icy mantles.^{20,25} These ices undergo many forms of energetic processing, as discussed in Chapter 1, and the interaction of icy mantles with impinging light affects the radiative transfer of energy within regions of the ISM. Hence, knowledge of the complex refractive index, *N*, is essential for modelling this process in order to determine the amount of light absorbed, reflected and refracted.^{10,14} Here N = n + ik, where *n* is the real part of the refractive index, related to diffraction, and *k* is the imaginary part which is related to extinction.

Previous studies of ice analogues adsorbed onto surfaces have used the Kramers-Kronig relation, equation (1.13), to simulate infrared (IR) spectra of interstellar ices by

determining N.^{10,12–17} As discussed in Chapter 1, the Kramers-Kronig relation allows the determination of the real and imaginary parts of the complex refractive index as a function of wavelength, $N(\lambda)$.

Whilst the Kramers-Kronig method has been widely used to determine *N* of several astronomically relevant ice systems in the literature,^{10,12–17} several issues must be taken into consideration. The Kramers-Kronig relation requires an accurate value of the real part of the refractive index in the UV/vis range, n_0 , and of the ice thickness, d, as it is used to determine k alongside the Fresnel coefficients.¹³ Variations in n_0 and d can cause the Kramers-Kronig relation to give conflicting results for n and k even for the same ice system.¹⁶ Clearly determining accurate values of n_0 and d for interstellar ice analogues is an extremely important research aim. However, it has been shown that, depending on the method used, uncertainties in the measurement of ice thickness can be up to 50%.¹⁵

In one method of determining d, a He-Ne laser is reflected off the surface onto which the ice is being grown, producing interference fringes during deposition. The fringes are used to determine *d* using equation (1.15).^{10,16,17,35,41,50,140,185,186} This method of determining the ice thickness requires a value of *n* in order to determine the ice thickness. Often a value of *n* for a specific ice system is unavailable, and an assumed value, or the value for the ice constituents under ambient conditions, have been used.^{10,14} Given that experiments relevant to the ISM require extreme conditions in terms of pressure and temperature, as described in Chapter 2, it is questionable to assume that an ice will behave the same way as in the liquid under ambient conditions. In other cases, when ices of mixed compositions were studied, a weighted average value based upon the relative contributions of each ice component was used for n.¹⁵ However, this does not take into account interactions within the ice, and therefore the actual refractive index may vary significantly from that derived in this way.^{35,36} An additional consideration for this method of measuring d is that, because the measurement is made during deposition of the ice, only the thickness of the as-dosed ice is obtained. The effect on the thickness of an ice of any post-deposition processing cannot be measured.³⁴

In order to be able to measure the effect of processing on the ice thickness, an alternative method to determine ice thicknesses after deposition has been used which

uses IR band strengths and ice densities.^{37–40} Often band strengths are assumed or taken from the literature,³⁸ in which case care must be taken to ensure that the conditions used match those in the study being referenced. For example, if a mixed ice is being studied, band strengths of a pure ice spectrum may be inappropriate.¹⁰ In other cases, the band strength is given with no explanation of its origin,¹⁰⁹ meaning that it is impossible to verify the values. Similarly, the density value used in this method must also be accurate. In some cases densities are assumed to be equal to that of liquid water^{14,37,38} or taken to be a weighted average of the ice constituents. In reality, densities do not follow this behaviour,³⁵ and depend on the ice growth conditions.⁴¹

In order to avoid the need to assume the value of *n* in determining ice thickness, methods of directly determining *n* under astronomically relevant conditions have been developed. By splitting the emission of a He-Ne laser into two separate beams which reflect from the ice at different angles of incidence, *n* has been determined under high vacuum conditions for ammonia and hydrocarbon ices in the temperature range 80 K – 100 K.⁴⁷ Similar experiments have yielded *n* values for pure and binary mixed ices of carbon dioxide, molecular nitrogen and methane at temperatures as low as 14 K.^{35,41} These determined values of *n* can then be used to calculate *d* according to equation (1.15).

Whilst the methods presented above can provide values of *n* and *d* which may be used in the Kramers-Kronig analysis, the method has only been reported for transmission experiments, as the Fresnel coefficients for transmission are required.¹³ In this work, as described in Chapter 2, the surface onto which ices are grown is highly oriented pyrolytic graphite (HOPG). This material is chosen as an analogue of an interstellar dust grain, which are thought to be carbonaceous and silicaceous in nature.^{52,145} HOPG is optically opaque, therefore in this work the transmission Fresnel coefficients cannot be determined. In this case, only reflection experiments are possible. Kozlova *et al.*¹⁸⁷ have presented a method to determine *n* and *k* values as a function of wavelength for lithium niobate (LiNbO₃) films deposited on silicon substrates from UV/vis reflection spectra. The method involves solving an inversion problem, where the result (*i.e.* the measured reflection spectrum) is known, but certain parameters which lead to the result (*i.e. n* and *k*) are not. Kozlova *et al.*¹⁸⁷ presented a theoretical description of the optical behaviour
of the substrate/film system which showed the relationship between n and k and the reflection spectrum. This method was then used to fit a simulated spectrum to the experimental data by varying the values of n and k until a match was found, giving the correct n and k values. The theoretical description of Kozlova *et al*.¹⁸⁷ is explored in detail below, and has been developed in this work to analyse reflection spectra from a HOPG surface.

The information presented above gives several experimental considerations which must be taken into account when determining a material's refractive index. Both *n* and *d* for an ice need to be measured directly, without the need to make assumptions or to use potentially inappropriate literature values. Additionally, measuring both *n* and *d* using a single experimental procedure would be beneficial. The methods described above and in Chapter 1 require separate experiments to measure *n* and *d*. It is also desirable to measure *d* accurately at any point in an experiment, so that the effect of processing can be quantified. Finally, because an optically opaque HOPG surface is used in this work, the complex refractive index of an ice must be accessible from reflection data only.

In light of the above considerations, this chapter presents the design, installation and testing of a novel fibre-coupled UHV compatible variable angle reflection absorption UV/vis spectrometer. The apparatus has been developed to determine optical parameters and thicknesses of ices. The apparatus allows *n* and *d* for ices to be determined directly, avoiding the need to use assumed or literature values. Additionally, a method to determine wavelength dependent complex refractive indices is presented, based on a previously demonstrated experimental method.¹⁸⁷ The design and installation of the apparatus is discussed and test data for amorphous benzene ices are presented as a proof of concept. Benzene was selected as a test ice system as it has well defined UV/vis absorption peaks,^{186,188–190} therefore it offers an immediate way to check that the apparatus works as expected. Additionally, it has been detected in the ISM^{64,153,191,192} and is of interest as a potential building block of polycyclic aromatic hydrocarbons (PAHs), thought to account for up to 20% of interstellar carbon.^{75,145}

3.2 Equipment and Installation

The apparatus described in this chapter was designed by Professor Martin McCoustra of Heriot-Watt University (HW), Edinburgh, under a collaborative grant. It was constructed in the workshops at HW, then shipped to Sussex where it was installed on the UHV chamber described in Chapter 2 and tested. Some small modifications were made as required, which are detailed in this chapter.

3.2.1 Apparatus

The apparatus is shown in Figure 3.1 prior to installation onto the UHV chamber, with key components labelled. One of the key design elements is the rhombic mechanism. It is made of 30 mm long stainless steel plates held together at each vertex by rivets, allowing rhombic distortion to take place. The vertex at the extreme of the apparatus, closest to the left of Figure 3.1, is attached to a larger stainless steel plate on the end of a stainless steel arm. The plate is employed to add stability to the rhombic mechanism. This vertex remains in a fixed position. The opposite vertex is attached *via* a stainless steel bolt to a stainless steel arm and moves back and forth to introduce rhombic distortion. Collimating lenses (Ocean Optics) in threaded housings are screwed into machined stainless steel arms which are attached on the other two vertices *via* stainless steel screws. UV light is delivered to these lenses *via* fibre optic cables inside and outside of the chamber, coupled by a feedthrough. The UV light is provided by a UV/vis light source (Ocean Optics DH-2000-S-DUV-TTL), containing deuterium and halogen lamps, and collected using a spectrometer (Ocean Optics QE Pro).

The steel arms are welded to the inside of a linear translation stage with an attached millimetre scale (Vacgen ZTR1570), henceforth z-shift. The arm attached to the plate is welded at the stationary end of the z-shift so it is fixed in place. The other arm is welded at the moveable end. The attachment of these arms to the z-shift allows the linear motion to be translated into rhombic distortion. The mathematical details and testing of this mechanism are explored in detail below.



Figure 3.1 Labelled photograph of the apparatus prior to installation on the UHV chamber. Airside fibre optic cables are omitted but attach to the fibre optic feedthroughs.

The apparatus is attached to the chamber *via* a CF flange onto which a CF70-CF250 zero length adapter is attached. Additional spacers were also required. In Figure 3.1, all components to the left of the zero length adapter are housed inside the UHV chamber.

In designing the apparatus, several considerations had to be accounted for. Primarily, all the constituent materials needed to be UHV compatible, and able to withstand the temperatures reached when baking the UHV chamber (up to 120 °C). Additionally, because the lens assembly had to extend into the centre of the chamber to reach the HOPG surface, the components of this part had to be both lightweight and strong so as to not deform over time when installed. Finally, incident and reflected light had to be fed into, and subsequently collected from, the chamber.

With the above in mind, stainless steel was used to construct the lens support and rhombic mechanism, with PTFE bushes used for lubrication of the movable stainless steel arms inside the chamber. UHV compatible fibre optics were employed inside the apparatus, connected to fibre optic feedthroughs to allow the UV to enter and leave the chamber.

The rhombic mechanism described allows the reflection angle to be altered inside the UHV chamber. This mechanism is based on the fact that compressing a square along one of its diagonals changes the angles at its vertices, known as rhombic distortion. Therefore linear motion, provided by the z-shift, can be used to adjust the angle of incidence of the UV light impinging onto the HOPG surface. This is the key design element of the apparatus, and is shown schematically in Figure 3.2A and photographed in Figures 3.2B and 3.2C prior to its installation onto the UHV chamber.

The relationship between the diagonal distance of the quadrilateral and the angle of incidence from the surface, α in Figure 3.2A, can be determined using trigonometry. If the length of the side of the quadrilateral is given by h, shown in Figure 3.2A, and the two diagonals, d, intersect at right angles, the quadrilateral Q₁ is produced. This can be considered the zero position, where the angles at each vertex are equal to 90°. In this work, h = 30 mm. Q₁ can be split into two identical right-angled triangles, T₁, with hypotenuse d, two sides with length h and two 45° angles. Q₁ and T₁ are shown schematically in Figure 3.3.







Figure 3.2 Schematic and photographs of the apparatus in benchtop tests. A: Schematic of the design of the rhombic apparatus. B and C: Photographs of the completed assembly at wide (B) and narrow (C) angles of incidence. These photographs were taken before any modifications were performed, as discussed in the text. Reproduced from J. W. Stubbing et al., Rev. Sci. Instrum., 2018, **89**, 054102, with the permission of AIP Publishing.³⁴



Figure 3.3 Left: Schematic of the quadrilateral, Q₁, with lengths and angles indicated. Right: Q₁ can be split into two identical triangles, T₁.

The length of the diagonal d, the hypotenuse of triangle T₁, is given by equation (3.1), which becomes (3.2) given that $cos(45) = \sqrt{2}/2$. Alternatively, Pythagoras' theorem can be used to determine the length of d, which also leads to equation (3.2).

$$d = \frac{h}{\cos(45^\circ)}$$
(3.1)

$$d = \frac{2h}{\sqrt{2}} = h\sqrt{2}$$
 (3.2)

Any linear change in d, Δx , leads to (3.3).

$$d = h\sqrt{2} \pm \Delta x \qquad (3.3)$$

If a vertex of Q_1 is placed on a plane of the HOPG surface with *d* normal to it, Figure 3.4, a new triangle, T_2 , can be drawn with a side normal to the surface plane of length d/2 and hypotenuse *h*. This triangle is produced by splitting T_1 , illustrated in Figure 3.3, in half.



Figure 3.4 Schematic of triangle T_2 formed by splitting T_1 in half with one vertex placed on the plane of the surface.

By using equation (3.3), the angle θ can be found trigonometrically by equation (3.4),

$$\cos \theta = \frac{h\sqrt{2} \pm \Delta x}{2h}$$
(3.4)

which, given that α is 90 – θ , leads to the following expression for α , equation (3.5).³⁴

$$\alpha = 90 - \cos^{-1}\left(\frac{h\sqrt{2} \pm \Delta x}{2h}\right)$$
(3.5)

Using equation (3.5) with a value of h of 30 mm, a series of values for α can be determined. Values of θ are also given as they are equal to 90 – α . These are shown in Table 3.1.

Once the apparatus had been assembled, the veracity of equation (3.5) could be tested by measuring the angle θ (and hence α) as the z-shift position is changed. The measured angles are shown alongside those calculated using equation (3.5) in Table 3.1. The z-shift scale value is an arbitrary value, read off the millimetre scale for reproducibility. The errors in measured angle arise from the uncertainty of the measurement of the protractor used.

| Δx / mm | Calculated angles from equation (3.5) / ° | | Measured angles / ° | | z-shift scale value / |
|---------|--|----|---------------------|--------|-----------------------|
| | α | θ | α | θ | - 11111 |
| +10 | 61 | 29 | 59 ± 3 | 31 ± 3 | 110 |
| +5 | 52 | 38 | 51 ± 4 | 39 ± 4 | 115 |
| 0 | 45 | 45 | 44 ± 2 | 46 ± 2 | 120 |
| -5 | 39 | 51 | 37 ± 3 | 53 ± 3 | 125 |
| -10 | 33 | 57 | 32 ± 2 | 58 ± 2 | 130 |
| -15 | 27 | 63 | 26 ± 3 | 64 ± 3 | 135 |
| -20 | 22 | 68 | 22 ± 3 | 68 ± 3 | 140 |

Table 3.1 Reflection angles α and θ as a function of Δx as determined by equation (3.5) and as measured. Also shown is the z-shift scale value corresponding to each Δx value.

As shown in Table 3.1, the measured values of the angles are in excellent agreement with those calculated, with small deviations expected given the real material dimensions of the rhombic mechanism. This is shown graphically in Figure 3.5, where the measured and calculated values of θ are plotted as a function of z-shift position and Δx .



Figure 3.5 Variation in θ as a function of z-shift position with corresponding values of Δx . Black Squares: Measured angles. Red Line: Angles determined using equation (3.5). Reproduced from J. W. Stubbing et al., Rev. Sci. Instrum., 2018, **89**, 054102, with the permission of AIP Publishing.³⁴

Henceforth, when referring to the angle of reflection or angle of incidence, the angle from the surface normal, θ , is used.

3.2.2 Installation

Once the apparatus was constructed and shown to function as required in bench tests, installation onto the UHV chamber was performed. Figure 3.6 shows a photograph of the installed apparatus, taken from the inside of the chamber. It can be seen that the fibre optic cables are in contact with the chamber walls, as indicated, and that the rhombic mechanism extends beyond the gold plated radiation shield which houses the sample mount, and therefore the sample position. The contact between the fibre optics and the chamber walls introduced friction and consequently strain on the movement of the lenses, a key feature of the apparatus. The consequence of this was that a) movement of the lenses was hindered and b) the strain caused the arms to move out of position.



Figure 3.6 View inside the chamber after initial installation of the apparatus, prior to modifications. Circled are issues that required modifications to be made to the apparatus. Also visible are the outlet tubes extending from the leak valves on the chamber.

To alleviate these problems, modifications were required to allow the apparatus to be used. In order to correct the positioning of the rhombic mechanism, it was necessary to add spacers onto the flange used to attach the apparatus. This was preferable to using the translation stage for moving the sample as this would have meant that UV and RAIRS experiments could not have been performed simultaneously. This is because the sample position for RAIRS experiments is fixed by the optics described in Chapter 2. The reason that it is desirable to use the two techniques simultaneously is so that the effect of any processing of an ice could be examined by both RAIRS and UV experiments for a single ice sample, eliminating any variations between doses.

Adding a spacer would correct the sample position, but would increase the strain on the fibre optic cables as they would be pulled further towards the chamber walls. In order to overcome this, the design of the lens mounts was adapted so that the fibre optic cables hung downwards in the chamber, rather than horizontally, allowing them more space and thus avoiding the chamber walls. This was achieved by adding stainless steel right-angle mounts to the collimating lenses in the support arms. These components were purchased from Fibre Design (Part number: 502-90CLH/UHV) and were UHV and bake out compatible. Crucially they were also lightweight, so they would not strain the arms of the apparatus.

The spacers added to the apparatus are shown in Figure 3.7A and the right angle mounts are shown in Figure 3.7B. Figure 3.7A is external to the chamber and also shows the airside fibre optic cables connected to the UV/vis light source and spectrometer. Red asterisks show the spacer flanges. Figure 3.7B shows the apparatus inside the chamber. By comparing the position of the rhombic mechanism to that in Figure 3.6, it is clear that the sample now sits in the correct position above the extreme vertex of the quadrilateral. Additionally, the right angle mounts are shown to overcome the problem of the fibre optic cables touching the chamber walls.



Figure 3.7 Photographs of the apparatus installed after undergoing the modifications described. A: external part of the apparatus. Red asterisks mark the added spacer flanges. Also shown are the airside fibre optic cables coupled to the light source and spectrometer. B: view inside the chamber showing the right angle mounts installed on the lens supports. C: expanded section of B.

After the addition of the spacers and right angle mounts shown in Figures 3.7A and 3.7B respectively, it was found that over several passes back and forth of the z-shift, the steel arms became misaligned. This moved the rhombic mechanism, and hence lenses, out of position. In order to overcome this issue, a slot was milled into the stainless steel plate which supports the rhombic mechanism. The bolt which attaches the vertex of the quadrilateral furthest from the sample to the mobile stainless steel arm passes through the slot and the securing nut is placed below the plate in order to secure the arms in position. Figure 3.7C shows an expanded part of Figure 3.7B in order to more clearly show the milled slot in the steel plate. This addition stopped the arms from becoming misaligned in normal use without adding any new components, thus keeping the assembly lightweight.

3.3 Experimental

Initial test UV/vis reflection data was recorded for benzene, which was introduced into the chamber *via* one of the high precision leak valves shown in Chapter 2. In all cases, benzene was deposited at base temperature (approximately 25 K) in its amorphous form. Later chapters will examine the benzene ice phase in detail. Both backfilling and direct dosing were employed and are discussed below.

The UV/vis apparatus described above was connected *via* fibre optics to a light source and spectrometer. The procedure to obtain UV/vis spectra is outlined below. All spectra are the average of 128 scans with an integration time of 500 ms per scan. The integration time is analogous to the shutter speed of a photographic camera. A larger integration time will allow more reflected light to be collected but may introduce changes in the resultant spectra due to changes in the system during collection, analogous to motion blur in a photograph. These parameters were determined following trial and error tests to obtain the highest signal without saturating the spectrometer. In total a spectrum requires approximately 30 seconds to be recorded. The total area of the HOPG sample which is irradiated by the UV/vis light is estimated to be a spot of 1 cm diameter, smaller than the total HOPG area.

To collect a set of reflection-absorption spectra, background spectra of the clean HOPG surface were recorded at each reflection angle. The sample was then dosed with benzene and a sample spectrum at each angle was subsequently recorded. For each gas exposure, at least one repeat was performed to ensure reproducibility. In initial experiments, a background spectrum was recorded at a single reflection angle, the ice was grown, and a sample spectrum was then recorded at the same reflection angle. The sample was then cleaned and the process was repeated for a new angle. Subsequently, experimental efficiency was increased in terms of time and gas load in the chamber by recording background spectra at every angle, growing a single ice, and recording sample spectra at each angle for that ice. This improved the rate of data collection dramatically and ensured that the sample thickness was constant for all angles tested.

Identically to RAIRS, the data are plotted in the form of $\Delta R/R$ (shown in Chapter 2 equation (2.1)). This is to correct for the non-uniform intensity of the light source output

as a function of wavelength. This is shown in Figure 3.8. Figure 3.8A is from the Ocean Optics website and shows the spectral output of the light source.¹⁹³ Figure 3.8B shows the recorded reflectance spectrum of the clean HOPG surface.



Figure 3.8 Spectral output of the Ocean Optics DH-2000-S-DUV-TTL light source used in this work. A: Direct output from the manufacturer's website.¹⁹³ B: Recorded reflectance spectrum of the clean HOPG surface. The features circled in B are explained in the text.

From Figures 3.8A and 3.8B, the output is seen to be much less intense at shorter wavelengths. Additionally, the output contains features due to hydrogen emission at 486 nm and 656 nm. These are Balmer series emission lines originating from the $n = 4 \rightarrow n = 2$ and $n = 3 \rightarrow n = 2$ transitions in the deuterium lamp.¹⁹⁴ The feature at 581 nm is from the halogen lamp.¹⁹⁵

3.4 Test Data and Preliminary Analysis

Figure 3.9A shows reflectance spectra at a fixed angle of incidence of 31° for increasing exposures of benzene on HOPG dosed *via* backfilling, *i.e.* by allowing benzene vapour to fill the chamber as described in Chapter 2. Whilst these spectra show some features, described below, it is clear that they do not contain characteristic interference fringes which are necessary for the determination of optical parameters and ice thicknesses, as discussed in section 3.1. The small feature at 656 nm is an artefact arising from the ratioing of the raw data which contains features from the light source (shown in Figure 3.8) and can be ignored.



Figure 3.9 Reflectance spectra of increasing exposures of amorphous benzene on HOPG dosed via backfilling at a reflection angle of 31°. A: 50 Lm – 200 Lm of benzene across the wavelength range 185 nm – 850 nm. B: Expanded section of the 200 Lm spectrum between 185 nm – 350 nm.

At all exposures, a feature at 214 nm is present which increases in intensity with exposure. From an exposure of 100 L_m a second broad feature is present centred at 226 nm, which increases in intensity and broadens at 200 L_m. Figure 3.9B shows an expanded section of the 200 L_m spectrum between 185 nm – 350 nm. Weak absorption features are present centred at 255 nm with peaks at 249 nm, 255 nm and 262 nm. The peak at 214 nm is assigned to the ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ transition, 186,188,196,197 and those centred at 255 nm are assigned to the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transition of benzene. ${}^{186,188-190,196-198}$ In the

case of benzene, both the ${}^{1}B_{1u}$ and ${}^{1}B_{2u}$ states are dipole symmetry forbidden, but the transitions are observed due to Herzberg-Teller vibronic coupling which allows them to intensity steal from an allowed state, in this case the ${}^{1}E_{1u}$ state. The ${}^{1}E_{1u} \leftarrow {}^{1}A_{1g}$ transition is not consistently observed in this work, as it is at 190 nm, 186 just outside the reliable spectral range of the spectrometer. However, it may be the cause of the apparent peak on the 200 L_m spectrum at the short wavelength end of the x-axis (Figures 3.9A and 3.9B).

In order to observe interference fringes, it was necessary to dose thicker ices. This is because the fringes arise from constructive and destructive interference of light reflecting off all the interfaces present. In order for interference to occur, a suitable phase difference must be introduced in the reflected wave. This means that the ice thickness, *d*, must be on the order of the light wavelength, *i.e.* hundreds of nm thick. Figure 3.10 shows the reflections that occur in an example ice system when incident light, *I*, at an angle of incidence θ_0 illuminates the system. Reflections from the HOPG and upper ice surface introduce the phase difference in the reflected light, *R*. The angles of refraction are θ_1 and θ_2 and the optical parameters of the ice and HOPG are n_1 , k_1 , n_2 and k_2 respectively.



Figure 3.10 Schematic of the origin of interference fringes. n_0 is the refractive index of the vacuum (equal to 1). Adapted from Kozlova et al.¹⁸⁷

Figure 3.11 shows the raw background and sample reflection spectra for 400 L_m benzene on HOPG dosed directly, as opposed to backfilling. The details of the dosing methods are described in Chapter 2. Direct dosing was employed to produce thicker ices. The reflection angle in Figure 3.11 is 39°. As in Figure 3.8, spectral features from the light source output are observed.



Figure 3.11 Unprocessed UV/visible reflection spectra recorded at a reflection angle of 39°. Blue: Background spectrum of the clean HOPG surface. Red: After direct dosing of 400 L_m of benzene. The features at 486 nm, 581 nm, and 656 nm are hydrogen emission lines from the light source output. Reproduced from J. W. Stubbing et al., Rev. Sci. Instrum., 2018, **89**, 054102, with the permission of AIP Publishing.³⁴

It is also clear that the deposition of benzene on the surface has changed the reflection behaviour of the sample. The reflection intensity is reduced across the wavelength range and the profile of the refection curve has changed when compared to the clean surface. Subsequently the data is plotted in the form of $\Delta R/R$ as a function of wavelength. This is shown in Figure 3.12, at all reflection angles, for a 500 Lm exposure of benzene.



Figure 3.12 Reflectance spectra of 500 L_m amorphous benzene on HOPG dosed directly at all reflection angles.

The spectra in Figure 3.12 produced from ices grown *via* direct dosing show interference fringes, from approximately 270 nm upwards. This is as opposed to the data collected from ices grown by backfilling, shown in Figure 3.9. Below a wavelength of approximately 270 nm the previously assigned absorption bands are present, however they are much sharper and more intense than those in Figure 3.9. The absorption bands do not shift or vary with reflection angle, as expected. Similarly, the light source feature at 656 nm also remains at a constant wavelength. The higher intensity is to be expected as 19 times more benzene is deposited on the surface when directionally dosed than *via* backfilling.

The absorption features shown in Figures 3.9 and 3.12 agree excellently with the absorption bands observed by Dawes *et al.*¹⁸⁶ for benzene deposited on an MgF₂ substrate at 25 K. The bands observed by Dawes *et al.* are shown for comparison to this work in Figure 3.13. It should be noted that absorptions are shown as dips in the spectra in this thesis, compared to peaks in the spectra shown in Figure 3.13.



Figure 3.13 UV/vis absorption spectrum for benzene recorded by Dawes et al.¹⁸⁶ with the transitions *labelled.*

Whilst the absorption features remain constant, the fringes shift with changing reflection angle. The observation in Figure 3.12 of both interference fringes and the well-defined UV/vis absorptions of benzene indicates that the apparatus is working as designed, *i.e.* it is possible to observe UV/vis reflection spectra which are comparable to previous work.^{186,188–190,196–198}

Whilst direct dosing provides the thick ices required, it means that between recording the background spectra and the sample spectra, the sample must be rotated to face the leak valve and then returned to its starting position. The necessity of this is shown by the relative position of the sample housing and leak valve outlets in Figures 3.6 and 3.7B. In order to ensure that the sample is returned to its original position, the signal measured by the MCT IR detector is used, which is sensitive to the position. First, the measured signal on the MCT detector is noted before moving the sample. Upon returning the sample to the start position, the signal is monitored and matched to its starting value. This method gives a reasonable reliability but some change in the position is likely. However a test to determine the effect of a variation in reflection angle of $\pm 4^{\circ}$ on the initial analysis did not alter the results within the experimental error.

The fringes observed in Figure 3.12 are the basis for the analysis, and ultimate determination of the optical parameters of the ices. The initial method of analysis was chosen as a proof of concept of the apparatus. The method was adapted from that of Harrick.¹⁹⁹ Originally the method was applied to benchtop IR experiments which examined polyethylene terephthalate films. However, it was thought to be relevant to the ices in this work as it makes use of interference fringes, albeit in a different wavelength regime. Indeed, the method has been used as a basis to determine the thickness and refractive index of polystyrene films in transmission experiments.²⁰⁰

By examining the spacing between the maxima and minima of the interference fringes at different angles of incidence, the real part of the refractive index, n, and the film thickness, d, can be determined using equations (3.6) and (3.7).¹⁹⁹

$$n = \left[\sqrt{\left\{ \frac{\sin^2 \theta_1 \Delta \bar{v}_1^2 - \sin^2 \theta_2 \Delta \bar{v}_2^2}{\Delta \bar{v}_1^2 - \Delta \bar{v}_2^2} \right\}^2} \right]^{1/2}$$
(3.6)
$$d = \frac{m}{2(n^2 - \sin^2 \theta)^{1/2} \Delta \bar{v}}$$
(3.7)

In equation (3.6), spectra at two reflection angles, θ_1 and θ_2 , are compared. $\Delta \bar{v}_1$ and $\Delta \bar{v}_2$ represent the fringe spacings (in wavenumber) for the two spectra. For each exposure examined, spectra at every angle are compared to every other angle.

Once *n* is determined using equation (3.6), equation (3.7) is used to find *d* using each individual reflectance spectrum. *m* is the number of complete fringes in the spectrum, *n* is the determined refractive index from equation (3.6), θ is the reflection angle in degrees and $\Delta \bar{v}$, shown in Figure 3.14, is the spacing in wavenumber between the first and last maximum/minimum.

Figure 3.14 illustrates the use of the spectra in equations (3.6) and (3.7). It shows reflectance spectra of 400 L_m of benzene deposited on HOPG at 25 K at two reflection angles, 31° and 46° (the red and black traces respectively). The symbols on the plot in Figure 3.14 refer to those in equations (3.6) and (3.7). In equation (3.6), the two reflection angles, θ_1 and θ_2 , are 46° and 31° respectively. For equation (3.7), taking the minima at 284 nm and 639 nm of the 46° (black) spectrum gives m = 2 and

 $\Delta \bar{\nu} = 19531.1 \text{ cm}^{-1}$ (as shown on the plot). Equation (3.7) is applied to spectra from every reflection angle.



Figure 3.14 Reflectance spectra of 400 Lm of amorphous benzene on HOPG at two reflection angles of 31° (red trace) and 46° (black trace). The symbols refer to the terms in equations (3.6) and (3.7).
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Figure 3.15 shows the calculated value of *n* determined from equation (3.6) as a function of benzene exposure deposited at 25 K *via* direct dosing. Individual values of *n* for each dose are the mean of all the values that arise from comparing all the reflection angles, plus repeats. Error values are given as twice the standard error of the mean, as no individual error is associated with each value. All the values are consistent within error and give a mean value of $n = 1.43 \pm 0.07$ for amorphous solid benzene at 25 K. This is in good agreement with recent work which determined values of *n* for solid benzene at low temperatures ranging from $1.38 - 1.47 (\pm 0.06)$.¹⁸⁶ This confirms the validity of using Harrick's method¹⁹⁹ to analyse data in the UV/vis range. The determined value is lower than that of liquid benzene at 293 K (1.501^2), suggesting that assuming a value of *n* to be equal to that of the liquid may not be appropriate for application to astrochemistry. However given the error range, care must be taken in this conclusion. Reducing the error range of the determined n value would be useful. The simplest way to do this would be by increasing the number of repeats.



Figure 3.15 *Refractive index n as a function of dose for amorphous benzene on HOPG deposited at 25 K. Reproduced from J. W. Stubbing et al., Rev. Sci. Instrum., 2018, 89, 054102, with the permission of AIP <i>Publishing.*³⁴

Using the mean value of n, 1.43, the film thickness can be determined using equation (3.7). Figure 3.16 shows values of d as a function of dose for a fixed reflection angle of 31°. Error values are determined using the upper and lower values of n.



Figure 3.16 Amorphous benzene ice thickness as a function of dose, at a fixed reflection angle of 31°. Reproduced from J. W. Stubbing et al., Rev. Sci. Instrum., 2018, **89**, 054102, with the permission of AIP Publishing.³⁴

As surface concentration is known to be directly proportional to the dose,¹¹⁵ an expected linear relation between thickness and dose is observed. The mean values of thickness for all reflection angles for each dose are also shown in Table 3.2. The data in Figure 3.16 differ to those in Table 3.2 because they are for a single reflection angle.

| Dose / L _m | Thickness / nm |
|-----------------------|----------------|
| 100 | 127 ± 2 |
| 200 | 219 ± 4 |
| 250 | 261 ± 5 |
| 350 | 404 ± 11 |
| 400 | 401 ± 7 |
| 500 | 485 ± 9 |
| 1000 | 933 ± 18 |
| | |

 Table 3.2. Mean thicknesses of benzene ices for the examined doses

It is also expected that for a single dose, the thickness will not vary within error as a function of reflection angle. This is shown to be the case in Figure 3.17 for a dose of $250 L_m$ of benzene.

The data presented so far are a proof of concept of the apparatus described in this chapter. They demonstrate that the proposed method of analysis, based on that of Harrick,¹⁹⁹ can indeed be used in the UV/vis wavelength range under UHV and at low temperatures. Using this method, *n* and *d* for amorphous benzene ices deposited at 25 K have been determined. Crucially, both *n* and *d* have been determined using data from a single set of measurements, unlike previously reported methods.^{10,16,17,35,41,50,140,185,186} Additionally, no assumptions or literature values were required as *n* and *d* of benzene ices were directly determined.



Figure 3.17 Amorphous benzene ice thickness as a function of reflection angle, for a fixed dose of 250 L_m. The mean thickness is 261 ± 5 nm. Reproduced from J. W. Stubbing et al., Rev. Sci. Instrum., 2018, **89**, 054102, with the permission of AIP Publishing.³⁴

3.5 Determining the Complex Refractive Index

3.5.1 Theoretical Description of UV/vis Reflection Spectra

The analysis above provides a useful test of the system, however the refractive index is a wavelength dependent, complex parameter. Therefore the analysis needs to be extended in order to determine n and k as a function of wavelength. Knowledge of the variation of optical parameters of an ice as a function of wavelength are vital if spectra are to be simulated, as these parameters define how light interacts with a medium.

A challenge in determining wavelength dependent *n* and *k* values arises from the fact that the HOPG surface is optically opaque, therefore only reflection can be measured. Previous work determining optical parameters has relied on transmission experiments.^{10,13,200} In the case of this work, this means that no information on the transmitted light is known, and subsequently the Fresnel coefficients for transmission cannot be calculated. Shown above, these have been used in Kramers-Kronig analysis and other optical parameter studies.^{10,13,15}

Kozlova *et al.*¹⁸⁷ developed a method to determine both *n* and *k* as a function of wavelength using spectroscopic measurements recorded in reflection mode for LiNbO₃ films on opaque silicon. This technique requires no knowledge of the transmitted light and therefore can be developed for use with the data presented in this work. In this method, initial values of *n* and *d* were determined in a similar method to the Harrick¹⁹⁹ method used above. These values were then used as starting values to find wavelength dependent *n* and *k* values. The analysis is described in detail below.

To determine the starting values, reflectance spectra were recorded as a function of wavelength at two reflection angles, ϕ_1 and ϕ_2 , giving interference fringes similar to those recorded by the apparatus described in this work. This caused the fringes to shift analogously to the shift observed in Figure 3.14. The same maximum/minimum on each spectrum was selected and the wavelength of the maximum/minimum in each spectrum, λ_{ϕ_1} and λ_{ϕ_2} , were used to determine *n* using equations (3.8) and (3.9),^{187,201}

$$\left(\frac{n}{n_0}\right)^2 = \frac{\sin^2 \phi_1 - \beta \sin^2 \phi_2}{1 - \beta}$$
(3.8)

where n_0 is the refractive index of the vacuum, equal to 1, and β is given by:

$$\beta = \left(\frac{\lambda_{\varphi 1}}{\lambda_{\varphi 2}}\right)^2 \quad (3.9)$$

The values of *n* determined for amorphous benzene ice using equations (3.8) and (3.9) and the spectra shown in Figure 3.14 are 1.36 and 1.44. The values used in the equations are shown in Table 3.3. These values are in good agreement with the value determined above using the method of Harrick¹⁹⁹ of 1.43 \pm 0.07.

Table 3.3 Refractive index of amorphous benzene ice as determined using the method of Kozlova et al.¹⁸⁷

| φ ₁ /° | φ2/° | $\lambda_{\phi 1}$ / nm | $\lambda_{\phi 2}$ / nm | β | n |
|-------------------|------|-------------------------|-------------------------|------|------|
| 46 | 31 | 317 | 346 | 0.84 | 1.36 |
| | | 478 | 515 | 0.86 | 1.44 |

However the method used by Kozlova to estimate the film thickness does not agree with the results determined above by the Harrick method. Kozlova *et al.*¹⁸⁷ determine *d* using

the positions of adjacent interference maxima/minima, λ_1 and λ_2 , for a single reflection angle in equation (3.10), using the value of *n* from equations (3.8) and (3.9).

In the case of benzene ice, using n = 1.43 and the wavelengths in Table 3.3, d was determined to be 165 nm and 184 nm for a 400 L_m exposure, much lower than the value of 401 nm shown in Table 3.2. The reason for this discrepancy is unclear. However credibility is given to the values determined using the Harrick method by comparison with a common method used to estimate film ice thicknesses.¹⁰⁷ Using the estimate of the number of molecules on the surface, N_m given by equation (2.9) in Chapter 2, and the ice molecular density, ρ_s the thickness is determined. This is shown in equation (3.11).

$$d = \frac{N_m}{\rho_s}$$
(3.11)

It is necessary to multiply N_m determined by equation (2.9) by 19 to account for the fact that more molecules are deposited *via* direct dosing than backfilling, as outlined in Chapter 2. The density of benzene is taken as 0.8765 g cm⁻³,²⁰² which corresponds to a molecular density of 6.76×10^{21} molecules cm⁻³. This yields a thickness of 321 nm for a 400 L_m exposure from equation (3.11), closer to the 401 nm calculated in this work than the upper estimate of 184 nm determined using the method of Kozlova *et al.*¹⁸⁷ Therefore the values of *d* in Table 3.2 were used in the analysis outlined below.

With starting values for both *n* and *d* for the ice, and the wavelength dependent complex refractive index of the surface known from the literature (silicon²⁰³ in the case of Kozlova *et al.* and HOPG²⁰⁴ in this work), a method to determine the complex refractive index of the ice can be developed. This analysis is based upon that of Kozlova *et al.* and the theory behind it was further developed for the system described in this work by Professor Martin McCoustra.^{187,205}

The analysis works by taking a starting value of n, along with other parameters described below including an initial guess of k, and using these to simulate a reflectance spectrum. The simulated spectrum is compared to the experimental one, and a match parameter is determined. The values of n and k are then varied until a match between the experimental spectrum and simulated spectrum is found. With reference to Figure 3.10, the input parameters can be determined. The angle of incidence, θ_0 , refractive index of the vacuum, n_0 (equal to 1), complex refractive index of the ice, N_1 , where $N_1 = n_1 + ik_1$, thickness, d, and the complex refractive index of the HOPG, N_2 (equal to $n_2 + ik_2$) all contribute to the reflection spectrum, $\Delta R/R$. In the case of HOPG, there are two sets of optical parameters. One set for p-polarised light and one for s-polarised light. These parameters are defined as n_{2p} and k_{2p} for p-polarised light and one for s-polarised light. These parameters are defined as n_{2p} and $N_{2s} = n_{2s} + ik_{2s}$. The parameters θ_0 , n_0 , N_{2p} , N_{2s} and the experimental values, R_{0exp} and R_{exp} are known, alongside d from the Harrick analysis above. The relationship between the parameters and resulting spectra can be used to determine N_1 by fitting a simulated spectrum to the experimental data.

Using the parameters described, the Fresnel coefficients of reflection for s- and ppolarised light for the vacuum/ice and ice/substrate interfaces, which simulate the reflection behaviour of the ice, R_{sim} , can be determined. These are defined as r_{1p} and r_{1s} (vacuum/ice) and r_{2p} and r_{2s} (ice/substrate) by equations (3.12) – (3.15).^{2,187,205}

$$r_{1p} = \frac{N_1 \cos\theta_0 - n_0 \cos\theta_1}{N_1 \cos\theta_0 + n_0 \cos\theta_1}$$
(3.12)

$$r_{1s} = \frac{n_0 \cos\theta_0 - N_1 \cos\theta_1}{n_0 \cos\theta_0 + N_1 \cos\theta_1}$$
(3.13)

$$r_{2p} = \frac{N_{2p}\cos\theta_1 - N_1\cos\theta_{2p}}{N_{2p}\cos\theta_1 + N_1\cos\theta_{2p}}$$
(3.14)

$$r_{2s} = \frac{N_{1}cos\theta_{1} - N_{2s}cos\theta_{2s}}{N_{1}cos\theta_{1} + N_{2s}cos\theta_{2s}}$$
(3.15)

The Fresnel coefficients for reflection from the clean surface, $r_{0,2p}$ and $r_{0,2s}$ are also required in order to simulate the $\Delta R/R$ spectrum.^{2,187,205}

$$r_{0,2p} = \frac{N_{2p}\cos\theta_0 - n_0\cos\theta_{2p}}{N_{2p}\cos\theta_0 + n_0\cos\theta_{2p}}$$
(3.16)

$$r_{0,2s} = \frac{n_0 \cos\theta_1 - N_{2s} \cos\theta_{2s}}{N_{2s} \cos\theta_0 + n_0 \cos\theta_{2s}}$$
(3.17)

In equations (3.12) – (3.17), θ_1 , θ_{2p} and θ_{2s} are the complex angles of refraction at each interface given by equations (3.18) – (3.20).^{187,205}

$$\cos \theta_1 = \sqrt{1 - \frac{n_0^2 \sin^2 \theta_0}{N_1}}$$
 (3.18)

$$\cos \theta_{2p} = \sqrt{1 - \frac{n_0^2 \sin^2 \theta_0}{N_{2p}}}$$
 (3.19)

$$\cos \theta_{2s} = \sqrt{1 - \frac{n_0^2 \sin^2 \theta_0}{N_{2s}}}$$
 (3.20)

Using the Fresnel coefficients, it is possible to calculate R_{sim} and R_{0sim} , which are made up of the reflection coefficients for s- and p-polarised light, R_s and R_p respectively for the ice, and R_{0s} and R_{0p} for the clean surface. The reflection coefficients are calculated using equations (3.21) - (3.24).^{187,205}

$$R_{p} = \left| \frac{r_{1p} + r_{2p} e^{-2i\delta}}{1 + r_{1p} r_{2p} e^{-2i\delta}} \right|^{2} (3.21)$$

$$R_{s} = \left| \frac{r_{1s} + r_{2s} e^{-2i\delta}}{1 + r_{1s} r_{2s} e^{-2i\delta}} \right|^{2} (3.22)$$

$$R_{0p} = \left| r_{0,2p} \right|^{2} (3.23)$$

$$R_{0s} = \left| r_{0,2s} \right|^{2} (3.24)$$

In equations (3.21) and (3.22), δ is the complex phase thickness and describes the phase change introduced in the reflected light. It is given by equation (3.25)^{187,205}

$$\delta = \frac{2\pi dN_1 \cos\theta_1}{\lambda}$$
(3.25)

where λ is the wavelength. R_{0sim} and R_{sim} , are given by equations (3.26) and (3.27).^{187,205}

$$R_{sim} = R_p + R_s$$
 (3.26)
 $R_{0sim} = R_{0p} + R_{0s}$ (3.27)

Using equations (3.12) – (3.27), a simulated reflectance spectrum for a given ice can be produced. This can subsequently be compared to experimental data and *via* an iterative process the target parameters, n_1 and k_1 , can be determined. The optimisation is

performed by a least squares function, equation which minimises the goal function, *s*, given by equation (3.28).²⁰⁵

$$s = \sum_{\theta} \left[\left(\frac{R_{exp} - R_{0exp}}{R_{0exp}} \right) - \left(\frac{R_{sim} - R_{0sim}}{R_{0sim}} \right) \right]^2 = \sum_{\theta} \left[\left(\frac{\Delta R}{R} \right)_{exp} - \left(\frac{\Delta R}{R} \right)_{sim} \right]^2$$
(3.28)

In order to perform the analysis, a code was written using Python.²⁰⁶ The full code is shown in Appendix 1. A description of its operating procedure is outlined in Figure 3.18 and is explained below. Firstly however, the functions defined within the code are explained. In Python, a function is defined by the user and performs a set of specific actions. A function can then be called later on in the code to perform the specific task, without the need to repeat lengthy portions of code. When a function is written, the inputs of the function must be defined. These are the variables which will be used within the code within the code presented here, there are four defined functions within the code which are DR R func 1, func wrap, DR R func 2 and seq.

DR_R_func_1 takes a value of n_1 , k_1 and d calculates a value of $(\Delta R/R)_{sim}$ for a single wavelength for each reflection angle using the above equations. Subsequently it compares $(\Delta R/R)_{sim}$ for each angle to $(\Delta R/R)_{exp}$ to give a value of s according to equation (3.28) for the individual wavelength. The function inputs are d, λ , n_{2s} , k_{2s} , n_{2p} , k_{2p} , n_1 , k_1 and an index parameter j. This parameter, j, is used later in the code to repeat the process for each wavelength value in the spectral range examined. This is achieved *via* a feature called a "for loop", which is a statement allowing a certain action to be repeated. In this case each wavelength value is assigned an index, *i.e.* the first wavelength is indexed as 0, the second as 1, third as 2 etc. until the end of the wavelength range is reached. The for loop calls DR_R_func_1 for each j value, and therefore each wavelength value, to obtain s as a function of wavelength.

func_wrap is used in the optimisation step. It calls $DR_R_func_1$ and requires input parameters of n_1 and k_1 , the parameters that are being optimised. This function is required because the other input parameters of $DR_R_func_1$ are known and must not be varied in the code during the optimisation.

DR_R_func_2 is a variation of DR_R_func_1, but is called as the final step of the code. It takes as inputs θ , d, λ , n_{2s} , k_{2s} , n_{2p} , k_{2p} , n_1 and k_1 . The input variables for n_1 and

 k_1 used are the optimised values and this function returns optimised ($\Delta R/R$)_{sim} values which can be plotted for comparison with the experimental data.

Finally seq is a function written by Dr Adam Baskerville, research fellow at the University of Sussex, which allows a for loop in Python to iterate with a non-integer step size.²⁰⁷ This is used to determine starting guesses of n_1 and k_1 for use in the optimisation step, as explained below.

Figure 3.18 shows a flow chart of the operating procedure of the code. The octagonal box represents the input parameters, square boxes are individual code steps with arrows to show the processing order and circles represent outputs. Similarly thin grey arrows are input steps and thick grey arrows show outputs of procedures. The purple arrow is an iteration step.

The first step of the analysis is to collate $\Delta R/R_{exp}$ for all reflection angles and thicknesses, and the two sets of graphite optical parameters from Djurišić and Li²⁰⁴ as a function of λ , shown in Figure 3.18 by the octagonal input box. Next, for the first value of λ , an iterative brute force approach is used to determine a good starting guess of n_1 and k_1 . This step is required because the results were found to be very sensitive to the initial values for n_1 and k_1 used. This implies that a plot of n_1 and k_1 on the x and y axes against *s* from equation (3.28) on the z axis produces a surface which contains many local minima. Hence starting in the correct region of this surface is imperative to determine the global minimum. The starting guesses are produced by calling DR_R_func_1 for a series of initial n_1 and k_1 values to find the lowest value of *s*. Values of n_1 in the range 0.5 – 3.0 with a step size of 0.2 and values of k_1 in the range 0.000 – 1.000 with a step size of 0.001 were used in this step, with every value of n_1 tested with every value of k_1 . The ranges and step sizes were determined using a series of trial and error tests. This step was where the seq function was employed.



Figure 3.18 Flow diagram representing the process followed by the Python code.

Once n_1 and k_1 starting guesses are determined, func_wrap is called and given the starting guesses of n_1 and k_1 and the value of d determined via the method of Harrick.¹⁹⁹ The function is called within an intrinsic minimisation function (least squares) which means that n_1 and k_1 are varied to minimise s. The optimised values for the first value of λ are stored and used as the starting guesses for the next value of λ , in this way each wavelength is seeded by the previous one.

The final step of the code takes the optimised values of n_1 , k_1 and d as a function of wavelength and calls DR_R_func_2 to produce $(\Delta R/R)_{sim}$ for each reflection angle. It also compares $(\Delta R/R)_{sim}$ to $(\Delta R/R)_{exp}$ as in equation (3.28) and stores the residuals for each reflection angle, which can be summed to find s. Finally all the results of the code, that is n_1 , k_1 , and $(\Delta R/R)_{sim}$ at each reflection angle and thickness, and all residuals, are written to a single output file.

3.5.2 Benchmarking and Testing the Analysis Code

In order to test the theory and the code, a benchmarking procedure was performed using test data, with known values of n_1 and k_1 . The values of n_1 were determined using the work of Kofman *et al.*,¹³⁶ who determined thicknesses, *d*, and wavelength dependent *n* values for amorphous water ice.

Figure 3.19 shows a plot of n as a function of wavelength determined by Kofman *et al.*¹³⁶ The data is fitted with a polynomial equal to equation (3.29) in order to determine *n* across the full wavelength range used in this work. The maximum wavelength value used in the determination of the complex refractive index is 591 nm as shown by the blue line in Figure 3.19. The wavelength range examined using the code is smaller than that used in the Harrick¹⁹⁹ method, up to 800 nm, because the optical parameters for HOPG from Djurišić *et al.*²⁰⁴ are only available up to this value.

$$y = 5.51 \times 10^{-7} (x^2) - 8.54 \times 10^{-4} (x) + 1.60$$
 (3.29)



Figure 3.19 Real part of the refractive index, n, of amorphous water ice as a function of wavelength. Red squares: Values determined by Kofman et al.¹³⁶ Blue line: Fit to the data defined by equation (3.29) to give n across the wavelength range used to test the theory and code.

Kofman *et al.*¹³⁶ did not determine wavelength dependent values of *k* for amorphous solid water ice, therefore a constant value of 0.01 was assumed. This value was chosen as previously reported values in the relevant wavelength region tend to be small (<< 0.5) and positive for water.^{19,208} In any case, the specific value used is less important than the fact that it is known. The determined values of n_{λ} and the assumed values of k_{λ} were then used to simulate reflectance spectra such as those shown in Figures 3.12 and 3.14, with thicknesses between 100 nm and 500 nm. These spectra were simulated using a separate Python code which takes the known values of θ , d, λ , n_{2s} , k_{2s} , n_{2p} , k_{2p} , n_1 and k_1 and uses equations (3.12) – (3.27) to give simulated $\Delta R/R$ spectra, similar to the final step of the analysis described above and shown in Figure 3.18. The full code is shown in Appendix 2. Figure 3.20 shows examples of simulated reflectance spectra of amorphous water ice on HOPG at two thicknesses and several reflection angles.



Figure 3.20 Simulated reflectance spectra of amorphous water ice on HOPG using n values from Kofman et al.¹³⁶ and an assumed value of k = 0.01 at several reflection angles. A: spectra for a simulated ice thickness of 200 nm B: spectra for a simulated ice thickness of 500 nm.

In agreement with the experimental spectra for benzene ice shown in Figures 3.12 and 3.14, interference fringes are observed in the spectra shown in Figure 3.20. The position of the extrema of the fringes shifts as the reflection angle is changed. The number of fringes increases with ice thickness as expected. The spectra shown in Figure 3.20 are entirely simulated using equations (3.12) - (3.27), yet show similar behaviour, described above, to the experimental spectra in Figures 3.12 and 3.14. This gives an initial suggestion that the theoretical description of the production of UV/vis reflection spectra in equations (3.12) - (3.27) is valid.

The simulated amorphous water spectra were used as input $(\Delta R/R)_{exp}$ data for the analysis code. In this work, unlike the method of Kofman *et al.*,¹³⁶ no calibration point is required in order to determine n as a function of wavelength. This means that the results of the analysis are not biased by literature values which are potentially erroneous. Also unlike in Kofman *et al.*,¹³⁶ the imaginary part of the refractive index, *k*, is determined by

this method. Figure 3.21 shows the results of the analysis. These are the calculated wavelength dependent n and k values for the simulated amorphous water spectra, alongside those used to produce the simulated spectra.



Figure 3.21 Real (panel A) and complex (panel B) part of the refractive index of amorphous water ice as a function of wavelength. Blue lines: the values from Kofman et al.¹³⁶ Red open circles: the results of the analysis.

In Figure 3.21A, it is observed that the calculated *n* values from the simulated amorphous water spectra, shown by red open circles, agree perfectly with those used to produce the spectra from Kofman *et al.*,¹³⁶ shown by the blue line. Similarly, the determined *k* values are in excellent agreement with the assumed value of 0.01, with only very small variations observed around 350 nm and 560 nm, as shown in Figure 3.21B. However the determined values of *k* differ from the assumed value by < 0.05%. This is insignificant as shown in Figure 3.22, where a simulated spectrum used as the code input is plotted alongside an example spectrum produced by the analysis code using the calculated *n* and *k* values shown in Figure 3.21.



Figure 3.22 Comparison of the simulated reflectance spectrum of amorphous water ice on HOPG (blue line) and the spectrum produced by the code (red crosses) using the values of n and k shown in Figure 3.21. The reflection angle is 46° and the ice thickness is 400 nm.

It is clear from Figure 3.22 that the small variations in *k* do not adversely affect the output spectra from the code, shown by the red crosses in Figure 3.22, which reproduces the input data shown by the blue line excellently. The fact that the determined *n* and *k* values are in near perfect agreement to the known values, shown in Figure 3.21, and that the code reproduces the input spectra show that the theory is valid, and that the code is suitable for the analysis of the experimental data. The code was hence used to analyse the UV/vis spectra of benzene presented above.

3.5.3 Applying the Complex Refractive Index Analysis to Benzene

Figure 3.23 shows a comparison of an experimental UV/vis spectrum of benzene ice and the corresponding simulated output spectrum from the analysis code at a reflection angle of 53°. The benzene exposure is 400 L_m , corresponding to an ice thickness of 401 nm determined using the Harrick¹⁹⁹ method. The wavelength region shown is

between 200 nm and 300 nm, to highlight the previously assigned benzene absorption features.^{186,188–190,196–198}



Figure 3.23 Comparison of reflectance spectra of 400 L_m amorphous benzene on HOPG in the wavelength range 200 nm – 300 nm. Red trace: experimental spectrum. Blue trace: Simulated spectrum produced by the analysis code. The reflection angle is 53°.

The ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ transition at 214 nm^{186,188,196,197} and the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transitions at 255 nm^{186,188–190,196–198} are excellently reproduced in the simulated spectrum, both in terms of peak position and profile. This is important as the simulated water spectra used to benchmark the theory and code did not include any absorption features, and further indicates that the theory describes the physical processes occurring in the experiment
accurately. Whilst the data shown in Figure 3.23 show that the experimental spectra are well reproduced in the wavelength range 200 nm – 300 nm, Figure 3.24 shows that the interference fringes at longer wavelengths are not as well simulated.



Figure 3.24 Comparison of reflectance spectra of 400 L_m amorphous benzene on HOPG in the wavelength range 200 nm – 590 nm to show the entire wavelength range. Red trace: experimental spectrum. Blue trace: simulated spectrum produced by the analysis code. The reflection angle is 53°.

The analysis is shown to be valid in section 3.5.2, as it accurately reproduces input spectra. Therefore the reason for the discrepancy between the experimental and simulated spectra in Figure 3.24 must be due to some error in the experimental data. Given that the absorption features, which are shown in Figures 3.12 and 3.14 not to shift with reflection angle, are well reproduced by the code, but the interference fringes, which do shift with reflection angle, are not then the most likely source of this error is an uncertainty in the reflection angle. This uncertainty is due to the limits of precision of the differentially pumped rotary feedthrough (DPRF, see Chapter 2) which allows the sample to be rotated, and the need to rotate the sample between recording a background spectrum and a sample spectrum. This disparity in angle does not have a large effect on the Harrick¹⁹⁹ analysis, as shown by the relatively small errors on *n* and *d*. However, it may be significant in determining the complex refractive index.

reason that this has little effect on the Harrick¹⁹⁹ analysis is that equations (3.6) and (3.7) rely on the spacing of the fringes, rather than the exact position. Figure 3.25 shows two recorded UV/vis reflectance spectra of separate benzene ices grown following an exposure of $250 L_m$ of benzene at two reflection angles. The spectra in each panel should be the same, however clear differences are observed.



Figure 3.25 Comparison of two data sets, shown in red and blue, of reflectance spectra of 250 L_m amorphous benzene on HOPG at two reflection angles. A: at a reflection angle of 39°. B: at a reflection angle of 58°.

In Figure 3.25, the fringes are shifted in position between the two data sets, shown in red and blue, by approximately 15 nm – 20 nm. This suggests that the reflection angle between the two data sets is not the same (as it was expected to be), as in Figures 3.14 and 3.20 the fringe position is shown to change with reflection angle. Therefore the values of θ shown in Table 3.1 and Figure 3.5 may not be the true experimental values. In both sets of data in Figure 3.25, the fringe spacing is relatively constant (varying by approximately 2%), whereas the position is not, hence the Harrick¹⁹⁹ analysis is valid.

In order to test the effect of an uncertainty on the reflection angle on the complex refractive index analysis, amorphous water ice spectra were simulated using the *n* and *k* values determined above, but with the reflection angles changed by $\pm 2^{\circ}$. Examples of these spectra are shown for a reflection angle of 46° $\pm 2^{\circ}$ in Figure 3.26.



Figure 3.26 Simulated reflectance spectra of amorphous water ice on HOPG using n values from Kofman et al.¹³⁶ and an assumed value of k = 0.01 with an error in reflection angle of $\pm 2^{\circ}$ introduced. The ice thickness in all cases is 400 nm.

It is clear that the fringe spacing remains relatively constant, 184 nm at 44° compared to 176 nm at 48°, at the different reflection angles. However the extrema of the interference fringes are shifted by approximately \pm 6 nm by changing the reflection angle. The magnitude of this shift, compared to the shift of approximately 15 nm in Figure 3.25, shows that the experimental uncertainty in reflection angle may be greater than \pm 2°.

In order to test the effect that an error in the reflection angle has on the analysis to calculate *n* and *k*, the simulated spectra with changed reflection angles were analysed using the code. However, the values of θ used were those shown in Table 3.1 in order to introduce an error on the reflection angle. For example, if an input spectrum was produced with reflection angle of 29°, it was analysed using θ = 31°. Figure 3.27 shows

the *n* and *k* values determined from spectra with changed reflection angles using the θ values from Table 3.1. Also shown for comparison are the results shown in Figure 3.21, where there was no error on reflection angle.



Figure 3.27 Real (panel A) and complex (panel B) part of the refractive index of amorphous water ice as a function of wavelength. Red traces: as shown in Figure 3.21. Blue traces: the result of the code when the reflection angle error is + 2°. Green traces: the result of the code when the reflection angle error is -2°.

The red traces in Figures 3.27A and 3.27B show the results of the analysis for *n* and *k* when the reflection angles of the input spectra matched the values used in the analysis, *i.e.* there was no error on the reflection angle. These values were shown in Figure 3.21 to match the known values used to simulate the input spectra and show that the analysis code worked as intended and expected. The green traces are the resulting values of *n* and *k* when an error of -2° in the reflection angle was introduced, *i.e.* the reflection angle used to produce the simulated spectra was 2° less than the θ value used in the analysis. Blue traces show results for an introduced error of +2°. The *n* and *k* values used to simulate the traces were identical, yet when an error in the reflection angle of \pm 2° is introduced the analysis gives inaccurate values of *n* and *k* as outputs. This would lead to the simulated spectra not matching the experimental data, which is indeed observed in

Figure 3.25. Therefore in this case, the final wavelength dependent complex refractive index of amorphous benzene ice is not able to be determined due to experimental uncertainty on the reflection angle of the spectra obtained. However the theoretical description of UV/vis reflection absorption spectra put forward in this work is shown to be valid.

Further work is therefore required to allow the code to be applied to experimental UV/vis data. In order to overcome the issue of error in the reflection angle, two options may be considered. Firstly, introducing a mechanism to return the sample to its starting position more accurately than using the MCT signal may overcome the issue. This could be done by mounting a laser pointer to the DPRF, and selecting a point to which the laser dot must be returned. The further this point is from the DPRF, the higher the angular accuracy will be. An alternative option is to remove the need to rotate the sample between recording the background spectra and dosing. Section 3.4 showed that direct dosing is required in order to produce ices thick enough to show interference fringes. The current configuration of the UHV chamber means that this can only be achieved by rotating the sample. Therefore this option would require a reconfiguration of the chamber, or one of the leak valves to be moved.

3.6 Summary and Conclusions

A novel fibre-coupled UHV compatible variable angle reflection-absorption UV/visible spectrometer has been installed on the UHV chamber. The design and geometric relations governing its operation are presented and shown to accurately describe the change in angle of incidence with z-shift position, as shown in Table 3.1.

Upon installation, it was necessary to make some modifications to the initial design which included adding extra right-angle mounts to the lens assembly and introducing a slot in the baseplate to increase reliability of the movement. Subsequent testing showed that these modifications did not alter the operation of the apparatus and were in keeping with the initial design considerations of UHV compatibly, lightweight design and strength.

The ice system chosen on which to perform test experiments using the novel apparatus was benzene. Benzene was chosen as its well-defined UV/vis absorptions^{186,188–190,196–198}

provided a simple check as to whether the apparatus was working as designed. Figures 3.12 and 3.14 show these absorption features, and confirm that the apparatus can be used to collect accurate UV/vis data. An initial analysis method was developed from that of Harrick,¹⁹⁹ which was first used to analyse benchtop IR spectra of polymer films. It was shown to be adaptable to UHV, low temperature UV/vis spectra and for amorphous benzene ice, $n = 1.43 \pm 0.07$, in excellent agreement with the literature.¹⁸⁶ This value is lower than that of liquid benzene.² This suggests that, as discussed in the section 3.1, it may not be appropriate to use an n value that is taken under ambient conditions in experiments under astronomically relevant conditions. The determined values of ice thickness, d, are shown in Table 3.2, and are on the order of 10^2 nm, as expected by the presence of interference fringes.

Using the Harrick method to determine *n* and *d* overcomes several issues identified in section 3.1. In this work, *n* and *d* are measured directly, eliminating the need to use an assumed value of *n*. Additionally, a single set of measurements can be used to obtain both *n* and *d*, reducing experimental time. And finally, because the UV/vis spectra are recorded after dosing the sample to grow the ice, rather than during dosing, the effect of processing (such as annealing) on the ice in terms of *n* and *d* can be measured.

In order to determine the wavelength dependent complex refractive index of an ice, *N*, the Kramers-Kronig relation has previously been used.^{10,12–17} However this method is inapplicable to this work as knowledge of the transmission Fresnel coefficients is required.^{1,2} This is not possible in the system described in this thesis as the surface onto which ices are grown is optically opaque HOPG. In this case, the method of Kozlova *et al.*¹⁸⁷ was employed. The theoretical description of reflection spectra used in this method was developed in this work by Professor Martin McCoustra of Heriot-Watt University.²⁰⁵ The theoretical description, illustrated by equations (3.12) – (3.27), was used to develop a code, written in the Python language (Appendix 1), to determine *n* and *k* of an ice from input reflectance data. In order to test the theory and code, UV/vis reflectance spectra of amorphous water ice were simulated at the reflection angles shown in Table 3.1 and a range of thicknesses in the range 100 nm – 500 nm using wavelength dependent *n* values determined by Kofman *et al.*¹³⁶ and an assumed, constant value of *k* = 0.01. These spectra were used as the input data of the code and

were found to be excellently reproduced, and the calculated *n* and *k* values were in near perfect agreement to the known values used to simulate the spectra. Therefore it was concluded that the theoretical description of reflectance spectra presented here and the analysis code are valid.

The code was hence applied to the experimental reflectance data recorded from amorphous benzene ices. Unlike in the testing using amorphous water ice spectra, the experimental benzene spectra were not well reproduced by the code. Investigations showed that small variations in the reflection angle, equal to 2°, caused the determined n and k values to vary from their true value. The shift in fringe maxima/minima introduced by an angle change of 2° in simulated spectra was approximately 6 nm. This is less than the \approx 15 nm shift seen in the recorded benzene spectra. This suggests that the uncertainty on reflection angle in the experimental spectra is likely > 2°. The origin of this uncertainty is most likely due to the need to rotate the sample between recording the background spectrum and the sample spectrum in order to grow ices thick enough to produce interference fringes without putting too high a gas load into the chamber. Future work must address this experimental error in order to accurately determine complex refractive indices of ices using the described apparatus.

4 RAIRS and TPD of Pure Benzene and Toluene Ices

This chapter presents a comparative study of the behaviour of benzene and toluene adsorbed on a highly oriented pyrolytic graphite (HOPG) surface at 25 K as a function of both exposure and temperature. Reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) are used to examine the ices. Multilayers of benzene are shown to undergo a thermally induced phase change which is assigned to crystallization of benzene ice. Toluene is shown to remain in its amorphous form until desorption. TPD experiments of low exposures of each molecule show complex desorption behaviour. This is assigned to lateral repulsive interactions between adsorbed molecules. Desorption parameters for each molecule as a function of exposure are calculated and discussed with reference to their molecular size, polarity and polarizability. Whilst the ices in this chapter are not directly relevant to astronomical ices, as pure benzene and toluene ices are unlikely to exist in space, the data are a benchmark for further work in this thesis.

4.1 Introduction

Benzene and its methyl substituted derivative, toluene, are of interest to a range of fields and applications due to their use as solvents and the fact that they are common organic pollutants.^{131,209–213} A survey of many household items and materials found that both benzene and toluene were present on approximately 50% of the items.²¹⁰ They are also emitted as air pollutants by exhaust fumes and oil refineries.²⁰⁹ As air pollutants, they can be found in water sources and snowfall, where they are trapped from the atmosphere.^{214,215} Because of this, their adsorption and desorption behaviour is of interest as a potential environmental cleaning route.^{216–219} Benzene and toluene are also of interest to the astrochemical community. This is due to their potential as building blocks of polycyclic aromatic hydrocarbons (PAHs), which are thought to contain up to 20% of interstellar carbon⁷⁵ and be constituents of interstellar dust grains themselves.¹⁴⁵ Benzene has been detected in galactic and extra-galactic protoplanetary nebulae^{64,153,192} and toluene formation routes have been postulated.^{154,155} Experimentally, gas phase reactions of the ethynyl radical (C₂H) and isoprene (CH₂C(CH₃)CHCH₂) lead to toluene.¹⁵⁴

(CH₃CHCCH) is suggested to produce toluene along with *para* and *ortho* isomers of xylene as shown by *ab initio* calculations.¹⁵⁵ These reactions are closely related to suggested benzene formation routes¹⁵¹ and hence toluene is thought to be present in similar astrophysical environments to those in which benzene is found.¹⁵⁵

The surface behaviour of adsorbed benzene has been relatively well studied using surface science techniques. Temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), metastable impact electron spectroscopy (MIES) and infrared spectroscopy have all been used to examine the surface behaviour of benzene. TPD and HREELS experiments demonstrated that, on Ru(001), benzene deposited at 120 K initially chemisorbs and then forms three distinct physisorbed phases.^{220,221} The authors suggest that the first phase lies flat on top of the chemisorbed layer and desorbs at 167 K in TPD experiments.²²⁰ This physisorbed layer is stabilised by π - π stacking interactions. Subsequently deposited benzene forms two phases (with desorption temperatures of 144 K and 154 K respectively) which easily interconvert. In these phases, benzene molecules are oriented perpendicular to the first physisorbed phase.^{220,221} RAIRS of benzene multilayers deposited on Ru(001) at 55 K show that a thermally induced phase change occurs after annealing the ice to 127 K, evidenced by splitting of bands associated with C-H vibrations at 3088 cm⁻¹, 3033 cm⁻¹ and 1036 cm^{-1,221} Similar chemisorption behaviour was observed following the deposition of benzene on Cu(111) at 120 K. Chemisorption was followed by the formation of a perpendicularly oriented bilayer and a subsequent multilayer phase which desorbed at 157 K and 153 K respectively.²²² Non-metal surfaces have also been used in studies of benzene adsorption/desorption. Low coverages of benzene on carbon nanotubes (CNTs),²²³ amorphous silica (a-SiO₂)^{114,115} and graphene coated metal and SiO₂ supports^{122,224} all show a coverage dependent desorption temperature in TPD experiments. The desorption temperature of sub-monolayer coverages of benzene on these surfaces is shown to decrease with increasing exposure in TPD experiments. In the case of benzene adsorbed on a-SiO2^{114,115} and CNTs,²²³ this effect was attributed to benzene desorbing from a range of adsorption sites of different binding energies. However in the case of graphene coated Cu,²²⁴ lateral repulsions between adsorbed benzene molecules were given as the reason for the observed desorption behaviour.

By contrast, the surface behaviour of toluene is less well examined. A single study of toluene adsorbed on graphite at 20 K has been reported.¹¹⁹ In this study, the toluene monolayer was found to desorb at 179 K, and the second layer desorbed at approximately 140 K.¹¹⁹ Toluene deposited on Ru(001) at 120 K has been examined by HREELS and TPD and shows similar behaviour to that of benzene.²²⁵ The first layer of toluene chemisorbs with its ring plane parallel to the surface, and the subsequent layer physisorbs in the same orientation.²²⁵ In this study, in contrast to that of benzene by the same authors,^{220,221} no structural information on the multilayers of toluene was given.²²⁵

The surface behaviour of benzene and toluene on HOPG has not been previously examined, therefore TPD and RAIRS experiments have been performed at a range of exposures. The results for each molecule are compared in order to examine whether the addition of a methyl group has any effect on the adsorption/desorption behaviour of benzene and toluene on HOPG. The addition of this methyl group renders toluene slightly polar, with a dipole moment of 0.36 D,²⁰² compared to apolar benzene. These experiments are also used to characterise the behaviour of the molecules for comparison with UV/vis spectroscopy, discussed later in this work, and as a benchmark for their behaviour in the presence of water.

4.2 Experimental

The experimental methods used in this chapter were outlined in Chapter 2. In all cases, ices are grown *via* backfilling.

4.3 Results and Discussion

4.3.1 RAIRS of Benzene and Toluene on HOPG

Figure 4.1 shows RAIR spectra of increasing exposures of benzene deposited on HOPG at 25 K. The figure has been split into three spectral regions for clarity as the bands have different intensities. Figure 4.1A shows the wavenumber region from 3150 cm⁻¹ – 2950 cm⁻¹, Figure 4.1B shows the region 1550 cm⁻¹ – 1400 cm⁻¹ and Figure 4.1C shows the region 1080 cm⁻¹ – 980 cm⁻¹. No bands outside of these regions are present. Exposures of 0.5 Lm – 100 Lm were examined. At exposures below 5 Lm, no bands are observed in the spectrum, as shown in the 1 Lm spectrum in Figure 4.1.



Figure 4.1 RAIR spectra of increasing exposures of benzene on HOPG deposited at 25 K. Band intensities are shown in each panel and exposures in L_m are shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

As the exposure is increased to 5 L_m, bands appear in the spectrum at 3038 cm⁻¹ and at 1479 cm⁻¹. By comparison with the literature,^{31,127,226} the band at 3038 cm⁻¹ is assigned to a combination of C-H stretching modes, v(CH), and that at 1479 cm⁻¹ is assigned to the aromatic C-C stretching mode, v(CC)_{aromatic}. Band assignments for all the bands observed in Figure 4.1 are given with reference to the literature in Table 4.1. The band intensities increase as the exposure is increased to 10 L_m and at an exposure of 20 L_m an additional band at 1036 cm⁻¹ appears in Figure 4.1C. This is assigned to the C-H in plane deformation mode, δ (CH)_{in-plane}.^{31,127,226} After increasing the exposure to 30 L_m, a band at 3090 cm⁻¹ is also observed, assigned to the C-H stretching mode, v(CH)_{aromatic}.^{31,127,226} Aft 30 L_m the combination band red shifts to 3034 cm⁻¹. As the exposure is increased to 100 L_m, all bands continue to grow in intensity and no subsequent shifts are observed. The small shifts of the benzene RAIR bands upon adsorption when compared to the liquid,²²⁷ as shown in Table 4.1, suggest that benzene is physisorbed on the HOPG surface.

Table 4.1 Assignments of the bands observed in the RAIR spectra of benzene shown in Figure 4.1. Values on HOPG are from this work, comparison to the literature is also shown.^{31,127,227} Symbols: v = stretching, $\delta =$ deformation.

| | | Wavenumber / cm ⁻¹ | | | | |
|---------------------------|-----------|-------------------------------|----------------------------|---------------------------|------------------------|--|
| Band | HOPG at | HOPG at | Si(111) at | Ru at | Liquid | |
| Assignment | 25 K | 110 K | 77 K ¹²⁷ | 14 K ³¹ | benzene ²²⁷ | |
| v(CH) _{aromatic} | 3090 | 3091/3085 | 3088 | 3095 | 3091 | |
| v(CH) | | | | | | |
| Combination | 3038/3034 | 3037/3030 | 3036 | 3043 | 3036 | |
| band | | | | | | |
| v(CC) _{aromatic} | 1479 | 1479 | 1480 | 1481 | 1479 | |
| δ(CH) _{in-plane} | 1036 | 1040/1034 | 1040 | 1038 | 1038 | |

Figure 4.2 shows RAIR spectra for the adsorption of toluene. As for benzene, the spectra are divided into different spectral regions for clarity, and no bands outside these regions are present. Exposures of toluene from 5 L_m – 100 L_m were investigated. Figure 4.2A

shows the wavenumber region from $3050 \text{ cm}^{-1} - 2850 \text{ cm}^{-1}$, Figure 4.2B shows the region 1650 cm⁻¹ - 1450 cm⁻¹ and Figure 4.2C shows the region 1100 cm⁻¹ - 1000 cm⁻¹.

At the lowest exposure studied, 5 L_m, the only toluene RAIRS bands present are shown in Figure 4.2A. This exposure was the lowest investigated as it had extremely low signal intensity, as shown in Figure 4.2, and lower exposures did not show any bands. Table 4.2 shows the observed toluene bands and their assignments with reference to the literature. The bands observed at 2951 cm⁻¹ and 2915 cm⁻¹ are assigned to the asymmetric methyl stretch, v(CH₃)_{as}, and the symmetric methyl stretch, v(CH₃)_s, respectively.^{228,229} The presence of these bands at the lowest exposures is to be expected, as they are methyl modes and therefore at any molecular orientation, some component of the vibration's dynamic dipole will be in the surface normal. As can be seen from the scale bar in Figure 4.2A, the bands are very weak, and do not grow significantly with increasing exposure. Compared to the benzene bands in this region, shown in Figure 4.1A, the toluene bands are broader. This is most likely due to the fact that they are methyl vibrations as opposed to single C-H modes in benzene. As such they will have a wider distribution of orientations and therefore a broader energy range, as varying degrees of their dynamic dipoles will be in the surface normal.

At a toluene exposure of 10 L_m, two additional bands are observed at 1605 cm⁻¹ and 1496 cm⁻¹ (Figure 4.2B). Both of these bands are assigned to v(CC)_{aromatic} modes.^{228,229} More bands are observed in the RAIR spectra of toluene than of benzene due to the increased molecular complexity of toluene which means that it has more degrees of freedom.¹¹⁷ As the exposure is increased to 30 L_m, additional toluene bands are observed in Figure 4.2C. The band at 1084 cm⁻¹ is assigned to the δ (CH)_{in-plane} mode, and the very weak band at 1039 cm⁻¹ is assigned to the methyl rocking mode, ρ (CH₃).^{228,229} The final toluene bands are observed following an exposure of 50 L_m. One of these is shown in Figure 4.2A, at 3020 cm⁻¹. This band is extremely weak, with an intensity of < 0.02%. This band is assigned to the v(CH)_{aromatic} mode.^{228,229} The other band is at 1466 cm⁻¹, seen in Figure 4.2B. This is a combination band containing contributions from the v(CC)_{aromatic} and δ (CH₃)_{as} modes.^{228,229}



Figure 4.2 RAIR spectra of increasing exposures of toluene deposited on HOPG at 25 K. Band intensities are shown in each panel and exposures in L_m are shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

Table 4.2 Assignments of the bands observed in the RAIR spectra for toluene shown in Figure 4.2. Values for HOPG are from this work, comparison to the literature is also shown.^{228–230} Symbols: v = stretching, δ = deformation, $\rho =$ rocking, s = symmetric, as = asymmetric.

| | Wavenumber / cm ⁻¹ | | | |
|-----------------------------------|-------------------------------|------------------------------------|---|----------------------------------|
| Band Assignment | HOPG at 25 K | Ni(111) at 110 K ²²⁸ | Gas phase protonated toluene ²²⁹ | Liquid toluene ²³⁰ |
| v(CH) _{aromatic} | 3020 | 3027 | - | 3028 |
| v(CH ₃) _{as} | 2951 | 2922 | 3068 | 2948 |
| v(CH ₃)s | 2915 | 2876 | 2914 | 2873 |
| v(CC)aromatic | 1605 | 1605 | 1623 | 1605 |
| v(CC)aromatic | 1496/1495 | 1495 | 1487 | 1496 |
| v(CC) _{aromatic} and | | | | |
| δ(CH ₃) _{as} | 1466 | 1464 | 1473 | 1461 |
| combination | | | | |
| $\delta(CH)_{in-plane}$ | 1084/1082 | 1082 | - | 1082 |
| ρ(CH₃) | 1039 | 1030/1014 | 1028 | 1042 |

As for benzene, some wavenumber shifts as a function of exposure are observed in the RAIR spectra of increasing amounts of toluene. The v(CC)_{aromatic} band, which appears at 1496 cm⁻¹ in the 5 L_m and 10 L_m spectra, red shifts to 1495 cm⁻¹ for exposures of 30 L_m and above. This corresponds, as for benzene, to the monolayer to multilayer coverage regime change which is discussed in detail below. Similarly, the δ (CH)_{in-plane} mode is seen to shift, in the same exposure range, from 1084 cm⁻¹ – 1082 cm⁻¹. The small changes in the toluene band positions upon adsorption when compared the liquid IR spectrum²³⁰ indicate that toluene is physisorbed on the HOPG surface, as is the case for benzene.

As well as being used to examine the appearance of bands with increasing exposure, adsorption experiments can be used to examine the validity of the assumption that the sticking probability at base temperature is constant (set out in Chapter 2). Figure 4.3 shows the integrated area of the v(CC)_{aromatic} mode for benzene at 1479 cm⁻¹ (Figure 4.3A) and the v(CC)_{aromatic} mode for toluene at 1495 cm⁻¹ (Figure 4.3B). These bands were

chosen as the most intense bands in each set of RAIR spectra. For both molecules a linear relationship is shown between peak area and exposure, and a linear fit is shown on each plot, which indeed shows that the sticking probability remains constant. The constant sticking probability is also indicative of physisorption, in agreement with the previously observed small shifts upon adsorption of benzene and toluene IR bands. This conclusion relies on the assumption that no structural changes in the ice occur as a function of exposure as this would lead to changes in the RAIR band intensities.



Figure 4.3 Integrated band area of RAIR spectra of benzene and toluene as a function of exposure in L_m. A: red squares show the benzene band areas and the blue line shows a linear fit to the data. B: blue circles show the toluene band areas and the red line shows a linear fit to the data.

In addition to adsorption experiments, the effect of annealing ices of benzene and toluene adsorbed on HOPG was monitored by RAIRS. Annealing experiments are used to probe any thermally induced changes in the ice which affect the RAIR spectra. Figure 4.4 shows RAIR spectra of 100 L_m of benzene on HOPG deposited at 25 K and subsequently annealed in 10 K intervals until all the benzene had desorbed. The 100 L_m exposure is shown as a representative example of an annealing experiment as it has the highest band intensity, although exposure dependent annealing behaviour is discussed below. The figure is split into the same wavenumber regions as Figure 4.1 for clarity.



Figure 4.4 RAIR spectra showing the effect of annealing on 100 L_m benzene on HOPG deposited at 25 K. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure. Adapted from Salter et al.¹¹⁷

Between 25 K and 70 K, no changes in any of the bands occur and therefore these spectra are omitted from Figure 4.4. Upon annealing to 90 K, several changes in the spectra are apparent. At 90 K, the v(CH)_{aromatic} band at 3090 cm⁻¹, shown in Figure 4.4A, splits and blue shifts to 3091 cm⁻¹ with a shoulder growing in at 3085 cm⁻¹. As the temperature is increased, the shoulder increases in intensity until, at 110 K, the peak becomes a clearly defined double peak. Similarly at 90 K, the combination band at 3038 cm⁻¹ begins to split into two peaks at 3037 cm⁻¹ and 3030 cm⁻¹ which become most apparent at 100 K. In Figure 4.4B, the v(CC)_{aromatic} band at 1479 cm⁻¹ is seen to increase in intensity from 90 K – 110 K, nearly doubling in intensity without shifting in wavenumber. Finally, the δ (CH)_{in-plane} band at 1036 cm⁻¹ (Figure 4.4C) red shifts following annealing to 90 K to 1034 cm⁻¹, with a shoulder at 1040 cm⁻¹. As the temperature is increased to 110 K this shoulder sharpens. At 130 K, benzene begins to desorb from the surface, as shown by the decrease in intensity of all bands. At 140 K, all of the benzene has desorbed, indicated by the lack of any bands in the RAIR spectrum in Figure 4.4. The thermally induced changes in the bands are also shown in Table 4.1.

During the annealing experiment, no additional benzene is added to the system. Additionally, residual benzene does not persist in the chamber as the pressure measured by the ion gauge returns to base pressure when the leak valve is closed at the end of the dose. Therefore the changes in the spectra must occur due to a thermally induced change in the ice structure. Indeed thermally induced changes in RAIR spectra have been noted for ices of many molecules, such as acetylene,¹⁸ H₂O,^{137,142} CO,²³¹ CO₂,^{118,232} isomers of C₂H₄O₂^{233,234} and propan-2-ol¹¹⁶ to name a few. The nature of the structural change of the benzene ice can be determined by careful consideration of the observed changes. RAIRS experiments on *para*-xylene (1,4-dimethylbenzene)¹¹⁷ and isomers of C₂H₄O₂²³³ have shown that ordering and crystallisation cause different changes in the spectrum. Small shifts and increases in intensity of bands are attributed to ordering, whereas splitting of bands and larger shifts tend to indicate crystallisation.

In the case of benzene, the observed changes to the RAIR spectra upon annealing (Figure 4.4) are attributed to a phase transition from amorphous to crystalline benzene. The thermally induced crystallisation of adsorbed benzene has been observed using RAIRS on graphene coated Pt(111)²³⁵ and Ru(001)²²¹, by electron energy loss spectroscopy

(EELS) on polycrystalline Pt¹⁹⁸ and by vacuum ultraviolet (VUV) spectroscopy on MgF₂.¹⁸⁶ The splitting of bands upon crystallisation is explained by considering the initial deposition of the molecules at 25 K. At this temperature, the molecules will adsorb in random orientations. As a result, the oscillations of individual vibrational modes will be in a range of environments, affected to varying degrees by intermolecular interactions and oscillating in all directions. The effect of this anisotropic oscillation is that varying degrees of a vibrational mode are cancelled out and enhanced, therefore the frequency of the mode becomes spread over a range of energies. Hence a single band is observed in the RAIR spectrum, representing the spread of frequencies.

When the ice crystallises, molecules become aligned and ordered so that the oscillations of a vibrational mode become aligned within the ice, and their frequencies are less varied. This causes the sharpening of a band in the RAIR spectrum and splitting if there are multiple environments in the crystal structure. In the case of benzene, the bands associated with the C-H modes, at 3090 cm⁻¹, 3038 cm⁻¹ and 1036 cm⁻¹, split upon crystallisation, whereas the v(CC)_{aromatic} mode at 1479 cm⁻¹ sharpens and increases in intensity. This allows the possible structure of crystalline benzene ice to be examined. Jakob and Menzel^{220,221} studied the vibrational modes of benzene adsorbed on Ru(001) and concluded that benzene multilayers crystallise with their molecular plane oriented diagonally to that of the surface. Similarly, neutron^{236,237} and X-ray^{238,239} diffraction studies of solid benzene show a herringbone crystal structure, as shown in Figure 4.5.



Figure 4.5 Crystal structure (a) and molecular packing (b) of solid benzene shown along the c-axis. Reproduced from Nayak et al.²³⁷

It is hence likely that benzene adopts this structure on the HOPG surface upon annealing. The splitting of the C-H modes at 3090 cm⁻¹, 3038 cm⁻¹ and 1036 cm⁻¹ seen in Figure 4.4, is explained by the different C-H environments. Two of the C-H bonds, *para*- to one another, are pointing into the middle of the rings of the two adjacent benzene molecules, forming stabilising C-H··· π interactions.²³⁷ The other C-H bonds do not form these interactions and are therefore in a different chemical environment, giving the characteristic splitting observed in the RAIRS, as shown in Figure 4.4. Comparatively, the v(CC)_{aromatic} mode does not split, but grows in intensity in Figure 4.4. This is because all the aromatic rings are in the same environment between two stabilising C-H··· π interactions, therefore no splitting occurs. The intensity growth is a consequence of the ordering of benzene molecules when the ice crystallises. As this happens the number of molecules with a component of the v(CC)_{aromatic} dynamic dipole in the surface normal increases and therefore its intensity in the RAIR spectra increases, according to the metal surface selection rule.¹⁸⁰

The crystallisation of benzene as a function of temperature is also found to be dependent on the exposure of benzene. Figure 4.6 shows the change in the integrated area of the $v(CC)_{aromatic}$ band of benzene as a function of annealing temperature for several benzene exposures. It is assumed that the change in area of the $v(CC)_{aromatic}$ band is attributed to crystallisation and no other structural change in the ice occurs at any exposure.

At all exposures, as shown in Figure 4.4, the band area decreases above 120 K as the benzene desorbs from the HOPG surface. What is apparent in Figure 4.6 is that only for exposures of 30 L_m and above does the band area increase upon annealing. Below this exposure, the band area remains relatively constant until desorption. This indicates that the crystallisation of benzene is coverage-dependent. This has been observed previously where only multilayers of benzene undergo this phase change.^{198,221} This coverage dependence of crystallisation is discussed further below with reference to TPD data.

The thermal behaviour of benzene on HOPG provides an interesting comparison to that of toluene. Figure 4.7 shows the effect of annealing on the RAIR spectra of 70 L_m toluene on HOPG. The Figure is split into the same regions as Figure 4.2 for clarity.



Figure 4.6 Change in the integrated band area of the v(CC)_{aromatic} mode of benzene at 1479 cm⁻¹ as a function of annealing temperature for several exposures. In all cases the deposition temperature was 25 K.



Figure 4.7 RAIR spectra showing the effect of annealing on 70 L_m toluene on HOPG deposited at 25 K. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

The 70 L_m exposure was chosen as a representative example of the toluene annealing experiments. In contrast to benzene, the toluene spectra show very few changes upon annealing. In Figure 4.7A, following annealing to 110 K, the v(CH₃)_{as} band at 2951 cm⁻¹ and v(CH₃)_s band at 2915 cm⁻¹ sharpen slightly. However, because the intensities of these bands are so weak, they are less distinguishable from the spectral baseline and so care must be taken when examining these changes. Following annealing to 130 K (Figure 4.7) the bands all decrease in intensity as toluene begins to desorb from the surface.

The only other changes in the toluene spectra are shown in Figure 4.7B, after annealing to 80 K. The v(CC)_{aromatic} and δ (CH₃)_{as} combination band at 1466 cm⁻¹ decreases in intensity slightly. None of the bands show any thermally induced shifts. Due to the fact that no shift or splitting of any of the toluene RAIRS bands is observed upon annealing, and that only small intensity changes occur, crystallisation of toluene is not thought to occur on HOPG. Some thermal rearrangement may occur, which is responsible for the small reduction in intensity of the combination band at 1466 cm⁻¹. The lack of crystallisation observed here is in contrast to previous studies of toluene adsorbed on surfaces, which have shown crystallisation to occur. Coats et al.228 examined ices of toluene deposited on Ni(111) at 110 K and observed several changes to RAIRS peak intensity upon annealing. These included the decrease of intensity of the combination band, although to a much larger degree than in this work, upon annealing to 132 K. Similarly, crystallisation of toluene deposited at 15 K on Ni(111) was observed at 147 K by Souda²⁴⁰ via TPD and time-of-flight secondary ion mass spectrometry (TOF-SIMS). In both cases, the temperatures of crystallisation of toluene, 132 K²²⁸ and 147 K,²⁴⁰ are in the temperature range where toluene desorbs. Therefore it is likely that, in this work, toluene desorbs before it crystallises, although some rearrangement may occur before desorption.

The fact that crystallisation of toluene is not observed in this work is further shown by examining the peak areas of RAIRS bands as a function of annealing temperature. Figure 4.8 shows the change in area of the $v(CC)_{aromatic}$ and combination bands (1495 cm⁻¹ and 1466 cm⁻¹ respectively). No significant change in the $v(CC)_{aromatic}$ band is observed in Figure 4.8A, whereas a slight decrease in intensity is shown in the case of the combination band in Figure 4.8B. This is in contrast to the benzene data, shown in Figure

4.6, where significant increases in band area are observed, which are indicative of crystallisation. Exposures of 50 L_m and 100 L_m of toluene are shown and no coverage dependency is observed.



Figure 4.8 Integrated band areas of 100 L_m (blue squares) and 50 L_m (red circles) of toluene on HOPG as a function of annealing temperature. A: for the v(CC)_{aromatic} band at 1495 cm⁻¹. B: for the v(CC)_{aromatic} and δ (CH₃)_{as} combination band at 1466 cm⁻¹.

The crystallisation temperature of benzene observed in this work is in the range 90 - 110 K, as shown in Figures 4.4 and 4.6, which is lower than that of toluene observed in

the literature (110 K to > 130 K).^{228,240} This suggests that the barrier to crystallisation of toluene is higher than that of benzene. This can be rationalised by the crystal structure of toluene. Toluene is known to have two crystal structures, α -toluene^{237,241} and β -toluene.²⁴² Of the two forms, α -toluene is thermodynamically favoured, as it is produced at higher temperatures than the β form. Nayak *et al.*²³⁷ solidified toluene at 100 K and subsequently annealed it to 155 K to form α -toluene. Similarly Ibberson *et al.*²⁴¹ determined the structure of α -toluene grown at 162 K. Lower temperatures are required to obtain β -toluene, as shown by Andre *et al.*²⁴² who grew β -toluene nucleates at 132 K then rapidly cooled the sample to 122 K to ensure that only the metastable β form was formed. Therefore it is more likely that the low-temperature β -toluene is formed in the works of Coats²²⁸ and Souda²⁴⁰ as the observed crystallisation temperatures of 132 K and 147 K respectively are lower than that which forms the α -phase.



Figure 4.9 Molecular packing of β -toluene shown along the c-axis. Reproduced from Andre et al.²⁴²

Considering the β -toluene structure, shown in Figure 4.9, compared to that of benzene in Figure 4.5, the higher crystallisation temperature, and by implication barrier, can be explained. In crystalline benzene, all of the molecules are aligned and in the same environment, whereas in β -toluene the molecules are arranged with their methyl groups in alternate directions. The addition of a methyl group on toluene increases the molecular complexity and reduces its symmetry compared to benzene. This means that more dramatic rearrangement is required in the amorphous to crystalline phase transition, which would lead to a larger barrier and therefore require a higher temperature than benzene. Hence toluene crystallisation is not observed before desorption in this work.

4.3.2 TPD of Benzene and Toluene on HOPG

TPD experiments were also performed for both benzene and toluene adsorbed on HOPG and provide complementary data to the RAIRS results. Figure 4.10 shows TPD traces of low exposures ($\leq 20 L_m$) of benzene (Figure 4.10A) and toluene (Figure 4.10B) on HOPG deposited at 25 K. In order to make the data for the two molecules comparable, exposures in L_m are converted to approximate coverages in monolayers, ML.

In order to make this comparison, the area of a single molecule was initially calculated. Benzene was taken to be circular, and the radius was determined using the bond lengths taken from Bacon and Curry.²³⁶ Toluene was approximated as a benzene molecule plus a quadrilateral representing the methyl group, the size of which was determined using bond lengths from Ghosh and Ha.²⁴³ The calculated areas of the molecules were 1.93×10^{-19} m² and 2.10×10^{-19} m² for benzene and toluene respectively. The area was then multiplied by the estimate of the number of molecules on the surface, as determined by equation (2.9) in Chapter 2, to determine the total area of the surface covered by the molecules. Given the 2 cm² size of the HOPG surface, a coverage could then be determined. Using this method, approximately 1 ML coverage was found to correspond to exposures of 15 L_m – 20 L_m for benzene and toluene and the equivalent coverages in ML.

The validity of this assumption is examined in the analysis of the TPD data. The TPD traces shown in Figure 4.10 are for exposures of $1 L_m - 15 L_m$ of benzene and $3 L_m - 20 L_m$ of toluene. These exposures correspond to coverages of approximately 0.1 ML - 1 ML of each molecule on HOPG. For benzene and toluene, some TPD traces have been omitted from the figure for clarity, however they show the same trends as the data presented.

| Benzene | | Toluene | | |
|---------------------------|---------------|---------------------------|---------------|--|
| Exposure / L _m | Coverage / ML | Exposure / L _m | Coverage / ML | |
| 0.3 | 0.02 | 3 | 0.15 | |
| 0.5 | 0.03 | 5 | 0.24 | |
| 1 | 0.06 | 7 | 0.34 | |
| 2 | 0.1 | 10 | 0.49 | |
| 3 | 0.17 | 12 | 0.59 | |
| 4 | 0.23 | 15 | 0.73 | |
| 5 | 0.28 | 20 | 0.98 | |
| 7 | 0.40 | 25 | 1.22 | |
| 10 | 0.56 | 30 | 1.47 | |
| 15 | 0.85 | 40 | 1.96 | |
| 20 | 1.13 | 50 | 2.45 | |
| 30 | 1.69 | 70 | 3.43 | |
| 40 | 2.26 | 85 | 4.16 | |
| 50 | 2.82 | 100 | 4.89 | |
| 70 | 3.95 | 120 | 5.87 | |
| 100 | 5.64 | 150 | 7.34 | |
| | | 200 | 9.79 | |

Table 4.3 Equivalent coverages of benzene and toluene in ML for the exposure in L_m.

For both molecules at sub-monolayer exposures, the desorption temperature clearly decreases as the exposure increases. For benzene, in the coverage range 0.17 ML - 0.56 ML, the decrease in desorption temperature is 15 K, from 147 K to 132 K. For toluene the desorption temperature decreases by 12 K, from 158 K at 0.15 ML to 146 K at 0.59 ML. The decrease in desorption temperature for benzene is greater than that of toluene for equivalent coverages, the significance of which is discussed below. Both molecules exhibit very broad TPD peaks at low exposures. As the exposure is increased, the peak profile changes from broad and symmetrical to narrower and slightly asymmetrical with a steeper leading edge, as seen in Figure 4.10.



Figure 4.10 TPD traces for approximately 0.1 – 1.0 ML of benzene (A) and toluene (B) deposited on HOPG at 25 K.

Typical sub-monolayer TPD traces are characterised by mostly symmetrical peaks, with a peak temperature which does not change with coverage.^{25,29} This is clearly not the case for benzene and toluene, which exhibit complex desorption behaviour at low exposures. A decrease in peak temperature with increasing exposure has also been observed for benzene desorbing from amorphous silica (a-SiO₂),^{114,115} Pd(111),²⁴⁴ Cu(111),²²² bare and graphene coated Ru(0001)¹²² and graphene coated Cu and SiO₂.²²⁴ In the case of a-SiO₂,^{114,115} the decrease in desorption temperature and broad peak shape was attributed to benzene desorbing from a range of adsorption sites, which is consistent with the rough morphology of a-SiO₂.¹¹⁵ However the HOPG surface is generally smooth compared to a-SiO₂, and more comparable to the other surfaces. In the cases of Pd(111), Cu(111), bare and graphene coated Ru(0001), and graphene coated Cu and SiO₂, repulsive lateral interactions between adsorbed molecules have been suggested to account for the desorption behaviour observed.^{122,222,224,244} Therefore, it is concluded that these repulsions also occur for benzene adsorbed on HOPG. The repulsions, which occur between adjacent adsorbed benzene molecules, are due to the polarization upon adsorption of the π -electron system of benzene,^{117,121,224}

leading to the observed TPD behaviour. The TPD behaviour which has been observed here, of decreasing peak temperature with increasing exposure, has not previously been observed for toluene. However, due to the striking similarity in behaviour of toluene compared to benzene, the decrease in desorption temperature with increasing coverage is also assigned to lateral repulsions between adsorbed toluene molecules. The nature of these repulsive interactions is examined in more detail below.

Figure 4.11 shows TPD traces resulting from increasing the coverage of benzene (Figure 4.11A) and toluene (Figure 4.11B) compared to those shown in Figure 4.10. For both molecules the highest coverages shown in Figure 4.10 are shown for comparison. By comparison with the RAIRS data, Figure 4.11A shows the desorption of crystalline benzene from HOPG. The crystallisation is not observed in the TPD as it occurs at a lower temperature (90 K - 120 K) than the onset of desorption. Figure 4.11B shows the desorption of amorphous toluene as no crystallisation is observed in the RAIRS. In both cases, the behaviour is clearly different to the lower coverage TPD data shown in Figure 4.10. For both molecules, as the coverage is increased, the peak desorption temperature increases. For benzene the temperature increases from 136 K at a coverage of 1.13 ML to 140 K for 5.64 ML. For toluene the temperature increases from 138 K at 1.47 ML to 140 K at 4.89 ML. These data agree with the RAIRS data. In Figure 4.4, 100 Lm benzene (5.65 ML) is seen to have desorbed after annealing to 140 K, and in Figure 4.7, after annealing to 130 K, most of a 100 Lm exposure of toluene (4.89 ML) has desorbed.

At the coverages shown in Figure 4.11, the leading edges of the TPD traces for each molecule become shared. This is characteristic of multilayer desorption²⁵ and is in agreement with the coverage estimates made above, as at a coverage of > 1 ML, multilayer behaviour is observed. This shows that the estimation of coverage based on molecular size is reasonable, despite the fact that it assumes close packing. According to the coverage estimates described above, the coverages shown in Figure 4.11 are approximately 1 ML – 5.5 ML. By comparison with Figures 4.1 and 4.2, it can be concluded that sub-monolayer amounts of benzene and toluene are observable in the RAIR spectra.

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Figure 4.11 TPD traces for approximately 1 – 5.5 ML of benzene (A) and toluene (B) deposited on HOPG at 25 K.

The change from monolayer to multilayer desorption according to the TPD occurs at similar exposures to observed RAIRS band shifts. The bands that shift are the benzene combination band at 1034 cm⁻¹ (Figure 4.1) and the v(CC)_{aromatic} and δ (CH)_{in-plane} modes of toluene at 1496 cm⁻¹ and 1084 cm⁻¹ respectively (Figure 4.2). For both molecules, the shifts occur at an exposure of 30 L_m, which corresponds to coverages of 1.69 ML and 1.47 ML for benzene and toluene respectively. At this coverage, the multilayer behaviour is established. Therefore the band position can be used as an indicator of coverage in this work. This change from monolayer to multilayer desorption is also in agreement with the results of RAIRS annealing experiments, that show crystallisation of benzene occurring for exposures \geq 30 L_m. As suggested in the literature,^{198,221} only multilayers of benzene will undergo crystallisation. This is in agreement with the results of the proposed crystal structure of benzene, where stacks of molecules are required to form the herringbone structure.

The TPD data were analysed using leading edge analysis, discussed in Chapter 2, in order to determine the kinetic parameters for desorption. Figure 4.12 shows example plots used to determine *n* (Figure 4.12A) and E_{des} (Figure 4.12B) for benzene. Figure 4.12A shows a plot of ln[I(T)] against $ln(\theta_{rel})$ for coverages from 0.1 ML – 5.64 ML of benzene at a fixed temperature of 130 K. Plots of this type were constructed for temperatures between 127 K and 130 K. The gradient of the graph gives *n*, and the change in gradient shows the change from monolayer to multilayer desorption. In Figure 4.12A, the point at which the gradient is seen to change is at an exposure of 15 L_m benzene, in excellent agreement with the coverage estimation based on molecular size outlined above.



Figure 4.12 A: Plot of ln[l(T)] against $ln(\theta_{rel})$ for a fixed temperature of 130 K on the leading edge of TPD traces of coverages from 0.1 ML – 5.64 ML benzene. Blue crosses are individual data points and solid red lines are linear fits to the data. B: Plot of $ln[(T)] - nln(\theta_{rel})$ against 1/T for 3.95 ML of benzene on HOPG. Red circles are individual data points and the blue solid line is a linear fit to the data.

In Figure 4.12A, the gradients for the two linear portions of the plot are shown. Table 4.4 shows the gradients determined from each set of benzene TPD traces for both monolayer and multilayer exposures. The error in the mean of these gradients is taken as two times the standard error of the mean. This method was chosen to determine the error in n as each individual value did not have an associated error. In the case of the sub-monolayer value of *n*, the mean gradient of 3.27 is clearly unphysical, and therefore

leading edge analysis for these exposures (\leq 15 L_m, shown in Figure 4.10) was not taken further. An alternative analysis is discussed below. The reason for the spurious value of *n* for sub-monolayer benzene is due to the lateral repulsions. These interactions cause the deviation from typical sub-monolayer behaviour and hence cause the order to deviate from its typical value of 1.

| Fixed Temperature / K | Monolayer order (≤ 15 L _m) | Multilayer order (≥ 15 L _m) |
|-----------------------|--|---|
| 127 | 3.34 | 0.05 |
| 128 | 3.36 | 0.11 |
| 129 | 3.36 | 0.17 |
| 130 | 3.02 | 0.27 |

Table 4.4 Orders of desorption of sub-monolayer and multilayer benzene from HOPG for several fixed

 temperatures on the TPD traces determined using leading edge analysis for each set of data.

Taking the mean of the gradients of the order plots at each fixed temperature shown in Table 4.4 gives an order of 0.18 ± 0.06 for multilayer benzene desorption. This is higher than the expected value of 0 for multilayer desorption.²⁵ This fractional order of desorption is expected as the leading edges of the TPD traces in Figure 4.11A are not perfectly shared. It is also clear in Table 4.4 that there is a trend in the multilayer values of n, which increase as the fixed temperature on the leading edge is increased. This is because, as shown in the TPD traces in Figures 10 and 11, the contribution of the submonolayer desorption peak to the leading edge will increase as higher temperatures are used to determine *n*.

Using the determined multilayer desorption order, and equation (2.6) in Chapter 2, E_{des} can be determined from plots such as that shown in Figure 4.12B. Figure 4.12B shows a plot of $ln[l(T)] - nln(\theta_{rel})$ against 1/T for the 70 L_m TPD trace of benzene. The error bars are determined using the upper and lower values of the mean desorption order of 0.18 ± 0.06. The data were then fitted using a weighted least squares fit, and the desorption energy for multilayer crystalline benzene was taken as the mean of all the values from each TPD trace. Table 4.5 shows the individual values of E_{des} for each

multilayer TPD trace and the error, determined from the error on the straight line fit to the data. The overall error on the mean value was determined by propagation of errors.

 Dose / Lm
 Desorption Energy, Edes / kJ mol⁻¹

 30
 43.3 ± 4.6

 40
 44.9 ± 4.1

 50
 46.1 ± 4.3

 70
 46.5 ± 3.7

 100
 46.7 ± 3.5

 Table 4.5 Multilayer desorption energies of benzene determined by leading edge analysis for each set of data.

The determined E_{des} for multilayer benzene, the mean of the values shown in Table 4.5, is 45.5 ± 1.8 kJ mol⁻¹. This value is in good agreement with previously determined values of 46.6 ± 0.08 kJ mol⁻¹, 48.5 ± 3.0 kJ mol⁻¹ and 41.4 ± 0.9 kJ mol⁻¹ for a-SiO₂,¹¹⁵ Ru(001)²²⁰ and Cu(111)²²² respectively. Ulbricht *et al*.¹¹⁹ have calculated a value of E_{des} for multilayer benzene of 44 ± 7 kJ mol⁻¹ which is also in good agreement with the value determined in this work. The values in Table 4.5 vary with benzene exposure, initially there is an increase from 30 L_m to 50 L_m which then plateaus. This trend is explained below.

The final step of the leading edge analysis is to determine the pre-exponential factor, v, for the desorption of multilayer benzene. Using equations (2.7) – (2.10) in Chapter 2, the values for v shown in Table 4.6 were determined. Taking the mean of the values in Table 4.6 gives $v = 10^{29 \pm 1}$ molecules cm⁻² s⁻¹ for multilayer benzene desorption, which is reasonable given typical multilayer (0th order) values on the order of $10^{30} - 10^{35}$ molecules cm⁻² s⁻¹.¹⁴² The error on the value of v is determined by using the upper and lower values of n and E_{des} to give an error associated with each value of v. The error on the mean is determined using propagation of errors. This value is in excellent agreement with that of Thrower *et al.*, who determined v for multilayer benzene to be $5 \times 10^{29 \pm 1}$ molecules cm⁻² s⁻¹.

| Dose / L _m | Pre-exponential factor, v / molecules cm ⁻² s ⁻¹ |
|-----------------------|--|
| 30 | 10 ^{29±2} |
| 40 | 10 ^{29 ± 2} |
| 50 | 10 ^{29 ± 2} |
| 70 | 10 ^{29 ± 2} |
| 100 | 10 ^{29 ± 2} |

 Table 4.6 Multilayer desorption pre-exponential factors for benzene determined from leading edge

 analysis for each set of data.

The analysis was also applied to toluene, and example plots to determine n and E_{des} are shown in Figure 4.13. Overall mean gradients and E_{des} values are shown on the plots. Table 4.7 shows the individual desorption orders for each set of TPD traces.



Figure 4.13 A: Plot of ln[I(T)] against ln(θ_{rel}) for a fixed temperature of 133 K for exposures from 0.49 ML – 9.79 ML of toluene. Blue crosses are individual data points and solid red lines are linear fits to the data.
B: Plot of ln[(T)] – nln(θ_{rel}) against 1/T for 4.89 ML of toluene adsorbed on HOPG. Red triangles are individual data points and the blue solid line is a linear fit to the data.

Figure 4.13A shows an example plot of ln[l(T)] against $ln(\theta_{rel})$ for exposures from 10 Lm – 200 Lm of toluene at a fixed temperature of 133 K. Plots of this type were constructed for fixed temperatures in the range 130 K – 137 K. The exposure at which the gradient changes in Figure 4.13A, *i.e.* the change from monolayer to multilayer desorption, is 25 Lm which is in agreement with the coverage estimation. The gradients for each linear region of the graph are shown in the figure. The values of *n* determined for each fixed temperature are shown in Table 4.7. The mean monolayer gradient of 2.18 is unphysical, as it is for benzene, due to the lateral repulsive interactions. The mean order of desorption of multilayer toluene is 0.37 ± 0.04, larger than the typical value of 0,²⁵ and is expected due to the not perfectly shared leading edges of the TPD traces in Figure 4.11.

 Table 4.7 Orders for desorption of sub-monolayer and multilayer desorption of toluene from HOPG for

 several fixed temperatures on the leading edges of the TPD traces determined using leading edge

 analysis for each set of data.

| Temperature / K | Monolayer order (≤ 25 L _m) | Multilayer order (≥ 25 L _m) |
|-----------------|--|---|
| 130 | 2.12 | 0.34 |
| 131 | 2.03 | 0.30 |
| 132 | 2.07 | 0.34 |
| 133 | 2.13 | 0.31 |
| 134 | 2.15 | 0.36 |
| 135 | 2.22 | 0.38 |
| 136 | 2.30 | 0.44 |
| 137 | 2.43 | 0.52 |

A similar trend in the toluene multilayer desorption orders in Table 4.7 is observed as for benzene (Table 4.4), where n increases with exposure. As is the case for benzene, this is due to the increased contribution from the sub-monolayer peaks as the temperature is increased. As for benzene, the multilayer value of n, 0.37 ± 0.04 was used to determine E_{des} for the multilayer TPD traces. Figure 4.13B shows a plot of $ln[l(T)] - nln(\theta_{rel})$ against 1/T for points along the leading edge of the 100 Lm TPD trace of toluene. Table 4.8 shows the values of E_{des} for all the multilayer TPD traces. Errors on each value are determined from the upper and lower values of n.

| - | |
|-----------------------|--|
| Dose / L _m | Desorption energy, E _{des} / kJ mol ⁻¹ |
| 40 | 45.0 ± 3.9 |
| 50 | 45.2 ± 3.7 |
| 70 | 47.2 ± 3.4 |
| 85 | 48.4 ± 3.3 |
| 100 | 48.0 ± 3.2 |
| 120 | 48.9 ± 3.3 |
| 150 | 49.3 ± 3.2 |
| 200 | 48.8 ± 3.2 |

 Table 4.8 Multilayer desorption energies of toluene determined by leading edge analysis for each set of

 data

The values in Table 4.8 give a mean value for the desorption of multilayers of toluene of $E_{des} = 47.6 \pm 1.2$ kJ mol⁻¹. The only literature value for multilayer desorption of toluene is from Ulbricht *et al.*¹¹⁹ and is given as 54 ± 6 kJ mol⁻¹. Whilst in reasonable agreement with the value determined in this work, it should be noted that a desorption order of 1 was used to determine this value for multilayer toluene desorption.

There is a clear trend in the values of E_{des} for multilayer toluene shown in Table 4.8 which is similar to that for benzene in Table 4.5. Figure 4.14 shows a plot of multilayer E_{des} values for both benzene and toluene as a function of coverage. The highest toluene coverages are omitted for clarity. Between toluene coverages of 1.96 ML – 4.16 ML, and benzene coverages of 1.69 ML – 2.82 ML, E_{des} increases and then plateaus at higher exposures. The fact that the E_{des} values increase and then plateau suggests that, below the plateau point, some monolayer character is retained in the TPD traces. This is shown in Figure 4.11 by the non-perfectly shared leading edges of the multilayer TPD traces for both benzene and toluene. This may mean that the determined multilayer values of E_{des} of 45.5 ± 1.8 kJ mol⁻¹ for benzene and 47.6 ± 1.2 kJ mol⁻¹ for toluene are lower than the true values, as the values below the plateau point are used to calculate them. However,
this is not a large effect, as can be shown by taking the mean of the values of E_{des} for multilayer benzene (Table 4.5) and toluene (Table 4.8) with those below the plateau points excluded. This is shown in Table 4.9 not to change the values of E_{des} within the error range. Therefore it is valid to use the mean of all values of E_{des} to determine multilayer pre-exponential factors.



Figure 4.14 Variation of *E*_{des} as a function of coverage for multilayer benzene and toluene.

Table 4.9 Edes for multilayer benzene and toluene calculated from all data points on Figure 4.14 andexcluding those below the plateau points.

| Molecule | Mean multilayer E _{des} / kJ mol ⁻¹ | | |
|----------|---|---------------------------------------|--|
| | Using all coverages | Excluding coverages below the plateau | |
| Benzene | 45.5 ± 1.8 | 46.4 ± 2.2 | |
| Toluene | 47.6 ± 1.2 | 48.7 ± 1.4 | |

Finally, *v* for multilayer toluene is determined as for benzene using the determined values of *n* and *E*_{des}. Table 4.10 shows the values for each TPD trace. The mean value is found to be $10^{27 \pm 0.3}$ molecules cm⁻² s⁻¹. This value is slightly lower than benzene, as expected due to the higher desorption order of toluene.

| Dose / L _m | Pre-exponential factor, v / molecules cm ⁻² s ⁻¹ | | |
|-----------------------|--|--|--|
| 40 | 10 ^{27 ± 1} | | |
| 50 | 10 ^{27 ± 1} | | |
| 70 | 10 ^{27 ± 1} | | |
| 85 | 10 ^{27 ± 1} | | |
| 100 | 10 ^{27 ± 1} | | |
| 120 | 10 ^{27 ± 1} | | |
| 150 | 10 ^{27 ± 1} | | |
| 200 | 10 ^{27 ± 1} | | |

 Table 4.10 Multilayer desorption pre-exponential factors for toluene determined from leading edge

 analysis for each set of data.

As shown in Tables 4.4 and 4.7 and discussed above, the desorption orders for submonolayer TPD traces of benzene and toluene (3.27 and 2.18 respectively) determined using leading edge analysis are unphysical. This is a result of the decreasing desorption temperature with increasing exposure due to lateral repulsive interactions. Because of the unphysical desorption orders, an alternative method of analysis to determine desorption parameters was employed. The same decrease of desorption temperature with increasing exposure has been observed for benzene by Thrower et al.,¹¹⁵ who simulated TPD traces to determine E_{des} as a function of exposure by varying the deposition parameters until a fit to their experimental traces was found. In order to examine the validity of this method, the desorption parameters determined for multilayer benzene and toluene were used to simulate experimental TPD traces. To do this, the kinetics simulation program Kinetiscope was used.²⁴⁵ Kinetiscope is used to produce a simulated TPD trace by giving input parameters of order *n*, pre-exponential factor v and desorption energy E_{des} , to the Polanyi-Wigner equation (equation (2.2) in Chapter 2) and a coverage in molecules cm⁻² as determined by equation 2.9 in Chapter 2. These parameters are used in conjunction with defined chemical processes to produce a simulated TPD trace. The processes used to produce the simulated TPD traces presented in this work are shown below.

The desorption step uses *n*, E_{des} and *v* to determine the rate of desorption *via* the Polanyi-Wigner equation where molecules adsorbed on the surface (X_(ads)) go into the gas phase (X_(g)). The gaseous molecules are then removed from the system as they become pumped away (X_(p)) with a constant pumping speed, the value of which is determined *via* trial and error tests.

Figure 4.15 shows a comparison of experimental multilayer TPD traces of toluene and simulations produced by Kinetiscope. Only coverages of 3.43 ML and 7.34 ML are shown for clarity, but all multilayer coverages show the same agreement between experimental and simulated TPD traces.



Figure 4.15 *Comparison of experimental (dashed traces) and simulated by Kinetiscope (solid traces) TPD traces of multilayer coverages of toluene deposited on HOPG at 25 K. Coverages are shown on the graph.*

The peak temperature and leading edge of the experimental (dotted traces) data are excellently reproduced by the simulations (solid traces), as well as the relative

intensities. The experimental trailing edges are not well reproduced, which is a consequence of the idealised pumping simulated by Kinetiscope. The good overall agreement between the simulated and experimental traces suggests that using Kinetiscope to simulate TPD traces is valid, and shows that the determined multilayer parameters of benzene and toluene desorption are reasonable as they can be used to simulate reasonable TPD traces.

In order to determine values of E_{des} for sub-monolayer quantities of benzene and toluene, shown in Figure 4.10, Kinetiscope was used to produce simulated TPD traces by giving input parameters of n, v and E_{des} , and a coverage in molecules cm⁻². The simulated trace was compared to the experimental data and the parameters varied until a good match was achieved. The method of Thrower *et al.*¹¹⁵ was employed, which was used to examine sub-monolayer desorption of benzene from a-SiO₂. The values of n and v were fixed as 1 and 10^{13} s⁻¹ respectively. These values were chosen as they are typical of sub-monolayer desorption.^{25,29} Fixing the values of n and v is an oversimplification of the complex desorption behaviour but allows the variation of E_{des} as a function of coverage to be determined.

Figure 4.16 shows a comparison of the Kinetiscope simulations and experimental TPD data for benzene and toluene. The peak temperatures and leading edges are well simulated, which suggests that the assumption of first order desorption, n = 1, is reasonable. However, the trailing edge is not well reproduced in the simulations. This is because Kinetiscope simulates ideal pumping, which experimentally is not achieved. Additionally, as some of the molecules on the surface desorb, the coverage decreases and therefore the repulsive interactions are reduced which effectively increases E_{des} and causes the observed broad peaks.

Simulations, such as those shown in Figure 4.16, were also performed with varying values of v in order to examine the validity of the assumed value of 10^{13} s⁻¹. In each case values were varied from 10^{12} s⁻¹ – 10^{14} s⁻¹. Figure 4.17 shows a comparison between the simulations using the different values of v for 0.28 ML of benzene on HOPG.



Figure 4.16 TPD traces of benzene and toluene adsorbed on HOPG at 25 K, and corresponding
 Kinetiscope simulations. A: Experimental TPD traces of benzene. B: Experimental TPD traces of toluene.
 C: Kinetiscope simulations for benzene with coverages corresponding to those in A. D: Kinetiscope
 simulations for toluene with coverages corresponding to those in B. Adapted from Salter et al.¹¹⁷

The effect on the determined E_{des} of this variation is found to be small. For $v = 10^{12} \text{ s}^{-1}$, in order to match the experimental TPD trace, the value of $E_{des} = 42.0 \text{ kJ mol}^{-1}$ determined using $v = 10^{13} \text{ s}^{-1}$ (the blue trace in Figure 4.17) must be reduced to 39.5 kJ mol⁻¹. Similarly, when $v = 10^{14} \text{ s}^{-1}$ is used, E_{des} is determined to be 44.5 kJ mol⁻¹. This process was repeated for all exposures of benzene and toluene and leads to each determined value of E_{des} being given an uncertainty of ± 2.5 kJ mol⁻¹.



Figure 4.17 Comparison of Kinetiscope simulations of TPD of 0.28 ML of benzene deposited on HOPG at 25 K using differing values of v. In all cases n = 1 and $E_{des} = 42.0$ kJ mol⁻¹.

Figure 4.18 shows the results of the Kinetiscope analysis for benzene and toluene in a plot of E_{des} as a function of dose. The individual values of E_{des} are also shown in Table 4.11. For both molecules, E_{des} is seen to decrease as the coverage is increased. Additionally, as can be predicted from the higher desorption temperature of toluene compared to equivalent coverages of benzene, toluene is more strongly bound to HOPG than benzene. The decrease in E_{des} from coverages of approximately 0.1 ML – 1 ML is larger for benzene than toluene, 6.2 kJ mol⁻¹ compared to 5.2 kJ mol⁻¹, in agreement with the larger difference in temperature for benzene compared to toluene. This coverage range is equivalent to exposures of 1 L_m – 15 L_m of benzene and exposures of 3 L_m – 20 L_m of toluene, corresponding to the TPD traces shown in Figure 4.10. The difference in temperature and E_{des} difference between the molecules suggests that the lateral repulsions are stronger in benzene than toluene.



Figure 4.18 Change in desorption energy, E_{des} , as function of coverage for sub-monolayer benzene and toluene deposited on HOPG at 25 K determined using Kinetiscope. Error bars represent \pm 2.5 kJ mol⁻¹. Adapted from Salter et al.¹¹⁷

The cause of the lateral repulsive interactions of sub-monolayer coverages of benzene and toluene was attributed to the polarization of the π -electron system of each of the molecules.^{117,121,224} Therefore it follows that a molecule with a higher polarizability will experience stronger lateral repulsions. However, the polarizability of toluene is 11.861 Å³ compared to a value of 9.959 Å³ for benzene.²⁴⁶ This is expected, as polarizability generally increases with the volume occupied by electrons.²⁴⁷ The reason that the lateral repulsions are in fact stronger for benzene, as discussed above, is due to the fact that polarizability is also related to the strength of binding to the surface. It has been shown that the heat of adsorption increases with polarizability for hydrocarbons²⁴⁸ adsorbed on activated carbon. Additionally, a similar trend is observed for noble gases, where the enthalpy of adsorption on MgO increases in the order Ar < Kr < Xe^{249,250} which is the same order as the increase in their polarizabilities.²⁵¹ A more recent study also determined that making the substrate more polarizable (in this case a metal organic framework) increases the binding strength of several gaseous adsorbates.²⁵² Therefore, the more polarizable toluene should be bound more strongly to HOPG than benzene, as is shown to be the case in Figure 4.18. The stronger adsorption of toluene compared to benzene means that it can overcome the lateral repulsions to a degree, whereas benzene cannot. Hence the decrease in E_{des} for toluene is less than for benzene (Figure 4.18).

Table 4.11 Desorption energies for sub-monolayer coverages of benzene and toluene determined using Kinetiscope to fit to the experimental data using n = 1 and $v = 10^{13}$ s⁻¹. Errors are determined by varying vby \pm an order of magnitude.

| | Benzene | Toluene | | |
|--|----------------------------|------------|---------------------------------------|--|
| Coverage / Desorption energy, E _{des} / | | Coverage / | Desorption energy, E _{des} / | |
| ML | ± 2.5 kJ mol ⁻¹ | ML | ± 2.5 kJ mol ⁻¹ | |
| 0.02 | 51.0 | 0.15 | 48.0 | |
| 0.03 | 49.2 | 0.24 | 47.5 | |
| 0.06 | 47.5 | 0.34 | 46.1 | |
| 0.1 | 45.6 | 0.49 | 44.8 | |
| 0.17 | 44.1 | 0.59 | 43.7 | |
| 0.23 | 43.1 | 0.73 | 43.3 | |
| 0.28 | 42.0 | 0.98 | 42.8 | |
| 0.40 | 41.5 | 1.22 | 42.4 | |
| 0.56 | 41.2 | | | |
| 0.85 | 41.3 | | | |

The values of E_{des} determined for sub-monolayer desorption of benzene are in excellent agreement with a previously determined value of benzene desorbing from HOPG of 48 ± 8 kJ mol^{-1.253} Other values reported in the literature are in good agreement with the data reported here in terms of the range of values as coverage is increased, although they are not directly comparable as a different surface is used. For example on the a-SiO₂ surface values range from 52 kJ mol⁻¹ – 39.5 kJ mol^{-1.115} Only one value of E_{des} for submonolayer exposures of toluene was found in the literature, 68 ± 7 kJ mol⁻¹, determined by Ulbricht *et al.*¹¹⁹ This is considerably higher than any value determined in this work. This may be because lower coverages were examined by Ulbricht, or that the value of $v = 10^{19}$ s⁻¹ used was higher than the assumed value here. Indeed, by using $v = 10^{19}$ s⁻¹ in our simulations, a value E_{des} = 57 kJ mol⁻¹ is required to match the experimental TPD traces, closer to the lower limit of Ulbricht's value.¹¹⁹

4.4 Summary and Conclusions

A comparison of the adsorption and desorption behaviour of benzene and toluene on HOPG was performed. RAIR spectra of increasing exposures of both molecules show that sub-monolayer exposures are detectable by RAIRS and have been used to confirm that the sticking probability at 25 K is constant. Upon increasing the exposure from submonolayer to multilayer exposures, some RAIR bands are seen to shift, which can be used as an estimate of benzene coverage on HOPG.

Multilayers of benzene are shown to undergo a crystallisation between 90 K – 120 K, as shown by thermally induced changes in the RAIR spectra, whereas no such process is observed for toluene before desorption occurs. However, some thermal rearrangement may occur. This may be because toluene has a more complex crystal structure than benzene, with two molecular environments compared to one in benzene, leading to a larger barrier to crystallisation. This is most likely due to the addition of the methyl group which decreases the molecular symmetry of toluene compared to benzene.

The nature of the observed changes in the RAIR spectra of benzene upon annealing is rationalised by examination of its crystal structure. Splitting is observed in vibrational bands associated with C-H modes, in agreement with the two environments of C-H bonds in the crystal structure. Conversely, the band associated with the ring of benzene does not split upon crystallisation, instead it sharpens and grows. This is due to the alignment of the rings in the crystal structure, which only exist in a single environment.

At sub-monolayer exposures, both molecules exhibit lateral intermolecular repulsions, which manifest themselves in the TPD with a decreasing desorption temperature with increasing coverage until the completion of the monolayer. At this point the desorption behaviour changes in both molecules, with fractional order desorption. The origin of these repulsive interactions is due to the polarization of the π -electron cloud of the aromatic ring in both molecules becoming polarized upon adsorption. This effect has been previously observed for benzene adsorbed on several surfaces, ^{114,115,122,222,244} but this work represents the first observation of this behaviour in toluene. Leading edge

analysis was performed on multilayer benzene and toluene TPD traces and yielded the mean parameters shown in Table 4.12.

| | n | E _{des} / kJ mol ⁻¹ | v / molecules cm ⁻² s ⁻¹ |
|---------|-----------------|---|--|
| Benzene | 0.18 ± 0.06 | 45.5 ± 1.8 | 10 ^{29±1} |
| Toluene | 0.37 ± 0.04 | 47.6 ± 1.2 | $10^{27 \pm 0.3}$ |

Table 4.12 Desorption parameters for multilayer benzene and toluene determined in this chapter.

The parameters in Table 4.12 were used to produce simulated TPD spectra using the Polanyi-Wigner equation which agreed well with the experimental data. This proof of concept of the simulations allowed them to be used to determine desorption energies for sub-monolayer benzene and toluene, where leading edge analysis was not applicable. The determined desorption energy ranges suggest that the lateral repulsions are stronger in benzene than toluene. This seems counterintuitive, given that toluene is more polarizable than benzene,²⁴⁶ but can be explained by the fact that a larger polarizability also means stronger adsorption, as shown by the determined sub-monolayer values of *E*_{des} for toluene and benzene. The stronger adsorption of toluene means that the repulsive interactions can be overcome to some degree, whereas they cannot in benzene.

The data in this chapter show that benzene and toluene behave in a broadly similar way when adsorbed on HOPG, but some differences are apparent. Both molecules experience lateral repulsive interactions at sub-monolayer coverages, however the addition of the methyl group on toluene causes it to adsorb more strongly to HOPG than benzene and overcome these repulsions somewhat. Additionally, multilayers of benzene are shown to crystallise, whereas toluene ices do not as a consequence of the lower symmetry leading to a larger barrier to crystallisation. It is concluded that the larger size of toluene is the main reason for the observed differences in behaviour of benzene and toluene ices on HOPG, rather than any polarity effects.

Benzene and toluene are relevant to astrophysical environments.^{64,153,154,192} Whilst the data in this chapter are not directly relevant to the chemistry of the ISM and other astrophysical environments, as regions of pure benzene and toluene ice are unlikely to

be present, they represent a benchmark to which more relevant data can be compared. Indeed in subsequent chapters, water bearing ices of benzene and toluene are examined and compared to this chapter. Additionally, the parameters of desorption determined in this chapter will be used to construct models of desorption on astronomical timescales.

5 RAIRS and TPD of Water Containing Benzene and Toluene Ices

This chapter builds upon the data presented in Chapter 4. The data presented in Chapter 4 are used as a benchmark to compare the behaviour of pure benzene and toluene ices to that of water containing ices of each molecule. These data are more astronomically relevant than pure ices, as water is abundant in the interstellar medium (ISM). RAIRS is used to probe any interactions between water and benzene or toluene, and the effect that water ice has on the benzene phase change. The effect of both amorphous and crystalline water on the adsorption and desorption of benzene and toluene is examined. Additionally, mixed ices are grown, which are most relevant to astronomical ices. The data in this chapter are used in a simple model of desorption of ices on astronomical timescales, highlighting the importance of laboratory data to astronomy.

5.1 Introduction

As outlined in Chapter 4, benzene and toluene are of interest to a range of fields and applications due to their importance as solvents and prevalence as pollutants.^{131,209–213} Both molecules are of interest to the astrochemical community, as building blocks of polycyclic aromatic hydrocarbons (PAHs).¹⁵⁰ Benzene has been detected in galactic and extra-galactic protoplanetary nebulae^{64,153,192} and gas-phase formation routes of toluene are postulated.^{154,155}

Chapter 4, described a range of investigations of pure benzene and toluene ices. This chapter focuses on water containing ices of benzene and toluene, which are less well studied by comparison to the pure ices. However these ice systems are more relevant to astronomical ices, where water is the most abundant component.^{25,54,67,86} Additionally, protoplanetary nebulae, the type of region in which benzene has been detected, have been shown to have dusty shells⁶³ and contain water rich ice.²⁵⁴ Therefore the data are highly relevant to both benzene and toluene in space. The data presented in this chapter are also relevant to benzene and toluene as organic pollutants in snow and ices on Earth.^{214–216}

Infrared (IR) studies of benzene deposited on top of amorphous solid water (ASW) show that benzene and water interact favourably in ices.^{255–257} This interaction occurs via a hydrogen bond (H-bond) between the aromatic π -electron system and dangling –OH and -OD bonds at the water ice surface. This interaction is shown by a shift in the dangling -OH IR band by approximately 100 cm⁻¹.^{255–257} Marchione *et al*.¹⁰⁸ also observed this interaction in RAIRS experiments as a small blue shift in the CC aromatic stretching mode of 2 cm⁻¹. A consequence of this H-bonding is that complex desorption behaviour is observed in benzene/water ice systems. For example, irradiation of benzene deposited on ASW ice by low energy (200 eV - 300 eV) electrons at various benzene overlayer thicknesses has been examined.^{108,132} Electron-promoted desorption (EPD) of both benzene and water was observed, with the process being more efficient for water.¹⁰⁸ However, at low exposures of benzene (approximately 1 ML coverage) benzene desorption was observed at higher efficiencies than the water EPD mechanism. The cause of this was energy transfer between electron-ionised water in the ice and the adsorbed benzene via the H-bond interaction.^{108,132} Photon irradiation has shown that energy transfer can also go from benzene to water. Irradiation of layered benzene on water ices by photons of wavelength at or near the ultraviolet (UV) absorption region of benzene leads to the desorption of both water and benzene as measured by mass spectrometry.^{132,184} This observation was assigned to an adsorbate-mediated desorption process where the electronically excited benzene can transfer sufficient energy to cause the underlying water ice to desorb.^{132,184}

The thermal desorption of water containing benzene ices has also been examined by TPD. Thrower *et al.*¹¹⁴ determined the desorption energy, E_{des} , of sub-monolayer amounts of benzene desorbing from ASW to be 41.0 ± 0.5 kJ mol⁻¹. Theoretical chemists have also studied the benzene/water system. A density functional theory (DFT) study of single molecule complexes of benzene and water confirms that an interaction occurs between a water H atom and the benzene π -system.²⁵⁸ The interaction energy varies little (0.6 kJ mol⁻¹) between two conformations which have either a single or both water H atoms pointing at the benzene ring.²⁵⁸ Classical molecular dynamics calculations agree well with experimental values for the desorption energy of benzene from ASW, with a value of 39 kJ mol⁻¹.²⁵⁹ A trend between increasing size of PAH and binding energy was

also observed. Similarly, quantum level calculations from the same authors gave values in good agreement with classical calculations, with a value of E_{des} of 42 kJ mol⁻¹.²⁶⁰ Classical calculations have also been used to give binding energies for benzene on crystalline ice (CI) of 40 kJ mol⁻¹,²⁵⁹ and no experimental values of this value have been reported to date.

Despite the fact that benzene and toluene are separated by the presence of a single methyl group, toluene's surface behaviour in the presence of water has not been examined. Toluene offers an interesting comparison to benzene as it has a small dipole moment of 0.36 D.²⁰² This may mean that its ice behaviour in the presence of water differs from benzene, which is apolar. In this chapter a comprehensive study of waterbearing benzene and toluene ices is undertaken with the data for each molecule compared and contrasted in order to determine if polarity affects the behaviour.

Given that several water containing ice systems are examined in this chapter, it is first useful to explore the known behaviour of water under astronomically relevant conditions. As outlined in Chapter 1, water ice exists in several forms.^{42–44,137,140} In this chapter, ASW is grown by depositing water at 25 K, and CI is grown by depositing water at 135 K. These two forms of water behave differently on a HOPG surface, and can be differentiated by their TPD traces and RAIR spectra, as shown in Figure 5.1.

In the TPD trace in Figure 5.1A, when water is deposited as ASW, it undergoes a phase change to CI at 147 K. This is shown as a shoulder on the leading edge of the trace. This shoulder is not present in the TPD trace of CI shown in Figure 5.1B. CI desorbs at 156 K, as shown in both TPD traces. The RAIR spectra of ASW and CI also show clear differences. Figures 5.1C and 5.1D show the OH stretching band of water, v(OH). In Figure 5.1C, ASW gives a broad slightly asymmetrical band, centred at 3423 cm⁻¹, whereas the CI v(OH) band in Figure 5.1D is highly asymmetrical, with a sharp peak at 3232 cm⁻¹ and features at 3365 cm⁻¹ and 3136 cm⁻¹. Species such as CO, N₂, OCS and CH₃CN have been found to undergo trapping in ASW ices.¹³³ It has also been shown that species which can from intermolecular bonds with the water molecules, such as propan-2-ol, can greatly influence the phase change and desorption kinetics of the water.¹¹⁶



Figure 5.1 Comparisons of the TPD (panels A and B) and RAIRS (panels C and D) behaviour of ASW and CI. A: TPD trace of 50 L_m ASW. B: TPD trace of 50 L_m CI. C: v(OH) band of ASW. D: v(OH) band of CI.

This chapter builds upon the work presented in Chapter 4, and the data presented in Chapter 4 are used as a comparison to the data presented here. RAIRS and TPD are used to examine the ices. Layered ices are examined, where benzene or toluene are deposited on top of ASW or CI. For benzene on CI, and toluene on ASW and on CI, these data have not been previously reported in the literature. Therefore this work adds to fundamental understanding of interactions between benzene and CI, and toluene and water in ices. Mixed ices are also grown and studied. These ices are the most relevant to astronomical ice systems, and have never previously been studied by TPD. The data are also used to run a model of the desorption of benzene and toluene on astronomical timescales, with the implications briefly discussed. This highlights the usefulness of laboratory data to astronomy, as experimentally derived desorption parameters can be used in astrochemical networks.

5.2 Experimental

The equipment and experimental procedures were presented in Chapter 2, however dosing techniques specific to the data presented in this chapter are discussed here. Several water bearing ice configurations are examined in this chapter, with various experimental requirements. In all experiments shown in this chapter, ices were grown *via* backfilling. Layered ices were grown by depositing water, allowing the chamber pressure to return to its base value and subsequently depositing benzene or toluene.

Figure 5.1 shows that water can be deposited on the HOPG surface used in this work as ASW or Cl. In order to deposit Cl, the sample is heated to 135 K and held at this temperature during the dose. The TPD trace in Figure 5.1B is recorded after depositing water at 135 K, and indeed shows that only Cl is present as the ASW to Cl phase change at 147 K (shown in Figure 5.1A) is not observed. The crystalline nature of the water ice grown at 135 K was also confirmed by RAIRS, where the band was shown to match that shown in Figure 5.1D. Whilst increasing the deposition temperature allows Cl to be grown, it also lowers the sticking probability. This is indicated by the decrease in area under the TPD curve (proportional to amount of adsorbate) when the sample is exposed to the same dose of water at different temperatures, as shown in Table 5.1.

| Dose pressure | Dose | Deposition | Dose area / | TPD area / |
|----------------------|----------|-----------------|-----------------------|------------------------|
| / mbar | time / s | temperature / K | arbitrary units | arbitrary units |
| 2.0×10^{-7} | 250 | 25 | 2.03×10^{11} | 3.67 × 10 ⁶ |
| 2.0×10^{-7} | 250 | 135 | 1.86×10^{11} | 2.88×10^{6} |
| 2.0×10^{-7} | 320 | 135 | 2.44×10^{11} | 3.59×10^{6} |

Table 5.1 Areas under the dose and TPD curves for water ice at different deposition temperatures.

In order to ensure that data recorded for different water bearing ices are comparable, the same amount of water must be present on the HOPG surface. Therefore, the ratio of the areas under the TPD curves for water ice grown at 25 K and 135 K for an identical dose was used as a correction factor. This ratio is the ratio of the sticking probabilities at the two temperatures, and was found in this work to be 1.28 for water. This means that 1.28 times more water is deposited at 25 K than 135 K, and in order to grow an equivalent amount of CI the dose must be adjusted accordingly. Hence, the dose time was increased by a factor of 1.28. This correction was found to bring the area under the TPD curve for water deposited at 135 K in line (within 2%) with that of water deposited at 25 K, as shown in Table 5.1. In all cases, the amount of water on the HOPG was equivalent to 50 L_m of ASW.

Growing mixed ices is more challenging than layered systems, as both components are deposited simultaneously. An additional consideration is how to determine the ratio of components in the ice. As in the layered systems, the amount of water on the surface is 50 L_m. Therefore the amount of benzene or toluene deposited is varied to change the ice composition. Initially, calibration doses are performed to determine the relative sensitivity of the quadrupole mass spectrometer (QMS) to each component of the ice. These doses are performed at the same pressure and time for each component, and the areas under the dose curves are used to determine a QMS sensitivity ratio. Figure 5.2 shows an example of calibration doses of 20 L_m of water and benzene.

Despite the fact that each dose was performed at identical pressures (2×10^{-7} mbar in this case), the QMS intensity is not equal. This shows that the QMS is more sensitive to water than benzene, with a sensitivity ratio, S, of 4.40. The sensitivity ratio is used to successfully grow an ice of the desired composition. Practically, this is achieved by introducing the major ice component, water in this case, into the chamber up to the desired dose pressure and then introducing the minor component up to a target QMS intensity value, I_{target}. The target QMS intensity is calculated using equation (5.1).

$$I_{\text{target}} = \frac{P \times I_{\text{H}_2\text{O}}}{S}$$
(5.1)



Figure 5.2 Calibration doses of 20 L_m of water (blue trace) and benzene (red trace). The dose pressure and time for both molecules was 2×10^{-7} mbar and 100 s respectively.

In equation (5.1), P is the proportion of the minor component in the ice and I_{H_2O} is the average QMS intensity for water at the water dose pressure, as determined from the calibration doses. Figure 5.3 shows the recorded dose file for an initial test dose of 17% benzene in water ice.



Figure 5.3 Initial test dose of a 17% benzene in water mixed ice deposited at 25 K. The benzene QMS intensity was determined using equation (5.1). The dotted lines are a guide to show the point at which each molecule reaches its peak intensity and the arrow shows the offset between these points.

It is clear from Figure 5.3, and indicated on the figure by the arrow, that there is an offset between the water (blue trace) and the benzene (red trace) reaching their desired intensities. This is a practical consequence of using both leak valves and leads to lower than expected proportions of the minor component being present in an ice, as calculated from the dose areas. In order to correct for this offset, the desired proportion is divided by the actual proportion to give a correction factor, C. This correction factor is typically small, for example for benzene, C = 1.12. The correction factor causes equation (5.1) to become equation (5.2).

$$I_{\text{target}} = \left(\frac{P \times I_{\text{H}_2\text{O}}}{S}\right) C \quad (5.2)$$

A range of benzene or toluene proportions in water ice were examined in this thesis. These percentages range from 7% - 50%. These proportions were chosen as they correspond to the exposures of benzene or toluene deposited onto 50 L_m ASW or CI in the layered ices, and allow direct comparisons between the systems. Exposures in L_m and their corresponding percentages in mixed ices are shown in Table 5.2.

| Exposure in layered ices / L _m | Equivalent proportion in a mixed ice / % |
|---|--|
| 5 | 9 |
| 7 | 12 |
| 10 | 17 |
| 15 | 23 |
| 20 | 29 |
| 25 | 33 |
| 30 | 38 |
| 40 | 44 |
| 50 | 50 |

 Table 5.2 Comparison of exposures of benzene or toluene in layered ices to the equivalent percentage in

 mixed ices.

5.3 Results and Discussion

5.3.1 RAIRS of Water Containing Benzene and Toluene Ices

Figure 5.4 shows RAIR spectra of benzene in different water environments; 20 L_m benzene deposited on 50 L_m ASW, 20 L_m benzene deposited on 50 L_m CI and a mixed ice of 23% benzene in water. A spectrum of 20 L_m benzene on HOPG is also shown for comparison. In all cases the benzene deposition temperature was 25 K. The wavenumber regions shown are 1550 cm⁻¹ – 1400 cm⁻¹ in Figure 5.4A and 1080 cm⁻¹ – 980 cm⁻¹ in Figure 5.4B. The bands shown are the same as those presented in Chapter 4, and are assigned in Table 5.3. The high wavenumber bands at 3090 cm⁻¹ and 3034 cm⁻¹, corresponding to the v(CH)_{aromatic} and combination band respectively, are omitted from Figure 5.4. This is because the v(CH)_{aromatic} band is obscured by the broad water OH stretch ,v(OH), and the intensity of the combination band is hard to distinguish from the noise at the exposures shown.



Figure 5.4 RAIR spectra of benzene deposited at 25 K in different water environments. Band intensities are shown in the panels and the ice configuration is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

| | Wavenumber / cm ⁻¹ | | | |
|-------------------------|-------------------------------|-----------|--------------------|--------------------|
| Band | HOPG at HOPG at | | 23% benzene in | 50% benzene in |
| Accignment | | 110 10 81 | mixed water ice at | mixed water ice at |
| Assignment | 23 K | 110 K | 25 K | 25 K |
| v(CC)aromatic | 1479 | 1479 | 1481 | 1479 |
| $\delta(CH)_{in-plane}$ | 1036 | 1040/1034 | 1036 | 1036 |

Table 5.3 Assignments of the bands observed in the RAIR spectra of benzene shown in Figure 5.4. Values on HOPG are from Chapter 4 and mixed ice values are from this chapter. Assignments are made from the literature.^{31,127,227} Symbols: v = stretching, $\delta =$ deformation.

Compared to the pure benzene ice, the v(CC)_{aromatic} mode in the presence of water is slightly blue shifted to 1481 cm⁻¹ from 1479 cm⁻¹ in Figure 5.4A. Conversely the δ (CH)_{in-plane} mode does not shift in the presence of water as shown in Figure 5.4B. A small blue shift of 2 cm⁻¹ – 3 cm⁻¹ in the v(CC)_{aromatic} band has been observed by Marchione *et al.*¹⁰⁸ and is due to a H-bond interaction between the π -electron system of the aromatic ring and a hydrogen atom on the water molecule. This same behaviour has been observed more recently by Dawes *et al.*²⁵⁷ The δ (CH)_{in-plane} mode would not be expected to shift analogously to the v(CC)_{aromatic} mode as this part of the benzene molecule does not take part in the benzene-water interaction.

As the amount of benzene is increased from the amounts shown in Figure 5.4, the $v(CC)_{aromatic}$ band shifts back to 1479 cm⁻¹, analogous to the pure system. Figure 5.5 shows a comparison of the same bands as seen in Figure 5.4, but at higher exposures/proportions of benzene. The wavelength regions shown are the same as in Figure 5.4. In Figure 5.5, RAIR spectra of 50 L_m benzene on 50 L_m ASW, 50 L_m benzene on 50 L_m CI and a 50% benzene and water mixed ice are shown alongside 50 L_m of benzene on HOPG for comparison.



Figure 5.5 RAIR spectra of benzene deposited at 25 K in different water environments. Band intensities are shown in the panels and the ice configuration is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

It is clear that the v(CC)_{aromatic} band in all cases is now comparable to the pure benzene spectrum, shown in Figure 5.5A and centred at 1479 cm⁻¹. A slight change in peak profile is observed between the pure benzene and benzene on CI spectra, which have sharp, symmetrical peaks, and the benzene on ASW and mixed ice spectra, where there is a slight asymmetry to the peak on the high wavenumber side. Similar to the lower amounts of benzene shown in Figure 5.4, the δ (CH)_{in-plane} band at 1036 cm⁻¹ in Figure 5.5B shows no changes between the ice systems. The return to 1479 cm⁻¹ of the v(CC)_{aromatic} band as the amount of benzene is increased suggests that the benzenewater H-bond interaction becomes less important as more benzene is added to the system. This is because benzene molecules in the ice become less surrounded by water and therefore the level of benzene/water interaction decreases. In the mixed ice, and in the benzene on ASW ice, some degree of interaction is retained, as shown by the asymmetric feature on the v(CC)_{aromatic} band at 1481 cm⁻¹ in Figure 5.5. Conversely, the benzene on CI spectrum does not show this feature, suggesting that the benzene/water

interaction is either not present or present to a lesser degree than in the other systems. This can be rationalised by considering the relative roughness and porosity of amorphous versus crystalline water ices. The rough and porous water ices in the benzene on ASW and mixed ice systems will have regions where benzene molecules will be trapped in a local environment which has a low proportion of benzene, leading to a shifted v(CC)_{aromatic} vibration. The CI surface is smoother and does not have these regions. Therefore the shift is not observed in the v(CC)_{aromatic} band.

The blue shift of the v(CC)_{aromatic} mode in the presence of water for small amounts of benzene, which moves back to match the pure spectrum as the amount of benzene is increased, has been observed in mixed ices by Dawes *et al.*²⁵⁷ It has also been observed in layered benzene and water ices,¹⁰⁸ where the band shifts to match the pure benzene ice as the amount of benzene is increased. The decrease in the benzene-water interaction as the amount of benzene is increased is further shown in Figure 5.6, where the v(CC)_{aromatic} band of mixed benzene and water ices of increasing benzene proportion is shown. Band positions are also shown in Table 5.3.



Figure 5.6 RAIR spectra showing the effect of increasing benzene proportion in mixed ices on the $v(CC)_{aromatic}$ band. The benzene proportion increases from top to bottom and the proportion is shown to the right of each spectrum. A pure benzene spectrum is shown for comparison. Dotted lines are included as guides and their position is shown on the figure.

The v(CC)_{aromatic} band for a 23% benzene in water ice is initially positioned at 1481 cm⁻¹. As the proportion of benzene is increased, it shifts to 1479 cm⁻¹ to match the pure ice. As discussed above, the 50% benzene and water mixed ice has a feature on the high wavenumber side of the peak due to the benzene/water interaction.

Similarly to benzene, RAIR spectra of toluene in water containing ices show differences compared to the pure toluene system. These changes are listed in Table 5.4. Figure 5.7 shows RAIR spectra of 50 L_m toluene deposited on 50 L_m ASW, 50 L_m toluene deposited on 50 L_m CI, a 50% toluene and water mixed ice and 50 L_m toluene deposited on HOPG. Figure 5.7A shows the wavenumber region from 1650 cm⁻¹ – 1580 cm⁻¹, Figure 5.7B shows the region 1520 cm⁻¹ – 1450 cm⁻¹ and Figure 5.7C shows the region between 1100 cm⁻¹ and 1000 cm⁻¹. In all cases the toluene deposition temperature was 25 K and the bands shown are the same as those described in Chapter 4, which are assigned in Table 5.4. RAIR spectra of lower exposures are not shown as the signal-to-noise ratio was low and bands were not seen clearly. However, no wavelength shift or band profile changes were observed as a function of amount of toluene. The high wavenumber bands at 3020 cm⁻¹, 2951 cm⁻¹ and 2915 cm⁻¹ are also not shown due to their low intensity. Unlike benzene, even when a relatively large proportion or exposure of toluene is present in the ice, the bands are shifted when compared to the pure ice.

| Table 5.4 Assignments of the bands observed in the RAIR spectra of toluene shown in Figure 5.7. Values |
|---|
| for HOPG are from Chapter 4 and water containing systems are from this chapter. Assignments are from |
| the literature. ^{228–230} Symbols: $v =$ stretching, $\delta =$ deformation. |

| | Wavenumber / cm ⁻¹ | | | |
|--|-------------------------------|--------------------------------|------------------------------------|-----------------------------------|
| Band Assignment | HOPG at 25 K | On 50 L _m ASW at | On 50 L _m CI at 25 K | 50% toluene in water mixed ice at |
| | | 25 K | | 25 K |
| v(CC)aromatic | 1605 | 1605 | 1605 | 1602 |
| v(CC) _{aromatic} | 1495 | 1497 | 1497 | 1497 |
| $v(CC)_{aromatic}$ and $\delta(CH_3)_{as}$ combination | 1466 | 1468 | 1468 | 1469 |
| $\delta(CH)_{in-plane}$ | 1082 | 1082 | 1082 | 1083 |



Figure 5.7 RAIR spectra of toluene deposited at 25 K in different water environments. Band intensities are shown in the panels and the ice configuration is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

In Figure 5.7A the v(CC)_{aromatic} band is at 1605 cm⁻¹ in all systems except the mixed ice, where it is red shifted to 1602 cm⁻¹. The second v(CC)_{aromatic} band, shown in Figure 5.7B, which in the pure ice is at 1495 cm⁻¹, is shifted to 1497 cm⁻¹ in the mixed ice. In the toluene on ASW system, the band is also at 1497 cm⁻¹ with a feature at 1495 cm⁻¹. In the toluene on CI system the band is almost matching that of the pure toluene ice, with a slightly dominant feature at 1497 cm⁻¹. Also shown in Figure 5.7B, the combination band shifts from 1466 cm⁻¹ in the pure toluene ice to 1468 cm⁻¹ for toluene on ASW and CI and then shifts further to 1469 cm⁻¹ in the mixed ice. Finally, in Figure 5.7C, the δ (CH)_{in-plane} shows similar behaviour to the v(CC)_{aromatic} band at 1605 cm⁻¹. It is seen at 1082 cm⁻¹ in all systems except the mixed ice, where it is shifted to 1083 cm⁻¹ and the band profile is broadened.

These shifts in bands are indicative of a toluene/water interaction. This is the first time that this interaction has been observed in RAIRS experiments. A change in the

fluorescence behaviour of toluene on solid ice surfaces compared to the liquid however has been observed, and has been tentatively assigned to a toluene/water ineteraction.²⁶¹ The shifts that are present in the mixed ice only, or which become more pronounced in the mixed ice, are due to the locally water rich environments where isolated toluene molecules will be surrounded by water. The nature of this interaction is likely to be similar to that of benzene, where the aromatic π -electron system acts as a H-bond acceptor and a hydrogen atom in a water molecule acts a H-bond donor. The less prominent shift in the toluene on CI system suggests that, analogous to benzene, the porosity of the water in the toluene on ASW system and mixed ice increases the degree of interaction.

Unlike in benzene, bands which are not associated with the aromatic ring in toluene exhibit shifts in the presence of water when compared to pure toluene ice. This may suggest that there is another interaction mechanism between toluene and water in the ices. This is rationalised by considering the relative polarities of the molecules. Benzene is apolar whereas, due to the addition of a methyl group, toluene has a small dipole of 0.36 D.²⁰² This allows a polar interaction to occur between toluene and water, which is not possible with benzene. This manifests itself in shifts in bands related to ring and methyl C-H bonds, as shown in Figure 5.7. This additional interaction is likely also the reason that the shifts are observed even at higher exposures or proportions of toluene in the presence of water, where they are not in benzene, as the overall toluene/water interaction is stronger than the benzene/water interaction.

Annealing experiments were also performed on water containing benzene and toluene ices to examine the effect of water on the thermal evolution of the ices. Figure 5.8 shows RAIR spectra of 70 L_m toluene on 50 L_m ASW as a function of annealing temperature. This toluene exposure was chosen as it gives a good signal to noise ratio and is representative of other toluene exposures. Figure 5.8A shows the wavenumber region from 3800 cm⁻¹ – 2800 cm⁻¹, Figure 5.8B shows the region from 1650 cm⁻¹ – 1450 cm⁻¹ and Figure 5.8C the region from 1130 cm⁻¹ – 1030 cm⁻¹. Figure 5.8A shows the characteristic phase change of water from ASW to Cl, as discussed in section 5.1.



Figure 5.8 RAIR spectra showing the effect of annealing on 70 L_m toluene on 50 L_m ASW deposited at 25 K. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

In Figure 5.8B the v(CC)_{aromatic} is seen at 1497 cm⁻¹ after deposition at 25 K with a slight asymmetrical feature at 1495 cm⁻¹, in agreement with the toluene on ASW spectrum in Figure 5.7. As the temperature is increased to 60 K, the low wavenumber feature becomes more intense and becomes dominant at 100 K. By 120 K the band has shifted to 1495 cm⁻¹, in agreement with the pure toluene spectrum shown in Figure 5.7. At 130 K all toluene bands reduce in intensity as toluene begins to desorb and have disappeared at 140 K, when water has fully crystallised, as shown in Figure 5.8A. No other band shifts in the toluene RAIR spectra are observed as a function of temperature. The shift of the v(CC)_{aromatic} band to match the pure toluene spectrum suggests that toluene and water segregate to some degree upon annealing.

The segregation of toluene and water is also suggested by annealing experiments performed on mixed toluene and water ices. Figure 5.9 shows RAIR spectra of a 50% mixed ice as a function of annealing temperature. This proportion is chosen as it is representative of the other proportions, but had the highest toluene band intensity. The wavenumber regions shown are the same as those in Figure 5.8. The characteristic water phase change is shown in Figure 5.9A and is unchanged between the mixed and layered ice systems.

In Figure 5.9B the v(CC)_{aromatic} band at 1602 cm⁻¹ shifts to 1605 cm⁻¹ upon annealing to 70 K, as the water band is beginning to become slightly asymmetric. This shift means that the band matches the pure toluene spectrum, shown in Figure 5.7. The other v(CC)_{aromatic} band at 1497 cm⁻¹ does not shift upon annealing, unlike in the layered ice system. The final band shown in Figure 5.9B is the combination band which is at 1469 cm⁻¹ upon deposition at 25 K. After annealing to 70 K, the band shifts to 1466 cm⁻¹, matching the pure ice. The δ (CH)_{in-plane} band at 1083 cm⁻¹ does not shift at any annealing temperature.



Figure 5.9 RAIR spectra showing the effect of annealing on a 50% toluene and water mixed ice deposited at 25 K. The total dose is 100 L_m. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

Whilst the mixed ice and toluene on ASW ices behave relatively similarly, the toluene on CI system is slightly different. Figure 5.10 shows the effect of annealing on RAIR spectra of 50 L_m toluene on 50 L_m Cl, with the same wavenumber regions shown as in Figures 5.8 and 5.9. In Figure 5.10A, the water band is characteristic of CI, with an intense asymmetric peak with maximum intensity at 3232 cm⁻¹. This band does not change with increasing annealing temperature, indicating that the water ice is deposited in its fully crystalline form. In Figure 5.10B, the $v(CC)_{aromatic}$ band at 1605 cm⁻¹ does not shift at any annealing temperature. Instead it reduces in intensity at an annealing temperature of 130 K as toluene begins to desorb from the CI surface, before disappearing completely after annealing to 140 K. All toluene bands are no longer apparent in the spectra after annealing to 140 K. The second v(CC)_{aromatic} band, which has a slightly dominant feature at 1497 cm⁻¹ upon deposition at 25 K, indicative of a small toluene/water interaction as discussed above, does not definitively shift upon annealing. Indeed in the spectra shown, the feature is slightly less dominant in the spectra taken after annealing to 50 K, 70 K and 100 K, but is dominant from 120 K until the band is no longer visible after annealing to 140 K. Because of this, the band is not thought to shift as a function of annealing temperature to match the pure toluene spectrum, where the band is at 1495 cm⁻¹. Similarly, the combination band, which is at 1466 cm⁻¹ in the pure toluene spectrum, does not shift from 1468 cm⁻¹ as a function of annealing temperature. There is also no shift in the band at 1082 cm⁻¹ as a function of annealing temperature.

In both the toluene on ASW system and the mixed ice, toluene bands shift to match the pure toluene ice, but this is not observed in the toluene on CI system. The difference between these systems is that water undergoes a phase change, as shown by the RAIR spectra in Figures 5.8A and 5.9A, in the layered and mixed ices, and does not in the toluene on CI system. This suggests that the segregation of toluene and water arises due to the mobility of water undergoing its compaction and phase change rather than toluene mobility. In the toluene on CI system, the water is already in the crystalline form, meaning that it does rearrange, and therefore any toluene/water interaction is preserved. The competing interaction which causes the segregation, in spite of the toluene/water interaction, is the formation of a water H-bonding network in CI.



Figure 5.10 RAIR spectra showing the effect of annealing of 50 L_m toluene on 50 L_m CI. CI is deposited at 135 K and toluene at 25 K. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.

This is rationalised by considering the relative strengths of the toluene/water and water/water interactions. As discussed above, the toluene/water interaction is a combination of an H-bond involving the aromatic π -system and a polar interaction. The H-bond is likely to be the major contributor to the overall interaction. Although the toluene/water interaction has not been examined in detail, the benzene/water interaction, which is dominated by the H-bond component,²⁶² can be used as a comparison. A consideration in this assumption is the possibility that a small inductive effect of the toluene methyl group may increase the interaction strength in toluene compared to benzene. Experimental work by Cheng et al.²⁶³ puts the strength of the benzene/water interaction at 9.41 ± 1.17 kJ mol⁻¹, and *ab initio* calculations give a value of 7.45 kJ mol^{-1.264} More recent theoretical work using diffusion Monte Carlo methods gives water/benzene interaction strengths as 9.98 kJ mol⁻¹ and 11.55 kJ mol⁻¹ depending on the potential energy surface used.²⁶⁵ A theoretical approach based on electrostatic potentials gives the highest value of the benzene/water interaction, 12.13 kJ mol⁻¹, although the authors suggest that this is a slight overestimate.²⁶² Even taking the highest value of the benzene/water interaction, it is still lower than experimentally derived water/water interaction strengths of 15 ± 2 kJ mol⁻¹ by Curtiss et al.²⁶⁶ and 13.2 kJ mol⁻¹ by Rocher-Casterline et al.²⁶⁷ It is also lower than theoretically derived values from several studies which range from 13.2 kJ mol⁻¹ up to 16.87 kJ mol⁻¹.^{265,268,269} The fact that the water/water interaction is shown to be stronger than the toluene/water (as approximated using benzene/water) shows that this is the driving force of the observed segregation.

Segregation of benzene and water is also suggested by RAIRS annealing experiments. Figure 5.11 shows the effect of annealing on RAIR spectra of 30 L_m benzene on 50 L_m ASW deposited at 25 K. This exposure is low enough that the shifts due to the benzene/water interaction are still present, but high enough to give a clear signal. Figure 5.11A shows the water v(OH) band which undergoes the characteristic phase change, and shows that water has fully desorbed after annealing to 150 K. Figure 5.11B shows the wavenumber region 1550 cm⁻¹ – 1400 cm⁻¹ which contains the v(CC)_{aromatic} band. Figure 5.11C shows the wavenumber region 1080 cm⁻¹ – 980 cm⁻¹. At this exposure, the shift of the v(CC)_{aromatic} band, shown in Figure 5.4, is slightly diminished. However a feature on the band at 1481 cm⁻¹ is apparent in Figure 5.11B, indicative of the benzene/water interaction. This feature is no longer present after annealing to 90 K and the band is symmetric and centred at 1479 cm⁻¹, matching the spectrum of pure benzene ice in Figure 5.4. The disappearance of this feature, alongside the change in the water peak profile, suggests that water mobility towards CI is responsible for the segregation of benzene and water. This is analogous to water containing toluene ices, in spite of the benzene/water interaction. After annealing to 130 K, all the benzene bands decrease in intensity as benzene begins to desorb from the surface and the water band is becomes very asymmetric as the water phase change continues. After annealing to 140 K, benzene has mostly desorbed. The water band in Figure 5.11A shows that the water has undergone its phase change and is in its fully crystalline state. After annealing to 150 K, no bands are present, indicating that all species have desorbed from the surface.

It is apparent in Figure 5.11 that the crystallisation of benzene does not occur in the benzene on ASW ice system. This crystallisation is characterised by the v(CH)_{aromatic}, combination and δ (CH)_{in-plane} bands splitting upon annealing, as shown in Table 5.3. Additionally, the v(CC)_{aromatic} band increases in intensity upon annealing. The crystallisation of benzene is also not observed in mixed ices (data not shown).

Contrasting behaviour is observed when annealing ices of 30 L_m benzene on 50 L_m Cl, as shown in Figure 5.12. An exposure of 30 L_m is shown as a comparison to Figure 5.11. The v(OH) region is omitted as it does not change from the characteristic Cl peak in the temperature range shown. Figure 5.12A shows the wavenumber region from 3050 cm⁻¹ – 3000 cm⁻¹, and shows the v(CH) combination band. Figure 5.12B shows the region from 1550 cm⁻¹ – 1400 cm⁻¹, containing the v(CC)_{aromatic} band, and Figure 5.12C shows the region from 1080 cm⁻¹ – 980 cm⁻¹ containing the δ (CH)_{in-plane} band. After annealing to 110 K, the benzene bands have changed, indicating that benzene has crystallised. The combination band in Figure 5.12A has shifted and split from a single peak at 3038 cm⁻¹ to two peaks at 3038 cm⁻¹ and 3030 cm⁻¹, the v(CC)_{aromatic} at 1479 cm⁻¹ has increased in intensity by a factor of two and the δ (CH)_{in-plane} band has shifted to 1034 cm⁻¹ from 1036 cm⁻¹ and developed a shoulder at 1040 cm⁻¹. After further annealing to 120 K, the δ (CH)_{in-plane} band fully splits to give two peaks at 1034 cm⁻¹ and 1040 cm⁻¹. These spectral changes all indicate that benzene has crystallised, analogous to pure benzene on HOPG.



Figure 5.11 RAIR spectra showing the effect of annealing of 30 L_m benzene on 50 L_m ASW deposited at 25 K. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure. Dotted lines are included as guides and their positions are shown on the figure.



Figure 5.12 RAIR spectra showing the effect of annealing of 30 L_m benzene on 50 L_m Cl. Cl is deposited at 135 K and benzene is deposited at 25 K. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure.

A comparison of the crystallisation, or lack thereof, behaviour in water containing benzene ices is illustrated in Figure 5.13, where the area of the benzene $v(CC)_{aromatic}$ mode at 1479 cm⁻¹ is shown as a function of annealing temperature. It is assumed that any observed change in the band area is only due to crystallisation. In all cases the amount of benzene is approximately the same, 30 L_m for pure benzene, benzene on ASW and benzene on CI systems and equivalent to 25 L_m in the mixed ice. For the pure benzene ice and the benzene on CI system, the increase in intensity (and hence area) of the band indicates that crystallisation occurs. This is not the case in the benzene on ASW and mixed ice systems.



Figure 5.13 Integrated band area of the v(CC)_{aromatic} band at 1479 cm⁻¹ of benzene as a function of annealing temperature for different ice configurations. In the layered and pure ice system the benzene exposure is 30 L_m and in the mixed ice the benzene proportion is 29%.

Figure 5.13 shows that the presence of water in its amorphous form inhibits the crystallisation of benzene. This is rationalised by considering the structure of amorphous water ice. The porous nature of amorphous water in both the benzene on ASW system and mixed ice will trap benzene and prevent its rearrangement to its crystalline phase. When benzene is deposited on top of crystalline water, no pore system is present and therefore at sufficient exposures the crystallisation of benzene is observed. Therefore,
the crystallisation of benzene is physically inhibited by amorphous water due to trapping. Other molecules such as glycolaldehyde^{32,270} and propan-2-ol¹¹⁶ also have their phase change inhibited in the presence of water.



Figure 5.14 RAIR spectra showing the effect of annealing on 70 L_m benzene on 50 L_m ASW deposited at 25 K (panels A-C) and on a 50% benzene and water mixed ice (panels D-F). Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure.

The fact that the physical inhibition of crystallisation by the pore system is responsible, as opposed to any chemical effect, is further shown by annealing higher exposures of benzene on ASW. Figure 5.14 shows RAIR spectra of 70 L_m benzene on 50 L_m ASW (panels A - C) and a 50% mixed ice (panels D - F). Spectra recorded after deposition at 25 K and after annealing to 120 K are shown. The wavenumber regions shown are the same as those shown in Figure 5.12. Clearly shown in Figures 5.14A – 5.14C are the changes in benzene RAIRS bands associated with the crystallisation of benzene. These changes are not observed in Figures 5.14D – 5.14F. This indicates that at higher exposures of benzene will not be trapped and can hence crystallise. This conclusion will be examined with respect to the TPD data below. Even at the highest proportion of benzene in water mixed ice,

no crystallisation is observed. This is due to the fact that the ices are co-deposited and therefore, in contrast to the benzene on ASW system, no saturation of the pore system occurs and all the benzene is trapped, *i.e.* prevented from undergoing crystallisation.

5.3.2 TPD of Water Containing Benzene and Toluene Ices

TPD experiments were also performed for all of the systems described above. The resulting data provide complementary information to the RAIRS results, as well as information which RAIRS experiments cannot probe. Figure 5.15 shows TPD traces of increasing exposures of benzene deposited at 25 K on 50 L_m Cl. An example water trace is shown (black trace), which is characteristic of Cl desorption due to the lack of shoulder on the leading edge. Exposures of benzene range from 5 L_m – 50 L_m, corresponding to approximately 0.3 ML – 3.0 ML according to the estimations made in Chapter 4. This direct comparison is only valid when benzene (or toluene) is deposited on Cl. This is because the Cl surface is relatively smooth, analogous to HOPG. When benzene or toluene are deposited on the ASW, which has a rough and porous surface, the same exposure in L_m will not give the same coverage in ML as on HOPG. In this section, all data will be presented in terms of exposure in L_m, with the equivalent coverage on HOPG in ML stated.

At exposures of 5 L_m and 10 L_m (equivalent to 0.28 ML and 0.56 ML respectively on HOPG), a single broad peak is observed, which has peak intensity at 131 K and 129 K for 5 L_m and 10 L_m exposures respectively. As the exposure of benzene is increased to 15 L_m (0.85 ML on HOPG), a second, high temperature, peak is apparent in the trace. The first peak remains at approximately 129 K, with a small shift to lower temperature, and the second peak is at 134 K. The high temperature peak becomes dominant as the exposure is increased and shifts to 136 K at an exposure of 20 L_m (1.13 ML). The high temperature peak is the only peak observed in the 30 L_m and 50 L_m traces with peak temperatures of 137 K and 138 K respectively. These exposures are equivalent to coverages of 1.69 ML and 2.82 ML on HOPG. The high temperature feature increases in peak temperature with increasing exposure, characteristic of multilayer desorption.^{25,29} This peak is identical to the TPD peak arising from the same exposure of pure benzene ice, as shown in Figure 5.16. Simulations in Kinetiscope²⁴⁵ using the parameters determined in Chapter

4 ($n = 0.18 \pm 0.06$, $E_{des} = 45.5 \pm 1.8$ kJ mol⁻¹ and $v = 10^{29 \pm 1}$ molecules cm⁻² s⁻¹) confirm that the desorption parameters are the same in the two systems, as expected. For these reasons, the high temperature peak is assigned to multilayer crystalline benzene desorption. The low temperature peak, apparent in exposures from 5 L_m – 20 L_m, is assigned to sub-monolayer quantities of benzene desorbing directly from the CI surface. This assignment is made as this peak is present before the appearance of multilayer desorption. The shift to lower temperature as the exposure is increased is analogous to the behaviour of benzene on HOPG, and is assigned to lateral repulsions between adsorbed benzene molecules on the surface. The shift is less pronounced than in the pure benzene ice, which may be a consequence of the benzene/water interaction described above. The interaction may compete with repulsive interactions, and make the temperature shift less pronounced. This is examined with respect to the desorption parameters below.



Figure 5.15 TPD traces of increasing exposures of benzene deposited at 25 K on 50 L_m CI. Benzene exposures are equivalent to 0.28 ML – 2.82 ML on HOPG. The black trace is a 50 L_m CI TPD trace for comparison.



Figure 5.16 Comparison of the TPD traces of 50 L_m (2.82 ML) of benzene desorbing from HOPG or from 50 L_m of Cl.

The same procedure as in Chapter 4 was applied to the sub-monolayer benzene on CI desorption peaks, where Kinetiscope was used to determine the desorption energy, E_{des} , using an assumed desorption order (*n*) of 1, and pre-exponential factor (*v*) of 10^{13} s⁻¹ according to the method of Thrower *et al*.¹¹⁵ The values of *n* and *v* are typical values for sub-monolayer desorption.^{25,29} An example of the simulated TPD traces compared to the experimental data is shown in Figure 5.17. The peak temperatures and leading edges of the experimental traces are well reproduced by the simulation. The trailing edge is not well simulated, which is due to the fact that Kinetiscope assumes ideal pumping which is not representative of the experiment. As the exposure of benzene on CI is increased from 5 L_m to 10 L_m, the decrease in *E*_{des} is found to be 0.5 kJ mol⁻¹, from 39.8 ± 2.5 kJ mol⁻¹ to 39.3 ± 2.5 kJ mol⁻¹. This decrease is smaller than the decrease of 0.8 kJ mol⁻¹ found for the same change in exposure of benzene on HOPG. This indicates that the lateral repulsions between adsorbed benzene molecules are weaker in the presence of water which may be due to the benzene/water interaction.



Figure 5.17 Comparison of experimental and simulated by Kinetiscope TPD traces of sub-monolayer exposures of benzene on 50 L_m Cl. Benzene exposures are 5 L_m and 10 L_m, equivalent to 0.28 ML and 0.56 ML of benzene on HOPG.

By comparison, as shown in Figure 5.18, TPD of toluene on CI does not show similar behaviour to toluene on HOPG, nor to that of benzene on CI. Figure 5.18A shows TPD traces of exposures of 5 $L_m - 25 L_m$ (0.17 ML – 1.22 ML) of toluene on 50 L_m CI and Figure 5.18B shows those arising from 25 $L_m - 200 L_m$ (up to 9.79 ML). In both Figures 5.18A and 5.18B an example water trace is shown for comparison. The lower exposure TPD traces in Figure 5.18A are mostly symmetrical with a single peak temperature of 141 K. As the exposure of toluene is increased to 40 L_m , a second peak becomes apparent at 138 K which grows and becomes dominant at an exposure of 60 L_m . The low temperature peak also shifts to higher temperatures as the exposure is increased, and it is the only peak in the TPD at an exposure of 150 L_m of toluene. At an exposure of 200 L_m the peak has shifted to 143 K.



Figure 5.18 TPD traces of increasing exposures of toluene deposited at 25 K on 50 L_m Cl. A: toluene exposures equivalent to 0.17 ML – 1.22 ML. B: toluene exposures equivalent to 1.22 ML – 9.79 ML. In both panels the black trace is an example of a 50 L_m Cl TPD trace for comparison.

Symmetrical peaks with a constant peak temperature with increasing exposure are typical of sub-monolayer desorption.^{25,29} Therefore the TPD traces in Figure 5.18A are assigned to sub-monolayer desorption of toluene from CI. This peak is also present in Figure 5.18B up to an exposure of 85 L_m (4.16 ML on HOPG). Leading edge analysis using the Polanyi-Wigner equation was applied to the TPD traces shown in Figure 5.18A in order to determine desorption parameters for toluene desorbing from a CI surface. Figure 5.19A shows a plot of ln[l(T)] against $ln(\theta_{rel})$ for exposures of 10 L_m – 25 L_m of toluene on CI at a fixed temperature of 136 K, where the gradient is equal to *n*. This exposure range is equivalent to a coverage range of 0.49 ML – 1.22 ML on HOPG. Figure 5.19B shows a plot of $ln[l(T)] - nln(\theta_{rel})$ for an exposure of 25 L_m toluene on CI. The parameters determined for sub-monolayer toluene desorption are shown in Tables 5.5 and 5.6.



Figure 5.19 A: plot of ln[l(T)] against $ln(\theta_{rel})$ for a fixed temperature of 136 K for exposures from 10 L_m – 25 L_m toluene on CI, equivalent to coverages of 0.49 ML – 1.22 ML. Blue crosses are individual data points and the solid red line is a linear fit to the data. B: plot of $ln[(T)] - nln(\theta_{rel})$ against 1/T for 25 L_m of toluene on CI. Red circles are individual data points and the blue solid line is a linear fit to the data. Error bars are determined using the upper and lower values of n.

| Temperature / K | n |
|-----------------|------|
| 132 | 0.87 |
| 133 | 0.80 |
| 134 | 0.96 |
| 135 | 1.06 |
| 136 | 1.18 |
| 137 | 1.11 |
| 138 | 1.22 |
| 139 | 1.32 |
| 140 | 1.35 |

 Table 5.5. Orders of desorption of sub-monolayer toluene from CI determined using leading edge

 analysis for each set of data.

Table 5.6. Sub-monolayer desorption energies and pre-exponential factors for toluene on CI determinedfrom leading edge analysis for each set of data. The exposure range in L_m is equivalent to coverages of0.49 ML - 1.22 ML on HOPG.

| Exposure / L _m | E _{des} / kJ mol ⁻¹ | v / s ⁻¹ |
|---------------------------|---|----------------------|
| 10 | 39.8 ± 9.8 | 10 ^{16 ± 2} |
| 15 | 45.4 ± 11.3 | 10 ^{16 ± 2} |
| 20 | 51.9 ± 11.2 | 10 ^{16 ± 2} |
| 25 | 50.0 ± 11.6 | 10 ^{16 ± 2} |

The values above give mean desorption parameters for sub-monolayer toluene desorption from CI as follows, $n = 1.11 \pm 0.09$, $E_{des} = 46.8 \pm 5.5$ kJ mol⁻¹ and $v = 10^{16 \pm 1}$ s⁻¹. The value of v is higher than typical sub-monolyaer desorption pre-exponential factors, which are typically 10^{13} s⁻¹.^{25,29} High sub-monolayer pre-exponential factors have been observed previously for larger molecules such as n-alkanes,^{120,121} benzene²⁷¹ and its fluorinated derivatives,¹²³ cyclohexane²⁷¹ and p-xylene.¹¹⁷ They are due to the fact that large molecules have greater differences in the molecular degrees of freedom between adsorbed and desorbed states, increasing the entropy change upon desorption and thus the pre-exponential factor.^{117,120,121,271}

The low temperature peak shown in Figure 5.18B, which grows and shifts to higher temperature with increasing exposure, is assigned to the desorption of multilayers of toluene. This is because the traces for exposures of 150 L_m and 200 L_m toluene (equivalent to 7.34 ML and 9.79 ML on HOPG respectively), where only the multilayer peak is observed, agree in terms of peak temperature and profile with the equivalent exposure of toluene on HOPG. This is analogous to multilayers of benzene on CI, shown in Figure 5.16.

The constant peak temperature of sub-monolayer TPD traces of toluene on CI is in contrast to pure toluene (and benzene) and suggests that lateral repulsive interactions do not affect the desorption temperature when toluene is adsorbed on CI. The behaviour of toluene on CI can be rationalised with reference to the RAIRS data presented in this chapter and the TPD data in Chapter 4. In the case of benzene on CI, the decrease in desorption temperature compared to pure benzene ice is reduced due to the benzene/water interaction. In section 5.3.1, it was concluded that the toluene/water interaction is stronger (due to its polarity) than that of benzene and water. Indeed this is supported by comparing the values of E_{des} for desorption from CI presented above, 39.8 ± 2.5 kJ mol⁻¹ for benzene compared to 46.8 ± 5.5 kJ mol⁻¹ for toluene. Additionally, in Chapter 4, the lateral repulsions between adsorbed benzene molecules are shown to be stronger than those between adsorbed toluene molecules, as shown by the relative decreases in E_{des} for equivalent coverages. The combination of these factors is the likely explanation for the observed difference in behaviour *i.e.* benzene shows repulsive behaviour on CI due to stronger repulsions and a weaker interaction with water whereas toluene does not show repulsive behaviour on CI due to weaker repulsions and a stronger interaction with water.

The TPD behaviour of benzene and toluene in the presence of ASW, in layered systems or in mixed ices, is more complex than that on CI due to the morphological differences between the water systems. Indeed in the RAIRS data shown in section 5.3.1, the pore system of ASW is shown to inhibit the crystallisation of benzene. Figure 5.20 shows TPD traces of low exposures (\leq 30 L_m, or 1.69 ML on HOPG) of benzene deposited on 50 L_m ASW. Also shown is an example water trace, with the characteristic feature on the leading edge of the peak at 147 K present, indicative of the ASW to CI water phase change.

From exposures of 1 L_m – 20 L_m (0.06 ML – 1.13 ML on HOPG), two clear peaks are present in the traces, at 147 K and 156 K. The lower temperature peak is sharp and occurs at the same temperature as the water phase change. Therefore this is assigned to volcano desorption of benzene trapped in the pore system of the ASW ice, which desorbs rapidly when the pores collapse during the water phase change.^{28,139} The second peak at 156 K occurs concurrently with the desorption of Cl on the water trace, and is therefore assigned to co-desorption of benzene which remained trapped and was not able to desorb during the phase change with Cl. Both of these peaks grow in intensity as the benzene exposure is increased at the exposures shown in the figure. At all benzene exposures, a small feature is also seen at 130 K which increases in intensity slightly as the exposure is increased to 20 L_m. As the exposure is increased to 30 L_m (1.69 ML on HOPG), this peak grows dramatically in intensity. This peak is hence assigned to the desorption of benzene from the water ice surface, as it occurs before the onset of water desorption and is in good agreement with the peak observed by Thrower *et al*.¹¹⁴ for benzene desorbing from an ASW surface.



Figure 5.20 TPD traces for increasing exposures of benzene deposited at 25 K on 50 L_m ASW. Benzene exposures are equivalent to coverages of 0.06 ML – 1.69 ML on HOPG. The black trace is an example of a 50 L_m ASW TPD trace for comparison

Figure 5.21 shows TPD traces of exposures up to 30 L_m of toluene deposited on 50 L_m ASW, alongside an example water trace. This is up to a corresponding toluene coverage on HOPG of 1.47 ML. As in the benzene system, two high-temperature peaks are present in the TPD trace, at 147 K and 156 K. Similarly to benzene, these peaks are assigned to volcano and co-desorption respectively, as they are concurrent with the ASW to CI phase change of water and the desorption peak of CI. The volcano and co-desorption peaks increase in intensity as the exposure in increased, similarly to benzene. Up to an exposure of 20 L_m (0.98 ML on HOPG) a small feature is also present at 137 K. As the toluene exposure is increased further to 30 L_m this peak grows in intensity rapidly and shifts in temperature to 141 K. This peak is assigned to desorption of toluene from the ASW surface.



Figure 5.21 TPD traces of increasing exposures of toluene deposited at 25 K on 50 L_m ASW. Toluene exposures are equivalent to coverages of 0.24 ML – 1.47 ML on HOPG. The black trace is an example of a 50 L_m ASW TPD trace for comparison

The rapid growth of the surface component for both benzene and toluene on ASW, compared to the steady increase of the volcano and co-desorption peaks with increasing exposure, suggests that there is a threshold exposure of surface desorption below which it is only a minor component of desorption. This is seen in Figure 5.22, which shows TPD traces of \geq 30 L_m benzene on ASW (\geq 1.69 ML on HOPG).

The volcano and co-desorption peaks in all the benzene traces in Figure 5.22 are of equal intensity, unlike the steady increase in peak intensity in Figure 5.20. This means that the ASW pore system is saturated, and subsequently deposited benzene will only adsorb onto the surface of the ice. This effect is further exemplified in Figure 5.23, where the integrated areas (proportional to the amount of benzene desorbing) of each desorption component are shown as a function of benzene exposure. The area of the surface desorption component is measured between 100 K and 143 K, the area of the volcano desorption component is measured between 143 K and 152 K and the area of the co-desorption component is measured between 152 K and 200 K.



Figure 5.22 TPD traces of increasing exposures of benzene deposited at 25 K on 50 L_m ASW. Benzene exposures are equivalent to coverages of 1.69 ML – 5.64 ML on HOPG. The black trace is an example of a 50 L_m ASW TPD trace for comparison.



Figure 5.23 Integrated peak areas of each desorption peak in the benzene on ASW TPD traces as a function of benzene dose. Red crosses: surface desorption. Blue squares: volcano desorption. Green circles: co-desorption.

Up to an exposure of 30 L_m benzene (1.69 ML on HOPG), the area of the volcano and codesorption components steadily increase, and above this exposure they level off as the pore system is saturated. The surface component increases slowly and steadily up to an exposure of 20 L_m (1.13 ML on HOPG), and starts to increase rapidly in area at 30 L_m, as shown in the TPD traces in Figure 5.20. Subsequently it increases linearly as the exposure is increased, as expected. This effect is a consequence of the water pore system, where initially most of the adsorption sites available are in this porous network and hence volcano desorption dominates. Some surface desorption occurs due to the low deposition temperature and likely limited mobility of benzene on the surface at 25 K. Once the pore network is filled, at a benzene exposure of 30 L_m, surface desorption becomes more important and therefore the peak in the TPD trace rapidly increases in intensity. This applies to both benzene and toluene as both show similar low exposure behaviour in the TPD experiments, shown in Figures 5.20 and 5.21. This also agrees well with the RAIRS data shown above, since at low exposures of benzene on ASW no crystallisation is observed due the trapping of benzene in the pore system of water. RAIR spectra of exposures > 30 Lm benzene on ASW show crystallisation. This is after the saturation of the pore network as shown by the TPD traces in Figure 5.22.

The surface desorption component in Figure 5.22 changes with increasing benzene exposure. Initially at an exposure of 30 L_m, a single peak at 130 K is observed. This peak increases in intensity and remains at 130 K as the exposure is increased to 40 L_m (2.26 ML on HOPG). At an exposure of 50 L_m (2.82 ML on HOPG) the peak shifts slightly to 131 K and a second, high-temperature, peak becomes apparent at 137 K. This high temperature peak becomes dominant as the exposure is increased and shifts to higher temperature. At an exposure of 100 L_m (5.64 ML on HOPG) the peak is at 140 K, and is the only peak in the TPD trace. The peak at 140 K in the 100 L_m trace is assigned to multilayer desorption of benzene, as it matches the peak for benzene desorbing from HOPG for similar exposures. The low temperature peak in exposures < 100 L_m is assigned to sub-monolayer amounts of benzene desorbing from the ASW surface. It is in agreement with the peak observed by Thrower *et al.*¹¹⁴ and is at a similar temperature of the sub-monolayer surface desorption peak does not decrease in temperature with

increasing exposure, unlike in the benzene on CI system. This suggests that lateral repulsive interactions do not occur on ASW, which is likely due to the surface roughness compared to the relatively smooth CI (and HOPG) surfaces.

Leading edge analysis was applied to the traces of 30 L_m – 50 L_m in order to determine the sub-monolayer desorption parameters of benzene desorbing from ASW. In the pure ice, the relative coverage term, θ_{rel} , is determined simply by the taking the area under the TPD trace as only a single peak was present in the TPD trace. However, in the traces shows in Figure 5.22, this is not the case due to the presence of volcano and codesorption peaks. In order to determine the value of θ_{rel} to be used in the analysis, a peak fitting procedure was performed. This procedure determines the relative contribution of each individual peak to the whole TPD trace. This is especially important for the 50 L_m benzene TPD trace shown in Figure 5.22, as the surface desorption peaks. Each peak is fitted using a Lorentzian function, which when summed are found to reproduce the overall TPD trace. Figure 5.24 shows the results of the peak fitting procedure for the 50 L_m benzene on ASW TPD trace. The TPD peaks do not follow the Lorentzian profile exactly. However, as shown in Figure 5.24, this function does allow the overall TPD trace to be reproduced well.



Figure 5.24 Example of the peak fitting procedure applied to TPD traces of benzene on ASW to determine the relative contribution of each desorption event to the total trace.

A total of four peaks are fitted in the trace. These are, from lowest temperature to highest, sub-monolayer benzene desorption, multilayer benzene desorption, volcano desorption and co-desorption. Also shown in Figure 5.24 is the sum of the fitted peaks, which agrees well with the experimental trace, suggesting that the peak fitting procedure is valid. Once the relative contributions of each desorption peak were determined, leading edge analysis was applied and the desorption parameters for sub-monolayer desorption were determined. Figure 5.25A shows a plot of ln[l(T)] against $ln(\theta_{rel})$ for exposures of 30 L_m – 50 L_m of benzene on ASW (1.69 ML – 2.82 ML on HOPG) at a fixed temperature of 126 K, where the gradient is equal to n. Figure 5.25B shows a plot of $ln[l(T)] - nln(\theta_{rel})$ for an exposure of 40 L_m benzene on ASW. The parameters determined for sub-monolayer benzene desorption from ASW are $n = 0.83 \pm 0.08$, $E_{des} = 41.7 \pm 6.4$ kJ mol⁻¹ and $v = 10^{19 \pm 2}$ s⁻¹.



Figure 5.25 A: plot of ln[I(T)] against ln(θ_{rel}) for a fixed temperature of 126 K for exposures from 30 L_m – 50 L_m benzene on ASW, equivalent to coverages of 1.69 ML – 2.82 ML on HOPG. Blue crosses are individual data points and the solid red lines is a linear fit to the data. B: plot of ln[(T)] – nln(θ_{rel}) against 1/T for 40 L_m of benzene on ASW. Red circles are individual data points and the blue solid line is a linear fit to the data. Error bars are determined using the upper and lower values of n as shown in A.

The value of the pre-exponential factor of $10^{19 \pm 2}$ s⁻¹ is higher than typical values for submonolayer desorption, which are approximately 10^{13} s⁻¹,^{25,29} and is likely due to the fact that benzene is a large molecule, analogously to the case of toluene on CI shown above. Indeed sub-monolayer desorption of benzene from graphene has been shown to occur with a pre-exponential factor of 10^{17} s⁻¹.²⁷¹ The desorption energy of sub-monolayer amounts of benzene from ASW of 41.7 ± 6.4 kJ mol⁻¹ is in excellent agreement with previous experimental work,¹¹⁴ which gives a value of 41.0 ± 0.5 kJ mol⁻¹. It is also in good agreement with recent theoretical work at classical²⁵⁹ and quantum²⁶⁰ levels, giving values of 39 kJ mol⁻¹ and 42 kJ mol⁻¹ respectively.



Figure 5.26 TPD traces of increasing exposures of toluene deposited at 25 K on 50 L_m ASW. Toluene exposures are equivalent to coverages of 1.47 ML – 9.79 ML on HOPG. The black trace is an example of a 50 L_m ASW TPD trace for comparison.

TPD traces of higher exposures (\geq 30 L_m, or 1.47 ML on HOPG) of toluene on ASW are shown in Figure 5.26. At an exposure of 30 L_m, a single surface desorption peak is present at 141 K. This peak is assigned to sub-monolayer desorption of toluene desorbing from the ASW surface as it is at the same temperature as that of sub-monolayer toluene desorption from CI. As the exposure is increased, a second, low temperature, peak becomes apparent at 140 K, whilst the sub-monolayer peak shifts to 143 K. The low temperature peak becomes dominant from an exposure of 70 L_m (3.43 ML on HOPG) and shifts slightly to higher temperature, to 142 K at an exposure of 200 L_m (9.79 ML on HOPG). The sub-monolayer peak remains at 143 K at all exposures and is present as a feature on the trailing edge of all the surface desorption components of the TPD traces. The low temperature peak is assigned to multilayer desorption of toluene, as it agrees well with previously assigned multilayer desorption peaks.

In TPD traces of toluene exposures below 150 L_m (7.34 ML on HOPG) in Figure 5.26, the volcano desorption peak is shown to saturate. In the 150 L_m and 200 L_m TPD traces, the volcano peak appears to increase in intensity, however this is due to the fact that all the peaks in the TPD traces, that is surface desorption, volcano and co-desorption peaks, are close together in temperature and overlap significantly. This overlap causes the volcano peak to appear as a feature on the trailing edge of the surface desorption component at 147 K, rather than a resolved single peak which is saturated. The co-desorption peak at 156 K is also saturated at an exposure of 30 L_m, however this is not clear in Figure 5.26 due to its low relative intensity compared to the other peaks.

The significant overlap of the peaks means that the peak fitting procedure applied to the benzene on ASW system could not be applied to the toluene on ASW system. As such no desorption parameters could be calculated for sub-monolayer toluene desorption from ASW. However, the sub-monolayer peak is in agreement with the peak in the TPD traces for toluene on CI in terms of peak temperature. Therefore an estimation can be made that the desorption energy calculated above for toluene desorbing from CI, of 46.8 ± 5.5 kJ mol⁻¹, is likely to be close to the value for sub-monolayer toluene desorption from ASW. This value is higher than the value of benzene sub-monolayer desorption from ASW. This agrees with the earlier conclusion that the toluene/water interaction is larger than that of benzene/water, as a consequence of toluene's polarity.

TPD traces arising from mixed benzene and water ices with increasing proportions of benzene are shown in Figure 5.27. The behaviour of benzene in a mixed ice is broadly similar to that of the benzene on ASW system. In all traces there is clearly a sharp peak at 147 K, concurrent with the water phase change, and clearly a less intense peak at 156 K which matches the desorption temperature of the water trace. These peaks are

assigned to volcano desorption and co-desorption respectively, and indicate that benzene is trapped in the pore system of the water ice. In the main panel, from a benzene proportion of 29%, a low temperature peak is apparent centred at 131 K, which grows in intensity as the proportion of benzene is increased. This peak is assigned to small amounts of benzene desorbing from the ice surface. It is in good agreement with the sub-monolayer desorption peak of benzene on ASW in terms of peak profile and temperature. As shown in the inset of Figure 5.27, where a TPD trace of 7% benzene in water mixed ice shown, even at the lowest proportions of benzene a broad surface desorption feature is present. This is analogous to the layered ice system where small amounts of surface desorption are observed before the saturation of the volcano peak.



Figure 5.27 TPD traces of increasing proportions of benzene in a mixed water ice deposited at 25 K. The water exposure in all cases is 50 L_m. The black traces are an example of a 50 L_m ASW TPD trace for comparison.

At no proportion of benzene do the volcano or co-desorption peaks saturate in the mixed ice, unlike in the layered benzene on ASW ice. This is because the two molecules are co-deposited, therefore benzene is trapped within the pore system through the entire ice. This is as opposed to in the sequentially deposited layered ice, where benzene molecules can only enter pores that are accessible from the top surface of the ASW

layer. The co-deposition of the molecules also explains the fact that the surface desorption peak does not rapidly increase in intensity as shown in Figure 5.20 for the layered ice, as the pore system does not saturate. The proportion of benzene in the ice, which does have an effect on the RAIRS data (Figure 5.6), is not shown to alter the desorption behaviour of benzene. This is shown in Figure 5.28, where the relative contribution of each desorption peak to the total TPD trace in terms of percentage of the total integrated area is shown as a function of benzene proportion. The peak areas of each desorption feature are measured between 100 K – 143 K, 143 K – 152 K and 152 K – 200 K for surface, volcano and co-desorption respectively. The relative contribution of each desorption event, surface, volcano and co-desorption, is constant for all benzene proportions. The contributions due to surface, volcano and co-desorption are 14%, 75% and 11% respectively.



Figure 5.28 Integrated peak areas of each desorption peak in the benzene in water mixed ice TPD traces as a function of benzene proportion expressed as percentage of the total TPD trace area. Red crosses: surface desorption. Blue squares: volcano desorption. Green circles: co-desorption.

Similar to benzene, TPD traces of mixed toluene ices also show 3 desorption features, as shown in Figure 5.29. The first peak is at 139 K – 140 K, shifting to higher temperature

as the toluene proportion is increased. This peak is assigned to sub-monolayer amounts of toluene desorbing from the surface of the mixed ice. Similar to benzene, no rapid increase in intensity of this peak is observed due to the co-deposition of toluene and water. The peaks at 147 K and 156 K are assigned to volcano and co-desorption respectively. As is the case for mixed benzene and water ices, neither volcano nor codesorption peaks saturate in the mixed toluene and water ice, whereas they do in the layered toluene on ASW ice. As discussed above, this is a consequence of the differences in dosing the layered and mixed ices.



Figure 5.29 TPD traces of increasing proportions of toluene in a mixed water ice deposited at 25 K. The water exposure in all cases is 50 L_m. The black trace is an example of a 50 L_m ASW TPD trace for comparison.

Unlike in benzene, as shown in Figure 5.30, the relative contributions of each desorption feature in the toluene and water mixed ices do not remain constant as the proportion of toluene is increased. The peak areas of each desorption feature are measured between 100 K – 141 K, 141 K – 153 K and 153 K – 180 K for surface, volcano and codesorption respectively. The relative contributions of the surface and volcano desorption peaks increase slightly from 9% – 16% and 59% – 73% respectively of the total, as the toluene proportion is increased from 9% - 50%. The relative contribution of

the co-desorption peak over the same increase in toluene proportion is seen to decrease from 32% - 12%. This decrease in proportion of toluene desorbing as co-desorption with water may be a consequence of toluene's increased molecular size compared to benzene, meaning that volcano desorption becomes more important due to steric effects, although this is not clear.



Figure 5.30 Integrated peak areas of each desorption peak in the toluene in water mixed ice TPD traces as a function of toluene proportion expressed as percentage of the total TPD trace area. Red crosses: surface desorption. Blue squares: volcano desorption. Green circles: co-desorption.

5.3.3 Astrophysical Implications

The models presented in this section were run by Dr Tara Salter, using data collected and analysed by the author.

The desorption parameters determined above, and in Chapter 4, alongside the observed trapping behaviour, can be used in a model to examine how benzene and toluene would behave in astronomical ices in terms of their desorption temperatures. This information is useful to astronomers as the presence of gas phase species with known desorption parameters can give information about the local environment such as temperature, or about the age of a nearby stellar object.^{25,143}

In order to examine benzene and toluene desorption in astronomically relevant environments, a model developed in the Brown group which uses a heating profile developed by Viti *et al.*¹³⁴ is employed. It is a single-point time-dependent model which simulates the local heating near a star of a given mass and gives desorption profiles of target molecules. The model uses the Polanyi-Wigner equation,^{25,183} shown in Chapter 2 (equation (2.2)), to determine the rate of desorption at a given temperature, using the experimentally determined desorption parameters *n*, *E*_{des} and *v*.

Some assumptions must be made about the ice composition and thickness, and the heating rate in order for the model to give astronomically relevant results. The heating rate used in this work was 0.5 K s⁻¹, whereas heating rates of a dust grain in a hot core have been shown to be closer to 1 K century⁻¹.^{134,143} Equally, non-linear heating rates are more appropriate for interstellar heating.^{134,272} The heating rate in the desorption model of Viti *et al*.¹³⁴ is given by equation (5.3).¹³⁴

T is the temperature of the star, t is the time in years and A and B are constants which are specific to stars of a certain mass, where the mass is expressed in number of solar masses (M_{\odot}). A and B arise from correlating the observed luminosity, taken from Molinari *et al.*²⁷³, and hence temperature, with the age of a star of a given mass. This temperature-time relation is found to obey the power law (5.3) from which A and B can be found.¹³⁴ Example temperature profiles are shown in Figure 5.31 for a 5 M_{\odot} and 25 M_{\odot} star. In both cases the temperature increase over time is non-linear, and is more rapid for the more massive star. For example for a 25 M_{\odot} star, a temperature of 70 K is reached after 22 000 years, compared to 112 000 years for a 5 M_{\odot} star.

The thicknesses of the ices grown in this chapter are not representative of astronomical ices, which have been estimated to be 0.3 μ m thick.¹³³ This thickness corresponds to a coverage of 9.5 × 10¹⁷ molecules cm⁻², which is the total initial coverage used in the model. This coverage value is calculated from the published density and porosity of water ice deposited at 10 K,^{43,274} and has been used previously in this model.^{133,143} According to the coverage estimates based on molecular size in Chapter 4, a coverage of 1 ML refers to 5.2 × 10¹⁴ molecules cm⁻² of benzene and 4.7 × 10¹⁴ molecules cm⁻² of

toluene. Therefore the model simulates desorption of ices which are comfortably in the multilayer regime, and so appropriate desorption parameters must be used.



Figure 5.31 The temperature evolution of stars of two masses as a function of time. Blue trace: for a star of 25 M_@ Red trace: for a star of 5 M_@. Figure credit: Professor Wendy A. Brown.

As well as the thickness, the ice composition must be considered. In an astronomical environment, water is the most abundant molecule adsorbed on dust grains.⁸⁶ Therefore mixed ices with the lowest proportions of benzene or toluene and layered ices with small amounts of benzene or toluene deposited on top of water are the most representative of astronomical ices, and the TPD data from these systems should be used to construct the model. Indeed it is thought that benzene or toluene may only make up 1% of the total ice in which they would be present.²⁷² This represents 9.5×10^{15} molecules cm⁻² in a 0.3 µm thick ice. However, in the ASW containing layered and mixed ices, not all the aromatic molecules desorb in the surface desorption component. As discussed above, volcano and co-desorption are dominant in these systems. Therefore in order to accurately model these systems, the percentage of molecules desorbing in each desorption process must be known. Table 5.7 shows the determined percentages,

from the contributions of each peak to the total TPD trace area. For benzene mixed ices, the percentages of each desorption event are the average value of all benzene proportions, which is shown to be constant in Figure 5.28. For toluene mixtures, the percentages used in the model are those for the lowest proportion of toluene, 9%, as the percentages do not remain constant with increasing toluene proportion. Even the lowest percentage of surface desorption, 9% in the mixed toluene ice, represents a coverage of 8.6×10^{14} molecules cm⁻², therefore multilayer desorption parameters should be employed in the model.

| | | Proportion of molecules desorbing at each event / | | | |
|----------|-----------|---|---|----------------|--|
| Molecule | System . | | % | | |
| | | Surface | Surface Volcano esorption desorption | Co decorretion | |
| | | desorption | | co-desorption | |
| Benzene | On Cl | 100 | - | - | |
| | On ASW | 13 | 70 | 17 | |
| | Mixed ice | 14 | 75 | 11 | |
| Toluene | On Cl | 100 | - | - | |
| | On ASW | 13 | 64 | 23 | |
| | Mixed ice | 9 | 59 | 32 | |

 Table 5.7 Percentages of the total amount of adsorbate which desorb during each desorption process
 according to the experimental TPD traces.

Whilst surface desorption of benzene and toluene is modelled using the multilayer desorption parameters determined in Chapter 4, which are applicable to the TPD data in this chapter as well, the desorption parameters of volcano and co-desorbing benzene and toluene have not been determined. However, these desorption events are not determined by the desorption kinetics of benzene or toluene, they are consequences of the presence of water. Therefore, they can be modelled using the desorption kinetics of ASW, in the case of volcano desorption, and CI in the case of co-desorption. The parameters for volcano and co-desorption are those determined by Fraser *et al.*²⁸, and all the desorption parameters used in the model are shown in Table 5.8.

| | | Desorption | Pre-exponential |
|----------------------|----------|-------------------------------|--|
| Molecule | Order, n | energy, E _{des} / kJ | factor, v / |
| | | mol ⁻¹ | molecules cm ⁻² s ⁻¹ |
| Benzene ^a | 0.18 | 45.5 | 10 ²⁹ |
| Toluene ^a | 0.37 | 47.6 | 10 ²⁷ |
| ASW ^b | 0.01 | 46.6 | 10 ³⁰ |
| Clp | 0.01 | 47.9 | 10 ³⁰ |

 Table 5.8 Desorption parameters derived from experimental data used in the model. ^a Determined in

 Chapter 4 and presented in Salter et al.^{117 b} Determined by Fraser et al.²⁸

The final consideration is which A and B parameters in equation (5.3) to use, that is what stellar mass is to be used in the model. In practice, any stellar mass for which the A and B parameters are known, which range from 5 M_{\odot} - 60 M_{\odot},¹³⁴ can be used. However, in order to produce models which will be of use to astronomers, relevant environments must be simulated. Benzene has been detected in CRL 618¹⁵³ and SMP LMC 11^{64,192} which are both examples of protoplanetary nebulae. These types of stellar objects are characteristic stages in the life cycle of stars of 0.8 M_{\odot} – 9 M_{\odot},⁶⁴ therefore the heating profile of a 5 M_{\odot} star has been used in the model below, where A = 4.856 × 10⁻² and B = 0.6255.¹³⁴

Figure 5.32 shows the results of the model for benzene and toluene in layered ices on CI and on ASW and in a mixed ice. Benzene or toluene make up 1% of the total ice, as discussed above. In the CI system, a single desorption event is observed for both molecules, in contrast to the three events in the ASW bearing systems. This is due to the lack of trapping of benzene and toluene by CI compared to ASW. In all cases the desorption of benzene or toluene occurs at lower temperatures than in the laboratory experiments. For the CI layered system, it is interesting to note that benzene desorbs at a slightly higher temperature than toluene, at 86.0 K compared to 85.6 K, or approximately 900 years later. This is in contrast to the laboratory experiments where toluene desorbs at higher temperatures to benzene and highlights the need to use experimental data to model suitable astronomical heating rates and timescales.



Figure 5.32 Gas-phase concentration profiles for 1% of benzene or toluene in different water ice configurations, using astrophysical timescales for a 5 M_{\odot} star.

The on ASW system and mixed ices behave broadly similarly, with small differences caused by the differences in contributions of each desorption event. In both cases, the surface desorption component occurs at around 86 K and the gas phase concentration plateaus for approximately 30 000 years, as all of the molecules on the surface have desorbed. After this time, the temperature has reached 95 K and volcano desorption

begins as the ASW to CI phase change occurs. This continues to a temperature of 104 K and, in layered and mixed ices, releases the majority of the benzene and toluene into the gas phase. This is shown in Table 5.7 and the TPD traces in Figures 5.20, 5.21, 5.27 and 5.29 where volcano desorption dominates. The final desorption step, co-desorption of CI and benzene or toluene occurs at temperatures above 104 K, reached after approximately 210 000 years in a 5 M_☉ star.

The model shows that the desorption behaviour of benzene and toluene in astrophysical ices will vary depending on their environment. Real ices will be more complex in terms of composition than the 2-component ices modelled, but it clearly illustrates the fact that the ice system will affect desorption. For example observations of gas phase benzene or toluene at a temperature of 90 K may indicate that the ice environment is made up of CI, whereas higher temperature observations may point to layered or mixed ASW ices, although these two may be hard to distinguish from one another based on the model results.

5.4 Summary and Conclusions

TPD and RAIRS experiments of benzene and toluene ices in the presence of water were performed. Three water containing ices were examined, layered benzene or toluene on CI ices, layered benzene or toluene on ASW ices and co-deposited mixed ASW/benzene or ASW/toluene ices. RAIR spectra of benzene in all water systems deposited at 25 K show band shifts compared to the spectra of pure benzene ice, indicating that there is a benzene/water interaction. This interaction has been described previously^{108,255–257} and is assigned to a benzene/water H-bond. Toluene also exhibits shifts in its RAIR spectra compared to the interaction likely to be of a similar nature to the benzene/water interaction with an added polar component due to toluene's small dipole moment.

The presence of water is shown to affect the thermal evolution of RAIR spectra compared to the pure ice system. Annealing mixed ices and layered, ASW containing ices of both benzene and toluene causes the bands which were shifted from their positions in the pure benzene or toluene ice to return to their original positions, although some asymmetry of the bands remains. This is assigned to thermally induced

segregation of the aromatic and water upon annealing the ice. In contrast, the benzene or toluene on CI ices do not show any evidence of segregation. Therefore the mobility of water during the phase change from ASW to CI upon annealing is thought to be responsible. Indeed the water/water interaction is shown to be stronger than that of aromatic/water and is hence the driving force for segregation.

In Chapter 4, the crystallisation of benzene was presented. In the presence of ASW the crystallisation of benzene is inhibited at exposures \leq 30 L_m, which is shown in the TPD to be the exposure at which the pore system saturates (as shown by the saturation of the volcano and co-desorption peaks). This, coupled with the fact that crystallisation is observed for the benzene on CI system at exposures where it is not for the on ASW system, suggests that the inhibition is physical rather than chemical in nature.

The interactions between benzene and toluene and water are shown by TPD experiments to have an effect on their desorption behaviour compared to the pure ices. Sub-monolayer coverages of benzene on CI show a decrease in peak temperature with increasing coverage as in the pure benzene ice. This is due to lateral repulsive interactions between adsorbed benzene molecules. However, the determined decrease in E_{des} for this system is less than that for the pure benzene on HOPG case, due to the benzene/water interaction competing with the repulsive interaction. For toluene on CI, the toluene/water interaction is strong enough, due to its polarity, that it overcomes the repulsive lateral interactions observed for toluene on HOPG and no decrease in desorption temperature with exposure is observed.

In the presence of ASW, either in layered or mixed systems, lateral repulsions are not shown in the TPD traces due to the roughness of the ASW surface. These systems are dominated by the desorption kinetics of water, where volcano and co-desorption are the most significant desorption events at low exposures in the layered system and in all cases in mixed ices.

Desorption parameters were determined for sub-monolayer coverages of benzene on ASW, benzene on CI and toluene on CI. Multilayer desorption parameters are the same as those determined in Chapter 4. The sub-monolayer desorption parameters determined in this chapter are shown in Table 5.9.

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| Molecule | System | Order, n | Desorption energy, | Pre-exponential |
|-----------|--------|-----------------|---|-----------------------------|
| | | | E _{des} / kJ mol ⁻¹ | factor, v / s ⁻¹ |
| Benzene _ | On Cl | 1 | 39.8 - 39.3 ± 2.5 | 10 ¹³ |
| | On ASW | 0.83 ± 0.08 | 41.7 ± 6.4 | $10^{19 \pm 2}$ |
| Toluene | On Cl | 1.11 ± 0.09 | 46.8 ± 55 | $10^{16 \pm 1}$ |

Table 5.9 Sub-monolayer desorption parameters determined in this chapter.

The TPD data presented in this chapter were used to construct astrophysically relevant desorption models of benzene and toluene containing ices composed primarily of water. The ice composition was chosen to be as representative as possible of a real astronomical ice. The model results suggested that the desorption temperature/time of benzene and toluene may be useful to distinguish between environments containing CI and ASW, but that layered and mixed ASW containing ices are harder to differentiate. In this case, the RAIRS data may be useful as subtle differences between mixed and layered ASW containing ices, particularly in the case of toluene, have been shown.

The data presented here show that the addition of the methyl group to apolar benzene to form the slightly polar toluene does affect its surface behaviour in the presence of water. Although this difference becomes small on an astronomical desorption timescale, it may be spectroscopically significant for detection of benzene and toluene in different ice environments.

6 UV/vis Spectroscopy of Benzene and Toluene Ices

This chapter presents an ultraviolet/visible (UV/vis) study of benzene and toluene ices deposited on highly oriented pyrolytic graphite (HOPG). Both amorphous and crystalline benzene ices are examined, whereas only amorphous toluene is studied. This is because toluene ice was not shown to undergo a phase change in this thesis. Clear UV/vis absorption bands are observed for both molecules and are assigned by comparison to the literature. The effect of the benzene phase change on its electronic spectrum is examined in detail, with reference to the RAIRS data shown in previous chapters. The effect of this phase change on the refractive index, *n*, of benzene is also discussed. Toluene is found to have a lower refractive index than benzene. The data presented in this chapter are of interest to the astrochemical community, as the optical parameters and electronic spectra of the molecules are shown to vary with phase.

6.1 Introduction

In Chapter 4 and in published work from this laboratory,¹¹⁷ multilayers of benzene deposited on HOPG at 25 K have been shown to undergo a phase change after annealing to 90 K. This phase change was shown by changes in the reflection absorption infrared (RAIR) spectrum of benzene upon annealing. Other authors have also observed this thermally induced phase change using vibrational spectroscopy methods. Jakob and Menzel²²¹ deposited multilayers of benzene on Ru(001) at 53 K in its amorphous form, and observed splitting of several RAIRS bands upon annealing the ice to 127 K. Specifically splitting was observed in those bands assigned to bending and stretching modes of the C-H bonds, identically to the observations in Chapter 4. Swiderek et al. also used electron energy loss spectroscopy (EELS) to show that films of benzene deposited on Pt at 32 K gave different spectra compared to films deposited at 100 K.¹⁹⁸ Specifically, vibronic bands assigned to the ${}^{3}B_{1u} \leftarrow {}^{1}A_{1g}$ transition were sharper and shifted to higher energy loss in crystalline benzene compared to amorphous ice.¹⁹⁸ Raman spectra recorded by Ishii et al. show band splitting after annealing benzene ices deposited at 17 K on gold coated copper to 58 K, indicative of crystallisation.²⁷⁵ In the same study, Ishii et al.²⁷⁵ also performed X-ray diffraction measurements, which confirmed the lack of order in the initially deposited films, and confirmed that the annealed films were fully crystalline.

As well as examining the phase change itself, several authors have found that benzene deposited at elevated temperatures forms an ordered or crystalline phase directly. When benzene is deposited at 110 K on Cu(111), an initial chemisorbed layer forms, lying flat on the surface.²²² Subsequently deposited benzene adsorbs as an almost parallel oriented physisorbed bilayer, followed by multilayers which follow the crystal structure proposed in Chapter 4.²²² This behaviour was shown by a combination of temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and near edge X-ray absorption fine structure (NEXAFS) measurements.²²² Similar results were also observed for benzene deposited at 120 K on Ru(001), shown by TPD and HREELS.²²⁰ On graphite, neutron diffraction experiments suggest that an initial, flat-lying, physisorbed monolayer forms when benzene is deposited at 100 K, followed by crystalline multilayers.²⁷⁶

The effect of the benzene phase change on the electronic spectrum of benzene ice was recently examined in detail by Dawes *et al.*¹⁸⁶ Transmission spectra were recorded for benzene deposited on a MgF₂ window at 25 K in the wavelength range 115 nm – 340 nm. Benzene was crystallised by annealing the ice deposited at 25 K to 90 K for 2 minutes and several band shifts and profile changes were observed in the spectrum.

Whilst the benzene phase change has previously been described spectroscopically, the effect of the phase change on the refractive index of benzene ices has not been examined. Indeed only one study has determined the refractive index of crystalline benzene ice. Romanescu *et al.* split the emission of a HeNe laser into two beams which were reflected off a gold substrate at different reflection angles during deposition of benzene at 100 K.⁴⁷ The period of the resulting interference fringes, and the known reflection angles, were used to determine an *n* value of 1.54 ± 0.02 for benzene ice.⁴⁷ It was assumed from the literature²⁷⁵ that the ice grown under these conditions was crystalline, although no other analytical technique was used to confirm this.⁴⁷

Toluene has not been shown to undergo any thermally induced phase change in this thesis, and only a single, amorphous form of toluene ice has been observed.

Additionally, in contrast to benzene, the UV/vis behaviour of toluene ices has not been examined. As such, the refractive index of toluene ice has never been measured. The UV/vis spectrum of toluene gas, however, has been measured by several authors.^{189,190,277} Sharp absorption bands were observed in the 243 nm – 277 nm region by Fally *et al.*,¹⁹⁰ however these were not assigned. The observations of Fally *et al.*¹⁹⁰ were in good agreement with similar UV/vis absorption experiments of toluene gas by Etzkorn *et al.*¹⁸⁹ The same features have also been observed, and assigned, by Serralheiro *et al.*²⁷⁷ They are shown by *ab initio* calculations to be of mixed valence and Rydberg nature.

Knowledge of the refractive index of an ice is useful to the astrochemical community, as it allows the interaction of ices with photons to be simulated.^{10,14} It is therefore relevant to investigate whether the local environment affects not only the structure of an ice, but also the optical parameters of the ice. If this is the case, then care must be taken to use the correct optical properties when modelling spectra from different astrophysical environments.

In light of the above, this chapter examines the differences in UV/vis reflectance spectra between amorphous and crystalline benzene ices. These data were recorded using the apparatus described in Chapter 3. The analysis method of Harrick,¹⁹⁹ detailed in Chapter 3, is applied to both systems and the variation in ice thickness, *d*, and real part of the refractive index, *n*, between the two benzene phases is discussed. Additionally, the UV/vis spectra of toluene ices have been recorded and analysed using the Harrick¹⁹⁹ method. No phase change was observed for toluene ice, therefore only amorphous toluene ices have been examined.

6.2 Experimental

The equipment and experimental procedures were presented in Chapter 2. However, dosing techniques specific to the data presented in this chapter are discussed here. Benzene and toluene are examined in their amorphous form. Additionally, crystalline benzene ices are examined. The methods which were used to produce these ices are discussed. In all experiments shown in this chapter, ices were grown *via* direct dosing, as described in Chapter 2.

Depositing benzene on HOPG at 25 K will lead to an amorphous ice. This is regardless of the dosing method used (backfilling or direct dosing). Upon annealing, benzene undergoes crystallisation, as shown by several changes in its RAIR spectrum.¹¹⁷ The ices examined in Chapter 4 were grown *via* backfilling. In order to test whether growing the thicker ices *via* direct dosing had an effect on the crystallisation of benzene, a RAIRS annealing experiment was performed for a thick ice. Figure 6.1 shows the effect of annealing on RAIR spectra of 500 L_m benzene deposited *via* direct dosing at 27 K. Figure 6.1A shows the wavenumber region 3150 cm⁻¹ – 2950 cm⁻¹ and Figure 6.1B shows the region 2050 cm⁻¹ – 950 cm⁻¹.

No bands are observed outside of the regions shown in the figure. The bands at 3090 cm^{-1} , 3032 cm^{-1} , 1479 cm^{-1} and 1036 cm^{-1} are the same as those observed in Chapters 4 and 5. These are assigned, with reference to the literature, 31,127,227 to the C-H stretch (v(CH)_{aromatic}), v(CH) combination, aromatic C-C stretch (v(CC)_{aromatic}) and C-H in plane deformation (δ (CH)_{in-plane}) modes of benzene respectively.

In addition to the bands described above, several additional features are observed in the spectra, which are also assigned by comparison to the literature.^{31,127,220,221,227} The band at 3068 cm⁻¹ is assigned to the v(CH)_{aromatic} mode of benzene. The bands at 1176 cm⁻¹ and 1148 cm⁻¹ are assigned to δ (CH)_{in-plane} modes and the band at 973 cm⁻¹ is the δ (CH)_{out of plane} mode. Tentative assignments of the bands at 1402 cm⁻¹ and 1012 cm⁻¹ are given based on their frequencies. These are assigned to v(CC)_{aromatic} and δ (CH) modes respectively. The bands at 1967 cm⁻¹ and 1824 cm⁻¹ remain unassigned. The observed bands and their assignments are shown in Table 6.1.

Of the additionally observed bands, only those at 3068 cm⁻¹, 1176 cm⁻¹, 1148 cm⁻¹ and 973 cm⁻¹ have been definitively assigned, ^{31,127,220,221,227} as shown in Table 6.1. The other bands are tentatively assigned based on their frequencies. The additionally observed bands have been previously observed in IR spectra of solid benzene.²⁷⁸ This confirms that only benzene is present on the HOPG surface in this work, and that the additional bands are a product of the ice thickness (due to the dosing method) rather than from contaminants.



Figure 6.1 RAIR spectra showing the effect of annealing on 500 L_m benzene on HOPG deposited at 27 K via direct dosing. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure.

Table 6.1 Assignments of the bands observed in the RAIR spectra of benzene shown in Figure 6.1. Values for ices grown by backfilling are from Chapter 4 and values for ices grown by direct dosing are from this chapter. Assignments are from the literature.^{31,127,220,221,227} Symbols: v = stretching, $\delta =$ deformation.^{*a*} tentative assignment.

| | Wavenumber / cm ⁻¹ | | | |
|--|-------------------------------|----------------|---------------|---------------|
| Band | Backfilling at | Backfilling at | Direct dosing | Direct Dosing |
| Assignment | 25 K | 110 K | at 27 K | at 70 K |
| v(CH) _{aromatic} | 3090 | 3091/3085 | 3090 | 3091/3085 |
| v(CH) _{aromatic} | - | - | 3068 | 3066 |
| v(CH) | | | | |
| Combination | 3034 | 3037/3030 | 3032 | 3037/3030 |
| band | | | | |
| unknown | - | - | 1967 | 1982/1975 |
| unknown | - | - | 1824 | 1840/1830 |
| v(CC) _{aromatic} | 1479 | 1479 | 1479 | 1479 |
| v(CC) _{aromatic} ^a | - | - | 1402 | 1416/1404 |
| $\delta(CH)_{in-plane}$ | - | - | 1176 | - |
| $\delta(CH)_{in-plane}$ | - | - | 1148 | 1148/1142 |
| $\delta(CH)_{in-plane}$ | 1036 | 1040/1034 | 1036 | 1040/1034 |
| δ(CH)ª | - | - | 1012 | 1011 |
| $\delta(CH)_{out of plane}$ | - | - | 973 | 987/974 |

After annealing the ice to 50 K, the combination band at 3032 cm⁻¹ shifts to 3030 cm⁻¹ and develops a shoulder at 3035 cm⁻¹. After annealing to 60 K, several more changes are apparent in the spectra, as listed in Table 6.1. These changes indicate that benzene has begun to crystallise. By an annealing temperature of 70 K, the changes in the bands are complete, as shown by spectra of the ice after annealing to temperatures > 70 K in Figure 6.1. This indicates that after annealing to 70 K, the phase change is complete. Annealing the ice to 150 K causes benzene to desorb from the HOPG surface, as shown in Figure 6.1 by the disappearance of all of the bands. The phase change observed in Figure 6.1 is confirmed as crystallisation by comparison to the observed changes in RAIRS bands

shown in Chapter 4. Table 6.1 lists the bands, and observed changes due to crystallisation, observed in Chapter 4. The bands in Figure 6.1 and their thermally induced changes match the behaviour in Chapter 4, and therefore are assigned to crystalline benzene. In all cases the annealing time was 3 minutes.

The crystallisation temperature of thick ices deposited by direct dosing is lower than that of the thinner ices deposited via backfilling. In Chapter 4, the onset of crystallisation was 90 K, compared to only 50 K in Figure 6.1. Different temperatures of crystallisation for benzene have been observed in the literature. Ishii et al.²⁷⁵ observed crystallisation of benzene films when amorphous benzene deposited at 30 K was annealed to 60 K, in agreement with the spectra in Figure 6.1. Alternatively, Dawes et al. 186 observed a phase change in benzene ice deposited at 25 K after annealing to 90 K, in agreement with the results presented in Chapter 4. Jakob and Menzel²²¹ showed that the temperature of crystallisation of benzene deposited at 45 K decreases with increasing thickness, which explains the observed results in this thesis. The reason for this difference is not clear, however it is possible that there is a difference in benzene ice morphology between the ices grown via direct dosing and backfilling which may make crystallisation more favourable in the former case. Indeed the morphology and porosity of water ice has been shown to be sensitive to deposition rate, angle and dosing method.^{25,42,43,45,46,279} Alternatively, the thicker ice may increase the chance of a crystalline nucleation point forming, making crystallisation occur at lower temperatures.

Given that benzene ices grown *via* direct dosing are shown to crystallise, further tests were performed in order to determine if it was possible to grow crystalline benzene ice directly. It was shown in Chapter 5 that water could be deposited in its CI form by depositing at 135 K. In order to dose crystalline benzene ice, a deposition temperature of 70 K was chosen as it is far below the desorption temperature of 150 K but high enough to cause crystallisation, as shown in Figure 6.1. Figure 6.2 shows RAIR spectra of 500 L_m of benzene deposited at 70 K and subsequently annealed to 80 K and 100 K. The figure is split into the same wavenumber regions as Figure 6.1 for clarity.


Figure 6.2 RAIR spectra showing the effect of annealing on 500 L_m benzene on HOPG deposited at 70 K via direct dosing. Band intensities are shown in the panels and the annealing temperature is shown on the right of the figure.

It is clear that the ice deposited at 70 K is crystalline, shown by the splitting of several bands identically to those in Figure 6.1. Upon annealing to 80 K and 100 K, where the ice is shown in Figure 6.1 to be completely crystalline, no changes in the bands are observed. This shows that 70 K is a sufficiently high deposition temperature to grow fully crystalline benzene ice.

It was shown in Chapter 5 that, whilst dosing water at an elevated temperature allowed CI to be grown directly, it did reduce the sticking probability. Therefore, a dose correction was required in order to deposit equivalent amounts of water compared to doses performed at base temperature. In order to test whether any dose correction was required when dosing benzene at 70 K, identical doses of 10 L_m were performed at base temperature and at 70 K and a TPD experiment was performed for each ice. The dose curves and TPD traces for each ice are shown in Figure 6.3.



Figure 6.3 A: dose curves for 10 L_m of benzene deposited at 29 K (red trace) and 70 K (blue trace). The dose pressure and time in each case was 1×10^{-7} mbar and 100 s respectively. B: TPD traces corresponding to the doses shown in panel A.

The ratio of the areas of the dose curves in Figure 6.1A is shown in Table 6.2 to be 0.93 (29 K to 70 K). This matches the ratio of the corresponding TPD areas, also shown in Table 6.2, and shows that the sticking probability does not change between 29 K and 70 K. Therefore no dose correction was required for benzene ices.

| Dose pressure / mbar | Dose time / s | Deposition temperature / K | Dose area / arbitrary units | Ratio of dose areas 29 K / 70 K | TPD area / arbitrary units | Ratio of TPD areas 29 K / 70 K |
|----------------------------|---------------------|----------------------------------|-----------------------------------|--|----------------------------------|---|
| 1 × 10 ⁻⁷ | 100 | 29 | 7.21 × 10 ⁹ | 0.93 | 1.96×10^{6} | 0.93 |
| 1 × 10 ⁻⁷ | 100 | 70 | 7.74 × 10 ⁹ | | 2.11 × 10 ⁶ | |

Table 6.2 Areas under the dose and TPD curves for benzene ice at different deposition temperatures.

The effect of growing toluene ices *via* direct dosing as opposed to backfilling was also examined using RAIRS. Figure 6.4 shows the RAIR spectrum of 500 L_m toluene deposited on HOPG at 27 K. Figure 6.4A shows the wavenumber region 3250 cm⁻¹ – 2650 cm⁻¹ and Figure 6.4B shows the region 1700 cm⁻¹ – 850 cm⁻¹. No bands are observed outside of these regions.

The bands shown in Figure 6.4B at 1605 cm⁻¹, 1495 cm⁻¹, 1466 cm⁻¹, 1082 cm⁻¹ and 1039 cm⁻¹ are the same as those observed in RAIR spectra shown in Chapter 4. They are assigned with reference to the literature^{228–230} to the aromatic C-C stretch (v(CC)_{aromatic}), a second v(CC)_{aromatic}, a combination of the v(CC)_{aromatic} and asymmetric methyl deformation (δ (CH₃)_{as}), the C-H in plane deformation (δ (CH)_{in-plane}) and the methyl rock (p(CH₃)) modes of toluene respectively. Some bands that were observed in Chapter 4 are shifted in the spectra of toluene ice produced by direct dosing. In Figure 6.4A these are observed at 3022 cm⁻¹ shifted from 3020 cm⁻¹ in Chapter 4, 2948 cm⁻¹ shifted from 2951 cm⁻¹ and 2912 cm⁻¹ shifted from 2915 cm⁻¹. These bands are assigned to the aromatic C-H stretch (v(CH)_{aromatic}), asymmetric methyl stretch (v(CH₃)_{as}) and symmetric methyl stretch (v(CH₃)_s) modes of toluene respectively.^{228–230}

As is the case for benzene, several additional bands are observed in Figure 6.4 compared to the RAIR spectra of toluene in Chapter 4. These are at 3083 cm⁻¹ and 2850 cm⁻¹ in Figure 6.4A, and 1377 cm⁻¹, 1178 cm⁻¹ and 900 cm⁻¹ in Figure 6.4B. Both bands in Figure 6.4A are assigned to v(CH₃)_{as} modes of toluene.²²⁹ The bands observed in Figure 6.4B are assigned to the symmetric methyl deformation (δ (CH₃)_s) mode at 1377 cm⁻¹, ²²⁸ the δ (CH) mode²²⁸ at 1178 cm⁻¹ and the v(CC)_{aromatic} mode at 900 cm⁻¹.²²⁹ The bands and their assignments are shown in Table 6.3. No annealing experiments were performed on toluene ices grown *via* direct dosing, as no phase change was observed in Chapter 4.



Figure 6.4 RAIR spectrum of 500 L_m toluene on HOPG deposited at 27 K via direct dosing. Band intensities are shown in the panels. Dotted lines are included as guides and their positions are shown on the figure.

Table 6.3 Assignments of the bands observed in the RAIR spectra of toluene shown in Figure 6.4. Values for ices grown by backfilling are from Chapter 4 and values for ices grown by direct dosing are from this chapter. Assignments are from the literature.^{228–230} Symbols: v = stretching, δ = deformation, ρ = rocking, as = asymmetric and s = symmetric.

| Pond accignment | Wavenumber / cm ⁻¹ | | | |
|--|-------------------------------|-----------------------|--|--|
| Banu assignment | Backfilling at 25 K | Direct dosing at 27 K | | |
| v(CH ₃) _{as} | - | 3083 | | |
| v(CH) _{aromatic} | 3020 | 3022 | | |
| v(CH ₃) _{as} | 2951 | 2948 | | |
| v(CH ₃)s | 2915 | 2912 | | |
| v(CH ₃) _{as} | - | 2850 | | |
| v(CC) _{aromatic} | 1605 | 1605 | | |
| v(CC) _{aromatic} | 1495 | 1495 | | |
| v(CC) _{aromatic} and δ(CH ₃) _{as} combination | 1466 | 1466 | | |
| δ(CH ₃)s | - | 1377 | | |
| δ(CH) | - | 1178 | | |
| δ(CH) _{in-plane} | 1082 | 1082 | | |
| ρ(СН₃) | 1039 | 1039 | | |
| v(CC)aromatic | - | 900 | | |

6.3 Results and Discussion

6.3.1 Amorphous and Crystalline Benzene Ices

Figure 6.5 shows UV/vis reflectance spectra of amorphous benzene at two exposures and for different reflection angles. Figure 6.5A shows spectra for an exposure of 200 L_m and Figure 6.6B for an exposure of 400 L_m . As for the data shown in Chapter 3, increasing the exposure (and hence thickness) of the benzene causes the number of fringes observed to increase. These fringes are seen to shift in terms of the position of the maxima/minima with changing reflection angle. In all of the spectra in Figure 6.5, sharp absorption features are also present. These are seen at 214 nm, with several peaks also centred at approximately 255 nm. These absorption bands have been observed previously^{186,188–190,196–198} and are assigned to the ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ and ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transitions respectively. The absorption bands do not shift with reflection angle, as expected.



Figure 6.5 UV/vis reflectance spectra of amorphous benzene on HOPG deposited at 25 K at two reflection angles. A: exposure of 200 L_m. B: exposure of 400 L_m. The reflection angle is indicated on the figure.

Figure 6.6 shows UV/vis reflectance spectra of crystalline benzene at two exposures and for different reflection angles. Figure 6.6A shows spectra from an exposure of 250 L_m and Figure 6.5B from an exposure of 450 L_m . Similarly to the case of amorphous benzene ice shown in Figure 6.5, increasing the exposure increases the number of fringes observed in the spectrum. Additionally, the extrema of the fringes shift in position with reflection angle, as for the amorphous ice.

Whilst there are similarities between the amorphous and crystalline UV/vis reflectance spectra, as described and shown in Figures 6.5 and 6.6, there are differences in the absorption region between 200 nm and 300 nm. Figure 6.7 shows UV/vis reflectance spectra of 400 L_m amorphous and crystalline benzene at a reflection angle of 46° in the wavelength range 190 nm – 230 nm. This region contains the ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ transition of benzene.^{186,189,190,196,197}



Figure 6.6 UV/vis reflectance spectra of crystalline benzene on HOPG deposited at 70 K at two reflection angles. A: exposure of 250 L_m. B: exposure of 450 L_m. The reflection angle is indicated on the figure.



Figure 6.7 UV/vis reflectance spectra of amorphous (red trace) and crystalline (blue trace) benzene on HOPG in the wavelength range 190 nm – 230 nm. In each case the benzene exposure is 400 L_m and the reflection angle is 46°.

In the amorphous benzene spectrum in Figure 6.7 (red trace), the band is observed as a broad peak with maximum intensity at 214.8 nm. In the crystalline spectrum (blue trace) the intensity of the feature is lost, although a small feature is apparent at 201.5 nm. Work by Dawes *et al.*^{186,257} has shown that the bands arising from the ¹B_{1u} \leftarrow ¹A_{1g} transition red shift upon crystallisation by approximately 1 nm, suggesting that the feature at 201.5 nm observed in Figure 6.7 is not the blue shifted ¹B_{1u} \leftarrow ¹A_{1g} band of crystalline benzene, and is instead an artefact in the spectrum. The reason for the disappearance of the ¹B_{1u} \leftarrow ¹A_{1g} band upon crystallisation is unclear. However, it should be noted that the intensity of the reflected light below approximately 220 nm is very low, as shown in Figure 3.8, which may affect the clarity of the spectra below this wavelength. The difference in absorption behaviour in the different phases of benzene ice is more clearly demonstrated by examining the ¹B_{2u} \leftarrow ¹A_{1g} band, centred at around 255 nm. Figure 6.8 shows UV/vis spectra of the same ices as those in Figure 6.7, *i.e.* 400 Lm exposure of both amorphous and crystalline benzene at a reflection angle of 46°, in the wavelength range 230 nm – 280 nm.



Figure 6.8 UV/vis reflectance spectra of amorphous (red trace) and crystalline (blue trace) benzene on HOPG in the wavelength range 230 nm – 280 nm. In each case the benzene exposure is 400 L_m and the reflection angle is 46°.

It is clear from Figure 6.8 that the absorptions due to the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transition change upon crystallisation of benzene. The position of the peaks in the crystalline benzene spectrum (blue trace) are blue shifted compared to the amorphous spectrum (red trace) by 0.7 nm. Additionally, the bands are sharpened in the crystalline spectrum. The full width at half maximum (FWHM) of the central band at approximately 255 nm is 2.63 nm in the amorphous spectrum, compared to 1.94 nm in the crystalline spectrum. The sharpening and blue shift of the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ bands in crystalline benzene is in excellent agreement with work by Dawes *et al.*¹⁸⁶ The positions of the peaks in amorphous and crystalline benzene ice are shown in Table 6.4, alongside the observations of Dawes *et al.*¹⁸⁶ which are also shown in Figure 3.13.

| Band position in | n this work / nm | Band position observed by Dawes <i>et</i> <i>al</i> . ¹⁸⁶ / nm | | |
|-----------------------|------------------|--|-------------|--|
| Amorphous Crystalline | | Amorphous | Crystalline | |
| benzene ice | benzene ice | benzene ice | benzene ice | |
| 244.0 | 243.3 | 244.15 | 243.25 | |
| 249.4 | 248.7 | 249.80 | 248.85 | |
| 255.5 | 254.7 | 255.65 | 254.65 | |
| 261.5 | 260.9 | 261.60 | 260.80 | |
| 265.5 | 264.3 | 265.65 | 264.45 | |

Table 6.4 Band positions of the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transition in amorphous and crystalline benzene ice in this work and observed by Dawes et al.¹⁸⁶

The sharpening of the bands upon crystallisation is explained by the fact that they are vibronic bands of the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transition. That is, the electronic ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transition is accompanied by a change in vibrational energy level as a consequence of the Franck-Condon principle. The different vibrational transitions which occur, from the distribution of initial vibrational levels in the electronic ground state, give different vibronic bands. Sharpening of a vibrational band upon crystallisation is explained by the range of molecular orientations in an amorphous ice. This random orientation means that the frequency of a vibrational mode is spread over a range of energies due to cancelling out and enhancement to varying degrees. In crystalline benzene, the oscillations become

aligned and hence the band becomes sharper. The fact that sharpening of the vibronic structure of the UV/vis spectrum of crystalline benzene ice is observed when compared to the amorphous ice is in excellent agreement with RAIRS data for the two systems shown in Chapter 4. This highlights the usefulness of the novel UV/vis apparatus described in this thesis as an analytical tool, as it allows a wider range of information to be determined from interstellar ice analogues.

The analysis method of Harrick,¹⁹⁹ presented in Chapter 3, was used to determine the real part of the refractive index, n, and the thickness of amorphous and crystalline benzene ices. Figure 6.9 shows the calculated values of n as a function of benzene exposure deposited at 70 K. Individual values of n for each dose are the mean of all the values that arise from comparing all the reflection angles, plus repeats. All the values are consistent within error and give a mean value of $n = 1.63 \pm 0.08$. This value is in reasonable agreement with a value of 1.54 ± 0.02 determined by Romanescu *et al.*⁴⁷ for benzene deposited at 100 K on gold under high vacuum conditions.



Figure 6.9 *Refractive index n as a function of dose for crystalline benzene on HOPG deposited at 70 K, as determined by equation (3.6).*

The value of 1.63 \pm 0.08 for the real part of the refractive index of crystalline benzene ice is higher than that of amorphous benzene, which was found to be 1.43 \pm 0.07 in Chapter 3. This suggests that impinging light from a vacuum is slowed more upon entering a crystalline benzene medium than an amorphous one. Similar behaviour has been observed for germanium selenide, with the crystalline form having a higher refractive index than the amorphous form.²⁸⁰

Given that amorphous and crystalline benzene have been shown to have different spectroscopic behaviour, it is not necessarily surprising that their refractive indices will differ. However the reason for the change in *n* must be examined. This change can be rationalised by considering the concept of the optical impedance, *Z*, of a medium. The concept of optical impedance was proposed by Kronig²⁸¹ (of the Kramers-Kronig relation). Optical impedance is defined as the ratio of the amplitudes of the perpendicular wave vectors in a propagating light wave, *i.e.* the ratio of the electronic wave vector, *E*, to the magnetic wave vector, *H*, and is shown in equation (6.1).^{281,282}

$$z = \left|\frac{E}{H}\right| = \sqrt{\frac{\mu}{\epsilon}}$$
(6.1)

Also shown in equation (6.1) is the relation between impedance and the permeability, μ , and dielectric constant, ε , of a medium.²⁸² In the case of non-magnetic media, such as benzene, $\mu = 1$ and hence $Z \propto \varepsilon^{-1/2}$.²⁸²

In its amorphous form, benzene molecules are randomly aligned and hence the electronic environment is disordered. That is, the electron cloud of each benzene molecule is randomly aligned compared to its neighbours. Crystalline benzene, the structure of which is shown in Chapter 4, consists of aligned benzene molecules in a herringbone structure. Therefore there is a difference in the electronic environment in the ice, as shown in Figure 6.8 where the UV/vis spectra of amorphous and crystalline benzene are shown to be different. This will cause the dielectric constant, and hence impedance, of the material to change. It is therefore necessary to link *n* and *Z* to explain the difference in refractive index between amorphous and crystalline benzene. This is done by considering that *n* is shown to vary with $\varepsilon^{1/2} \cdot 2.282}$ Therefore $n \propto 1/Z$, hence a change in impedance must be accompanied by a change in refractive index.

In the case of benzene, the refractive index of crystalline ice is higher than that of amorphous ice, 1.63 ± 0.08 compared to 1.43 ± 0.07 . This implies that *Z* is lower for crystalline benzene ice than for amorphous ice, and subsequently that the dielectric constant, ε , of the crystalline ice is higher than for amorphous ice, as shown in equation (6.1). Indeed, crystalline materials have been shown to have higher values of ε than their amorphous counterparts.^{280,283–285} Therefore the above explanation is reasonable.

As well as n, d can also be determined from the UV/vis spectra shown in Figures 6.5 and 6.6 using equation (3.7). In Chapter 3, the thickness of amorphous benzene ice was shown to vary linearly with dose and the thickness values are shown in Table 6.5 below. Identical analysis was performed on the crystalline benzene ices and the determined d values are also shown in Table 6.5. Each thickness value is the mean of the values determined for each reflection angle at a single dose, plus repeats, and errors are determined using the upper and lower values of n.

| | Ice thickness / nm | | | |
|-----------------------|--------------------|---------------------|--|--|
| Dose / L _m | Amorphous benzene | Crystalline benzene | | |
| 100 | 127 ± 2 | 96 ± 2 | | |
| 150 | - | 159 ± 3 | | |
| 200 | 219 ± 4 | 171 ± 3 | | |
| 250 | 261 ± 5 | 193 ± 3 | | |
| 350 | 404 ± 11 | 315 ± 6 | | |
| 400 | 401 ± 7 | - | | |
| 450 | - | 409 ± 7 | | |
| 500 | 485 ± 9 | 359 ± 6 | | |

 Table 6.5 Mean thicknesses of amorphous and crystalline benzene ices for the examined doses according to equation (3.7).

From the values shown in Table 6.5 it is clear that, for equivalent benzene exposures, amorphous ices are thicker than crystalline ices. The difference in thickness between amorphous and crystalline ices can be expressed as a compaction factor, which is

calculated from Figure 6.10. Figure 6.10 shows the values of d for amorphous and crystalline benzene plotted as a function of benzene exposure.



Figure 6.10 Thickness of benzene ice as a function of benzene exposure as determined by equation (3.7). Black squares: amorphous benzene. Red circles: crystalline benzene. The lines represent weighted least squares linear fits to each set of data with a fixed intercept of 0.

Each set of data in Figure 6.10 is fitted with a weighted least squares linear fit, shown by the lines on the plot. The weighting is given by the error values shown in Table 6.5. The intercept of each plot is fixed at 0, as with an exposure of 0 L_m the ice thickness must be 0 nm. The compaction factor is the ratio of the gradients of the linear fits to each set of data and for benzene is found to be equal to 1.35 for amorphous to crystalline benzene ices. This means that an amorphous benzene ice is 1.35 times thicker than a crystalline ice of the same amount of benzene. Alternatively, amorphous benzene ice compacts to 0.74 times (1/1.35) its original thickness upon crystallisation. This compaction factor indicates that crystalline benzene ice is denser than amorphous benzene ices in this work is not known. For example, it is not clear if this compaction is only due to decreasing intermolecular distances in the ice or if amorphous ice is porous and the

compaction is due to the collapse of the pore network. Further work using volatile molecules as tracers for porosity and compaction would be useful in determining the morphology of amorphous benzene ice. This has been employed previously using CO₂ or N₂ to examine porosity and trapping in water ice deposited at different temperatures and deposition rates.^{42,43,45,46} Additionally, scattering techniques using neutrons, X-rays or electrons may be employed to gain structural information of the amorphous ice.

6.3.2 Amorphous Toluene Ice

Figure 6.11 shows the UV/vis reflectance spectra of toluene at two exposures and for different reflection angles. Figure 6.11A shows spectra for an exposure of 200 L_m and Figure 6.11B shows spectra for an exposure of 500 L_m . As for the benzene ice spectra, the higher exposure spectra exhibit more interference fringes than the lower exposure spectra. Additionally, the extrema of the fringes are seen to shift with reflection angle. Sharp absorption features are also present around 260 nm. A further possible absorption feature is seen at 222 nm. These features do not shift with exposure or reflection angle, as expected.



Figure 6.11 UV/vis reflectance spectra of amorphous toluene on HOPG deposited at 27 K at two reflection angles. A: an exposure of 200 L_m. B: an exposure of 500 L_m. The reflection angle is indicated on the figure.

Figure 6.12 shows a UV/vis spectrum of toluene focussed on the absorption region between 210 nm and 280 nm. The features are labelled on the figure. The lower energy bands are assigned to the $S_1 \leftarrow S_0$ ($\pi^* \leftarrow \pi$) transition by comparison to the literature.^{189,277,286} The bands observed in Figure 6.12 are shown alongside those observed in previous work in Table 6.6.



Figure 6.12 UV/vis reflectance spectrum of amorphous toluene on HOPG in the wavelength range 210 nm – 280 nm. The toluene exposure is 600 Lm and the reflection angle is 53°.

The lowest energy transition in this work is observed at a wavelength of 269.2 nm which is red shifted compared to the literature, as shown in Table 6.6. The other bands in this work are red shifted compared to the work of Serralheiro *et al.*²⁷⁷ but are similar energies to those observed by Koban *et al.*²⁸⁶ The red shift compared to Serralheiro *et al.*²⁷⁷ is explained by the fact that this work was conducted on toluene ices, whereas theirs was on gaseous toluene. Dawes *et al.*¹⁸⁶ showed that red shifts occur in UV bands of ices compared to their gas phase spectra for benzene (Figure 3.13), and this is likely to be the case for toluene. Koban *et al.*²⁸⁶ also studied toluene vapour, but at a lower resolution (approximately 75% lower) than Serralheiro *et al.*²⁷⁷ which may explain the

discrepancy in band position. The bands observed by Serralheiro *et al.*²⁷⁷ are shown in Figure 6.13 for reference.

Table 6.6 Band positions of the $S_1 \leftarrow S_0$ ($\pi^* \leftarrow \pi$) transition in amorphous toluene ice in this work and inthe literature. 189,277,286

| Band position / nm | | | | |
|--------------------|---------------------------------------|------------------------------------|-----------------------------------|--|
| This work | Etzkorn <i>et al</i> . ¹⁸⁹ | Koban <i>et al.</i> ²⁸⁶ | Serralheiro et al. ²⁷⁷ | |
| 269.2 | 266.6 | 266.8 | 265.0 | |
| 262.8 | - | 263.0 | 262.2 | |
| 256.4 | - | 260.3 | 255.8 | |



Figure 6.13 UV spectrum of gaseous toluene recorded by Serralheiro et al.²⁷⁷

One possible reason for the red shift of toluene bands in ices compared to the gas phase is that these bands have been shown by *ab initio* calculations to have mixed valence (HOMO - LUMO) and Rydberg state character in the gas phase.²⁷⁷ Dawes *et al.*¹⁸⁶ showed that, for benzene, observed Rydberg states in the gas-phase were suppressed in spectra of benzene ices. It is possible therefore, that in an ice, the Rydberg states of toluene are supressed and the Rydberg character of the transitions is lost, leading to a change in energy.

The high energy feature at 222.0 nm has been tentatively assigned to the $S_2 \leftarrow S_0$ ($\pi^* \leftarrow \pi$) transition of toluene. Serralheiro *et al.*²⁷⁷ observe the feature centred at 202 nm but with vibronic structure extending to approximately 212 nm. The red shift of 10 nm is larger than expected compared to the shifts observed in Table 6.6. Additionally, the reflection intensity at this wavelength is low. Because of these two factors, the band is not definitively assigned.

The analysis method of Harrick¹⁹⁹ was applied to the toluene UV/vis spectra in order to determine *n* and *d* for the ices. No thermal effects were examined in the case of toluene, as toluene was not shown to undergo any significant thermal rearrangement in Chapter 4, according to RAIRS annealing experiments. Figure 6.14 shows the determined *n* values of toluene as a function of dose.



Figure 6.14 *Refractive index n as a function of dose for amorphous toluene on HOPG deposited at 27 K, as determined by equation (3.6).*

The value is not seen to vary within error as a function of toluene dose, and the average value is found to be $n = 1.36 \pm 0.07$. This is the first time that the refractive index of toluene ice has been measured. The value differs from the refractive index of liquid toluene, determined to by 1.4942 by Martínez-Reina *et al.*²⁸⁷ This also reinforces the

importance of accurately determining the refractive index of ices under astronomically relevant conditions.

The refractive index of amorphous toluene is lower than that of amorphous benzene, 1.43 ± 0.07 . According to the above discussion, this implies that the optical impedance of toluene ice is greater than that of benzene and that the dielectric constant of toluene is therefore lower than for benzene. No literature value of the dielectric constant of either ice has been found, therefore this cannot be confirmed.

The determined value of n of 1.36 ± 0.07 was used to determine the thickness of toluene ices. Unlike benzene, no phase change of toluene has been observed in this work and therefore a compaction factor is not determined. Figure 6.15 shows the thickness of toluene ice as a function of exposure in L_m.





As expected, and as for amorphous and crystalline benzene, the relation between thickness and dose is linear. This is shown by a weighted least squares fit to the data with a fixed intercept of 0.

6.4 Summary and Conclusions

The UV/vis reflectance spectra of amorphous and crystalline benzene and amorphous toluene have been measured. The previously observed absorption features due to the $^{1}B_{1u} \leftarrow {}^{1}A_{1g} \text{ and } {}^{1}B_{2u} \leftarrow {}^{1}A_{1g} \text{ electronic transitions of benzene} {}^{186,188-190,196-198} \text{ are shown}$ to vary between the two benzene phases. The band due to the ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ transition at 214.8 nm is shown to disappear in the spectrum of crystalline benzene ice. Conversely, the vibronic structure bands of the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transition sharpen in the spectrum of crystalline benzene compared to the amorphous ice. This sharpening is accompanied by a blue shift of approximately 1 nm. Both of these observations are in excellent agreement with the recent work of Dawes et al.¹⁸⁶ The sharpening of the bands is related to the ordering of the individual benzene molecules within the ice in their crystalline form compared to the amorphous form, analogous to the sharpening and splitting of bands observed in the RAIR spectra of benzene ices. This directly comparable and complementary data from RAIRS and UV/vis data highlights the usefulness of the newly installed UV/vis reflection absorption spectroscopy apparatus. Toluene ices in this thesis do not undergo a phase change, and as such only spectra of amorphous ices were examined. These spectra also showed clear absorption features. The features around 260 nm have been assigned to the $S_1 \leftarrow S_0$ ($\pi^* \leftarrow \pi$) transitions.^{189,277,286} They are shown to red shift compared to previous observations of gas phase toluene, possibly due to a loss of Rydberg state character.²⁷⁷ The band at 222.0 nm is tentatively assigned to the $S_2 \leftarrow S_0 \ (\pi^* \leftarrow \pi) \ transition.$

The change in the electronic spectra between crystalline and amorphous benzene ices is also accompanied by a change in refractive index. Using the method of Harrick, ¹⁹⁹ the real part of the refractive index, n, was determined for both amorphous and crystalline benzene ices. For amorphous benzene $n = 1.43 \pm 0.07$ and for crystalline benzene $n = 1.63 \pm 0.08$. The difference in refractive index can be explained by a change in the electronic environment of the crystalline ice due to the ordered herringbone structure of crystalline benzene shown in Chapter 4. This change in electronic structure will change the optical impedance of the ice, which is related to the refractive index *via* the dielectric constant of the medium. For amorphous toluene ice, $n = 1.36 \pm 0.07$. This is the first measurement of the refractive index of toluene ice. The value is lower than for

amorphous benzene, which suggests that toluene ice has a lower dielectric constant than that of benzene. However no measurements of the electronic properties of amorphous toluene or benzene ices have been made, therefore this is not confirmed by the literature.

As well as optical differences, the thickness of amorphous and crystalline benzene ices have been shown to differ. Amorphous benzene ice is found to be 1.3 times as thick as an equivalent exposure of crystalline benzene, according to the Harrick analysis method.¹⁹⁹ This indicates that the amorphous ice is less dense than the crystalline ice, however it does not take into account any porosity of the benzene ice. Further work using volatile tracer molecules may be used to determine if this is an important affect for benzene ices. It is also shown in section 6.2 that this compaction must only be due to the crystalline ice, the sticking probability is unchanged compared to dosing at base temperature. The thickness of toluene ice is shown to vary linearly with exposure, as expected and in line with the data shown in Chapter 3.

The data presented in this chapter are of importance to the astrochemical community. It has been shown that the spectroscopic and optical properties of benzene ice are dependent on its phase. It has been shown in this thesis that the phase of benzene present is a temperature dependent effect, with the crystalline phase requiring higher temperatures to form than the amorphous form. In an astrochemical environment, the local temperature will therefore dictate the phase of the benzene ice present and the optical parameters determined in this chapter will allow the correct phase to be modelled. Additionally, the UV/vis absorption bands of toluene ice have been shown to vary from spectra of gaseous toluene, which may be used to determine the phase of toluene in space.

7 RAIRS and UV/vis Spectroscopy of Methyl Formate and Water Ices

The data presented in this chapter were collected under the supervision of the thesis author by Rebecca Bond and Victoria Geddis, who completed their MChem projects in this laboratory. The analysis was performed by the author who also produced all of the figures.

This chapter presents a reflection absorption infrared spectroscopy (RAIRS) and ultraviolet/visible (UV/vis) spectroscopy study of ices of methyl formate (HC(O)OCH₃) and water. Initially, single component ices of each species are examined in order to characterise their structure, thermal behaviour and refractive index. Subsequently, mixed ices of methyl formate and water were examined and compared to the pure ices. Previously, the refractive index of a mixed ice has been assumed to be equal to a weighted average of the refractive indices of the ice components. This chapter examines this assumption.

7.1 Introduction

As an example of an interstellar complex organic molecule (COM, molecules containing > 6 atoms),¹⁵⁷ methyl formate has received considerable attention in the literature. It was first detected in 1975 in the dense molecular cloud Sagittarius B2 (Sgr B2).¹⁵⁶ Since then, it has been detected in several astrophysical environments, including hot cores²⁸⁸ and protoplanetary nebulae.¹⁹¹ It has also been detected in comets.²⁸⁹ Due to its observed abundance, which cannot be reproduced using gas phase chemistry alone, its formation on surfaces has been the focus of many ice analogue studies.^{39,110,290–292} Modelling the formation of methyl formate in regions of dense molecular clouds undergoing warming suggests that gas-phase and grain surface chemistry are coupled in its formation.^{290,292} Combination of HCO and CH₃O radicals in ices lead to adsorbed methyl formate recombination reactions lead to methyl formate.²⁹² The proposed formation in the models is supported by experimental studies. Irradiation of ices of pure methanol and binary methanol/carbon monoxide ices with electrons has been shown to produce

methyl formate *via* radical mechanisms.^{110,291} The thermal processing of methyl formate ice adsorbed on HOPG at 20 K has shown that it undergoes structural rearrangement after annealing to 95 K, as shown by RAIRS.²³³ There is disagreement in the literature as to the nature of this structural change. Burke *et al*.²³³ suggest that it is not due to methyl formate crystallisation, but an ordering, possibly as a consequence of a glass transition. Bertin *et al*.²⁹³ however, assign a change in the RAIR spectrum at 115 K to crystallisation, by comparison with spectra of polycrystalline solid methyl formate samples.²⁹⁴

Despite its importance, only a single value of the refractive index of methyl formate ice has been reported. This value was determined from the interference fringes produced by reflecting a He-Ne laser off a silicon substrate during the deposition of the ice at 16 K and is given as n = 1.30.¹¹⁰ This value differs from that for methyl formate under ambient conditions, 1.3412,²⁹⁵ and highlights the need to directly measure the optical parameters of interstellar ices.

Whilst examining methyl formate ices alone is useful to benchmark its behaviour and spectra, pure methyl formate ices are astronomically unlikely. Therefore it is also important to examine the adsorption and optical properties of multi-component ices, in particular in the presence of water. Sgr B2 is known to be water rich,²⁹⁶ and water is known to dominate cometary ices.²⁹⁷ Therefore the icy mantles within regions known to contain methyl formate will likely be water dominated.

Before examining mixed ices, it is also necessary to examine pure water ices as a benchmark. Water, due to its importance in the interstellar medium, has received a lot of experimental attention. In particular, the structure and morphology of water ice have been examined and shown to be sensitive to the deposition method and temperature.^{42–45,141,298} Amorphous solid water, ASW, is known to exist in porous and compact forms.^{42–44,298} Depositing by backfilling produces ASW which is more porous than that produced by direct deposition.^{43,44,298} At temperatures above approximately 130 K, water ice becomes crystalline and non-porous.^{25,28,298}

The refractive index, n, of water ice has also been examined previously. Dohnálek *et al.*⁴⁴ measured n for both ASW and crystalline ice (CI) using interference fringes produced by reflecting a He-Ne laser off the substrate during deposition of the water ice. The

refractive index of ASW and CI was found to be identical, at 1.285 \pm 0.01.⁴⁴ This is in agreement with the work of Westley *et al.*,¹⁴⁰ who showed that *n* did not vary with the deposition temperature of water between 30 K and 140 K. More recently, the wavelength dependent real part of the refractive index of ASW has been determined by Kofman *et al.*¹³⁶ and was found to range from approximately 1.43 – 1.26 in the wavelength range from 250 nm – 750 nm.

It is important to measure the optical parameters of pure ices in order to examine the bearing they have, if any, on the refractive index of mixed ices. Elsila *et al.*¹⁵ used a weighted average of the refractive indices of ice components to give the overall refractive index of a mixed ice. However Mukai and Krätschmer³⁶ suggested that using the refractive index of the ice components to predict the refractive index of a mixed ice is not valid. They concluded that interactions between constituents will affect the ice optical parameters.³⁶ Therefore only the refractive index of non-interacting mixed ices could be predicted from the refractive indices of its constituents.

Burke *et al.*²⁷⁰ have shown that, in mixed ices, methyl formate and water interact. This interaction is shown by shifts and changes in the profile of C=O and C-O associated bands in RAIR spectra. However, little effect is observed on the water bands due to the presence of methyl formate, indicating that the interaction is relatively weak. Given this interaction, and in order to examine the assumption of Elsila *et al.*¹⁵, mixed ices of methyl formate and water have been examined by RAIRS and UV/vis spectroscopy. Pure ices consisting of amorphous and crystalline phases of methyl formate and water have also been examined. These are used to characterise the behaviour of the molecules on HOPG and to compare to mixed ices. The refractive indices of the ices have been measured, using the UV/vis apparatus described in Chapter 3. These refractive indices are compared to those of the pure ices in order to test whether using a weighted average value is appropriate.

7.2 Experimental

The experimental equipment and procedures were detailed in Chapter 2. In all cases in this chapter, ices were grown *via* direct dosing. Crystalline and amorphous ices of both methyl formate and water were formed and the details of their characterisation by

RAIRS are discussed in sections 7.3.1 and 7.3.2 respectively. Briefly, amorphous water and methyl formate ices were grown by depositing the molecules at base temperature. Crystalline ices were grown by depositing at elevated temperatures. In order to grow CI, the deposition temperature was 135 K, with a correction factor of 1.08 applied to the dose time to account for the reduced sticking probability at higher temperature. This is lower than that determined in Chapter 5, which was 1.28. This is because the ices in Chapter 5 were grown *via* backfilling. Crystalline methyl formate was grown by depositing at 105 K, with a sticking probability correction factor of 1.06 applied to the dose time.

As well as pure ices, mixed ices were also examined in this chapter. The total exposure in L_m was kept constant whilst the proportions of methyl formate and water were changed. The method of varying the amount of both components whilst keeping the total ice dose constant was chosen to keep the gas load on the UHV chamber low when cleaning the surface, as thick ices were deposited *via* direct dosing. In all mixed ices described in this chapter, the total dose was 200 L_m. In order to successfully grow an ice of the desired proportion, calibration doses were performed to determine the QMS sensitivity ratio, *S*. This was determined by performing identical doses of water and methyl formate. An example of doses of 20 L_m of methyl formate and water is shown in Figure 7.1. The value of *S* was found to be 5.98 for the ratio of water to methyl formate.



Figure 7.1 Calibration doses of 20 L_m of water (black trace) and methyl formate (blue trace). The dose pressure and time for both molecules was 2×10^{-7} mbar and 100 s respectively.

This *S* value was used to grow ices of the desired composition. Water was introduced into the chamber to the desired pressure, and the second component (methyl formate) was then introduced up to a target QMS intensity value, I_{target} . Equation (7.1) is employed to determine the value of I_{target} .

$$I_{\text{target}} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{MF}}} \times \frac{I_{\text{H}_2\text{O}}}{S}$$
(7.1)

In equation (7.1), P_{H_2O} and P_{MF} are the proportions of water and methyl formate in the ice, I_{H_2O} is the QMS intensity of water at the chosen dose pressure and *S* is the QMS sensitivity ratio. As in Chapter 5, a correction factor, *C*, is applied to account for the practical consequence of operating both leak valves simultaneously which leads to a lower than expected proportion of methyl formate in the ice. Therefore equation (7.1) becomes equation (7.2).

$$I_{\text{target}} = \left(\frac{P_{H_2O}}{P_{MF}} \times \frac{I_{H_2O}}{S}\right) \times C \quad (7.2)$$

In this case C = 1.07. An additional consequence of varying the amount of both components to keep the total dose constant is that the dose time must be varied depending on the overall composition. For example, dosing 200 L_m of a 50% methyl formate/water mixed ice, requires half the time compared to dosing 200 L_m of a pure ice, because 100 L_m of each component are dosed simultaneously. Table 7.1 shows the dosing conditions for ices of a range of compositions with the same total dose of 200 L_m.

 Table 7.1 Dosing conditions for mixed methyl formate/water ices of different compositions. ^a For this

 dose the pressure is of methyl formate.

| Methyl Formate % | Water % | Water dose pressure / mbar | Total dose time / seconds | Water dose / L _m | Methyl formate dose / L _m |
|---------------------|---------|----------------------------------|---------------------------------|--------------------------------|--|
| 0 | 100 | | 1000 | 200 | 0 |
| 25 | 75 | | 750 | 150 | 50 |
| 50 | 50 | 2 × 10 ⁻⁷ | 500 | 100 | 100 |
| 75 | 25 | | 250 | 50 | 150 |
| 0 ^a | 100 | | 1000 | 0 | 200 |

7.3 Results and Discussion

Initially, experiments were performed to examine the adsorption behaviour of pure methyl formate and pure water. RAIRS was used to examine the structure and behaviour of the ices in their amorphous and crystalline forms, and UV/vis spectroscopy was used to determine the optical parameters of these ices. These data were then used to compare with the data for mixed ices.

7.3.1 RAIRS and UV/vis Spectra of Methyl Formate Ice

Methyl formate is known to undergo a thermally induced phase change,^{233,293} although there is some debate about the exact nature of this change, with varying results presented in the literature. Therefore, in order to determine the nature of the ices examined by UV/vis spectroscopy, the thermal behaviour of methyl formate ices was examined by RAIRS.

Figure 7.2 shows the effect of annealing on the RAIR spectra of $300 L_m$ of methyl formate deposited at 27 K on HOPG. For all exposures, the annealing behaviour is the same and $300 L_m$ data is presented as a representative example. Assignments have been made by comparison with the literature.^{110,233,285,299–302} Figure 7.2A shows the wavenumber region from 3500 cm⁻¹ – 2500 cm⁻¹ and Figure 7.2B shows the region from 1900 cm⁻¹ – 850 cm⁻¹ for clarity. No bands outside of these regions are observed.

In Figure 7.2A, six bands are observed. At 27 K the band at 3412 cm⁻¹ is assigned as an overtone of the C=O stretching mode, v(C=O)_{OT}.³⁰² Whilst overtones are typically weak, the thickness of the methyl formate ice in this case allows the band to be observed with appreciable intensity. The band at 3010 cm⁻¹, with a shoulder at 3037 cm⁻¹, is assigned to the asymmetric CH₃ stretching mode, v(CH₃)_{as} and that at 2960 cm⁻¹ is a C-H stretch, v(C-H).^{110,233,285,299–302} The bands at 2845 cm⁻¹ and 2594 cm⁻¹ have not been assigned in the literature. However, given their positions they are tentatively assigned to the overtones of the CH₃ symmetric deformation, δ (CH₃)_s, and C-O stretching modes, v(C-O), respectively. This is because they are located at approximately twice the frequencies of these two bands, as shown in Table 7.2.



Figure 7.2 RAIR spectra showing the effect of annealing on 300 L_m of methyl formate deposited on HOPG at 27 K. The annealing temperature is shown on the right of the

Table 7.2 RAIRS bands of methyl formate observed in this work using several deposition temperatures. Assignments are made by comparison to the literature.^{110,233,285,299–302} Symbols: v = stretching, $\delta =$ deformation, $\beta =$ bending, $\rho =$ rocking, OT = overtone, as = asymmetric, s = symmetric, (sh) = shoulder and * = tentative assignment.

| | Wavenumber / cm ⁻¹ | | | |
|---------------------------------------|-------------------------------|-----------------------|---------------------|--|
| Assignment | Deposited at | Deposited at 27 K and | Deposited at 105 K | |
| Assignment | 27 K | annealed to 100 K | Deposited at 105 K | |
| v(C=O) от | 3412 | 3390 | 3388 | |
| v(CH ₃) _{as} | 3037 (sh) | 3055 | 3053 | |
| v(CH ₃) _{as} | 3010 | 3010 | 3010 | |
| v(C-H) | 2960 | 2978/2960 | 2978/2960 | |
| *δ(CH ₃) _{as-OT} | - | 2900 | 2900 | |
| *δ(CH ₃) _{s-OT} | 2845 | 2852 | 2852 | |
| * v(С-О) от | 2594 | 2600 | 2600 | |
| v(C=O) 1740 | | 1728 | 1728 (sh) | |
| v(C=O) 1714 (sh) 1 | | 1714 (sh) | 1712 | |
| v(C=O) | 1678 | 1695 | 1695 | |
| δ(CH ₃) _{as} | 1454 | 1460/1454 (sh) | 1460/1450 | |
| δ(CH₃)₅ | 1437 | 1441 | 1441 | |
| β(С-Н) | 1387 | 1392 | 1392 | |
| v(C-O) | 1234 | 1242/1209 | 1242 (sh)/1209 | |
| ρ(CH₃) | 1175 | 1180/1169/1159 (sh) | 1180/1169/1161 (sh) | |
| v(C-O) | 914 | 906 | 906/900 (sh) | |

Figure 7.2B shows a further seven bands. The band at 1740 cm⁻¹ with a shoulder at 1714 cm⁻¹ and the band at 1678 cm⁻¹ are assigned to the v(C=O) mode.^{110,233,285,299–302} The two bands at 1454 cm⁻¹ and 1437 cm⁻¹ are assigned to the asymmetric and symmetric δ (CH₃) modes.^{110,233,285,299–302} The band at 1387 cm⁻¹ is assigned to the C-H bending mode, β (C-H).^{110,233,285,299–302} The bands observed at 1234 cm⁻¹ and 914 cm⁻¹ are due to v(C-O) modes.^{110,233,285,299–302} The band at 1175 cm⁻¹ is assigned to the CH₃ rocking mode.^{110,233,285,299–301} The observed bands are listed with their assignments from the

literature in Table 7.2. Between 27 K and 80 K, there are no changes in the bands. After annealing to 100 K, the spectrum changes dramatically as seen in Table 7.2.

Upon annealing methyl formate ice to 100 K, as shown in Figure 7.2A, the v(C=O)_{OT} band red shifts to 3390 cm⁻¹. The band due to the v(CH₃)_{as} mode, which was at 3010 cm⁻¹ with a shoulder at 3037 cm⁻¹, splits into two well defined bands at 3055 cm⁻¹ and 3010 cm⁻¹. The band at 3010 cm⁻¹ also sharpens and increases in intensity upon annealing to 100 K. The v(C-H) band at 2960 cm⁻¹ splits into two sharp bands at 2978 cm⁻¹ and 2960 cm⁻¹. A new band at 2900 cm⁻¹ also appears upon annealing to 100 K, which is tentatively assigned to the overtone of the $\delta(CH_3)_{as}$ mode due to its position at twice the frequency of the δ (CH₃)_{as} band. The other overtone bands both blue shift after annealing to 100 K, by 7 cm⁻¹ for the δ (CH₃)_{s-OT} mode and 6 cm⁻¹ for the v(C-O)_{OT} mode. The v(C=O) modes at around 1740 cm⁻¹ undergo dramatic changes. The band at 1740 cm⁻¹ shifts to 1728 cm⁻¹ and the shoulder remains at 1740 cm⁻¹, whilst the band at 1678 cm⁻¹ undergoes a large increase in intensity and sharpens, with a corresponding shift to 1695 cm⁻¹. The δ (CH₃)_{as} mode changes from a single, broad, band at 1454 cm⁻¹ to a sharp band at 1460 cm⁻¹ with a shoulder at 1454 cm⁻¹ and the δ (CH₃)_s band blue shifts by 4 cm⁻¹ to 1441 cm⁻¹. A similar blue shift of 5 cm⁻¹ is observed for the β (C-H) mode at 1387 cm⁻¹. The v(C-O) band splits upon annealing, going from a single band at 1234 cm⁻¹ to two overlapping bands at 1242 cm⁻¹ and 1209 cm⁻¹. The ρ (CH₃) mode at 1175 cm⁻¹ also splits upon annealing to 100 K, showing two peaks at 1180 cm⁻¹ and 1169 cm⁻¹, the latter showing a shoulder at 1159 cm⁻¹. Finally, the v(C-O) band at 914 cm⁻¹ shifts to 906 cm⁻¹ and increases in intensity. Further annealing of the ice showed no more spectral changes until 130 K, where the loss of all bands indicates that methyl formate has desorbed, as shown in Figure 7.2.

Previous RAIR spectra by Burke *et al.*²³³ showed that annealing methyl formate, deposited on HOPG at 20 K, to 95 K gave rise to several changes in the RAIR bands. These changes were assigned to a structural change of the amorphous methyl formate ice, possibly due to a glass transition. The observed changes were not assigned to a crystallisation of methyl formate because, whilst splitting of the v(C=O), δ (CH₃)_{as}, and v(C-O) modes was observed, no intensity increases of any bands were observed and it did not correspond to spectra of crystalline methyl formate shown by Katon and

Ranieri.²⁹⁴ The changes in the RAIR spectra upon annealing in this work, shown in Table 7.2, do not correspond to those observed by Burke *et al*.²³³ This is most likely because the ices grown in this work are much thicker than those examined by Burke *et al*.²³³ Instead, the splitting of several bands, along with the increases in intensity upon annealing to 100 K, leads to the conclusion that methyl formate undergoes a phase change from an amorphous to a crystalline form at this temperature.

Based on the RAIRS annealing data in Figure 7.2, in order to grow crystalline methyl formate ice directly, methyl formate was deposited at a temperature of 105 K. This temperature was selected as it was above the observed phase change temperature, but below the desorption temperature of approximately 130 K. Figure 7.3 shows a comparison of RAIR spectra of 300 L_m methyl formate deposited at 27 K, deposited at 27 K and annealed to 100 K, and deposited at 105 K. The figure is split into the same regions as Figure 7.2 for clarity.

It is clear that the annealed and high deposition temperature spectra are different to one another, as well as different when compared to the amorphous spectrum. The differences in the bands are summarised in Table 7.2. No changes between the annealed and high deposition temperature spectra are observed in the $v(CH_3)_{as}$ band at 3010 cm⁻¹, the split v(C-H) band at 2978 cm⁻¹ and 2960 cm⁻¹, the overtone bands at 2900 cm⁻¹, 2852 cm⁻¹ and 2600 cm⁻¹, the v(C=O) band at 1695 cm⁻¹, the δ (CH₃)_s band at 1441 cm⁻¹ and the β (C-H) band at 1392 cm⁻¹. Conversely, the v(C=O)_{OT} band is at 3388 cm⁻¹, compared to 3390 cm⁻¹ in the annealed spectrum. Similarly, the $v(CH_3)_{as}$ band is red shifted to 3053 cm⁻¹ from 3055 cm⁻¹. The v(C=O) region around 1740 cm⁻¹ is very different for the two high temperature spectra. In the high deposition temperature spectrum (Figure 7.3), the band at 1728 cm⁻¹ is now a shoulder rather than the dominant band as in the annealed spectrum, and the band at 1714 cm⁻¹ is now the second most intense band, where it was a shoulder in the spectrum of methyl formate deposited at 27 K. The δ (CH₃)_{as} is split into 2 bands at 1460 cm⁻¹ and 1450 cm⁻¹ rather than a band with a shoulder at 1460 cm⁻¹ in the annealed ice spectrum. The v(C-O) band shows the opposite behaviour. In the high deposition temperature spectrum it is a band at 1209 cm⁻¹ with a shoulder at 1242 cm⁻¹, compared to 2 bands in the annealed spectrum. The $\rho(CH_3)$ bands show a difference in intensity ratio between the two high temperature spectra. The band at 1169 cm⁻¹ is dominant in the high deposition temperature spectrum over that at 1180 cm⁻¹, whereas in the annealed spectrum where they are of similar intensities. Additionally, the shoulder is slightly shifted from 1159 cm⁻¹ in the annealed spectrum to 1161 cm⁻¹ in the high deposition temperature spectrum. Finally the v(C-O) band at 906 cm⁻¹ has a shoulder at 900 cm⁻¹ when methyl formate is deposited at 105 K.



Figure 7.3 RAIR spectra of 300 L_m methyl formate deposited at 27 K (red trace), deposited at 27 K and annealed to 100 K (blue trace) and deposited at 105 K (green trace).

The differences in the RAIR spectra shown in Figure 7.3 and Table 7.2 show that annealing methyl formate ice and depositing at high temperature lead to different structured ices. The phase of methyl formate deposited at 105 K is assigned to a second crystalline form, due to its sharp split peaks compared to the amorphous spectrum, as shown in Figures 7.2 and 7.3. Indeed two crystalline forms of methyl formate were previously observed by Katon and Ranieri.²⁹⁴ More recently, Roman et al.²⁸⁵ showed that the RAIR spectra of multilayers of methyl formate deposited on amorphous silica showed different structures depending on the deposition temperature. The spectrum of methyl formate deposited at 105 K shown in Figure 7.3 matches that observed by Roman et al.²⁸⁵ for methyl formate deposited at 108 K. Additionally, the RAIR spectrum of methyl formate deposited at 105 K in Figure 7.3 agrees well with the spectrum observed by Modica and Palumbo,¹¹⁰ which was assigned to crystalline methyl formate. Similar behaviour has also been observed in this laboratory for the related molecule ethyl formate, which exhibits two crystalline phases in RAIRS and TPD experiments.³⁰³ The precise structure of the two crystalline forms of methyl formate are not known, and there is little literature available. However the high deposition temperature phase has been described by Roman et al.²⁸⁵ as containing dimers of cis-methyl formate. This is the most stable gas phase dimer according to *ab initio* calculations.²⁸⁵ These dimers are formed by intermolecular hydrogen bonds between methyl formate molecules. The structure of this dimer is shown in Figure 7.4.



Figure 7.4 Structure of the most stable dimer of methyl formate according to Roman et al.²⁸⁵, thought to be present in the high deposition temperature form of crystalline methyl formate. The dashed lines indicate H-bonds.

In this chapter, the two methyl formate phases examined by UV/vis spectroscopy are the amorphous form, which is deposited on HOPG at base temperature, and the high deposition temperature phase which is formed by growing the ice at 105 K. The two phases are referred to as amorphous and crystalline methyl formate henceforth. The crystalline phase formed by annealing is not studied further in this work. However, future work which examines this phase would be useful, in particular to the field of spontelectrics.^{285,304,305}

Figure 7.5 shows UV/vis reflectance spectra of amorphous methyl formate deposited at 27 K on HOPG. As is the case for benzene and toluene, the characteristic interference fringes in the spectra are seen to shift with reflection angle. Additionally, the number of fringes increases with dose.



Figure 7.5 UV/vis reflectance spectra of amorphous methyl formate deposited on HOPG at 27 K. A: at an exposure of 250 L_m. B: at an exposure of 500 L_m. The reflection angle is indicated in the legend.

Conversely to benzene and toluene, no sharp absorption features are observed in the spectra. However, methyl formate has been shown to exhibit a broad absorption feature centred at 223 nm, caused by the electronic transition $\pi^*(C=O) \leftarrow n_0$, *i.e.* from a non-bonding oxygen orbital to the antibonding C=O orbital.³⁰⁶ It is not clear why this feature is not observed in UV/vis reflectance spectra of methyl formate in this thesis, especially

given that the reported absorption cross section for the band is of a similar magnitude to that of benzene.^{186,306} It may be a consequence of the fact that, as described in Chapter 3, the benzene absorption bands arise due to intensity borrowing from an allowed state *via* Herzberg-Teller vibronic coupling.¹⁸⁶ This may lead to an increase in absorption intensity of the benzene bands, which is not observed for methyl formate.

Because there are no visible absorption features in the UV/vis spectra of methyl formate, unlike in the RAIR spectra, there is little distinction between the spectra of amorphous and crystalline methyl formate. Examples of UV/vis reflectance spectra of crystalline methyl formate for ices of different thicknesses and at different reflection angles are shown in Figure 7.6.



Figure 7.6 UV/vis reflectance spectra of crystalline methyl formate deposited on HOPG at 105 K. A: at an exposure of 200 L_m. B: at an exposure of 600 L_m. The reflection angle is indicated in the legend.

Analogous to the amorphous spectra, the fringes are seen to shift with reflection angle, and the number of fringes increases for the higher dose. The analysis method of Harrick,¹⁹⁹ set out in Chapter 3, was applied to both amorphous and crystalline methyl formate. The resulting values of the real part of the refractive index, *n*, are shown in Table 7.3.

The upper limit of the *n* value for amorphous methyl formate is close to the value measured by Modica and Palumbo,¹¹⁰ although the slight variation may be due to a difference in deposition method. No literature values for the refractive index of crystalline methyl formate are available. However, the values of *n* determined in this thesis for amorphous methyl formate, and amorphous and crystalline benzene (Chapter 6), are in good agreement with the literature. Therefore, it is thought that the value for crystalline methyl formate is reasonable.

 Table 7.3 Real part of the refractive index of amorphous and crystalline methyl formate ice from this

 work and compared to the literature. ^aFrom Modica and Palumbo.^{110 b}From Yang et al.²⁹⁵

| Methyl formate | 2 | Literature value of | Under ambient | |
|----------------|-----------------|---------------------|---------------------|--|
| ice phase | п | n for an ice | conditions | |
| amorphous | 1.23 ± 0.05 | 1.30 ^a | 1.3412 ^b | |
| crystalline | 1.40 ± 0.08 | - | - | |

It is also likely that the refractive index of crystalline and amorphous methyl formate would differ, as shown in Table 7.3. In the RAIRS data above (Figures 7.2 and 7.3) a clear structural rearrangement is observed which will affect the bulk electronic structure of the ice. Indeed a thermally induced change of the electronic properties of methyl formate ice has been directly observed.^{285,305} As outlined in Chapter 6, the electronic properties of a material, namely its dielectric constant, are related to its optical impedance, *Z*. It was also shown that $n \propto 1/Z$. Therefore, a change in electronic structure will lead to the observed change in *n*.

It is also important to note that the determined *n* value for methyl formate ice is not in agreement with that of methyl formate under ambient conditions determined by Yang *et al.*²⁹⁵, highlighting the need to examine the optical properties of ices under relevant conditions when using them in astrochemical studies.

The values of *n* for amorphous and crystalline methyl formate ice were also used to determine the thickness of the ices. The method used was that outlined in Chapter 3.

Figure 7.7 shows the variation in thickness as a function of methyl formate exposure for amorphous and crystalline ices. For both ice phases, a weighted linear fit to the individual data points was produced and the ratio of the gradients gives a compaction factor for methyl formate of 1.35. In each case the linear fit was constrained to have an intercept of 0, as dosing nothing on the surface would give an ice thickness of 0 nm. As for benzene, the exact morphology of amorphous methyl formate ice is unknown and therefore it cannot be conclusively stated that this compaction factor is solely due to a change in phase. Therefore more work to examine the structure of each phase of methyl formate would be useful.



Figure 7.7 Thickness of methyl formate ice as a function of exposure as determined by equation (3.7). Red circles: amorphous methyl formate. Green squares: crystalline methyl formate. The lines represent weighted least squares linear fits to each set of data with a fixed intercept of 0.

7.3.2 RAIRS and UV/vis Spectra of Water Ice

As discussed in Chapter 5, water deposited at base temperature forms an amorphous ice structure which is porous. Upon annealing to 140 K, the ice structure changes to crystalline ice, CI, which involves the collapse of the pore network as the water
molecules rearrange. It was also shown in Chapter 5 that depositing water at 135 K led to the growth of CI, as shown by changes in the RAIR spectra and TPD traces. Figure 7.8 shows RAIR spectra of 100 L_m of water deposited at 27 K and at 135 K *via* direct dosing.



Figure 7.8 RAIR spectra of 100 L_m of water ice deposited on HOPG at different deposition temperatures.

The 27 K spectrum clearly shows several bands. There is a broad feature centred at approximately 3350 cm⁻¹, and a weaker broad band at 1685 cm⁻¹. Additionally, two sharper and much less intense bands are observed at 3720 cm⁻¹ and 3696 cm⁻¹. The band at 3350 cm⁻¹ is assigned to the O-H stretching mode, v(O-H),^{111,142,257} which is split into its asymmetric and symmetric modes at 3481 cm⁻¹ and 3209 cm⁻¹ respectively. The band at 1685 cm⁻¹ is due to the H₂O scissor mode.^{111,142} Both the v(O-H) and scissor mode bands indicate that the water is in an amorphous form, as they are broad features. This is due to the spread of frequencies of the vibrational modes and differing degrees of H-bonding occurring. The two bands at 3720 cm⁻¹ and 3696 cm⁻¹ are due to dangling –OH bonds of two- and three-coordinate water molecules respectively at the ice surface.^{108,111,114,257} These bands were not observed in RAIR spectra of water bearing ices

in previous chapters. In this case they are observed due to the fact that the water ice is grown *via* direct dosing and is therefore much thicker.

Due to the different deposition method, it is likely that the ASW ice grown in this chapter is not the same as that in Chapter 5. It has been shown that ASW ice can exist in several forms, for example in its porous or compact forms, and the form grown is extremely sensitive to the precise dosing procedure.^{42–46,111} Dosing *via* direct dosing, as in the work described here, is thought to give a compact, less porous form of ASW,^{42,43} in contrast to the ASW grown in Chapter 5.

When water is dosed at 135 K, the RAIR spectrum is markedly different to the amorphous spectrum at 27 K. The dangling –OH bands at 3720 cm⁻¹ and 3696 cm⁻¹ are no longer observed, nor is the scissor mode at 1685 cm⁻¹. The v(O-H) mode now shows two distinct sharp bands, one at 3433 cm⁻¹ with a shoulder at 3327 cm⁻¹ and a second at 3099 cm⁻¹ with a shoulder at 3176 cm⁻¹, which are red shifted and at higher intensity compared to the amorphous form. These bands are assigned to the asymmetric and symmetric modes of the v(O-H) respectively. The sharpening, splitting and increase in intensity of the v(O-H) bands suggest that the water ice is in its CI form. The loss of dangling –OH bonds is also consistent with water being in its CI form, as the molecules will be aligned in a H-bonded network, reducing the number of free –OH bonds at the ice surface. Additionally, the loss of the scissor mode is also indicative of crystallisation, as the molecular freedom will be reduced in CI compared to ASW, and will hinder the scissor motion of the water molecules.

Figure 7.9 shows UV/vis reflectance spectra of ASW deposited at 27 K on HOPG. Water is not known to have any UV absorption bands at wavelengths beyond 180 nm,^{138,257,307,308} hence no absorption features are observed in Figure 7.9. As with previously shown spectra (Figures 7.5 and 7.6), the position of the interference fringes shifts with reflection angle, and increasing the ice dose increases the number of observed fringes.



Figure 7.9 UV/vis reflectance spectra of ASW deposited on HOPG at 27 K. A: at an exposure of 100 L_m. B: at an exposure of 200 L_m. Reflection angle is indicated by the legend.

UV/vis reflection spectra of CI show no significant differences to those of ASW, and hence are not shown here. Similar differences between different reflection angles and exposures are observed as in Figure 7.9. The fringe extrema shift with reflection angle and the number of fringes increases with water exposure. Table 7.4 shows the determined real part of the refractive indices of ASW and CI, alongside literature comparisons.

The determined values of *n* for ASW and CI are almost identical and agree within the error ranges. Similar behaviour has been observed in the literature, where the refractive index of water ice does not vary as a function of deposition temperature.^{44,140} The values determined in Table 7.4 are higher than those determined by both Dohnálek *et al.*⁴⁴ and Westley *et al.*¹⁴⁰, however agree within error. Dohnálek *et al.*⁴⁴ showed that the refractive index of water will vary with different deposition methods, which may explain the observed differences between this work and theirs. It should therefore be noted that the values shown in Table 7.4 can only be considered accurate for directly deposited

ASW at 27 K and directly deposited CI at 135 K. Future work examining the effect on *n* of different dosing conditions, *e.g.* backfilling or at different temperatures, analogous to that of Dohnálek,⁴⁴ would be useful.

| Water ice phase | n | Literature value of <i>n</i> for an ice | Literature value under ambient conditions | |
|-----------------|-----------------|--|---|--|
| ASW | 1.38 ± 0.08 | 1.285ª | 1.33 ^c | |
| | | 1.29 ± 0.01^{b} | | |
| CI | 1.40 ± 0.12 | 1.285ª | | |
| | | 1.29 ± 0.01^{b} | | |

Table 7.4 Real part of the refractive index of ASW and CI from this work and compared to the literature.aFrom Dohnálek et al.44 bFrom Westley et al.140 From Hecht.2

In the case of water, the refractive indices for the ice grown in this work and under ambient conditions are quite similar, although not identical. It may therefore be valid to assume an *n* value for water under ambient conditions for ice models. However, as shown for methyl formate above, this is not a universally applicable assumption.

The values of *n* for ASW and CI determined in Table 7.4 were used to calculate the thicknesses of water ices. Figure 7.10 shows the ice thickness as a function of dose for ASW and CI. Also shown is a weighted linear fit to each data set, with the intercept set to 0.

Despite the fact that the refractive index of water varies very little with ice phase, there is a clear difference between thicknesses of ASW and CI, as shown in Figure 7.10. The compaction factor of ASW to CI is found to be 1.22 from the ratio of the gradients of the linear fits. The ASW grown in this chapter is believed to be compact ASW, which is still porous, but less so than other ASW forms.^{42,43} Therefore, at least to some degree, the observed compaction of water ice will be due to the collapse of porosity. Westley *et al.*¹⁴⁰ measured the density of water ice as a function of deposition temperature and found that, in the range 20 K – 140 K, the density remained constant at 0.82 ± 0.01 g cm⁻³. In this case, the loss of porosity would be the sole reason for the compaction of

water ice. This means that porosity represents 18% of the ASW thickness, based on the fact that CI is found to 0.82 times as thick as ASW (1/1.22). Measurements of ASW porosity tend to give a value of 0.1,^{140,298} which suggests that there must be a change in density in the water ice as well as loss of porosity leading to the observed compaction, in contrast to the measurements of Westley *et al.*¹⁴⁰ Indeed an increase in density as a function of surface temperature has been observed,^{44,141} and therefore a combination of pore collapse and increasing density is thought to be responsible for the observed compaction in this work.



Figure 7.10 Thickness of water ice as a function of exposure as determined by equation (3.7). Blue circles: ASW. Green squares: Cl. The lines represent weighted least squares linear fits to each set of data with a fixed intercept of 0.

7.3.3 RAIRS and UV/vis of Mixed Methyl Formate and Water Ices

The data presented above for pure methyl formate and water ices was used as a benchmark with which to compare mixed ice systems. In all cases, the total ice dose was 200 L_m, with the proportion of methyl formate in water increasing from 0% - 100% in 25% intervals. Figure 7.11 shows RAIR spectra of mixed methyl formate/water ices, with

the pure spectrum of each component also shown for comparison. The figure is split into different wavenumber regions for clarity. Figure 7.11A shows the region 3800 cm⁻¹ – 2600 cm⁻¹ and Figure 7.11B shows the region 1950 cm⁻¹ – 850 cm⁻¹.

It is clear that the mixed ices exhibit different behaviour to the pure ice spectra. The v(O-H) peak of water, shown in Figure 7.11A, decreases in intensity as the amount of water is decreased and loses its structure. However the positions of the asymmetric and symmetric components of the band do not shift in the presence of methyl formate, therefore the changes observed are likely to be a consequence of decreasing the amount of water in the ice rather than due to the presence of methyl formate. Similarly the dangling –OH bands at 3720 cm⁻¹ and 3696 cm⁻¹ decrease in intensity but do not shift with increasing methyl formate proportion, and are no longer visible in the 75% methyl formate spectrum (Figure 7.11A). The scissor mode band of water at 1685 cm⁻¹ (Figure 7.11B) also decreases in intensity as the amount of water is decreased in the ice, but still shows a contribution in all mixed spectra. This band overlaps with the v(C=O) mode of methyl formate at around 1740 cm⁻¹ and therefore its development is not as clear as the other water bands. The conclusion that the presence of methyl formate does not greatly affect the RAIRS bands of water in a mixed ice is in agreement with the work of Burke *et al.*²⁷⁰

In contrast to the water bands, the methyl formate bands do show some shifts between the pure ice spectrum and the mixed systems. In the spectra shown in Figure 7.11, the overtone bands (listed in Table 7.1) are not observed, which is likely due to the lower dose of methyl formate compared to in Figures 7.2 and 7.3. The bands associated with C-H and CH₃ modes do not show any shifts, and simply increase in intensity as the amount of methyl formate in the ice is increased. These are the v(C-H) band at 2960 cm⁻¹, the asymmetric and symmetric δ (CH₃) modes at 1454 cm⁻¹ and 1437 cm⁻¹, the β (C-H) band at 1387 cm⁻¹ and the ρ (CH₃) mode at 1175 cm⁻¹. Conversely, bands associated with both the C=O and C-O bonds in methyl formate do exhibit shifts. These are summarised in Table 7.5.



Figure 7.11 RAIR spectra of mixed methyl formate/water ices deposited on HOPG at 27 K. In all cases the total ice dose is 200 L_m. The percentage of methyl formate in the ice is shown on the right of the figure.

| | Wavenumber / cm ⁻¹ | | | | |
|------------|-------------------------------|------------|------------|-------------|--|
| Accianment | 25% methyl | 50% methyl | 75% methyl | 100% methyl | |
| Assignment | formate | formate | formate | formate | |
| v(C=O) | 1718 | 1724 | 1728 | 1740 | |
| v(C-O) | 1238 | 1238 | 1238 | 1234 | |
| v(C-O) | 918 | 916 | 916 | 914 | |

Table 7.5 RAIRS bands of methyl formate in mixed ices with water of differing compositions.

The observed shifts due to the presence of water in the methyl formate RAIRS bands are in good agreement with similar shifts observed by Burke et al.²⁷⁰ For a 27% methyl formate in water mixed ice, a red shift of 21 cm⁻¹ of the v(C=O) band was observed compared to the pure ice. This is in excellent agreement with the shift of 22 cm⁻¹ shown in Figure 7.11B and Table 7.5 in this work. Additionally, Burke et al.²⁷⁰ observed a broadening of the v(C=O) band in the mixed ice, with a contribution from the water scissor mode on the low wavenumber side of the band, in agreement with the spectrum shown in Figure 7.11B. The v(C-O) mode at 1234 cm⁻¹ in this work is shifted in the mixed ices to 1238 cm⁻¹, whereas Burke et al. observed a shift from 1233 cm⁻¹ to 1240 cm⁻¹. A small blue shift is observed in the second v(C-O) band in the mixed ices in this work. This band is not shown in the work of Burke *et al.*,²⁷⁰ but the shift is consistent with the other bands listed in Table 7.5. These band shifts are indicative of an interaction between water and methyl formate. The fact that the C-H associated bands do not shift in the presence of water, but the C-O/C=O bands do so, suggests that the interaction involves only these more polar bonds. However the lack of shifts in the water bands suggest that this is not a strong interaction. Indeed, Burke *et al.*²⁷⁰ also examined the effect of the presence of water on the RAIR spectra of glycolaldehyde and acetic acid (two isomers of methyl formate) and concluded that the interaction between methyl formate and water was the weakest of the three molecules. The effect of this interaction on the optical behaviour of the ices is discussed below.

Figure 7.12 shows UV/vis reflectance spectra of ices of different compositions from pure water to pure methyl formate at a reflection angle of 31° . In all cases the total ice dose is 200 L_m.



Figure 7.12 UV/vis reflectance spectra of mixed methyl formate/water ices deposited on HOPG at 27 K. In all cases the total ice dose is 200 L_m. The percentage of methyl formate in the ice is shown on the right of the figure. The reflection angle is 31°.

It is clear that the ice composition has an effect on the UV/vis spectra shown. The mostly water ices exhibit more interference fringes, with a smaller fringe amplitude than the methyl formate dominated ices. The number of fringes is the most for pure water, and the least for pure methyl formate, in agreement with Sections 7.3.1 and 7.3.2 that equivalent doses of water produce thicker ices than methyl formate. This is shown in Figures 7.7 and 7.10. This is examined in the analysis below. The difference in amplitude of the fringes in the different ices is due to the difference in optical properties of the ices causing varying amounts of reflection and interference to occur.

Previously, when examining mixed ices, a weighted average of the refractive indices of each ice component has been taken as the overall ice refractive index.¹⁵ Whilst this has been shown to be appropriate for non-interacting mixed systems such as emulsions of latex in water,³⁰⁹ its applicability to ices is less certain. Mukai and Krätschmer³⁶ attempted to determine refractive indices for mixed ices of water and NH₃, and found discrepancies between calculated values of *n* and experimentally determined values due

to interactions within the ice. They concluded that assuming an *n* value based on the ice components may be appropriate for non-interacting mixed ices but not for interacting species. In order to examine this assumption further, the Harrick¹⁹⁹ analysis was applied to the UV/vis spectra of mixed ices in order to determine *n*.

Figure 7.13 shows the determined *n* values for the mixed methyl formate/water ices as a function of the methyl formate and water proportion. The values for pure ASW and amorphous methyl formate (1.38 and 1.23 respectively) are shown with a line between them representing the weighted average of each individual value as a function of ice composition. According to the assumption of Elsila *et al.*¹⁵, the determined *n* values of the mixtures will sit along this line.



Figure 7.13 Real part of the refractive index, n, of mixed methyl formate/water ices as a function of ice proportion. Red circles: n for the pure ices. Blue triangles: n for mixed ices. The dashed black line is a weighted average based on the pure ice values.

It is clear that the *n* values of mixed ices do not sit along the weighted average line. This is most likely a consequence of the interaction between the molecules shown by the RAIR spectra. It is therefore clear that, for mixed ice systems, it is not appropriate to assume a refractive index based on the ice components. The previous assumption may be valid for ice systems in which there is not significant interaction between the components. However, the range of detected interstellar molecules with diverse chemical properties, shown in Table 7.1.1,⁵⁶ means that this is likely to be a minimal number of systems.

It is therefore necessary to experimentally measure the refractive index of mixed interstellar ice analogues for the most part, highlighting the importance of the new apparatus described in this thesis.

With reference to the number of observed fringes in the UV/vis spectra (Figure 7.12), it was suggested that more water-heavy ices would be thicker than those dominated by methyl formate. The determined n values shown in Figure 7.13 were used to calculate the thickness of mixed ices. It should be noted that a value of thickness for the 25% methyl formate ice was not determined. This is a consequence of its low refractive index (0.95 ± 0.12) which means that in equation (3.7), the $sin^2\theta$ term becomes larger than n^2 and the denominator cannot be calculated as it requires the square root of a negative number. Therefore the analysis outlined in Chapter 3 to determine the ice thickness is restricted to approximately values of n > 1. In spite of this, the thickness of 50% and 75% methyl formate ices have been calculated, along with the pure ice values. These are shown in Figure 7.14.

There is an upwards trend in ice thickness between pure methyl formate and pure water, as expected from Figure 7.12. The thickness of the 75% methyl formate ice is lower than expected, which may be a consequence of dosing errors, however thickness variations will not affect the determined *n* values.

The thermal behaviour in terms of the optical parameters and thickness of mixed methyl formate/water ices has not been examined in this work. Work by Burke *et al.*²⁷⁰ showed that, in mixed ices, the methyl formate phase change is inhibited but that of water is not. It was also shown that some methyl formate is effectively trapped on the surface

by water above its natural desorption temperature. Future work would examine the effect of annealing on methyl formate/water mixed ices in order to determine whether the reduction of the amount of methyl formate in the ice leads to the refractive index moving back towards that of pure water.



Figure 7.14 Thickness of mixed methyl formate/water ice as a function of ice proportion. The green line is a weighted linear fit to the data to illustrate the trend.

7.4 Summary and Conclusions

RAIRS and UV/vis spectroscopy experiments have been performed for single component ices of methyl formate and water. These data were used as a benchmark for comparison with mixed ices of the two molecules. Both methyl formate and water ices are known to undergo thermally induced phase changes. Methyl formate was found to have two high temperature crystalline phases, which are accessed by different thermal routes. The first form is produced when an amorphous methyl formate ice, deposited at 27 K, is annealed to 100 K. The second phase is formed when methyl formate is deposited directly onto HOPG at 105 K. These observations are in good agreement with the literature for methyl formate, ^{110,285,294} and similar behaviour has been observed for ethyl formate.³⁰³ The

second crystalline phase, that which was grown at 105 K, was further examined in this work. Both amorphous and crystalline methyl formate ices were examined using the newly developed apparatus described in Chapter 3. It was shown that, analogous to benzene, the real part of the refractive index of amorphous methyl formate ice is not the same as that for methyl formate under ambient conditions.²⁹⁵ The discrepancy between the *n* value for the liquid and for methyl formate ice highlights the need to measure refractive indices of ices experimentally under conditions relevant to the ISM.

The structural difference between amorphous and crystalline methyl formate (shown in Figure 7.3) leads to a change in the refractive index. The refractive index of amorphous methyl formate is found to be 1.23 ± 0.05 , whereas it increases to 1.40 ± 0.08 for its crystalline phase. This difference must be taken into account when using the refractive index to model spectra of methyl formate. It would be useful in future work to examine the first crystalline phase of methyl formate, in order to be able to model spectra of ices with different thermal histories.

In addition to methyl formate, this chapter also presents RAIRS and UV/vis data for water ices. RAIR spectra showed that when deposited at 135 K, water adsorbs in its crystalline form, CI. When deposited at 27 K, ASW is formed. It is likely that the ASW in this chapter is in its compact form, due to the fact that it is dosed directly.^{42,43}

Unlike methyl formate, the refractive index of ASW is similar to that of the liquid under ambient conditions, 1.38 ± 0.08 compared to 1.33.² Therefore in the case of directly deposited, compact ASW, it may be valid to assume that the *n* value of the liquid is similar to that of the ice. However because water ice can exist in many forms,^{25,28,42–} ^{45,141,298} it must be stressed that this may not be the case for all water ices. It would be useful to examine the optical properties of water ices grown under different conditions in order to further examine this.

The pure ice data was used to compare to the behaviour of mixed methyl formate/water ices. Previously, a weighted average of the refractive indices of each ice component has been taken as the refractive index of a mixed ice.¹⁵ This assumption was tested by taking a weighted average of the pure amorphous methyl formate and ASW *n* values and comparing it to experimentally determined *n* values for mixed ices. It was found, as

shown in Figure 7.13, that the refractive indices of mixed ices do not follow this trend. Therefore it is questionable to assume that a weighted average of component refractive indices is relevant to a mixed ice's optical properties. The most likely cause of the discrepancy is interactions between the constituents of the ice. Indeed RAIR spectra of mixed methyl formate/water ices show several differences to the pure ice spectra. These were most notable in bands associated with the C=O and C-O bonds in methyl formate. This indicates that these polar bonds are involved with the interaction. The interaction is not thought to be strong, however, as the water bands are not affected by the presence of methyl formate. The RAIRS results here are in good agreement with previous RAIRS data of methyl formate/water mixed ices.²⁷⁰

The results presented in this chapter show that measuring refractive indices of interstellar ice analogues is vital. This is because it has been shown that ices do not always have the same optical parameters as their constituents under ambient conditions. Additionally, when interactions between constituents of mixed ices occur, the optical parameters of the ice do not follow a trend based on the refractive indices of the pure constituents. Hence experimental data is required. The data highlight the usefulness of the newly developed UV/vis apparatus described in this thesis.

8 Concluding Remarks

8.1 Summary and Conclusions

This thesis aimed to measure the thickness and refractive indices of interstellar ice analogues in a way which overcame several issues with previously reported methods. Ices made of several astronomically relevant molecules, deposited on a highly oriented pyrolytic graphite (HOPG) surface, were examined. The ices investigated consisted of benzene, toluene, methyl formate and water. HOPG was used as a carbonaceous dust grain analogue surface. Ultraviolet/visible (UV/vis) reflection absorption spectroscopy was used to determine the refractive index and thickness of ices, using a newly developed piece of equipment. The ices were also characterised in terms of their structure, thermal behaviour and desorption from HOPG by reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD).

Chapter 3 presented the design, installation and testing of the novel UV/vis spectroscopy apparatus. The key design element, a variable angle lens assembly, was described in detail. Upon installation, it became apparent that modifications to the original design were required, which were also discussed. This chapter presented the initial test data which was recorded for benzene ices. It was determined that ices grown via backfilling were not sufficiently thick to use for the analysis, and therefore ices grown via direct dosing were examined. Benzene was chosen as a test system because it has well studied UV/vis absorptions which could be used as a simple test of the apparatus. Absorptions due to the ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ and ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transitions were observed in UV/vis spectra of benzene at 214 nm and 255 nm respectively. Interference fringes were also observed in the UV/vis spectra of benzene, which occur due to multiple reflections within the ice. The spacing of these fringes was used to determine the real part of the refractive index, n, and the thickness, d, for benzene ices. A refractive index of 1.43 ± 0.07 was determined, and the thickness was found to vary linearly with benzene exposure. Table 8.1 shows the refractive indices for all the single component ices determined in this thesis. In the case of benzene, the value of n is not the same as the value under ambient conditions,² highlighting the importance of measuring refractive indices of ices under astronomically relevant conditions. The apparatus was shown to

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allow *n* and *d* to be measures in a single experimental procedure, without the need for assumptions.

| Ice system | Refractive index | |
|----------------------------|------------------|--|
| Amorphous benzene | 1.43 ± 0.07 | |
| Crystalline benzene | 1.63 ± 0.08 | |
| Amorphous toluene | 1.36 ± 0.07 | |
| Amorphous methyl formate | 1.23 ± 0.05 | |
| Crystalline methyl formate | 1.40 ± 0.08 | |
| Amorphous solid water | 1.38 ± 0.08 | |
| Crystalline water ice | 1.40 ± 0.12 | |

 Table 8.1 Refractive indices for the pure ices determined in this work

Furthermore, a program was written using the Python language to determine the wavelength dependent, complex refractive index, N, of an ice; N = n + ik where k is the imaginary part of the refractive index, related to extinction of light. N can be used to simulate spectra of interstellar ices. The program was tested using data from the literature for amorphous solid water (ASW) ice,¹³⁶ and shown to accurately determine n and k as a function of wavelength. However, when the program was applied to the experimental data, an error in the reflection angle meant that n and k for benzene could not be determined. Potential methods to overcome this issue are discussed in section 8.2.

Chapters 4 and 5 presented RAIRS and TPD data for benzene and toluene ices. Chapter 4 examined pure benzene and toluene ices, and Chapter 5 used this benchmarking work to compare to the behaviour of water containing ices of benzene and toluene. RAIR spectra of benzene show that multilayers of benzene ice undergo a thermally induced crystallisation, whereas no phase change is observed for toluene. The fact that benzene crystallises and toluene does not is rationalised with reference to their likely crystal structures.^{237,241,242} Benzene requires less significant rearrangement to crystallise compared to toluene, therefore its barrier to crystallisation is likely to be lower than that for toluene. Both molecules showed complex desorption behaviour on HOPG at sub-

monolayer coverages. The desorption temperature was shown to decrease with increasing exposure, which has been assigned to lateral repulsions between adsorbed molecules. This was the first observation of this effect for toluene. The determined desorption energies led to the conclusion that the lateral repulsions were stronger for benzene than toluene. Multilayer desorption parameters were also determined using leading edge analysis. The determined desorption parameters are shown in Table 8.2.

Table 8.2 Desorption parameters for the ices examined in this work. ^a units of pre-exponential factor are s^{-1} for sub-monolayer systems and molecules $cm^{-2} s^{-1}$ for multilayer systems. ^b desorption order and pre-
exponential factor values were fixed at the values shown.

| Molecule | lce system | Desorption order, n | Desorption energy, E _{des} / kJ mol ⁻¹ | Pre-exponential factor, v ^a |
|--------------|--|------------------------|--|---|
| Benzene _ | Pure ice, sub- monolayer ^b | 1 | 41.3 – 51.0 (± 2.5) | 10 ¹³ |
| | Pure ice, multilayer | 0.18 ± 0.06 | 45.5 ± 1.8 | 10 ^{29±1} |
| | On CI, sub- monolayer ^b | 1 | 39.3 – 39.8 (± 2.5) | 10 ¹³ |
| | On ASW, sub- monolayer | 0.83 ± 0.08 | 41.7 ± 6.4 | 10 ^{19 ± 2} |
| - Toluene | Pure ice, sub- monolayer ^b | 1 | 42.4 – 48.0 (± 2.5) | 10 ¹³ |
| | Pure ice, multilayer | 0.37 ± 0.04 | 47.6 ± 1.2 | $10^{27 \pm 0.3}$ |
| | On Cl, sub- monolayer | 1.11 ± 0.09 | 46.8 ± 5.5 | 10 ^{16 ± 1} |

Water was shown to have an effect on the RAIR spectra of both benzene and toluene. For benzene, the aromatic C-C stretching mode (v(CC)_{aromatic}) was shifted to 1481 cm⁻¹ in the presence of water, from 1479 cm⁻¹ in the pure benzene spectrum. This shift is due to a hydrogen bonding (H-bond) interaction between the π -electron system of benzene and a H atom of water. As the amount of benzene in the ice was increased, the shift in the $v(CC)_{aromatic}$ band disappeared, and the benzene RAIR spectrum resembled that of pure benzene. For toluene, a similar shift in the $v(CC)_{aromatic}$ modes of toluene in the presence of water was observed, although it was more pronounced in the mixed ices. The interaction is also due to H-bonds, analogous to the benzene/water interaction, but with an added polar interaction due to the dipole of toluene.

Annealing experiments showed that ASW containing ices, in layered or mixed ices, segregate into regions of water and benzene or toluene as the temperature is increased. However, this effect was not observed when benzene or toluene were deposited on a crystalline ice (CI) surface. Therefore segregation was concluded to be a consequence of water mobility towards the crystalline state, which overcomes the benzene/water or toluene/water interaction. TPD experiments showed that ASW traps both benzene and toluene in its pore system. The TPD traces of both molecules were dominated by volcano desorption, with co-desorption also important. This trapping was shown to inhibit the crystallisation of benzene.

The RAIRS experiments performed clearly show phase changes and interactions by splitting or shifting of bands. However, it must be noted that the resolution used in this work, of 4 cm⁻¹, is superior to any current observational technologies. Therefore, care must be taken that the IR spectra in this work are not directly compared to observations of the ISM. Instead they illustrate that ices will vary in structure and composition under different conditions and may in the future be used as a direct comparison to observations.

The TPD data were used to construct a simple model of desorption of different water bearing ices of benzene and toluene on astronomical timescales. These models were applied to the specific regions of space where benzene has been detected and toluene is thought to form. It was shown that the desorption of benzene and toluene in these regions is highly dependent on the phase of water ice. ASW containing ices are dominated by the desorption kinetics of water, whereas those containing CI are more dependent on the desorption parameters of benzene and toluene. These data show that laboratory data can be used to determine the conditions in environments where molecules are detected. Chapter 6 presented data collected using the novel apparatus described in Chapter 3 for amorphous and crystalline benzene ices, and for amorphous toluene ices. For both molecules, clear UV/vis absorption features were observed and assigned with reference to the literature.^{186,188–190,196–198,277,286} These features were found to differ to gas phase UV/vis spectra for each molecule, suggesting that the position of the absorptions could be used to identify the phase of the molecules in space. The UV/vis spectra of amorphous and crystalline benzene were shown to differ, with a sharpening of the vibronic bands accompanied by an approximately 1 nm blue shift. The phase change was also found to cause a change in the refractive index and thickness of benzene ices. Crystalline ices were found to be 0.74 times as thick as amorphous ices, suggesting that crystalline benzene is denser than amorphous benzene. The refractive index was found to increase from 1.43 \pm 0.07 for amorphous benzene to 1.63 \pm 0.08 for crystalline benzene. This is rationalised by considering the optical impedance, Z, and dielectric constant of the ices. Crystalline benzene will have a higher dielectric constant than amorphous benzene, and therefore a lower impedance and higher refractive index, given that $n \propto 1/Z$.

The final chapter presented a study to examine an assumption that the refractive index of a mixed ice can be taken to be equal to a weighted average of the refractive indices of its components. Mixed ices of the interstellar complex organic molecule (COM) methyl formate and water were examined. Initially, the pure ices were characterised by RAIRS and UV/vis spectroscopy in order to benchmark the ice behaviour compared to mixed ices. Methyl formate was found to adsorb at 27 K in an amorphous form. Two crystalline forms of methyl formate were identified by RAIRS, one produced by annealing the amorphous ice to 100 K, and a second by depositing methyl formate directly at 105 K. The amorphous and high deposition temperature forms were examined by UV/vis spectroscopy to determine *n* and *d* for the ices. As for benzene, the crystalline form was found to have a higher refractive index than the amorphous form and was also found to be thinner. ASW and CI conversely were found to have similar refractive indices, but the loss of the pore system in water meant that CI films were thinner than ASW. RAIRS of mixed ices showed that methyl formate and water interact, as the methyl formate bands associated with the C-O and C=O bonds were shifted from their positions in the spectrum of pure methyl formate ice. The C=O stretch, v(C=O), was observed at 1740 cm⁻¹ in pure methyl formate ice, but was seen at 1718 cm⁻¹ in a 25% methyl formate in water mixed ice. The two v(C-O) bands were shifted from 1234 cm⁻¹ and 914 cm⁻¹ in the pure ice to 1238 cm⁻¹ and 918 cm⁻¹ in the mixed ice. No shifts were observed in the methyl formate bands associated with the CH bonds, therefore the interaction is likely to only involve the polar C-O and C=O bonds. UV/vis spectroscopy was used to determine the refractive indices of the mixed ices. It was found that the refractive index of a mixed ice was not equal to a weighted average of the refractive indices of methyl formate and water. This is a key finding of this thesis, and further highlights the requirement to use accurate laboratory data in astronomical models and studies.

8.2 Future Work

Whilst this thesis provides data that is of importance to the chemical and astronomical communities, further studies would be useful to expand on the conclusions presented. The first and most important issue to address is the fact that the reflection angle of the UV/vis experiments has an error which means that the data cannot be analysed by the program to find the complex refractive index. Two options are available to overcome this issue. The first is to remove the need to rotate the sample between recording background spectra and dosing. This would require redesigning the dosing lines to allow the leak valves to be positioned on the opposite side of the ultra-high vacuum (UHV) chamber than they are currently. For single component ices, this alone would be sufficient to solve the issue. However at present, only one port is available on the chamber to allow this, so the current method of growing mixed ices, using two leak valves simultaneously, would not be possible. Therefore, in addition to rearranging the gas lines, a mixing manifold would be required before the leak valve which would allow gases to be mixed in the desired proportions before dosing.

An alternative option would be to design a mechanism which allowed the sample to be rotated back to its original position more accurately. This would not require the dose lines to be changed, but a suitable mechanism would need to be devised and installed which would not hinder the sample movement. A possible method is to mount a laser onto the rotation stage of the sample which would shine onto a point on the laboratory wall some distance from the chamber. This point would be marked and used to return the sample to its original position. The greatest distance from the chamber to the laser point would be used to obtain the greatest angular accuracy.

Whilst the conclusion drawn in Chapter 7, that the refractive index of a mixed ice made up of interacting components cannot be assumed to be a weighted average of the individual components' refractive indices, is a key finding of this thesis, it requires further investigations in order to be made more certain. Firstly, several more ice compositions should be tested, in particular at the lowest and highest proportions of methyl formate (< 25 % and > 75%). The overall trend in Figure 7.13 is the opposite of the expected trend if a weighted average were used, the extreme ends of the methyl formate proportion would give a more detailed illustration of how n varies with ice composition. This would ultimately aid in explaining more clearly the observed behaviour, which is currently thought to be a consequence of intermolecular interactions within the ice.

Ices that have not been examined in this thesis would be of interest to the astrochemical community if studied using the novel UV/vis apparatus. It was stated in Chapter 7 that the refractive index of ASW determined was only valid to the specific form grown in this work, thought to be a compact form of ASW. Therefore, it would be beneficial to examine more ASW forms and determine any effect on the refractive index of this. Additionally, annealing experiments of the methyl formate and water mixed ices to examine the effect on the refractive index would be useful to allow spectra of a range of astronomical environments to be modelled.

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Appendix 1: Code to determine the complex refractive index of an ice

#Code to determine wavelength dependent complex refractive indices (n and k)
values of ices.
#Written in Python 3.5 in July/August 2018 by James Stubbing, with much
assistance from Dr. Adam Baskerville.
#The code calculates a deltaR/R value, which is then optimised by the least
squares method by comparison to
#experimental data at a range of reflection angles.

#import relevant modules
import numpy as np
mathematical operations
from scipy.optimize import least_squares
from scipy module
import pandas as pd
files
import time
program takes to run to be recorded

#numpy module for
#least squares operation
#pandas module for reading
#allows the time the

start = time.time()

#sets pandas to show all data in the output files
pd.set_option('display.max_rows', 10000)
pd.set_option('display.max_columns', 10000)

#list conaining all experimental reflection angles angle = [np.deg2rad(31), np.deg2rad(39), np.deg2rad(46), np.deg2rad(53), np.deg2rad(58), np.deg2rad(64), np.deg2rad(68)]

```
#empty lists for results
#Add in as many d values as required
ntarget = []
ktarget = []
sim 31 1 = []
sim 39 1 = []
sim 46 1 = []
sim_{53_1} = []
sim_58_1 = []
sim_64_1 = []
sim 68 1 = []
sim_{31_2} = []
sim_{39_2} = []
sim_{46_{2}} = []
sim_53_2 = []
sim_58_2 = []
sim 64 2 = []
sim 68 2 = []
sim_{31_{3}} = []
sim_39_3 = []
sim_46_3 = []
sim 53 3 = []
sim_{58_3} = []
sim_{64_3} = []
sim_68_3 = []
sim_31_4 = []
sim 39 4 = []
sim 46 4 = []
sim 53 4 = []
sim_58_4 = []
sim_64_4 = []
```

| sim 68 4 | = | [] |
|-----------------------|---|------------|
| sim 31 5 | = | [] |
| oim 20 5 | _ | с л г л |
| SIII_39_3 | _ | |
| sim_46_5 | = | [] |
| sim_53_5 | = | [] |
| sim_58_5 | = | [] |
| sim 64 5 | = | [] |
| sim 68 5 | = | ٢٦ |
| sim 31 6 | = | [] |
| oim 20 6 | _ | L J |
| SIII_39_0 | _ | [] |
| sim_46_6 | = | [] |
| sim_53_6 | = | [] |
| sim_58_6 | = | [] |
| sim 64 6 | = | [] |
| sim 68 6 | = | [] |
| sim 31 7 | = | [] |
| 31m_31_7 | _ | L J F 1 |
| SIM_39_/ | = | |
| sim_46_/ | = | IJ |
| sim_53_7 | = | [] |
| sim 58 7 | = | [] |
| sim 64 7 | = | [] |
| sim 68 7 | = | Г 1 |
| xog 21 1 | _ | L J |
| 162_31_1 | _ | [] |
| res_39_1 | = | IJ |
| res_46_1 | = | [] |
| res 53 1 | = | [] |
| res 58 1 | = | [] |
| res_64_1 | = | [] |
| ros 68 1 | _ | Г 1 |
| 103_00_1 | _ | L J |
| res_31_2 | = | |
| res_39_2 | = | IJ |
| res_46_2 | = | [] |
| res 53 2 | = | [] |
| res 58 2 | = | [] |
| $res 64^{-2}$ | = | [] |
| rog_69_2 | _ | L J |
| res_00_2 | _ | [] |
| res_31_3 | = | [] |
| res_39_3 | = | [] |
| res 46 3 | = | [] |
| res 53 3 | = | [] |
| res 58 3 | = | [] |
| reg 64 3 | _ | Г I |
| 103_04_3 | _ | [] |
| res_08_3 | = | [] |
| res_31_4 | = | [] |
| res_39_4 | = | [] |
| res 46 4 | = | [] |
| res 53 4 | = | [] |
| res 58 4 | = | Г 1 |
| rog_64_4 | _ | с ј Г ј |
| 105_04_4 | _ | |
| res_68_4 | = | [] |
| res_31_5 | = | IJ |
| res_39_5 | = | [] |
| res 46 5 | = | [] |
| res 53 5 | = | [] |
| res 58 5 | = | [] |
| res_50_5 | _ | L J F 1 |
| 104_3 | | L] |
| res_68_5 | = | IJ |
| res_31_6 | = | [] |
| res_39 6 | = | [] |
| res 46 6 | = | [] |
| res 53 6 | = | [] |
| res 58 6 | = | [] |
| TEP_00_0 | _ | L J F P |
| res_64_6 | = | Ľ |
| res_68_6 | = | [] |
| res_31_7 | = | [] |
| res 39 ⁻ 7 | = | [] |
| res_46_7 | = | [] |
| res_53_7 | = | [] |
| / | | |

```
res 58 7 = []
res_{64_7} = []
res 68 7 = []
#Reads in all the data from the formatted input file
exp_data = pd.read_csv('N:\Documents\Python\Input files (copied to C for
use)\Benzene xtal\_all thickness benzene xtal b.csv')
                                                                           #reads in
file, CHANGE DIRECTORY AS NEEDED
exp_lambda1 = exp_data['lambda1']
                                                                      #grabs data from
column with given header (header excluded)
exp n21s = exp data['n21s']
exp_k21s = exp_data['k21s']
exp_n21p = exp_data['n21p']
exp_k21p = exp_data['k21p']
exp 31 1 = exp data['31 1']
exp 39 1 = exp data['39 1']
exp_46_1 = exp_data['46_1']
exp_53_1 = exp_data['53_1']
exp_58_1 = exp_data['58_1']
exp_64_1 = exp_data['64_1']
exp_68_1 = exp_data['68_1']
exp 31 2 = exp data['31 2']
exp_39_2 = exp_data['39_2']
exp_{46_2} = exp_{data['46_2']}
exp_53_2 = exp_data['53_2']
exp_58_2 = exp_data['58_2']
exp_64_2 = exp_data['64_2']
exp_68_2 = exp_data['68_2']
exp_31_3 = exp_data['31_3']
exp_39_3 = exp_data['39_3']
exp_46_3 = exp_data['46_3']
exp_53_3 = exp_data['53_3']
exp 58 3 = exp data['58 3']
exp_64_3 = exp_data['64_3']
exp_68_3 = exp_data['68_3']
exp_31_4 = exp_data['31_4']
exp_39_4 = exp_data['39_4']
exp_46_4 = exp_data['46_4']
exp_53_4 = exp_data['53_4']
exp_58_4 = exp_data['58_4']
exp_64_4 = exp_data['64_4']
exp_68_4 = exp_data['68_4']
exp_31_5 = exp_data['31_5']
exp_39_5 = exp_data['39_5']
exp_46_5 = exp_data['46_5']
exp_53_5 = exp_data['53_5']
exp_58_5 = exp_data['58_5']
exp 64 5 = exp_data['64_5']
exp 68 5 = exp data['68 5']
exp_31_6 = exp_data['31_6']
exp_39_6 = exp_data['39_6']
exp_46_6 = exp_data['46_6']
exp_53_6 = exp_data['53_6']
exp_58_6 = exp_data['58_6']
exp_64_6 = exp_data['64_6']
exp_68_6 = exp_data['68_6']
exp_31_7 = exp_data['31_7']
exp_39_7 = exp_data['39_7']
exp_46_7 = exp_data['46_7']
exp 53 7 = exp data['53 7']
exp_58_7 = exp_data['58_7']
exp_64_7 = exp_data['64_7']
exp_68_7 = exp_data['68_7']
d 1 = exp data.at[0, 'd 1']
d 2 = exp data.at[0, 'd 2']
d_3 = exp_data.at[0, 'd_3']
d_4 = exp_data.at[0, 'd_4']
```

d 5 = exp data.at[0, 'd_5'] d_6 = exp_data.at[0, 'd_6'] d 7 = exp_data.at[0, 'd_7'] #Calculates sum of difference squared across all angles for a given wavelength def DR_R_func_1(j, d, lambda1, n21s, k21s, n21p, k21p, n11, k11): $sum_diff_sqrd = 0$ n0 = 1N11 = complex(n11, k11)N21s = complex(n21s, k21s) N21p = complex(n21p, k21p)#print(N21s) for i in angle: theta0 = iif theta0 == (np.deg2rad(31)): **if** d == d_1: exp_value = exp_31_1[j] **elif** d == d 2: exp_value = exp_31_2[j] **elif** d == d 3: exp_value = exp_31_3[j] **elif** d == d 4: exp_value = exp_31_4[j]
elif d == d_5: $exp_value = exp_31_5[j]$ **elif** d == d 6: exp_value = exp_31_6[j] **elif** d == d 7: exp_value = exp_31_7[j] elif theta0 == (np.deg2rad(39)): **if** d == d 1: exp_value = exp_39_1[j] **elif** d == d 2: exp_value = exp_39_2[j] **elif** d == d_3: exp_value = exp_39_3[j] **elif** d == d 4: $exp_value = exp_39_4[j]$ **elif** d == d 5: $exp_value = exp_39_5[j]$ **elif** d == d 6: $exp_value = exp_39_6[j]$ **elif** d == d 7: exp_value = exp_39 7[j] elif theta0 == (np.deg2rad(46)): **if** d == d 1: $exp value = exp_{46_1[j]}$ **elif** d == d_2: $exp_value = exp_46_2[j]$ **elif** d == d 3: $exp_value = exp_46_3[j]$ **elif** d == d 4: exp value = exp 46 4[j]**elif** d == d_5: $exp_value = exp_46_5[j]$ **elif** d == d 6: $exp_value = exp_46_6[j]$ **elif** d == d 7: $exp_value = exp_46 7[j]$ elif theta0 == (np.deg2rad(53)): **if** d == d 1: exp_value = exp_53_1[j] **elif** d == d 2: $exp_value = exp_53_2[j]$ **elif** d == d_3:

exp value = exp 53 3[j] **elif** d == d 4: $exp_value = exp_53_4[j]$ **elif** d == d 5: $exp_value = exp_53_5[j]$ **elif** d == d 6: $exp_value = exp_53_6[j]$ **elif** d == d_7: exp_value = exp_53 7[j] elif theta0 == (np.deg2rad(58)): **if** d == d 1: $exp value = exp_58_1[j]$ **elif** d == d 2: exp_value = exp_58_2[j] **elif** d == d 3: $exp_value = exp_58_3[j]$ **elif** d == d 4: exp value = exp 58 4[j]**elif** d == d_5: $exp_value = exp_58_5[j]$ **elif** d == d 6: exp_value = exp_58_6[j] **elif** d == d 7: $exp_value = exp_58_7[j]$ elif theta0 == (np.deg2rad(64)): **if** d == d 1: $exp_value = exp_64_1[j]$ **elif** d == d 2: exp value = exp 64 2[j]**elif** d == d_3: exp_value = exp_64_3[j] **elif** d == d 4: exp_value = exp_64_4[j] **elif** d == d 5: $exp_value = exp_64_5[j]$ **elif** d == d 6: exp_value = exp_64_6[j] **elif** d == d_7: exp value = exp 64 7[j] elif theta0 == (np.deg2rad(68)): **if** d == d 1: $exp_value = exp_68_1[j]$ **elif** d == d_2: $exp_value = exp_68_2[j]$ **elif** d == d 3: $exp_value = exp_68_3[j]$ **elif** d == d 4: exp value = exp 68 4[j] **elif** d == d 5: exp value = exp 68 5[j]**elif** d == d 6: exp_value = exp_68_6[j] **elif** d == d 7: $exp_value = exp_68_7[j]$ costheta1 = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0))**2)) / N11))) costheta2s = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0))**2)) / N21s))) costheta2p = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0)) ** 2)) / N21p))) deltaa = (2 * np.pi * d * N11 * costheta1) / lambda1 rlp = ((N11 * np.cos(theta0)) - (n0 * costheta1)) / ((N11 * np.cos(theta0)) + (n0 * costheta1)) rls = ((n0 * np.cos(theta0)) - (N11 * costheta1)) / ((n0 *np.cos(theta0)) + (N11 * costheta1)) r2p = ((N21p * costheta1) - (N11 * costheta2p)) / ((N21p * costheta1))+ (N11 * costheta2p)) r2s = ((N11 * costheta1) - (N21s * costheta2s)) / ((N11 * costheta1) +

```
(N21s * costheta2s))
                        r02p = ((N21p * np.cos(theta0)) - (n0 * costheta2p)) / ((N21p * np.cos(theta0))) / (
np.cos(theta0)) + (n0 * costheta2p))
                        r02s = ((n0 * costheta1) - (N21s * costheta2s)) / ((N21s *
np.cos(theta0)) + (n0 * costheta2s))
                        RP = abs((r1p + (r2p * np.exp(-2j*deltaa))) / (1 + (r1p * r2p *
np.exp(-2j*deltaa))))**2
                        RS = abs((r1s + (r2s * np.exp(-2j*deltaa))) / (1 + (r1s * r2s *
np.exp(-2j*deltaa))))**2
                        ROP = (abs(rO2p)) * * 2
                        ROS = (abs(rO2s)) * * 2
                        R = RP + RS
                        R0 = R0P + R0S
                        deltaR_over_R = (R-R0)/R0
                        diff = abs(exp value - deltaR over R)
                        sum_diff_sqrd += (diff**2)
            return sum_diff_sqrd
#Gives simulated spectra using optimised values
def DR R func 2(theta0, d, lambda1, n21s, k21s, n21p, k21p, n11, k11):
           n0 = 1
           N11 = complex(n11, k11)
           N21s = complex(n21s, k21s)
           N21p = complex(n21p, k21p)
           costheta1 = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0))**2)) / N11)))
costheta2s = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0))**2)) / N21s)))
costheta2p = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0)) ** 2)) / N21p)))
           deltaa = (2 * np.pi * d * N11 * costhetal) / lambdal
           rlp = ((N11 * np.cos(theta0)) - (n0 * costheta1)) / ((N11 *
np.cos(theta0)) + (n0 * costheta1))
            rls = ((n0 * np.cos(theta0)) - (N11 * costheta1)) / ((n0 * np.cos(theta0)))
+ (N11 * costhetal))
            r2p = ((N21p * costheta1) - (N11 * costheta2p)) / ((N21p * costheta1) +
 (N11 * costheta2p))
           r2s = ((N11 * costhetal) - (N21s * costheta2s)) / ((N11 * costheta1) +
 (N21s * costheta2s))
           r02p = ((N21p * np.cos(theta0)) - (n0 * costheta2p)) / ((N21p * np.cos(theta0)) - (n0 * costheta2p)) / ((N21p * np.cos(theta0)) / ((N21p * np.cos(theta0)) - (n0 * costheta2p)) / ((N21p * np.costheta2p)) / ((N21p
np.cos(theta0)) + (n0 * costheta2p))
           r02s = ((n0 * costheta1) - (N21s * costheta2s)) / ((N21s * np.cos(theta0))
+ (n0 * costheta2s))
            RP = abs((r1p + (r2p * np.exp(-2j*deltaa)))) / (1 + (r1p * r2p * np.exp(-
2j*deltaa))))**2
           RS = abs((r1s + (r2s * np.exp(-2j*deltaa)))) / (1 + (r1s * r2s * np.exp(-
2j*deltaa))))**2
           ROP = (abs(rO2p)) * * 2
           ROS = (abs(rO2s)) * * 2
           R = RP + RS
           R0 = R0P + R0S
           deltaR_over_R = (R-R0)/R0
           return deltaR over R
#pulls n and k as separate variables
def func wrap(x):
            n11, k11 = x
            fx = ((DR R func 1(j, d 1, exp lambda1[j], exp n21s[j], exp k21s[j]),
exp n21p[j], exp k21p[j], n11, k11)+
                            (DR_R_func_1(j, d_2, exp_lambda1[j], exp_n21s[j], exp_k21s[j],
exp_n21p[j], exp_k21p[j], n11, k11))+
```

```
(DR R func 1(j, d 3, exp lambda1[j], exp n21s[j], exp k21s[j],
exp_n21p[j], exp_k21p[j], n11, k11))+
         (DR_R_func_1(j, d_4, exp_lambda1[j], exp_n21s[j], exp_k21s[j],
exp_n21p[j], exp_k21p[j], n11, k11))+
         (DR R func 1(j, d 5, exp lambda1[j], exp n21s[j], exp k21s[j],
exp n21p[j], exp k21p[j], n11, k11))+
         (DR_R_func_1(j, d_6, exp_lambda1[j], exp_n21s[j], exp_k21s[j],
exp_n21p[j], exp_k21p[j], n11, k11))+
(DR_R_func_1(j, d_7, exp_lambda1[j], exp_n21s[j], exp_k21s[j], exp_n21p[j], exp_k21p[j], n11, k11)))
   return fx
#Allows iteration with float step size
def seq(start, stop, step=1):
   n = int(round((stop - start) / float(step)))
   if n > 1:
       return ([start + step * i for i in range(n + 1)])
   else:
       return ([])
#Finds the starting guess for n and k by brute force approach
s = 20
for j in range(0, 1):
    #print(exp_lambda1[j])
    for n11 in seq(0.5, 3, 0.2):
        for k11 in seq(0.000, 1, 0.001):
           sol_1 = DR_R_func_1(j, d_1, exp_lambda1[j], exp_n21s[j],
exp_k21s[j], exp_n21p[j], exp_k21p[j], n11, k11)
           sol_3 = DR_R_func_1(j, d_3, exp_lambda1[j], exp_n21s[j],
exp_k21s[j], exp_n21p[j], exp_k21p[j], n11, k11)
           sol_4 = DR_R_func_1(j, d_4, exp_lambda1[j], exp_n21s[j],
exp_k21s[j], exp_n21p[j], exp_k21p[j], n11, k11)
           sol_6 = DR_R_func_1(j, d_6, exp_lambda1[j], exp_n21s[j],
exp_k21s[j], exp_n21p[j], exp_k21p[j], n11, k11)
sol_7 = DR_R_func_1(j, d_7, exp_lambda1[j], exp_n21s[j],
exp_k21s[j], exp_n21p[j], exp_k21p[j], n11, k11)
           sol sum = sol 1 + sol 2 + sol 3 + sol 4 + sol 5 + sol 6 + sol 7
           if sol sum < s:</pre>
               s = sol sum
               n11 guess = n11
               k11 \text{ guess} = k11
#Seeding part
#Takes previous value of n and k for starting guess
for j in range(0,len(exp_lambda1)):
   if j == 0:
       res_wrapped = least_squares(func_wrap, (n11_guess, k11_guess),
bounds=([0, 0], [5, 5]))
                         #optimisation using guess
       z = res_wrapped.x[0] + res_wrapped.x[1] * 1j
       ntarget.append(res wrapped.x[0])
       ktarget.append(res_wrapped.x[1])
    elif j != 0:
       res_wrapped = least_squares(func_wrap, (ntarget[j-1], ktarget[j-1]),
bounds=([0, 0], [5, 5])) #optimisation using previous wavelength value
       z = res wrapped.x[0] + res wrapped.x[1] * 1j
       ntarget.append(res wrapped.x[0])
       ktarget.append(res_wrapped.x[1])
```

```
#Calls function to give simulated spectra for each angle
for i in angle:
    theta0 = i
    for x in range(0, len(exp lambda1)):
        if theta0 == np.deg2rad(31):
            a = DR R func 2(i, d 1, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim_31_1.append(a)
            residual_a = (a - exp_31_1[x])**2
            res_31_1.append(residual_a)
            b = DR_R_func_2(i, d_2, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 31 2.append(b)
            residual_b = (b - \exp_{31_2[x]}) * * 2
            res 31 2.append(residual b)
            c = DR_R_func_2(i, d_3, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 31 3.append(c)
            residual_c = (c - exp_{31_3[x]}) * * 2
            res_31_3.append(residual_c)
            dd = DR_R_func_2(i, d_4, exp_lambdal[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim \overline{31} 4.append(dd)
            residual d = (dd - exp 31 4[x]) ** 2
            res_31_4.append(residual_d)
ee = DR R func_2(i, d_5, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 31 5.append(ee)
            residual e = (ee - exp 31 5[x]) ** 2
            res_31_5.append(residual_e)
            f = DR_R_func_2(i, d_6, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 31 6.append(f)
            residual f = (f - exp 31 6[x]) ** 2
            res 31 6.append(residual f)
            g = DR_R_func_2(i, d_7, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim_31_7.append(g)
            residual g = (g - \exp_{31}7[x]) ** 2
            res_31_7.append(residual_g)
        elif theta0 == np.deg2rad(39):
            a = DR_R_func_2(i, d_1, exp_lambdal[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 39 1.append(a)
            residual a = (a - exp 39 1[x]) **2
            res 39 1.append(residual a)
            b = DR_R_func_2(i, d_2, exp_lambdal[x], exp_n21s[x], exp_k21s[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim 39_2.append(b)
            residual b = (b - exp 39 2[x]) **2
            res 39 2.append(residual b)
            c = DR_R_func_2(i, d_3, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 39 3.append(c)
            residual c = (c - exp 39 3[x]) * * 2
            res 39 3.append(residual c)
            dd = DR_R_func_2(i, d_4, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 39 4.append(dd)
            residual d = (dd - exp 39 4[x]) ** 2
            res 39 4. append (residual d)
            ee = DR_R_func_2(i, d_5, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 39 5.append(ee)
            residual e = (ee - exp 39 5[x]) ** 2
            res 39 5.append(residual e)
            f = DR_R_func_2(i, d_6, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
```

sim 39 6.append(f) residual f = $(f - \exp 39 6[x]) ** 2$ res_39_6.append(residual_f) g = DR R func 2(i, d 7, exp lambdal[x], exp n21s[x], exp k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 39 7.append(g) $residual_g = (g - exp_{39_7[x]}) ** 2$ res_39_7.append(residual_g) elif theta0 == np.deg2rad(46): a = DR_R_func_2(i, d_1, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim 46 1.append(a) residual $a = (a - \exp 46 1[x]) * * 2$ res_46_1.append(residual_a) b = DR_R_func_2(i, d_2, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 46 2.append(b) residual b = $(b - \exp 462[x]) * * 2$ res 46 2.append(residual b) c = DR_R_func_2(i, d_3, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 46 3.append(c) residual c = (c - exp 46 3[x]) * * 2res_46_3.append(residual_c) dd = DR_R_func_2(i, d_4, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim_46_4.append(dd) residual d = $(dd - exp_46_4[x]) ** 2$ res 46 4.append(residual d) ee = DR_R_func_2(i, d_5, exp_lambdal[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 46 5.append(ee) residual e = (ee - exp 46 5[x]) ** 2 res 46 5.append (residual e) $f = DR_{r_1}(x), c_1(x), c_2(x), c_2$ exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_46_6.append(f) residual_f = $(f - \exp_{46}[x]) * 2$ res 46 6.append(residual f) g = DR_R_func_2(i, d_7, exp_lambdal[x], exp_n21s[x], exp_k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_46_7.append(g) residual $g = (g - \exp 467[x]) ** 2$ res 46 7.append(residual g) elif theta0 == np.deg2rad(53): a = DR_R_func_2(i, d_1, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_53_1.append(a) $residual_a = (a - exp_{53_1[x]})**2$ res 53 1.append(residual a) b = DR R func 2(i, d 2, exp lambdal[x], exp n21s[x], exp k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) $sim \overline{5}3$ 2.append(b) residual b = $(b - \exp 53 2[x]) * * 2$ res 53 2.append(residual b) c = DR_R_func_2(i, d_3, exp_lambdal[x], exp_n21s[x], exp_k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_53_3.append(c) residual c = $(c - \exp 53 3[x]) * * 2$ res 53 3.append(residual_c) dd = DR R func 2(i, d 4, exp lambda1[x], exp n21s[x], exp k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_53_4.append(dd) residual d = (dd - exp 53 4[x]) ** 2res 53 4.append(residual d) ee = DR R func 2(i, d 5, exp lambda1[x], exp n21s[x], exp k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_53_5.append(ee)

residual e = (ee - exp 53 5[x]) ** 2res_53_5.append(residual_e) $f = DR_R func_2(i, d_6, exp_lambda1[x], exp_n21s[x], exp_k21s[x],$ exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 53_6.append(f) residual $f = (f - \exp 53 6[x]) ** 2$ res_53_6.append(residual_f) g = DR_R_func_2(i, d_7, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_53_7.append(g) residual_g = $(g - \exp_53_7[x]) ** 2$ res 53 7.append(residual g) elif theta0 == np.deg2rad(58): a = DR_R_func_2(i, d_1, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 58 1.append(a) residual a = (a - exp 58 1[x]) * *2res 58 1.append(residual a) b = DR_R_func_2(i, d_2, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 58 2.append(b) residual b = $(b - \exp 58 2[x]) * * 2$ res 58 2.append(residual b) c = DR_R_func_2(i, d_3, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim 58 3.append(c) residual_c = $(c - exp_58_3[x]) * *2$ res 58 3.append(residual c) dd = DR R func 2(i, d 4, exp lambda1[x], exp n21s[x], exp k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim 58 4.append(dd) residual d = (dd - exp 58 4[x]) ** 2res 58_4.append(residual_d) ee = DR R func 2(i, d 5, exp lambda1[x], exp n21s[x], exp k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 58 5.append(ee) residual e = (ee - $exp_{58}[x]$) ** 2 res_58_5.append(residual_e) f = DR_R_func_2(i, d_6, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x]) sim_58_6.append(f) residual_f = $(f - \exp_{58}[x]) ** 2$ res 58 6.append(residual f) g = DR_R_func_2(i, d_7, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 58 7.append(g) residual_g = $(g - \exp_58_7[x]) ** 2$ res 58 7.append(residual g) elif theta0 == np.deg2rad(64): a = DR R func 2(i, d 1, exp lambdal[x], exp n21s[x], exp k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim_64_1.append(a) residual_a = $(a - \exp_{64}[x]) * * 2$ res 64 1.append(residual a) b = DR_R_func_2(i, d_2, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim_64_2.append(b) residual_b = $(b - \exp_{64} 2[x]) * * 2$ res 64 2.append(residual b) c = DR_R_func_2(i, d_3, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim 64 3.append(c) residual_c = $(c - \exp_{64_3[x]}) * * 2$ res 64 3.append(residual_c) dd = DR_R_func_2(i, d_4, exp_lambda1[x], exp_n21s[x], exp_k21s[x], exp n21p[x], exp k21p[x], ntarget[x], ktarget[x]) sim_64_4.append(dd) residual_d = $(dd - exp_{64_4[x]}) ** 2$

```
res 64 4.append(residual d)
            ee = DR_R_func_2(i, d_5, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 64 5.append(ee)
            residual e = (ee - exp 64 5[x]) ** 2
            res 64 5.append(residual e)
            f = DR_{r_1} (i, d_6, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim 64 6.append(f)
            residual f = (f - \exp 64 6[x]) ** 2
            res 64 6.append(residual f)
            g = DR R func 2(i, d 7, exp lambda1[x], exp n21s[x], exp k21s[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim 64 7.append(g)
            residual_g = (g - exp_64_7[x]) ** 2
res_64_7.append(residual_g)
        elif theta0 == np.deg2rad(68):
            a = DR R func 2(i, d 1, exp lambda1[x], exp n21s[x], exp k21s[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim 68 1.append(a)
            residual a = (a - exp 68 1[x])**2
            res 68 1.append(residual a)
            b = DR R func 2(i, d 2, exp lambdal[x], exp n21s[x], exp k21s[x],
exp_n21p[x], exp_k21p[x], ntarget[x], ktarget[x])
            sim_68_2.append(b)
            residual b = (b - \exp 68 2[x]) * * 2
            res_68_2.append(residual_b)
            c = DR_R_func_2(i, d_3, exp_lambdal[x], exp_n21s[x], exp_k21s[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim_68_3.append(c)
            residual_c = (c - exp_{68_3[x]}) * *2
            res 68 3.append(residual c)
            dd = DR_R_func_2(i, d_4, exp_lambda1[x], exp_n21s[x], exp_k21s[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim 68 4.append(dd)
            residual_d = (dd - exp_{68}_4[x]) ** 2
            res_68_4.append(residual_d)
            ee = DR_R_func_2(i, d_5, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim_68_5.append(ee)
            residual_e = (ee - \exp_{68} 5[x]) ** 2
            res_68_5.append(residual_e)
            f = DR_R_func_2(i, d_6, exp_lambdal[x], exp_n2ls[x], exp_k2ls[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim 68 6.append(f)
            residual_f = (f - \exp_{68}[x]) * 2
            res_68_6.append(residual f)
            g = DR R func 2(i, d 7, exp lambdal[x], exp n21s[x], exp k21s[x],
exp n21p[x], exp k21p[x], ntarget[x], ktarget[x])
            sim 68 7.append(q)
            residual_g = (g - exp_{68_7[x]}) ** 2
            res_68_7.append(residual_g)
        else:
            break
```

| | res si i, |
|--|--|
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| 'sim_46_2': | sim_46_2, |
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| 'sim_64_2': | sim_64_2, |
| 'sim 68 2': | sim 68 2, |
| 100 31 21. | rag 31 2 |
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| 'res_39_2': | res_39_2, |
| 'res 46 2': | res 46 2, |
| 'res 53 2' | res 53 2. |
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| 'res_58_2': | res_s8_2, |
| 'res 64 2': | res 64 2, |
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| <pre>'sim_46_4': 'sim_53_4': 'sim_58_4': 'sim_64_4': 'res_31_4': 'res_39_4': 'res_53_4': 'res_64_4': 'res_64_4': 'res_64_4': 'res_64_4': 'sim_31_5': 'sim_46_5': 'sim_53_5': 'sim_64_5': 'res_31_5': 'res_31_5': 'res_39_5': 'res_53_5': 'res_64_5': 'res_64_5': 'res_64_5': 'res_64_5': 'res_64_5': 'res_64_5': 'res_64_5': 'res_64_5': 'res_64_5': 'res_64_5': 'sim_31_6': 'sim_39_6': 'sim_53_6':</pre> | sim_46_4, sim_53_4, sim_58_4, sim_64_4, sim_68_4, res_31_4, res_39_4, res_53_4, res_64_4, res_68_4, sim_31_5, sim_32_5, sim_64_5, sim_53_5, sim_64_5, sim_64_5, res_31_5, res_32_5, res_32_5, res_58_5, res_58_5, res_58_5, res_58_5, res_64_5, res_53_5, res_64 |

| 'sim_64_6': | sim_64_6, |
|-------------|-----------|
| 'sim_68_6': | sim_68_6, |
| 'res 31 6': | res 31 6, |
| 'res 39 6': | res 39 6, |
| 'res 46 6': | res 46 6, |
| 'res 53 6': | res_53_6, |
| 'res 58 6': | res_58_6, |
| 'res 64 6': | res 64 6, |
| 'res_68_6': | res_68_6, |
| 'sim 31 7': | sim 31 7, |
| 'sim 39 7': | sim_39_7, |
| 'sim 46 7': | sim_46_7, |
| 'sim 53 7': | sim_53_7, |
| 'sim 58 7': | sim_58_7, |
| 'sim_64_7': | sim_64_7, |
| 'sim_68_7': | sim_68_7, |
| 'res_31_7': | res_31_7, |
| 'res_39_7': | res_39_7, |
| 'res_46_7': | res_46_7, |
| 'res_53_7': | res_53_7, |
| 'res_58_7': | res_58_7, |
| 'res_64_7': | res_64_7, |
| 'res_68_7': | res_68_7, |
| }) | |

```
#Make several outputs, all named accordingly with correct dataframe
ffile = open('benzene xtal all thicknesses b.txt', 'w+')  #RENAME AS
NEEDED
ffile.write(str(table))
ffile.close()
end = time.time()
print("Calculation took {} s".format((end - start)))
```

```
print("\nThis is it, James!")
```

Appendix 2: Code to simulate a UV/vis spectrum from

the refractive index

```
#Code to simulate a UV spectrum from the n and k values for an ice
#Written by James Stubbing
#Import relvant modules
import numpy as np
import pandas as pd
import time
start = time.time()
                                         #Allows time taken for the code to run
to be recorded
pd.set option('display.max rows', 2000)
                                                #Set panda to show all the
data
pd.set option('display.max columns', 2000)
#List of reflection angles
angle = [np.deg2rad(31), np.deg2rad(39), np.deg2rad(46), np.deg2rad(53),
np.deg2rad(58), np.deg2rad(64), np.deg2rad(68)]
#Reads in all relevant constant data
#wavelength and graphite optical parameters
graphite data =
pd.read csv('N:\Documents\Python\Testing\inputs\graphite linnartz water.csv')
lambda1 = graphite_data['lambda1']
n21s = graphite data['n21s']
k21s = graphite_data['k21s']
n21p = graphite data['n21p']
k21p = graphite data['k21p']
#Set thicknesses required
d 100 = 100 #thicknesses.at[0, 'd 100']
d_200 = 200 #thicknesses.at[0, 'd_200']
d_250 = 250 #thicknesses.at[0, 'd_250']
d_400 = 400 #thicknesses.at[0, 'd_400']
d_500 = 500 #thicknesses.at[0, 'd_500']
#Read in known ice n and k values
adsorbate =
pd.read csv('N:\Documents\Python\Testing\inputs\k n water linnartz.csv')
n11 = adsorbate['n11']
k11 = adsorbate['k11']
#Produces spectra using all input data
def DR_R_func(theta0, d, lambda1, n21s, k21s, n21p, k21p, n11, k11):
    n0 = 1
    N11 = complex(n11, k11)
    N21s = complex(n21s, k21s)
    N21p = complex(n21p, k21p)
    costheta1 = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0))**2)) / N11)))
    costheta2s = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0))**2)) / N21s)))
    costheta2p = np.sqrt((1 - ((n0 ** 2 * ((np.sin(theta0)) ** 2)) / N21p)))
    deltaa = (2 * np.pi * d * N11 * costhetal) / lambdal
    rlp = ((N11 * np.cos(theta0)) - (n0 * costheta1)) / ((N11 *
```

```
np.cos(theta0)) + (n0 * costheta1))
          rls = ((n0 * np.cos(theta0)) - (N11 * costheta1)) / ((n0 * np.cos(theta0)))
+ (N11 * costheta1))
          r2p = ((N21p * costheta1) - (N11 * costheta2p)) / ((N21p * costheta1) +
 (N11 * costheta2p))
          r2s = ((N11 * costheta1) - (N21s * costheta2s)) / ((N11 * costheta1) +
 (N21s * costheta2s))
          r02p = ((N21p * np.cos(theta0)) - (n0 * costheta2p)) / ((N21p * np.costheta0)) - (n0 * costheta2p)) / ((N21p * np.costheta0)) - (n0 * costheta2p)) / ((N21p * np.costheta0)) - (n0 * costheta0)) - (n0 * cos
np.cos(theta0)) + (n0 * costheta2p))
          r02s = ((n0 * costheta1) - (N21s * costheta2s)) / ((N21s * np.cos(theta0)))
+ (n0 * costheta2s))
          RP = abs((r1p + (r2p * np.exp(-2j*deltaa))) / (1 + (r1p * r2p * np.exp(-
2j*deltaa))))**2
          RS = abs((r1s + (r2s * np.exp(-2j*deltaa))) / (1 + (r1s * r2s * np.exp(-
2j*deltaa))))**2
          ROP = (abs(rO2p)) * * 2
          ROS = (abs(rO2s)) * * 2
          R = RP + RS
          R0 = R0P + R0S
          deltaR_over_R = (R-R0)/R0
          #print(deltaR over R)
          return deltaR_over_R
#lists for output values
sim 31 100 = []
sim 39 100 = []
sim_{46}100 = []
sim_53_100 = []
sim_58_100 = []
sim_{64} 100 = []
sim 68 100 = []
sim_31_200 = []
sim_{39}_{200} = []
sim_{46_{200}} = []
sim 53 200 = []
sim 58 200 = []
sim_{64}200 = []
sim_{68}200 = []
sim_31_250 = []
sim_39_250 = []
sim 46 250 = []
sim 53 250 = []
sim_{58}250 = []
sim_{64}250 = []
sim_{68}250 = []
sim_{31}^{-}400 = []
sim 39 400 = []
sim 46 400 = []
sim_53_400 = []
sim_58_400 = []
sim_64_400 = []
sim 68 400 = []
sim 31 500 = []
sim_{39}_{500} = []
sim_{46}500 = []
sim_{53}500 = []
sim 58 500 = []
sim 64 500 = []
sim 68 500 = []
#Calls function to produce spectra
```

#Calls function to produce spectr
for i in angle:
 theta0 = i
 #print(theta0)

for x in range(0, len(lambda1)): a = DR_R_func(i, d_100, lambda1[x], n21s[x], k21s[x], n21p[x], k21p[x], n11[x], k11[x]) $b = DR_R_func(i, d_{200}, lambda1[x], n21s[x], k21s[x], n21p[x],$ k21p[x], n11[x], k11[x]) c = DR R func(i, d 250, lambda1[x], n21s[x], k21s[x], n21p[x], k21p[x], n11[x], k11[x]) e = DR_R_func(i, d_400, lambda1[x], n21s[x], k21s[x], n21p[x], k21p[x], n11[x], k11[x]) f = DR_R_func(i, d_500, lambda1[x], n21s[x], k21s[x], n21p[x], k21p[x], n11[x], k11[x]) if theta0 == np.deg2rad(33): sim_31_100.append(a) sim_31_200.append(b) sim 31 250.append(c) sim 31 400.append(e) sim 31 500.append(f) elif theta0 == np.deg2rad(37): sim_39_100.append(a) sim_39_200.append(b)
sim_39_250.append(c) sim 39 400.append(e) sim 39 500.append(f) elif theta0 == np.deg2rad(48): sim_46_100.append(a) sim_46_200.append(b)
sim_46_250.append(c) sim 46 400.append(e) sim 46 500.append(f) elif theta0 == np.deg2rad(51): sim_53_100.append(a)
sim_53_200.append(b) sim 53 250.append(c) sim 53 400.append(e) sim 53 500.append(f) elif theta0 == np.deg2rad(60): sim_58_100.append(a) sim 58 200.append(b) sim 58 250.append(c) sim_58_400.append(e) sim_58_500.append(f) elif theta0 == np.deg2rad(62): sim 64 100.append(a) sim 64 200.append(b) sim 64 250.append(c) sim_64_400.append(e) sim_64_500.append(f) elif theta0 == np.deg2rad(70): sim 68_100.append(a) sim 68 200.append(b) sim 68 250.append(c) sim_68_400.append(e) sim 68 500.append(f) else: break

| 'sim_ | 48 | 200' | : | sim_ | 46 | 200, |
|-------|------|------|---|------|------|------|
| 'sim | 51 | 200' | : | sim_ | 53 | 200, |
| 'sim_ | 60 | 200' | : | sim_ | 58 | 200, |
| 'sim_ | 62 | 200' | : | sim_ | _64_ | 200, |
| 'sim_ | 70 | 200' | : | sim_ | _68_ | 200, |
| 'sim_ | 33 | 250' | : | sim_ | _31_ | 250, |
| 'sim_ | 37 | 250' | : | sim_ | _39_ | 250, |
| 'sim_ | 48 | 250' | : | sim_ | 46 | 250, |
| 'sim_ | 51 | 250' | : | sim_ | _53_ | 250, |
| 'sim_ | 60 | 250' | : | sim_ | _58_ | 250, |
| 'sim_ | 62 | 250' | : | sim_ | _64_ | 250, |
| 'sim_ | _70_ | 250' | : | sim_ | _68_ | 250, |
| 'sim_ | _33_ | 400' | : | sim_ | _31_ | 400, |
| 'sim_ | 37 | 400' | : | sim_ | 39 | 400, |
| 'sim_ | 48 | 400' | : | sim_ | 46_ | 400, |
| 'sim_ | 51 | 400' | : | sim_ | _53_ | 400, |
| 'sim_ | 60 | 400' | : | sim_ | _58_ | 400, |
| 'sim_ | 62 | 400' | : | sim_ | _64_ | 400, |
| 'sim_ | _70_ | 400' | : | sim_ | _68_ | 400, |
| 'sim_ | _33_ | 500' | : | sim_ | _31_ | 500, |
| 'sim_ | _37_ | 500' | : | sim_ | _39_ | 500, |
| 'sim_ | 48 | 500' | : | sim_ | _46_ | 500, |
| 'sim_ | 51 | 500' | : | sim_ | _53_ | 500, |
| 'sim_ | 60 | 500' | : | sim_ | _58_ | 500, |
| 'sim_ | 62 | 500' | : | sim_ | _64_ | 500, |
| 'sim_ | 70_ | 500' | : | sim_ | _68_ | 500 |
| }) | | | | | | |

```
#writes dataframe to file
ffile = open('SIMULATIONS_water_linnartz_angleplusandminus2.txt', 'w+')
ffile.write(str(table))
ffile.close
end = time.time()
print("Calculation took {} s".format((end - start)))
```