Systematic Mid-IR And VUV Studies Of Electron Irradiated CO$_2$\text{NH}_3 Interstellar Ice Analogues

Thesis

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Systematic mid-IR and VUV studies of electron irradiated CO$_2$:NH$_3$ interstellar ice analogues

A thesis submitted in partial fulfilment for the degree of

*Doctor of Philosophy*

Rachel Louise James

Astronomy
School of Physical Sciences
The Open University

December 2019
I would like to dedicate this thesis to my parents, I will never be able to convey just how much their unconditional love and support means to me.
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Abstract

Over 200 molecules have been detected in the interstellar medium (ISM) but the formation pathways for most of these molecules remains elusive. It is now believed that a major route of molecular synthesis lies within the processing of interstellar ices formed on microscopic dust grains created in the cycle of star birth and death. However, despite decades of experimental research on molecular synthesis in ice films, the lack of a systematic approach to ISM analogue experiments means that there is still no comprehensive understanding of the influence of discrete experimental parameters on the synthesis of any molecular system under ISM conditions.

To demonstrate the advantages of performing a systematic study, this thesis presents a comprehensive analysis of thermal and electron processing of CO$_2$:NH$_3$ binary mixtures as a function of mixing ratio. A combination of mid-IR and VUV spectroscopy is used to identify chemical products and explore the morphology within the ice mixture demonstrating the advantages of the complementarity of the two spectroscopic methods. Mid-IR spectroscopy of the thermal processing of CO$_2$:NH$_3$ mixtures revealed that the ice structure is ratio dependent and that products formed by electron processing of such ices is dependent on the initial ratio of the ice. VUV spectroscopy revealed a thermal reaction which is not observed from the mid-IR spectroscopic studies and allowed new products to be identified.

This thesis therefore establishes the need to adopt a more systematic approach to ISM analogue experiments. Such comprehensive and coherent experimental data will improve the interpretation of the next generation of astrochemical observations whilst simultaneously allowing more accurate models of molecular synthesis in the ISM to be developed which in turn allows for a better understanding of processes involved in star and planet formation.
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Chapter 1

Introduction

Laboratory astrochemical experiments are important for the interpretation of observational data, for providing parameters for astrochemical models and for understanding the chemistry that occurs within space, often very different from that occurring under terrestrial conditions. The next decade promises to provide opportunities to explore the chemical nature of our universe in new and in depth ways that will help to revolutionise our understanding of ‘astrochemistry’ and its role in star and planet formation and ultimately perhaps our knowledge of the origins of life. In particular, the launch of JWST will provide higher resolution observations allowing increasingly complex molecules to be detected in discrete regions of the interstellar medium (ISM) such that their role in star and planet formation may be explored. However, the interpretation of such observations and the underlying physics and chemistry of the environment in which such molecules are detected will crucially depend on the quality and coherence of the laboratory data that allows such observations to be interpreted.

Most of the larger, more complex molecules detected in space are thought to form in the icy mantles around interstellar dust grains before they are desorbed to be detected in the gas phase. Section 1.1 provides an inventory of molecules observed in the Universe with an emphasis on molecules observed in the solid phase. Section 1.2 gives examples of observations of ice in the ISM, on comets and the icy bodies of the Solar System. Background information about the routes to molecular synthesis in the solid phase is given in Section 1.3. Examples of different astrochemical models used to describe molecular synthesis and the role of astrochemistry in the ISM is provided in Section 1.4. Finally, a short review of the different types of astrochemical laboratory experiments is presented in Section 1.5 and the motivation for this thesis is given in Section 1.6.
1.1 Molecules in space

It has been just over 80 years since the first molecule was observed in the ISM and advances in telescope technology have resulted in an average of $\sim 3.7$ new molecules being detected per year.\textsuperscript{1} This section will list the molecules which have been detected in the ISM (and circumstellar shells) and discuss the link that these molecules have to star formation. A list of molecules detected on comets, the remnants of planetesimals, which contain information about the chemical composition during the early Solar System is also provided. Finally, a list of molecules detected in the ice phase on the icy bodies of the Solar System planets is given.

1.1.1 Molecules in the ISM and circumstellar shells

A variety of molecules have been detected in the ISM and circumstellar shells. Tables 1.1 and 1.2 show all the molecules which have been detected in the ISM and circumstellar shells as of August 2019. All of the molecules in Table 1.1 and 1.2 have been observed in the gas phase either through their rotational or electronic structure. The molecules highlighted in blue represent molecules which have also been detected in the solid phase in the form of ice and are exclusively observed via their vibrational modes.

Simple molecules, or molecules with $\leq 5$ atoms are shown in Table 1.1. So called ‘complex organic molecules (COMs)’ are shown in Table 1.2. COMs refers to molecules, mainly organic in nature, which have $\geq 6$ atoms. Compared to molecules on Earth and in terms of chemistry on Earth, these are not complex molecules but in astronomical terms they are considered complex. Large molecules are difficult to observe in space (see Section 1.2 for more details) and COMs represent some of the largest molecules observed to date. They also represent some of the most biologically interesting molecules in space. For example, glycolaldehyde\textsuperscript{4} and glycolonitrile\textsuperscript{5} have both been detected in space and both molecules are considered as building blocks for life.

Historically, the ISM was considered too hostile an environment for molecules to form. The interstellar radiation field (ISRF) which has components in the far-ultraviolet and vacuum ultraviolet region (or UV wavelengths $< 200$ nm) was thought to pervade all of the ISM dissociating any molecules which may have formed.\textsuperscript{6} However, the ISM is not homogeneous and the physical and chemical conditions can vary widely. The ISM may be classified by these variations as shown in Table 1.3.

The majority of the molecules shown in Table 1.1 and 1.2 were discovered in molecular clouds. Molecular clouds are the birthplace of stars and some of the coldest, densest regions of the ISM. The presence of interstellar dust grains in molecular clouds prevents the ISRF from penetrating deeply within the cloud. As a result, the interiors of molecular clouds are shielded from the ISRF and molecules present within the clouds are not dissociated.
1.1 Molecules in space

<table>
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<th>2 atoms</th>
<th>3 atoms</th>
<th>4 atoms</th>
<th>5 atoms</th>
</tr>
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<td>H₂</td>
<td>AlF</td>
<td>C₂</td>
<td>CH</td>
</tr>
<tr>
<td>CO⁺</td>
<td>CP</td>
<td>HCl</td>
<td>KCl</td>
</tr>
<tr>
<td>NaCl</td>
<td>OH</td>
<td>H₂O</td>
<td>H₂S</td>
</tr>
<tr>
<td>CS</td>
<td>AlCl</td>
<td>C₂S</td>
<td>CH₂</td>
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<tr>
<td>AlO</td>
<td>OH⁺</td>
<td>CN⁻</td>
<td>SH⁺</td>
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<tr>
<td>N₂</td>
<td>NO⁺</td>
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<td>HeH⁺</td>
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<td>HCS⁺</td>
<td>HOC⁺</td>
<td>H₂O</td>
<td>H₂S</td>
</tr>
<tr>
<td>H₂Cl⁺</td>
<td>KNC</td>
<td>FeCN</td>
<td>HO₂</td>
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<td>HCS</td>
<td>HSC</td>
<td>NCO</td>
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</tr>
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<td>3 atoms</td>
<td>4 atoms</td>
<td>5 atoms</td>
</tr>
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<td>C₂H</td>
<td>C₂O</td>
<td>C₂S⁺</td>
</tr>
<tr>
<td>HCNH⁺</td>
<td>HNCO</td>
<td>HNCS</td>
<td>HO⁻CO⁺</td>
</tr>
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<td>c-SiC₃⁺</td>
<td>CH₃</td>
<td>C₃N⁻</td>
<td>PH₃</td>
</tr>
<tr>
<td>C₃H⁺</td>
<td>HMgNC</td>
<td>HCCO</td>
<td>CNCN</td>
</tr>
<tr>
<td>2 atoms</td>
<td>3 atoms</td>
<td>4 atoms</td>
<td>5 atoms</td>
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<td>C₄H</td>
<td>C₄Si</td>
<td>l-C₃H₂</td>
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<td>HCOOH⁺(*)</td>
<td>H₃CNH</td>
<td>H₂C₃O</td>
</tr>
<tr>
<td>C₄H⁻</td>
<td>HC(O)CN</td>
<td>HNCNH</td>
<td>CH₃O</td>
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A simplified schematic diagram of star formation from a molecular cloud is shown in Fig. 1.1. Molecular clouds are not homogeneous in structure and possess regions of higher density which are referred to as clumps. If a clump gains enough mass it can collapse under gravity. Typically, low mass stars, or stars similar in size to the Sun, form from a self-collapsing clump. For collapse to continue interstellar gas and dust must initially radiate away the gravitational potential energy. Eventually the interstellar gas and dust cannot prevent the molecular cloud from heating up and a protostar forms at the centre of the clump. A molecular cloud usually possesses several clumps and it is typical for several protostars to form from a molecular cloud. The protostar will remain enveloped in the molecular cloud which continues to accrete onto the protostar. Rotation of the collapsing molecular cloud results in accretion of material around the protostar to form a protoplanetary disk due to conservation of angular momentum. Material from this disk can then accrete onto the protostar. A pre-main sequence phase called the T
### Table 1.2 Complex organic molecules (≥ 6 atoms) observed in the interstellar medium or circumstellar shells. Obtained from the Cologne Database for Molecular Spectroscopy. All molecules were detected in the gas phase. Molecules highlighted in blue have also been detected in the solid phase.

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<th>CH₃NC</th>
<th>CH₃OH</th>
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</tr>
<tr>
<td>CH₃SH</td>
<td>HC₃NH⁺</td>
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<td>1-HC₅H</td>
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<td>H₂NCH₂CN</td>
<td>CH₃CHNH</td>
<td>CH₃SiH₃</td>
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<th>C₆₀⁺</th>
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</tbody>
</table>

Tauri phase is sometimes characterised with bipolar outflows which release excess angular momentum. The bipolar outflows will disperse the envelope leaving a pre-main sequence star surrounded by a protoplanetary debris disk. The protoplanetary debris disk is the site of planet formation with rocky planets forming closer to the star and gaseous planets further away. When the temperature reaches $14 \times 10^6$ K the star will start burning hydrogen and enter the main sequence phase.

#### 1.1.2 Molecules in comets

An interesting question which arises from Section 1.1.1 is whether the chemical composition of a molecular cloud is retained through to planetary formation? Comets are remnant planetesimals from planet formation in the early Solar System and are considered some of the most pristine
1.1 Molecules in space

Table 1.3 Regions of the interstellar medium as defined by the temperature, density and state of hydrogen. Adapted from Bell Burnell et al. 7

<table>
<thead>
<tr>
<th>Region</th>
<th>Fractional Volume (%)</th>
<th>Temperature (K)</th>
<th>Density (particles cm⁻³)</th>
<th>State of hydrogen*</th>
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<td>Molecular Clouds</td>
<td>&lt; 1</td>
<td>10 – 20</td>
<td>10² – 10⁶</td>
<td>H₂</td>
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<tr>
<td>Cold Neutral Medium</td>
<td>1 – 5</td>
<td>50 – 100</td>
<td>20 – 50</td>
<td>H</td>
</tr>
<tr>
<td>Warm Neutral Medium</td>
<td>10 – 20</td>
<td>6000 – 10000</td>
<td>0.2 – 0.5</td>
<td>H</td>
</tr>
<tr>
<td>Warm Ionised Medium</td>
<td>20 – 50</td>
<td>8000</td>
<td>0.2 – 0.5</td>
<td>H⁺</td>
</tr>
<tr>
<td>H II Regions</td>
<td>~10</td>
<td>8000</td>
<td>10² – 10⁴</td>
<td>H⁺</td>
</tr>
<tr>
<td>Hot Ionised Medium</td>
<td>30 – 70</td>
<td>10⁶ – 10⁷</td>
<td>10⁻⁴ – 10⁻²</td>
<td>H⁺</td>
</tr>
</tbody>
</table>

* Hydrogen is the most abundant and ubiquitous element in space. The state of hydrogen is an indicator of the processing environment within a region e.g. the processing environment in molecular clouds does not dissociate H₂ molecules, whereas, the processing environment present in hot ionised medium is sufficient to ionise the H atom.

Icy bodies in the Solar System. 11 Comets are composed of a nucleus made up from rock, dust and ice. Volatile molecules within the ice sublimate as a comet gets closer to the Sun creating a coma which is also composed of dust. The dust tail is mainly composed of silicates and a plasma tail forms from ionisation of the gas in the coma due to solar radiation.

Periodic comets, those which orbit the Sun, are broadly classified into two categories: short period and long period comets. Short period comets (orbital period < 200 years) are thought to originate from the Kuiper belt. 12 Their short period orbit brings them close to the Sun where the ice is processed. Long period comets (orbital period > 200 years) are thought to originate from the Oort Cloud. 13 They have passed closer to the Sun less times than short period comets and are therefore less processed.

Table 1.4 shows a list of molecules which have been detected on comets mainly in the gaseous coma. The detection of molecules on comets can be done remotely through electronic, rotational and vibrational excitations. However, space missions to the comets have also enabled the detection of molecules through in situ mass spectrometry (e.g. mass spectrometers were onboard the Giotto, Deep Space 1 and Rosetta spacecraft) and retrieval of cometary material (e.g. the Stardust mission). There are 20 molecules (e.g. N₂⁺, S₄, CH₃CONH₂) detected in comets which have not been detected in ISM (or circumstellar shells) and these are highlighted in red in Table 1.4. Of these molecules, seven were detected by mass spectrometry, eight by UV-vis electronic transitions and the rest through rotational lines. UV-vis spectroscopy is more widely used in the detection of cometary molecules compared to ISM molecules. In contrast, long, unsaturated carbon chain molecules (e.g. C₇H, C₈H) have not been detected in comets although they are widely observed throughout the ISM.
**Introduction**

Table 1.4 Molecules observed in solar system comets. Molecules highlighted in red have not been detected in the ISM (or circumstellar shells) as of August 2019.

<table>
<thead>
<tr>
<th>2 atoms</th>
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</tr>
</thead>
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<td>CN</td>
<td>N₂⁺</td>
<td>CO⁺</td>
<td>CH</td>
<td>NH</td>
</tr>
<tr>
<td>OH</td>
<td>CH⁺</td>
<td>OH⁺</td>
<td>CO</td>
<td>CS</td>
<td>CN⁺</td>
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<tr>
<td>S₂</td>
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<td>SO</td>
<td>NS</td>
<td>H₂</td>
<td>HF</td>
</tr>
<tr>
<td>HCl</td>
<td>HBr</td>
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<td>C₃</td>
<td>NH₂</td>
<td>CO₂⁺</td>
<td>H₂O⁺</td>
<td>HCN</td>
<td>HCO</td>
</tr>
<tr>
<td>H₂S⁺</td>
<td>CO₂</td>
<td>H₂O</td>
<td>NCN</td>
<td>H₂S</td>
<td>HNC</td>
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<tr>
<td>HCO⁺</td>
<td>OCS</td>
<td>HDO</td>
<td>SO₂</td>
<td>CS₂</td>
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<th></th>
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</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>H₂CO</td>
<td>C₃H⁺</td>
<td>H₃S</td>
<td>H₃O⁺</td>
<td>C₂H₂</td>
</tr>
<tr>
<td>H₂CS</td>
<td>HNCO</td>
<td>S₄</td>
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<tr>
<td>CH₄</td>
<td>HC₃N</td>
<td>HCOOH</td>
<td>NH₄⁺</td>
<td>CH₃Cl</td>
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</table>

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<th>6 atoms</th>
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</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN</td>
<td>c-C₃H₃⁺</td>
<td>CH₃OH</td>
<td>NH₂CHO</td>
<td>CH₃SH</td>
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</tbody>
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<table>
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<th>7 atoms</th>
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<tbody>
<tr>
<td>HCOCH₃</td>
<td>CH₃NH₂</td>
<td>CH₃NCO</td>
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<table>
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<tr>
<th>8 atoms</th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>C₂H₆</td>
<td>HCOOCH₃</td>
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<table>
<thead>
<tr>
<th>9 atoms</th>
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</thead>
<tbody>
<tr>
<td>CH₃CONH₂</td>
<td>C₂H₆S</td>
<td></td>
</tr>
</tbody>
</table>

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<th>10 atoms</th>
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</thead>
<tbody>
<tr>
<td>HOC₂H₂CH₂OH</td>
<td>C₂H₅NH₂</td>
<td>(CH₃)₂CO</td>
<td>CH₂CHCHO</td>
<td>C₂H₅NO₂</td>
<td></td>
</tr>
</tbody>
</table>

**PAHs**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₄H₁₀</td>
<td>C₁₆H₁₀</td>
</tr>
</tbody>
</table>
1.1 Molecules in space

Fig. 1.1 Simplistic schematic diagram of the star formation process. Molecular clouds possess denser regions called clumps (i) which can collapse under gravity (ii). A protostar forms from gravitational collapse which is surrounded by an envelope of gas and dust and a circumstellar disk (iii). The T Tauri phase is characterised with bipolar outflows (iv) which eventually disperse the envelope to leave a pre-main sequence star with a protoplanetary debris disk (v). The star enters the main-sequence when it starts burning hydrogen (vi). Adapted from Greene et al. 8

1.1.3 Molecules on icy bodies of the Solar System

Molecules are abundant throughout the Solar System and apart from comets, molecules have been detected on asteroids, interplanetary dust, planets and planetary satellites. For brevity, this section mainly focusses on the icy bodies of the Solar System and Table 1.5 provides a list of molecules detected on these icy bodies.

Mercury and Mars

While Mercury and Mars are not icy bodies, they both contain deposits of ice. Water ice has been observed in the permanently shadowed regions of the north pole of Mercury. 15 Low albedo measurements also indicate that the ice contains non-water deposits possibly seeded to Mercury through cometary impacts. 16 Mars contains two permanent deposits of water ice at its
**Introduction**

Table 1.5 Molecules observed in the icy bodies of the outer Solar System along with the temperatures of these bodies.\textsuperscript{14}

<table>
<thead>
<tr>
<th>Planet</th>
<th>Satellite</th>
<th>Temperature (K)</th>
<th>Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jupiter</td>
<td>Io</td>
<td>80–130; 150–200 at hot spots; peaks of 400–1870</td>
<td>SO\textsubscript{2}, H\textsubscript{2}S, H\textsubscript{2}O, silicates</td>
</tr>
<tr>
<td></td>
<td>Europa</td>
<td>86–132</td>
<td>H\textsubscript{2}O, SO\textsubscript{2}, CO\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, O\textsubscript{2}, hydrates of H\textsubscript{2}SO\textsubscript{4}, MgSO\textsubscript{4} and Na\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td></td>
<td>Ganymede</td>
<td>90–160</td>
<td>H\textsubscript{2}O, SO\textsubscript{2}, CO\textsubscript{2}, O\textsubscript{2}, O\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>Callisto</td>
<td>80–158</td>
<td>H\textsubscript{2}O, SO\textsubscript{2}, CO\textsubscript{2}, O\textsubscript{2}, silicates</td>
</tr>
<tr>
<td>Saturn</td>
<td>Mimas</td>
<td>73</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>Enceladus</td>
<td>33–85, 120–160 at hot spots; peaks of \sim 195–223</td>
<td>H\textsubscript{2}O, CO, NH\textsubscript{3}, NH\textsubscript{3}·H\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OH</td>
</tr>
<tr>
<td></td>
<td>Tethys</td>
<td>86</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}, NH\textsubscript{3}·H\textsubscript{2}O</td>
</tr>
<tr>
<td></td>
<td>Dione</td>
<td>87</td>
<td>H\textsubscript{2}O, O\textsubscript{3}, CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>Rhea</td>
<td>53–99</td>
<td>H\textsubscript{2}O, O\textsubscript{3}, CO\textsubscript{2}, CH\textsubscript{4}</td>
</tr>
<tr>
<td></td>
<td>Hyperion</td>
<td>60–115</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>Iapetus</td>
<td>40–130</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}, NH\textsubscript{3}·H\textsubscript{2}O</td>
</tr>
<tr>
<td></td>
<td>Phoebe</td>
<td>72–113</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}, HC\textsubscript{3}N</td>
</tr>
<tr>
<td></td>
<td>Titan</td>
<td>70–200</td>
<td>H\textsubscript{2}O, CO, CO\textsubscript{2}, CH\textsubscript{4}, CH\textsubscript{3}D, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{8}, HCN, HC\textsubscript{3}N, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}N\textsubscript{2}, C\textsubscript{3}H\textsubscript{4}, C\textsubscript{6}H\textsubscript{6}</td>
</tr>
<tr>
<td>Uranus</td>
<td>Miranda</td>
<td>80–86</td>
<td>H\textsubscript{2}O, NH\textsubscript{3}, NH\textsubscript{3}·2H\textsubscript{2}O</td>
</tr>
<tr>
<td></td>
<td>Ariel</td>
<td>60–84</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}</td>
</tr>
<tr>
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<td>Umbriel</td>
<td>64</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}</td>
</tr>
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<td></td>
<td>Titania</td>
<td>60–64</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>Oberon</td>
<td>73</td>
<td>H\textsubscript{2}O, CO\textsubscript{2}</td>
</tr>
<tr>
<td>Neptune</td>
<td>Triton</td>
<td>36–39</td>
<td>N\textsubscript{2}, CH\textsubscript{4}, H\textsubscript{2}O, CO, CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>Nereid</td>
<td>60</td>
<td>H\textsubscript{2}O</td>
</tr>
<tr>
<td>Pluto</td>
<td>Charon</td>
<td>38–63</td>
<td>N\textsubscript{2}, CH\textsubscript{4}, CO, H\textsubscript{2}O, CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40–53</td>
<td>H\textsubscript{2}O, NH\textsubscript{3}·H\textsubscript{2}O, N\textsubscript{2}</td>
</tr>
</tbody>
</table>
poles with the south pole also containing CO$_2$.\textsuperscript{17,18} Atmospheric CO$_2$ also freezes out of the atmosphere during the winter months forming a CO$_2$ frost at both poles.\textsuperscript{19}

**The Galilean Moons**

The four largest moons of Jupiter are collectively known as the Galilean moons (Io, Ganymede, Callisto and Europa). All of the Galilean moons reside within the magnetosphere of Jupiter with Io acting as the main internal plasma source.

**Io:** The innermost Galilean moon, Io, is possibly the most volcanically active body in the Solar System\textsuperscript{20} releasing huge amounts of sulphur dioxide into the atmosphere. The contribution of plasma mass to the Jovian magnetosphere from Io is estimated to be 1000 kg s$^{-1}$ mainly in the form of sulphur- and oxygen-containing ions.\textsuperscript{21} As a result of tidal heating, which causes the volcanic activity on Io, only a thin frost of SO$_2$ covers the surface.\textsuperscript{22}

**Europa:** While a thick layer of water ice covers the surface of Europa, red-brown streaks are also present across the surface. These red-brown streaks or deposits have been attributed to that of a mixture of salts of unknown composition.\textsuperscript{23} A subsurface ocean of water is highly probable\textsuperscript{24} and may be salty in composition. Cryovolcanism has been tentatively suggested as a transport mechanism of material from the subsurface ocean to the surface.\textsuperscript{25}

**Ganymede:** Ganymede also possesses a thick covering of water ice over the surface. It is also the only moon in the Solar System to have its own magnetosphere\textsuperscript{26} and there is strong evidence to suggest that a salt-water subsurface ocean exists.\textsuperscript{27}

**Callisto:** Callisto has one of the most cratered surfaces in the Solar System\textsuperscript{28} and is less affected by the Jovian magnetosphere than the other Galilean Moons as it is the furthest away. The surface is mainly composed of water ice, probably in a crystalline form due to the warmer temperature.\textsuperscript{29} Like Europa and Ganymede there is a possibility of a subsurface ocean.\textsuperscript{30}

**Saturn’s moon: Enceladus**

The majority of Saturn’s moons are covered in thick water ice deposits. However, cryovolcanism in the south of Enceladus transports ice particles and gas from a subsurface ocean to the surface.\textsuperscript{31} Complex macromolecules observed in the ice particles suggests that the subsurface ocean contains an organic component possibly formed in hydrothermal vents.\textsuperscript{32}

**Pluto, Charon and Triton**

Pluto has a layer of volatile ice composed of N$_2$, CH$_4$ and CO which sits on top of a layer of water ice crust.\textsuperscript{33,34} Some of the mountainous regions of the Sputnik Planitia are believed to be formed from water ice as N$_2$, CH$_4$ or CO composed material would collapse under
Introduction

their own weight on geological time scales.\textsuperscript{35,36} Images of Pluto show that it is covered in red-brown deposits which are hypothesised as being due to tholins.\textsuperscript{37} The definition of tholin is vague and according to Stern et. al it is defined as ‘complex carbon-hydrogen-oxygen-nitrogen (CHON)-containing macromolecular material produced by irradiation of simpler organic precursors’.\textsuperscript{37} The resulting tholin material is characteristically of a red-brown colour. Tholins on Pluto’s surface most likely formed in the atmospheric haze before deposition onto the surface.\textsuperscript{37} There was an assumption that tholins on the surface of Pluto were largely inert. However, this assumption was challenged through a study of three distinct regions of Pluto which showed different colouration indicating different reactivity of tholins.\textsuperscript{38}

Pluto’s satellite Charon does not appear to have an atmosphere unlike Pluto.\textsuperscript{39} While most of Charon is covered in water ice,\textsuperscript{40} images of Charon show that there is a red coloured cap in the northern polar region. Tholin macromolecules are believed to be responsible for this colouration.\textsuperscript{41} These tholins are thought to form when CH\textsubscript{4}, escaping the atmosphere of Pluto, condenses onto coldest regions of Charon at the poles. Subsequent irradiation converts the CH\textsubscript{4} into the tholins.

Neptune’s moon Triton shares similar properties to Pluto and is believed to be a captured Kuiper Belt Object. Triton contains a mixture of CO and N\textsubscript{2} on its surface which are not spatially distinct.\textsuperscript{42}

1.2 Observations of ice in the Universe

The technique used to observe ice in space depends on the location of the ice. For example, observations of interstellar ice (and also interstellar gas phase molecules) rely solely on remote, spectroscopic techniques. Whereas, ice found on comets or the icy bodies of the Solar System can be observed by remote observations or direct observations on board spacecraft. This section gives examples of the different observation techniques used to observe ice throughout space and some of the information that is elucidated from these observations.

1.2.1 Interstellar ice

The gas phase molecules listed in Tables 1.1 and 1.2 have been observed using radio astronomy. Radio astronomy exploits the rotational modes of molecules and generally covers cm to mm to (sub)mm wavelengths. However, interstellar ice is exclusively observed using the vibrational transitions of the molecule usually through absorption IR spectroscopy covering wavelengths from 0.6–300 $\mu$m.\textsuperscript{43} Most IR telescopes are space or airbourne based to avoid telluric CO\textsubscript{2} and H\textsubscript{2}O present in the atmosphere of the Earth which absorb IR radiation. Observations of
1.2 Observations of ice in the Universe

interstellar ice in absorption IR spectroscopy requires an IR source either embedded within the molecular cloud or behind it. A detailed review of interstellar ice observations is given by Boogert et al. 43

![Image of IR spectrum](image_url)

**Fig. 1.2** A combined ISO SWS and LWS spectrum of interstellar ice and dust observed in the line-of-sight towards the massive young stellar object RAFGL 7009 S with strongest features labelled. The dashed line shows a calculated spectrum of H$_2$O ice spheres at 10 K indicating the multiple bands of H$_2$O. Republished with permission of Annual Reviews from Boogert et al. 43 Copyright 2015.

Fig. 1.2 shows the IR absorption spectrum of interstellar ice from the massive young stellar object (YSO) RAFGL 7009 S. A YSO refers to a star in the early phases of formation and a massive YSO refers to a star which will be greater than 5–8 times the mass of the Sun. This spectrum was taken by the International Space Observatory (ISO) using both the short wave spectrometer (SWS) and the long wave spectrometer (LWS). A calculated IR spectrum of spheres of H$_2$O is also shown indicating multiple features due to H$_2$O ice which is the most abundant form of ice in the Universe. Other contributors to the ice features include CO$_2$, CO, NH$_3$, CH$_4$ and CH$_3$OH. Strong silicate features due to interstellar dust are also observed at 10 µm and between 20–30 µm.
Introduction

From extensive observations, the 3.0, 4.67 and 15.2 μm features have been identified as good tracers for the physical environment in which the interstellar ice resides. For example, the CO$_2$ asymmetric bend or the 15.2 μm band varies significantly depending on the environment in which it is observed as shown in Fig. 1.3. The IR spectrum in Fig. 1.3 was interpreted using five different laboratory spectra of CO$_2$ ice in different environments. These environments were classified as follows: polar (CO$_2$/H$_2$O < 1), apolar (CO$_2$/CO ∼1), dilute (CO$_2$/CO ≪1), pure CO$_2$ and a shoulder (CH$_3$OH/CO$_2$ ≫1). Fig. 1.3 (a) shows the evolution of interstellar ice formation from a polar environment to an apolar environment at temperatures below 20 K. It also shows warmer environments between 20–70 K and 70–90 K which occur as star formation progresses. Fig. 1.3 (b) shows more extreme environments where CO$_2$ has experienced extreme thermal processing which affects the grain shape, high abundances of CH$_3$OH, high and low ‘metallicities’. $^a$

However, not all of the features detected in interstellar ice observations have been securely identified. $^{43}$ Molecules such as formaldehyde, OCN$^-$ and OCS have been identified on single absorption features with matches to laboratory data and hence, are still only tentatively assigned. $^{43}$ The environment in which the ice resides affects the IR spectrum making it more difficult to securely identify features in the the solid phase compared to gas phase. Silicate features of the interstellar dust grains also obscure regions of the IR spectrum. One region in particular between 5–7 μm has no secured identification, although it has been decomposed into five components which vary depending on the environment. $^{45}$ Larger molecules and molecules in low abundances also present a challenge in identification with overlapping or obscuring features preventing a good identification or even detection.

Evolution of interstellar ice

From Fig. 1.3 there is observational evidence of different thermal environments around YSO. Interstellar ice can reside at different distances from the forming protostar and can experience a thermal gradient. A schematic diagram of the evolution of interstellar ice is shown in Fig. 1.4. It shows the thermal gradient and density gradient as the molecular cloud goes from a precollapse phase through to protoplanetary disk formation. Interstellar ice observations have shown that a water-rich layer of ice will form around the dust grain first, followed by a CO-rich layer as freeze-out of CO occurs. This is described in more detail in Section 1.3. The molecules in the ice are sometimes called zeroth order molecules as they form in the gas or on the surface of the interstellar dust. Dissociation of molecules in the ice can occur through

$^a$In astronomy, the term metal refers to any element heavier than helium and metallicity refers to the abundance of elements which are not hydrogen or helium. The early Universe was metal-poor and therefore, a low metallicity environment refers to a star-forming region from the early Universe.
1.2 Observations of ice in the Universe

Fig. 1.3 Observations of the CO$_2$ asymmetric bending mode in different astrophysical environments. The colour components refer to polar (red), apolar (black), dilute (green), pure (yellow) and shoulder (blue) which were described in Section 1.2.1. (a) show the observations of the CO$_2$ bending mode as an evolutionary scenario with increasing density and subsequent temperature. (b) shows extreme environments such as an extreme heating event (HOPS 68), high CH$_3$OH abundance (W33A), high (SSTGC 797384) and low (LMC 05222.46) metallicities. Republished with permission of Annual Reviews from Boogert et al. 43 Copyright 2015.

several processing techniques which are described in Section 1.3. As star formation progresses, radicals which formed from dissociation become mobile and react to form larger molecules which are called first generation molecules. Second generation molecules are formed from the sublimation of ices and when subsequently gas phase chemistry is predominant. Larger molecules are destroyed in the gas phase unless they are incorporated into the protoplanetary disk. In the protoplanetary disk the molecules and dust move to the cold midplane where formation of ice can occur, enabling additional ice chemistry.

**Future observations: The James Webb Space Telescope**

Previous space-based IR telescopes used to observe interstellar ice included ISO, Spitzer and Akari. While eliminating the risk of atmospheric contaminants, space-based IR telescopes
Introduction

Fig. 1.4 Schematic diagram of the evolution of interstellar ice from precollapse to circumstellar disk formation. A thermal and density gradient is observed as star formation progresses which influences the composition of interstellar ice. Zeroth- (0), first- (1) and second- (2) generation molecules are labelled (see text for more details). The temperature and density scale refer to the envelope and not to the protoplanetary disk. Adapted with permission of Annual Reviews from Herbst and van Dischoeck. Copyright 2009.
1.2 Observations of ice in the Universe

have a limited lifetime due to the requirement of a coolant to prevent thermal emission of the telescope interfering with IR measurements.

The James Webb Space Telescope (JWST), an IR, space-based telescope is set to launch in 2021. It will cover a wavelength range from 0.6–28.5 µm making it ideal for observing interstellar ice. One of the biggest advantages of JWST for the observation of interstellar ice is the increased angular resolution and sensitivity. JWST will have a significantly better angular resolution compared to ISO, Spitzer or Akari due to the size of the aperture. ISO, Spitzer and Akari had apertures between 0.6–0.85 m whereas JWST has an aperture of 6.5 m. Currently when observations of interstellar ice are made, like that of Fig. 1.3, all of the interstellar ice in the line of sight towards an embedded protostar or a background star are observed without spatial distinction. JWST will allow for a spatial distinction to be made and hence map the evolution of interstellar ice in regions at different stages of star formation as shown schematically in Figure 1.1.

As part of the Cycle 0 or Early Release Science proposals, the proposal ‘IceAge: Chemical evolution of ices during star formation’ was accepted. Using the improved resolution that JWST will provide, the investigators propose to map the spatial distribution of interstellar ice to ~20–50 AU, identify new molecules, and distinguish between the morphology, thermal history and mixing environment of the interstellar ice. In order to interpret this data, a public laboratory ice database must be built to provide reference spectra, as well as astrochemical models which will be used to fit ice abundances. Systematic laboratory data such as the work detailed in this thesis is therefore paramount to the interpretation of ice features in the different environments.

1.2.2 Cometary ice

Unlike interstellar ice, observations of comets are not limited to telescopic observations and there have been 10 successful missions in which spacecraft have visited comets (International Cometary Explorer, Vega-1, Vega-2, Sakigake, Suisei, Giotto, Deep Space 1, Stardust, Deep Impact, Rosetta/Philae). One advantage of space missions to comets is the use of mass spectrometry measurements. Mass spectrometry measures the mass-to-charge of the ionised sample to identify the molecule which allows for a better identification of larger, more complex molecules. For example, glycine, the simplest amino acid, was detected in the gaseous phase in the coma of 67P/Churyumov-Gerasimenko via in situ mass spectrometric measurements. Large and complex molecules are difficult to detect in the ISM through spectroscopic studies even in the gas phase and this is clearly evidenced through several non-detections and a disconfirmed detection of glycine. While the origin of cometary glycine is speculated as being from molecular clouds or protostar environments, there is no direct evidence to corroborate
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this. However, as mass spectrometry relies on direct sampling it is not a feasible technique for ISM observations of both gas and solid phase molecules.

Interestingly, three polycyclic aromatic hydrocarbons (PAHs), phenanthrene (C\textsubscript{14}H\textsubscript{10}),\textsuperscript{54} pyrene (C\textsubscript{16}H\textsubscript{10}),\textsuperscript{55} and anthracene (C\textsubscript{14}H\textsubscript{10}),\textsuperscript{56} were detected in the gaseous phase in the inner coma of comet 1P/Halley using the three-channel spectrometer on-board the spacecraft Vega 2. The PAHs were detected as near-ultraviolet emission spectra between 340–390 nm. PAHs have long been hypothesised to be responsible for the diffuse interstellar bands (DIBs) of the ISM, but no single identification has been made (for more details see review by McCabe\textsuperscript{57}).

There is widespread research into the chemical inheritance of molecular clouds to planetary formation (e.g. see review by Caselli and Ceccarelli\textsuperscript{58} for more details) and high deuterated ([D\textsubscript{2}O/HDO]/[HDO/H\textsubscript{2}O]) ratios in comet 67P indicate that water in comet 67P has a pre-solar origin.\textsuperscript{59} The idea that the short period and long period comets formed at different distances from the Sun is also invalidated through observations of the D/H ratio suggesting that comets formed over a large region of the protoplanetary disk.\textsuperscript{60}

So far most of the observations of molecules described above on comets have been made in the gas phase. In fact, the direct detection of ice in comets is small\textsuperscript{61–68} and the compositions are usually inferred from molecular detection in the gaseous coma.\textsuperscript{69}

Future spacecraft: Comet Interceptor

All previous comet missions have involved comets which have passed close to the Sun several times and therefore have undergone extensive processing. The comet mission Comet Interceptor set to launch in 2028 will intercept a comet from the Oort cloud which has not previously passed close to the Sun.\textsuperscript{70} The Comet Interceptor will wait in space until a suitable incoming comet is identified before making measurements of the coma. As the comet will be more pristine than any other comet observed to date the idea is that it will retain more of its original, unprocessed material from the solar nebula.\textsuperscript{70}

1.2.3 Icy bodies of the outer Solar System

Most of the information gained about the surface of the icy bodies is obtained through reflectance UV, visible or IR spectroscopy (for a detailed overview see reviews by Dalton\textsuperscript{14} and Clark et al.\textsuperscript{71}) Similar to interstellar ice observations, there is a reliance of laboratory spectra to interpret observations of the icy bodies of the Solar System. A key difference between these observations is that interstellar ices are usually observed through absorption spectroscopy, whereas icy bodies are observed through reflectance spectroscopy. Reflectance spectroscopy is influenced by the composition of the icy body surface or regolith. To overcome the fact that
1.2 Observations of ice in the Universe

Most icy surfaces will not be formed of just one pure material, models which range in varying degrees of complexity are used to interpret reflectance observations.  

For example, far-UV reflectance spectrum of the Saturnian moon Phoebe obtained from the Ultraviolet Imaging Spectrograph (UVIS) on board the Cassini spacecraft showed a distinctive water feature at 165 nm. This water feature and derived abundances confirmed earlier ground based IR observations. Mixing models incorporated different non-ice materials and results showed that regardless of the non-ice composition the best fits were obtained when ∼10% water ice was present with ice grain sizes of 7–9 µm.

A far-UV spectrum of Enceladus was also obtained using the UVIS instrument on board Cassini. The reflectance spectrum was noted to be much darker than expected for pure water ice and mixing models suggested that the darkening was possibly due to water mixed with small amounts of NH₃ and tholins. However, a lack of laboratory data at relevant temperatures, in particular optical constants, has hindered the interpretation of Enceladus’s far-UV reflectance spectrum.

The majority of observations of the icy bodies of the outer Solar System are made using near-IR spectroscopy. Near-IR spectroscopy probes the weak combination and overtone modes of a molecule and therefore laboratory ice samples need to be sufficiently thick to observe these features. An example of near-IR spectra of Charon taken using the Linear Etalon Infrared Spectral Array (LEISA) on board New Horizons spacecraft is shown in Fig 1.5. Crystalline water ice dominates the surface of Charon and marginal levels of an NH₃-containing species were also observed. Near the Organa crater the 2.2 µm band of the NH₃-containing species is stronger as shown in spectrum b of Fig. 1.5 (B). Radiolytic destruction of NH₃ ice on the surface of Charon timescale is estimated to take ∼10⁷ years. The higher levels of NH₃ suggest it is a recent deposit of NH₃ possibly due to recent exposure of previous subsurface material.

While most of the ice in the outer Solar System has been observed through reflectance spectroscopy, the icy plumes on Enceladus were sampled in situ using a mass spectrometer, the Cosmic Dust Analyzer which was on board the Cassini spacecraft. The salt-rich ice grains, which contained sodium and potassium, are hypothesised as originating from a salty, subsurface ocean.

Future spacecraft and telescopes

JUICE: The JUipter ICy moons Explorer (JUICE) mission, set to launch in 2022, will make observations of Jupiter and three of its icy moons of Ganymede, Callisto and Europa. Two instruments on board the spacecraft, the UV imaging Spectrograph (UVS: 55–210 nm) and
A composite base map of Charon obtained from the Long Range Reconnaissance Imager instrument on board New Horizons. Linear Etalon Infrared Spectral Array (LEISA) near-IR spectrum were obtained for four different regions on Charon (highlighted with blue and green boxes). (B) Offset spectra of the four regions indicated in (A). Characteristic, crystalline water ice bands are observed at 1.5, 1.65, and 2 μm for all four regions. Spectrum (b) is a region around the Organa crater which shows NH₃-containing absorption feature at 2.22 μm. (C) A close-up of the of the region near the Organa crater. Reproduced with permission of The American Association for the Advancement of Science from Grundy et al. Copyright 2016.

JWST: As mentioned in Section 1.2, JWST is a space based IR telescope set to launch in 2021. JWST will be able to characterise many of the icy bodies of the Outer Solar System.

1.3 Molecular synthesis in space

How do molecules form in space? The different physical conditions of space compared to Earth dictate a different chemistry and the study of chemistry in space is still a relatively new field. There are two major routes for molecular formation in the ISM: gas phase and solid
1.3 Molecular synthesis in space

phase routes. Gas phase reactions are briefly described in Section 1.3.1, but the focus of this thesis is on solid phase reactions which are described in detail in Section 1.3.2.

1.3.1 Gas phase synthesis

Even in environments like molecular clouds which have the highest densities in the ISM, the density is still $\sim 10^{13}$ orders of magnitude less dense than the atmosphere of the Earth at sea level ($10^{19}$ particles cm$^{-3}$). For a reaction to occur, the reactant molecules must collide with each other and in low density environments this is a slow process. Molecular clouds can have lifetimes of between 10–100 million years$^{80}$ and so the chemistry proceeds at a much slower rate than on Earth whilst the low densities of the ISM means that three-body reactions ($A + B + M \rightarrow AB + M$), which are common on Earth, rarely occur. The third body ($M$) carries away excess energy which helps stabilise the newly formed molecule ($AB$) preventing it from dissociating back into its constituent reactants ($A$ and $B$). Hence, bimolecular reactions are dominant in the gas phase in space.

The low temperature in molecular clouds also limits the types of reactions which can occur. Only exothermic reactions with small or no activation enthalpies occur in molecular clouds. In terms of gas phase chemistry, this limits the major reaction types to ion-molecule, neutral-neutral and radical-radical reactions. However, the efficiency of gas phase reactions in producing observed abundances in the ISM has been questioned especially for saturated molecules like methanol.$^{81,82}$ As the focus of this thesis is on solid-phase reactions, no more details about gas phase reactions are given and the reader is referred to reviews by Smith$^{83}$ and Millar$^{84}$ for more details.

1.3.2 Solid phase synthesis

Originally, it was thought that all molecules observed in the ISM could be explained by gas phase reactions. However, the formation of certain molecules including the most dominant molecule, H$_2$, cannot be explained by gas phase reactions at low temperatures.$^6$ The abundance of other molecules like methanol also can not be explained by gas phase reactions at low temperatures.$^{81}$ At temperatures of 10 K, the majority of atoms or molecules will condense onto the cold surface of an interstellar dust grain and form an icy mantle. In fact, it is now well established that the majority of COMs form within the icy mantles around interstellar dust grains. These COMs are then detected in the gas phase after thermal$^{85}$ or non-thermal desorption.$^{86}$

Chemistry can occur on the bare interstellar dust grain or within the bulk of the icy mantle. While the focus of this thesis is the chemistry within the bulk ice it is important to understand
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Fig. 1.6 Median abundances of CO$_2$, CO, CH$_3$OH, NH$_3$ and CH$_4$ ice relative to the abundance of H$_2$O ice. Error bars show the minimum and maximum detected abundance of the molecular species relative to water. Reprinted (adapted) with permission from Öberg. Copyright 2016 American Chemical Society.

how the bulk ice forms. During the formation of molecular clouds from diffuse clouds, the most abundant gas phase species are H, He, O, C and N atoms. Interstellar dust grains in the diffuse clouds are bare. As the molecular cloud starts to form and the temperature drops to $\sim$10 K and the density increases, H, O, C and N atoms condense onto the bare dust grain. The H atom is the most abundant and most mobile atom on the surface of the dust grain and hydrogenation reactions form H$_2$O, CH$_4$ and NH$_3$. CO forms in the gas phase and condenses onto the dust grain. While O atom condensation is occurring, OH radicals can form and CO$_2$ is produced from the reaction between OH+CO. As the density of the molecular cloud increases, ‘catastrophic’ CO freeze-out occurs. The H/CO ratio which was small to begin with is now large and the formation of CH$_3$OH, H$_2$CO, more CO$_2$ and other CO-bearing species occurs. Imperfect mixing of the interstellar ice is observed so that layers are formed. The first layer, the H$_2$O-rich (or polar) layer is dominated by H$_2$O, CH$_4$, NH$_3$ and some CO$_2$. The second layer, the CO-rich layer which forms after catastrophic freeze-out of CO contains CO, CO$_2$, CH$_3$OH, H$_2$CO and other species.

A schematic diagram of the interstellar ice layers is shown in Fig. 1.6 along with the variation of observed abundances of the six most abundant species.

Processing in the ISM

There are five main mechanisms in which the bulk interstellar ice can be processed to induce molecular synthesis. These are described in a review by Arumainayagam et. al and these are
1.3 Molecular synthesis in space

Fig. 1.7 Schematic diagram of the different types of non-energetic (atom- and radical-addition) and energetic processing (photochemistry, radiation chemistry and thermal chemistry) which may occur in interstellar ices with examples of how these processes can induce chemistry. See text for more details. Adapted with permission of the Royal Society of Chemistry from Arumainayagam et al. Copyright 2019.

shown in Fig. 1.7. Non-energetic processing includes atom- or radical-addition processes, while energetic processing includes thermal chemistry, shock chemistry, photochemistry and radiation chemistry processes. The study of interstellar ice analogue processing in the laboratory has greatly improved the knowledge of ice chemistry and a few select examples are given below.

**Thermal chemistry:** Thermal processing naturally occurs during the star formation process. Thermally induced acid-base, nucleophilic addition, elimination and condensation reactions can occur at cryogenic temperatures. For example, the acid-base reaction between NH$_3$ and formic acid can occur at 15 K to form the salt NH$_4^+$COO$^-$. An acid-base reaction between CO$_2$ and NH$_3$ can occur between 70–90 K to produce the ammonium carbamate salt or a nucleophilic reaction may occur and form carbamic acid.

**Atom- or radical-addition:** Atom- or radical-addition reactions have already been mentioned and are responsible for the formation of solid phase H$_2$O, CH$_4$, NH$_3$ and CH$_3$OH which contributes to the growth of the icy mantle. Laboratory experiments have also shown that larger
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molecules like glycolaldehyde and ethylene glycol can form from H-atom-addition reactions of CO:CH₃OH ice mixtures. Experimental studies have also shown that radical-addition reactions can also form larger molecules for example like the OH radical-addition with propyne to form propanols, propenols and propendiols.

Shock chemistry: Shock chemistry is a relatively understudied field with regards to molecular synthesis in interstellar ice. Highly energetic shocks are present throughout the ISM and are generated at various stages of star formation and evolution. For example, bipolar outflows of protostars, stellar winds and supernova shock fronts. Interstellar shocks most likely interact with interstellar ice at some point, but it is unknown whether these shocks only cause collisional-induced desorption of molecules or whether it also causes collisional-induced formation of molecules. A recent study by Surendra et al. has investigated the effect of shock chemistry on amino acids and nucleobases. Evidence of the formation of complex macrostructures was observed after shock chemistry was initiated. This study was used to understand the impact that an asteroid or meteorite might have on the evolution of life on Earth. However, it shows that molecular synthesis may be induced through shock chemistry of interstellar ices.

Photochemistry: Photochemistry refers to the absorption of photons in the visible or UV region of the electromagnetic spectrum and the subsequent physico-chemical processes which are induced from the decay of the electronically excited state. Some physico-chemical effects which might occur for example include photodissociation, isomerisation, bimolecular reactions and H-abstraction. Sources of photochemistry in molecular clouds include secondary UV photons generated from the interaction of cosmic rays with H₂. The cosmic ray excites the Lyman and Werner absorption bands of H₂ and as it decays back to the ground state it releases a UV photon in the energy range of 11.2–13.6 eV (Lyman-Werner UV photon). This is known as the secondary UV radiation field and has a much weaker UV flux compared to the ISRF UV flux. The UV photons from the ISRF do not penetrate deep enough into a molecular cloud due to shielding from the interstellar dust grains to contribute to photochemistry, but may be important at the boundary of such dust clouds. Purely photochemical reactions are difficult to study in interstellar ice analogue experiments as the energy used for the light source (e.g. microwave-discharge hydrogen-flow lamps) typically has an energy > 10 eV and high flux. The maximum energy to induce purely photochemical reactions is approximately < 10 eV dependent on the molecule under investigation and the flux used. Most laboratory studies using UV light sources will therefore have also initiated radiation chemistry.

Radiation chemistry: Radiation chemistry is characterised by the production of secondary electrons due to the absorption of ionising radiation to induce chemical change. Sources of radiation chemistry in the ISM come in the form of high energy particles (e.g. cosmic rays
1.3 Molecular synthesis in space

which are mainly composed of protons and helium nuclei\(^{91}\) and high energy photons from newly formed protostars (e.g. X-rays, \(\gamma\)-rays). When ionising radiation interacts with an icy dust grain \(\sim 4 \times 10^4\) electrons per MeV of energy deposited are produced which have an energy of \(< 20\) eV.\(^{101}\) Regardless of the type of ionising radiation, the inelastic collisions between the secondary electrons and molecules are thought to underpin radiation chemistry. There are numerous studies which initiate radiation chemistry in interstellar ice analogues. Studies which look at UV photon irradiation may also induce photochemical reactions and separating the effects of photochemistry and radiation chemistry is very challenging.\(^{91}\)

**Processing types in comets**

Thermal chemistry, shock chemistry, photochemistry and radiation chemistry all occur on comets, but the source of the processing is different compared to the ISM. For example the source of thermal chemistry in comets may occur during the formation of the comet from impact-induced or accretional heating.\(^{102}\) Once a comet is formed it is stored either in the Kuiper belt or the Oort cloud, before becoming active. Thermal processing may also occur in the storage phase via radiogenic heating which would affect the most volatile species (e.g. CO and \(\text{N}_2\)).\(^{102}\) Active comets will also experience thermal processing from the Sun. Space weathering can induce shock chemistry from micrometeorite impacts present throughout the Solar System, photochemistry from solar UV photons and radiation chemistry from solar particles and cosmic ray ions.\(^{103}\)

**Processing types in the icy bodies of the outer Solar System**

Similarly to comets, thermal, shock chemistry, photochemistry and radiation chemistry all occur on the icy bodies of the outer Solar System. Again the source of the processing is different compared to the ISM. Planetary bodies and their moons are significantly more processed than comets and the ice observed on these bodies is unlikely to be representative of the early Solar System. Thermal processing on the icy bodies may occur, for example, through seasonal changes or tidal heating.\(^{14}\) Impacts of asteroids and comets on planetary bodies may have seeded organic material and induced shock chemistry on the icy bodies of the outer Solar System.\(^{104,98}\) Space weathering as mentioned earlier can cause photochemistry and radiation chemistry, as well as shock chemistry.\(^{103}\) The magnetospheres of Jupiter and Saturn will process their nearby moons which will induce radiation chemistry and ion implantation. The Jovian magnetosphere is mainly composed of ions from \(\text{SO}_2\), such as \(\text{S}^+, \text{S}_2^+, \text{O}^+, \text{O}_2^+\), from the volcanic activity of Io.\(^{21}\) Whereas, \(\text{H}_2\text{O}\) based ions such as \(\text{O}^+, \text{H}_2\text{O}^+, \text{OH}^+\) dominate the magnetosphere of Saturn with the main source of water vapour from Enceladus.\(^{105}\)
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1.4 Astrochemical models

Astrochemical models are used both to understand how molecules form in ISM and predict their abundances. In fact astrochemical models were crucial in suggesting that the formation of COMs were more likely to occur in the solid phase than the gas phase. Modelling of gas phase reactions is more established than ice grain reactions, but both rely on the input of laboratory data. Laboratory experimental results also provide a well constrained environment for astrochemical modellers to verify the reliability of their models before extending to astrochemical time scales.

The type of astrochemical model used depends on the problem that is to be addressed and the amount of computing power and time available which usually requires a compromise. Similar to gas phase modelling, the majority of gas-grain models that incorporate a large network of chemical reactions will use the rate-equation model. In this rate-equation model, the gas and gas-grain phase chemical kinetics are described by ordinary differential equations. These equations are then solved to extract time dependent information about the abundance of chemical species for constant or evolving physical conditions. However, at low surface coverage of grains, rate-equation models can significantly overestimate formation rates in what is sometimes referred to as the accretion-limited case. To overcome this accretion limit, a modified rate equation may be used. However, this comes at the expense of more computation time and power.

Modelling is not only used for understanding the formation of interstellar ice and has been used in cometary ice. However, as the focus of this thesis is interstellar ice, the focus of this section is on astrochemical models (a few examples of cometary modelling are given here).

Select examples of how astrochemical models are used to solve different problems are given below but this is not an exhaustive list of problems (see reviews by Cuppen et al. and Garrod and Widicus Weaver for more examples).

1.4.1 Understanding reaction mechanisms from energetic processing

The majority of astrochemical models aimed at understanding the chemistry within interstellar ice from energetic processing have focussed on photochemistry. Individual reaction steps are rarely observed in astrochemical experiments and astrochemical models which include photochemical processes have been used to infer these reaction steps. Models which incorporate a ‘three-phase model’ where the gas phase, ice surface and bulk ice are treated separately are commonly used to investigate chemistry over astronomical timescales. Laboratory photodissociation rates are used in astrochemical models which are investigating the chemistry
of ice and typically, since often no solid phase data is available, gas phase data is used. However, gas phase data does not necessarily translate to solid phase data.\textsuperscript{6,114,115} Despite this, astrochemical models using photochemical reactions have been largely successful for reproducing the observational abundances of molecules in hot cores/corinos.\textsuperscript{91}

Few astrochemical models incorporate radiation chemistry despite the numerous laboratory studies on radiation chemistry in interstellar ice analogues. The lack of radiation chemistry in astrochemical models has been attributed to the quantity and complexity of fundamental processes which contribute to experimentally observed values.\textsuperscript{116,91} However, the need to explain how COMs form in molecular clouds has helped bring the inclusion of radiation chemistry into astrochemical models.

A general method for the inclusion of radiation chemistry into astrochemical models was first introduced in 2018.\textsuperscript{116} To assess how well this method worked in terms of simulating radiation chemistry in ice analogues a comparison was made with experimental data which is much more well constrained compared to interstellar chemistry.\textsuperscript{108} The rate equation model used provided results in good agreement with laboratory data. It was also noted that the traditional way of treating bulk chemistry of thermal diffusion or quantum tunnelling did not reproduce results in such good agreement especially at low temperatures.

### 1.4.2 Ice structure

Rate equation models like those discussed in Section 1.4.1 do not model the structure of the ice. However, astrochemical experiments show that porous ice can trap volatile molecules which may have the potential to enhance chemistry in the ISM. Porosity is ‘a concept related to texture, referring to the pore space in a material’.\textsuperscript{117} More porous ices will have larger surface areas enabling more trapping of volatile species.\textsuperscript{118} To model the ice structure, the positions of atoms or molecules need to be explicitly modelled.\textsuperscript{119} For example, a study by Clements et al. modelled the porosity of experimentally formed amorphous solid water ice using an off-lattice microscopic kinetic Monte Carlo model.\textsuperscript{107} An on-lattice microscopic kinetic Monte Carlo approach models the diffusion of atoms or molecules in a pre-defined lattice, whereas the off-lattice approach does not restrict the position of the atoms or molecules. However, off-lattice microscopic kinetic Monte Carlo models are more computational demanding than on-lattice models which in turn are more computational demanding than rate equation models. The off-lattice model presented in Clements et al. was a modified version of a model presented in Garrod\textsuperscript{119} with the modifications allowing laboratory experimental parameters to be incorporated. The results showed that non-thermal diffusion controlled the porosity of laboratory ice below 80 K. After simulating laboratory experiments the model was then extrapolated to protoplanetary conditions where direct deposition of water onto interstellar dust grains occurs.
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The results obtained indicate that the porosity of ices in protoplanetary conditions are less porous than laboratory ices.\textsuperscript{107}

1.5 Laboratory experiments

Experimental ice analogue investigations usually target a particular ice environment as both the physical and chemical conditions vary amongst the ISM and the Solar System environments. For experiments investigating planetary ice analogues the deposition temperatures of the ices will be higher than interstellar ice analogues.

As the experiments performed in this thesis used physical and chemical conditions relevant to interstellar ice analogues, this brief overview on laboratory experiments will focus on interstellar ice analogue experiments. Interstellar ice analogue experiments can be broadly split into two categories: experiments for the interpretation of observations (Section 1.5.1) and experiments for understanding molecular synthesis in ice (Section 1.5.2). Both types of experiments produce data (e.g. kinetic rates, abundances) which are included in astrochemical models.

1.5.1 Interpretation of observations

Identification of molecules

It is well recognised that laboratory experiments are important for the identification of molecules in interstellar ice through the IR absorption bands.\textsuperscript{43} Laboratory experiments involving mixtures of different ratios have been used to constrain the chemical and physical environments in which the molecules in the interstellar ice reside (e.g. see the series of papers on ‘Cores to Disks Spectroscopic Survey of Ices Around Low-Mass Young Stellar Objects\textsuperscript{45,120–122}).

An example of where laboratory experiments were used to identify and constrain the chemical and physical environments of CO\textsubscript{2} from several observations was given in Section 1.2.1. Fig. 1.3 showed observations of the CO\textsubscript{2} asymmetric bending mode in different environments. The identification of these different environments was made using laboratory spectra of CO\textsubscript{2} mixed with H\textsubscript{2}O, CO or CH\textsubscript{3}OH at different ratios.

Integrated IR band strengths

In addition to experiments aimed at the identification of specific molecules, laboratory experiments also provide crucial integrated band strengths, commonly referred to as A-values
1.5 Laboratory experiments

which are used to determine the column densities (N) of interstellar ices. The column density is determined from the integrated optical depth (τv) through the following equation:

\[ N = \frac{\int \tau_v dv}{A-value} \]  

(1.1)

In turn, laboratory determined A-values are obtained by using the thickness (t), density (ρ) and molecular mass (M) of the interstellar ice analogue from the following equation:

\[ N = \frac{t \times \rho \times N_A}{M} \]  

(1.2)

where \( N_A \) is Avogadro’s constant which is equal to 6.022 \( \times 10^{23} \) mol\(^{-1}\).

However, the accuracy of these experimentally determined A-values have been questioned.\(^{123,124}\) When calculating A-values, some studies have assumed the density of the interstellar ice analogue to be 1 g cm\(^{-3}\).\(^{125,126}\) This is an unfounded assumption usually from a lack of experimental data. For example, methane ice at 25 K has a value \( \sim \)0.45 g cm\(^{-3}\).\(^{124}\) This can contribute to large A-value errors and consequently interstellar ice abundances which are derived from column densities. However, recent studies have started to address some of these issues through new measurements.\(^{124,127-129}\)

Another assumption is that the A-values of pure ices can be applied to mixtures. However, several studies have shown that the integrated band strength of a vibrational mode of a pure ice changes when it is part of a mixture.\(^{126,130,131}\) Deposition temperature is also another experimental parameter known to affect A-values.\(^{127}\)

1.5.2 Molecular synthesis experiments

Molecular synthesis in interstellar ice analogues has been studied from the 1970s\(^{132}\) and can be broadly categorised into the following types:

(i) Molecular synthesis in pure ices

(ii) Molecular synthesis in binary ice mixtures

(iii) Molecular synthesis in multicomponent mixtures

(iv) Comparison of processing types

(v) Ice structure

The following section gives examples of the different types of molecular synthesis experiments.
Fig. 1.8 Proposed reaction diagram for the molecular synthesis induced by UV irradiation of CH$_3$OH ice displaying major dissociation and radical combination reactions. Note that other classes of reactions that may be active in the ice, including insertion and hydrogen abstraction reactions are not shown. Photodissociation steps are marked with purple arrows. Radical reaction steps are indicated with black arrows and the reaction partner is listed. Reprinted with permission from Öberg. Copyright 2016 American Chemical Society.

(i) Pure ice experiments

As mentioned in Section 1.2, interstellar ices are composed of several molecules. However, for the elucidation of chemical kinetics and formation mechanisms it is significantly easier to study the processing of pure ice analogues than ice analogue mixtures. A range of pure ices have been processed including the most abundant observed molecules in the ISM: H$_2$O, CO, CO$_2$, CH$_4$, NH$_3$, CH$_3$OH. Several molecules that have yet to be clearly identified in the ISM but are predicted in models have also been studied, for example, CH$_2$NH$_2$, NO, and NO$_2$.

As an example of some of the potential information which can be obtained from the study of a pure interstellar ice analogue, the study by Öberg et al. on the UV processing of CH$_3$OH ice is given. UV irradiation of pure methanol ice at 20 K produces a complex chemistry which is shown in Fig. 1.8 as a proposed reaction scheme diagram of the major dissociation and radical combination reactions.

The formation of several UV irradiation products including CO, H$_2$CO and CH$_4$, were measured as a function of fluence. Growth curves of CO, H$_2$CO and CH$_4$ as a function of UV fluence were obtained and are shown in Fig. 1.9. The growth curves of CO, H$_2$CO and CH$_4$ display different curve profiles which reflects the different chemical kinetics which form these
species. For example, the formation of $H_2CO$ is believed to form directly from the dissociation of $CH_3OH$ shown in C 1.1. The growth curve is characteristic of a first order reaction as the formation of $H_2CO$ relies solely on the concentration of methanol.

$$CH_3OH \xrightarrow{hv} H_2CO + H_2/2H \quad (C\ 1.1)$$

Whereas, the formation of $CH_4$ is dependent on the formation of $CH_3$ radicals (C 1.2) and $H$ (C 1.3) which form from the dissociation of $CH_3OH$. The growth curve of $CH_4$ is characteristic of a second order reaction (C 1.4) as the formation of $CH_4$ (C 1.4) relies on the concentration of both $CH_3$ and $H$.

$$CH_3OH \xrightarrow{hv} CH_3 + OH \quad (C\ 1.2)$$

$$CH_3OH \xrightarrow{hv} CH_2OH + H \quad (C\ 1.3)$$

$$CH_3 + H \longrightarrow CH_4 \quad (C\ 1.4)$$

The formation of CO (C 1.5) is the result of several dissociation reactions of $CH_3OH$ and as such the growth curve shows an increase at higher UV fluence.

$$CH_3OH \xrightarrow{hv} H_2CO \xrightarrow{hv} HCO \xrightarrow{hv} CO \quad (C\ 1.5)$$
Introduction

(ii) Binary ice experiments

The study of chemical kinetics and formation pathways are more difficult in binary mixtures compared to pure ices and results reported by different experiments are often conflictory. The focus of the experiment can also vary, for example, CO$_2$:NH$_3$ binary mixtures have been studied several times each with a different focus. Thermal processing of CO$_2$:NH$_3$ mixtures will induce molecular synthesis. For example, Rodríguez-Lazcano et al. presented the first study to investigate the effects of thermal processing on different stoichiometric ratios of CO$_2$:NH$_3$ in either a 1:1 ratio or excess NH$_3$. While Noble et al. also studied several different ratios of CO$_2$:NH$_3$, including a ratio with excess CO$_2$, the study was focussed on extracting chemical kinetic data as a function of the ratio. Other studies focussed on molecular synthesis induced by other energetic processing techniques such as low energy (9–20 eV) or high energy (1 keV) electrons. Also several studies compared the difference between thermal only processing and other energetic processes such as VUV photons or heavy ion bombardment.

Interestingly, in studies of CO$_2$:NH$_3$ binary mixture where processing with VUV photons, electrons or ions was conducted only experiments using a 1:1 ratio have been reported. However, a ratio dependency on the formation of products has been observed in energetically processed mixtures of H$_2$O:CO$_2$ mixtures. For example, carbonic acid is known to form in ratios where CO$_2$ is in excess but not when H$_2$O is in excess. Another example includes the formation of O$_3$. Energetic processing of pure CO$_2$ will form (O$_3$). However, when CO$_2$ is mixed with water, the production of O$_3$ appears inhibited when a H$_2$O/CO$_2$ ratio is > 2.5. The ratio of the mixture either inhibits (or introduces) different reaction pathways in the case of O$_3$ formation or the analytical technique is not sensitive to small concentrations of O$_3$.

(iii) Multicomponent ice experiments

Multicomponent ices have compositions which are more representative of interstellar ices and the products formed in these ice experiments are usually of biological interest (e.g. amino acids, ribose and its derivatives). Most multicomponent ice experiments focus on the detection and identification of the irradiation products. As such, and in contrast to most pure ice and binary mixture experiments, a typical multicomponent ice experiment will simultaneously deposit and irradiate in order to obtain enough sample for ex situ analysis.

It is difficult to elucidate formation pathways in multicomponent ices. However, isotopic substitution can provide some insight into mechanistic details or at least disprove some reaction mechanisms. For example, two reaction mechanisms were proposed for the formation of glycine in interstellar ice analogues and are shown in Fig 1.10. The first reaction mechanism
1.5 Laboratory experiments

Fig. 1.10 Glycine labelled with central and acid carbon atoms labelled. Proposed reaction mechanisms for the Strecker-type\textsuperscript{148} or the radical-radical\textsuperscript{151} reaction. The carbon and nitrogen atoms that originate from HCN are in bold. A modified radical-radical reaction proposed from isotopic investigations. Adapted from Elsila et al.\textsuperscript{149}

was a Strecker-type reaction where methanol dissociated to form H$_2$CO which could then react with HCN and NH$_3$ to form glycine. The central C would come from CH$_3$OH, the acid C from HCN and the N from NH$_3$. The second reaction mechanism was a radical-radical reaction where dehydrogenation of H$_2$O and CH$_3$OH and hydrogenation of HCN would form glycine. The central C and N would come from HCN and the acid C from CH$_3$OH.

In the study by Elsila et al. isotopic labelling was used to identify where the acid C, central C and N atom came from during the formation of glycine from UV irradiated H$_2$O:CH$_3$OH:HCN:NH$_3$ ice mixture. First of all, HCN or NH$_3$ was removed from the ice mixture to investigate the effects of glycine formation. Glycine was observed when HCN was removed or when NH$_3$ was removed, already suggesting a multireaction pathway. The yield of glycine was significantly lower when HCN was removed compared to NH$_3$. Isotopic labelling showed the acid C was always from HCN and the centre C was from HCN or CH$_3$OH. The majority of the N atoms were from HCN (\textasciitilde90 \%), hence the lower glycine yield when it was removed from the mixture. The major conclusions were that while the dominant formation pathway of glycine is through the HCN it can also form in the absence of HCN. Also that
the previously proposed Strecker-type and radical-radical reactions could not fully explain the synthesis of glycine.

(iv) Comparison of interstellar ice processing techniques

Apart from the composition of the interstellar ice analogues, experiments have compared products as a function of energy. For example, the irradiation of NH$_3$ ice with both low-energy (7 eV) and high-energy (1 keV) electrons by Shulenberger et al.$^{152}$ found little energy dependence on the formation of products. The lack of energy dependence on the formation of products is in keeping with a hypothesis that chemistry of high-energy electron irradiation is driven by low-energy secondary electrons.$^{153,101}$ In fact, a study on the UV irradiation (<7.4 eV) of NH$_3$ ice$^{154}$ showed that the photolysis products were the same as the electron irradiation products of an NH$_3$ ice.$^{152}$ From this the authors concluded that dissociation of an electronically excited molecule to form radicals is the dominant chemistry which underpins both the UV and electron irradiation chemistry.

Energetic and non-energetic processing have also been compared. For example, H-atom addition reactions and UV-irradiation of CO:CH$_3$OH mixtures were investigated by Chuang et al.$^{96}$ From this mixture of CO:CH$_3$OH ice which was processed via H-atom addition or UV irradiation (10.2 eV), methyl formate, glycolaldehyde and ethylene glycol were formed. A difference observed between H-atom and UV processing experiments was the yield of methyl formate. Formaldehyde is required to form methyl formate, however, in H-atom processing experiments the formation of formaldehyde is low and hence, so is the formation of methyl formate. This was not the case for UV processing experiments.

(v) Ice structure

Porosity was defined in Section 1.4.2 as ‘a concept related to texture, referring to the pore space in a material’.$^{117}$ More porous ices will have a larger surface area than less porous ices allowing for increased catalysis, adsorption of more molecules and trapping of volatiles.$^{118}$ Porosity of water ice can be experimentally controlled through the deposition rate, deposition temperature and the angle of deposition.$^{155–157}$ Studies show that pores in interstellar ice analogues can merge upon thermal processing allowing the transport of entrapped molecular species to meet and initiate further reaction.$^{158,159}$

Molecular transport upon phase changes is also thought to have an effect on the reactivity of the ice through the creation of structural cracks allowing for long-range diffusion.$^{160}$ For example, an isothermal kinetic study on H$_2$O:CO$_2$:NH$_3$ mixtures by Ghesquière et al.$^{160}$ showed an increase in thermal reactivity at temperatures where morphological changes were also
observed in amorphous solid water. The authors also suggested that these results would have implications on gas-grain astrochemical models which usually describe molecular transport using reaction-diffusion theory.

Similar to porosity, the phase of the interstellar ice analogue (i.e. whether the interstellar ice has a crystalline structure, that is the presence of three-dimensional order on the level of atomic dimensions) depends on experimental parameters such as the deposition temperature, deposition rate, thermal and energetic histories.

1.6 Thesis motivation and aim

1.6.1 Thesis motivation

From Section 1.5.2 there are many experimental parameters which can be adjusted depending on the defined focus of the experiment. For example, the deposition temperature can change the porosity and crystallinity of the ice which in turn can affect the shape and position of mid-IR peaks. Understanding how the mid-IR peaks vary is important for interpreting interstellar ice observations and inferring the physical and chemical conditions. Therefore it is also important to know that the porosity and crystallinity of the ice analogue can also be altered through deposition rate and angle. By having a comprehensive understanding of an interstellar ice analogue and how the experimental parameters affect the analogue, astrochemical models can be improved to better simulate interstellar ice experiments before extrapolation to an astrophysical environment.

This thesis is motivated by gaining a comprehensive understanding of the influence of experimental parameters on molecular synthesis in interstellar ice analogues. Comprehensive understanding of molecular synthesis in interstellar ice analogues is essential to help explain the presence and abundance of molecules in the ISM. It can also help target future observations with JWST. However, to have a comprehensive understanding of molecular synthesis in interstellar ice the experimental parameters must be investigated systematically. A systematic investigation refers to the concept of investigating one experimental parameter thoroughly while holding all other experimental parameters the same. There are many experimental parameters involved in astrochemistry experiments, for example, deposition temperature, deposition rate, deposition angle, deposition mixing ratio, irradiation technique and irradiation fluence. For direct comparison to interstellar ice observations, a mid-IR spectroscopic study must be conducted. However, to extract the most detail about molecular synthesis in interstellar ice analogues a second monitoring technique is usually employed e.g. UV spectroscopy or mass spectrometry.
Introduction

This thesis is motivated by the fact that to date, experiments involving investigations of molecular synthesis in multicomponent ices very rarely focus on systematic and thorough investigation of one experimental parameter at a time. Typically multicomponent ice experiments focus on identifying molecules, usually of biological interest to prove that they can form under an astrophysical environment. However, the experimental parameters are generally skewed to maximise product yield sometimes under physical and chemical conditions far from actual astrophysical conditions. Furthermore, since mid-IR spectroscopy has limitations in regards to identification of complex molecules this analytical technique is often not used in multicomponent ice experiments. However, multicomponent ice experiments are the most representative of the composition of interstellar ice and well constrained mid-IR spectroscopy of multicomponent ices is still useful even if without positive identification of vibrational modes.

Even the number of molecules in an ice mixture is an experimental parameter which should be systematically investigated. Understanding molecular synthesis in multicomponent ices is difficult especially if there is no understanding of the simpler mixture systems. Binary mixtures of interstellar ice analogues are therefore the most logical starting point, after pure ices, for an investigation into molecular synthesis in interstellar ice analogues before advancing to complex multicomponent ices. This thesis is motivated by the need to understand molecular synthesis in interstellar ice analogues which are representative of interstellar ices. However, it is also motivated by the need to gain a comprehensive understanding of an ice system which is best gained in a bottom-up approach, i.e. pure ices then binary ices then multicomponent ices.

1.6.2 Thesis aim

The aim of this thesis is to systematically investigate the thermal and radiation processing of one binary ice system as a function of deposition mixing ratio. The thermal processing represents the thermal gradient observed in interstellar ices around YSOs as depicted in Fig. 1.4. Radiation processing will be achieved through electron irradiation of the interstellar ice analogues. Electron irradiation will induce radiation chemistry to simulate secondary electrons which are released when a cosmic ray passes through interstellar ice as discussed in Section 1.3. Radiation processed interstellar ices will also experience a thermal gradient around a YSO and a combined electron irradiation at low temperatures plus subsequent thermal processing study will also be investigated. A median ice ratio is not representative of interstellar ice and this is a key experimental parameter to be comprehensively investigated to understand the effects it has on the thermal and radiation processing on the interstellar ice analogues. A binary ice system was chosen to demonstrate that a comprehensive study of the deposition mixing ratio on even a simple ice system has significant results.
To systematically investigate the thermal and radiation processing of a binary ice system as a function of deposition mixing ratio, the binary ice composition of CO$_2$:NH$_3$ was chosen.

- CO$_2$ and NH$_3$ were chosen as these molecules are two of the most abundant molecules observed in interstellar ice and their abundances vary depending on the source. NH$_3$ is the only confirmed source of N atoms in interstellar ice and mixed together with CO$_2$ this binary system contains the four most common elements to life (carbon, hydrogen, nitrogen and oxygen).

- Several literature studies exist on CO$_2$:NH$_3$ interstellar ice analogues\textsuperscript{94,95,162,163,140–143} which were briefly discussed in Section 1.5.2 (ii) Binary mixtures. These literature studies provide a reference to which the results of this thesis can be compared.

- While previous thermal processing studies of CO$_2$:NH$_3$ mixtures have investigated the mixing ratio, the energetic processing studies have only investigated the 1:1 ratio.

The parameter that was systematically studied was the initial deposition mixing ratio of the CO$_2$:NH$_3$ mixtures for an ice system which had been thermally processed after deposition at 20 K and an ice system which had been energetically processed with 1 keV electrons at 20 K and then subsequently thermally processed. The reasons for studying this parameter are given below:

- The mixing ratio is usually adjusted to maximise product yield, especially in multicomponent ices without understanding the effects of several different ratios. To understand multicomponent ices, the way in which molecules interact on a smaller scale is required. While thermal studies of CO$_2$:NH$_3$ mixture have investigated the mixing ratio, irradiation studies have only investigated the 1:1 ratio.

- As the ratios of CO$_2$:NH$_3$ in previous studies have not been varied, it is unknown whether molecular synthesis in all ratios is the same i.e. does the ratio of the ice affect product formation in energetic processing?

In order to monitor changes in the CO$_2$:NH$_3$ binary ice analogue system \textit{in situ} mid-IR and vacuum UV spectroscopy are used. As non-destructive techniques, mid-IR and vacuum-UV spectroscopy provide information on both the end products and the complex process involved in forming these products.
1.7 Thesis Outline

This thesis systematically investigates the thermal and radiation processing of a CO$_2$:NH$_3$ binary ice system as a function of deposition mixing ratio and is comprised of seven chapters.

Chapter 1 has provided an inventory of the molecules found in space with emphasis on solid phase molecules. It has given background information on the observations used in different regions of space, and provided the main molecular synthesis pathways in interstellar ices. An overview of astrochemical models and laboratory experiments were also given alongside the thesis motivation and thesis aim.

Chapter 2 introduces the background theory to IR and UV spectroscopy, ice structure and radiation processing with an electron gun. It also describes the experimental set-up and methodology used throughout this thesis.

Chapter 3 describes and discusses the mid-IR spectroscopic results of the thermal processing of CO$_2$:NH$_3$ binary ice mixtures which were deposited at 20 K as a function of deposition mixing ratios.

Chapter 4 describes and discusses the mid-IR spectroscopic results of the radiation processing of CO$_2$:NH$_3$ binary ice mixture which were deposited and processed at 20 K as a function of deposition mixing ratio. It also describes and discusses the subsequent thermal processing of the CO$_2$:NH$_3$ binary ice mixtures. These results are then compared to the thermal processing results in Chapter 3.

Chapter 5 describes and discusses the vacuum-UV spectroscopic results of the thermal processing of CO$_2$:NH$_3$ binary ice mixtures which were deposited at 20 K as a function of deposition mixing ratios. These results are then compared to the mid-IR spectroscopic thermal processing results in Chapter 3.

Chapter 6 describes and discusses the vacuum-UV spectroscopic results of the radiation processing of CO$_2$:NH$_3$ binary ice mixture which were deposited and processed at 20 K as a function of deposition mixing ratio. It also describes and discusses the subsequent thermal processing of the CO$_2$:NH$_3$ binary ice mixtures. The results are then compared to the thermal processing results in Chapter 5. These results are also compared to the mid-IR spectroscopic thermal processing results in Chapter 4.

Chapter 7 presents a summary of the results from Chapters 3, 4, 5 and 6, and briefly discusses the implications of these results in the context of astrochemical laboratory experiments, models and observations. Finally, ongoing work is presented and future work is suggested.
Chapter 2

Experimental

This chapter introduces the relevant theory that is required to interpret the spectroscopic results presented in this thesis and describes in detail the experimental methods employed to obtain these results. The theory includes the fundamental concepts which underpin IR and UV spectroscopy, the different types of morphology of ice and the role of energetic processing. The experimental methods include a detailed description of the experimental apparatus used and the techniques employed to determine the ice thickness, ratio of the mixture and penetration depth of the electrons. A description of the general experimental procedure is given and the limitations of the experimental apparatus together with the possible implications are also given.

2.1 Spectroscopy

Spectroscopy is the study of the interaction of matter with electromagnetic radiation. Matter in this thesis refers to the molecules in the interstellar ice analogues. While molecules can absorb, emit and scatter electromagnetic radiation this chapter mainly focusses on the absorption of IR and UV radiation.

Classical physics describes electromagnetic radiation as oscillating electric and magnetic fields which propagate as a harmonic wave through a vacuum at the speed of light ($c$). The different regions of the electromagnetic spectrum are characterised by the wavelength ($\lambda$) or frequency ($\nu$) which are related via the following equation:

$$c = \nu \lambda$$  \hspace{1cm} (2.1)

where $c = 3 \times 10^8$ m s$^{-1}$.

Quantum physics describes electromagnetic radiation as consisting of photons which are uncharged particles with zero mass at rest. Photons have quantised packets of energy ($E$) and the
different regions of the electromagnetic spectrum can also be characterised by the energy. The energy of the photons is directly proportional to its frequency through the following equation:

\[ E = h \nu \]  

(2.2)

where \( h \) is the Planck constant which is equal to \( 6.626 \times 10^{-34} \) J s.

The electromagnetic spectrum is shown in Fig. 2.1 as well as the associated atomic or molecular transitions. UV spectroscopy will provide information on the transitions of the valence (or outer shell) electrons and IR spectroscopy will provide information on the molecular vibrational transitions. Sometimes in UV spectroscopy the energy is quoted in units of electron-volts (eV) where 1 eV = \( 1.60218 \times 10^{19} \) J. Whereas, for IR spectroscopy the wavenumber, \( \tilde{\nu} \) (cm\(^{-1}\)) is most commonly used and is the reciprocal of wavelength where:

\[ \tilde{\nu} = \frac{1}{\lambda(\text{cm})} \]  

(2.3)
2.1 Spectroscopy

Fig. 2.2 Example of an IR spectrum of CO$_2$ ice deposited at 20 K with labelled vibrational modes. Note: this mid-IR spectrum was taken with the substrate at normal incidence to the IR beam.

Fig. 2.1 also shows the subregions of IR and UV radiation. However, precise definitions vary between the literature for the subregions of both IR and UV radiation and so the given subregions in Fig. 2.1 are just approximate.

The theory and application of IR and UV spectroscopy is described in detail in Sections 2.1.1 and 2.1.2, respectively.

### 2.1.1 Infrared spectroscopy

IR spectroscopy can identify functional groups present within a molecule and is routinely used for identifying unknown compositions. Fig. 2.2 shows an example of an IR spectrum of CO$_2$ ice deposited at 20 K. An IR spectrum is simply the plot of IR radiation intensity versus the wavelength (or wavenumber). In Fig. 2.2, the x-axis is in wavenumbers (\(\bar{\nu}, \text{cm}^{-1}\)) which is related to wavelength through Eq. 2.3. Wavenumbers are related to frequency, (\(\nu, \text{s}^{-1}\)) through the speed of light (c, cm s$^{-1}$) via the following equation:

\[
\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}
\] (2.4)
The y-axis of Fig. 2.2 is in absorbance (A) which is the ratio of the incident ($I_0$) to transmitted ($I_t$) IR light intensity and is dependent on the inverse transmittance (T) via the following equation:

$$A = \log_{10} \left( \frac{I_0}{I_t} \right) = \log_{10} \left( \frac{1}{T} \right)$$

The y-axis of an IR spectrum is also commonly plotted in transmittance, but throughout this thesis all IR results will be plotted in absorbance which is easier for any quantitative analysis.

(i) How do molecules absorb IR radiation?

Typically, diatomic molecules can be considered using the ‘ball and spring’ model where the atoms are represented as balls and the chemical bond is represented as a spring. Fig. 2.3 shows the diatomic molecule of hydrogen chloride (HCl). HCl is a polar molecule because the Cl atom has a larger electronegativity compared to the H atom. Electronegativity is the power of an atom to attract electrons to itself when it is part of a compound. The difference in the electronegativity between the H and Cl atoms results in a higher probability of finding electrons around the Cl atom compared to the H atom. Hence, in Fig. 2.3 the H atom is labelled with a partial positive charge ($\delta^+$) and the Cl atom is labelled with a partial negative charge ($\delta^-$). This asymmetry of the electric charges through the chemical bond is referred to as the dipole moment, ($\mu$) and can be calculated through the following equation:

$$\mu = Qr$$
where Q is the magnitude of the charge and r is the distance between the charges.

As the electric field of IR radiation alternates polarity it can interact with molecules with both positive and negative polarity. For molecules like HCl which has a permanent dipole, when the polarity of the electric field is positive it will repel the partial positive end of HCl. When the polarity of the electric field is negative it will attract the partial positive end of HCl. This attraction and repulsion is shown in Fig. 2.3. When HCl is repelled the bond length between the H and Cl atoms contracts and when HCl is attracted the bond length extends. This extension and contraction of the bond length is referred to as a vibration. Molecules will only interact with IR radiation if the frequency of the IR radiation corresponds to the natural vibration of the molecule. IR spectroscopy exploits this phenomenon and a spectrum can be acquired over a range of wavenumbers.

The interaction of molecules with IR radiation is not just limited to molecules with permanent dipole moments. Any molecule which can have an induced dipole moment will also absorb IR radiation. For example, CO$_2$ has a net dipole moment of zero as the dipole moments between the two C–O bonds are equal, but opposite, in magnitude as CO$_2$ is a linear molecule. However, once an electric field is applied to CO$_2$ some of the electrons will still be attracted or repelled. This will cause a temporary asymmetry in the electron distribution within the molecule and an induced dipole moment can occur. The formation of an induced dipole moment is depicted in Fig. 2.4.
Fig. 2.5 Parabolic potential energy of a classical harmonic oscillator with vibrational quantum numbers (v) labelled. \( R_e \) is the equilibrium bond length.

The gross selection rule for IR spectroscopy requires that a net change in the electric dipole moment of the molecule must occur during the vibration. Consequently, homonuclear diatomic molecules such as \( \text{N}_2 \) and \( \text{O}_2 \), which do not experience a change in dipole moment upon vibration, cannot absorb IR radiation and are said to be IR inactive.

(ii) Vibrational peak positions: the harmonic oscillator and fundamental modes

To understand the origin of the vibrational peak positions, the following must first be considered. Using the ‘ball and spring’ model, the vibrating chemical bond can be considered as a spring in harmonic oscillation which obeys Hooke’s Law. Hooke’s Law states that the restoring force is proportional to the displacement:

\[
\text{Restoring force} = -kx
\]  

where \( k \) is the restoring force constant (N m\(^{-1}\)) and \( x \) is the displacement (m).

Stiffer springs or chemical bonds will have higher force constants. In the case of a vibrating molecule the displacement, \( x \), corresponds to the displacement from the equilibrium bond distance \( (R_e) \) and is referred to as \( (R-R_e) \).

Fig. 2.5 shows the parabolic potential energy characteristic of a classical harmonic oscillator and the potential energy \( (V) \) is in the form of:
2.1 Spectroscopy

\[ V = \frac{1}{2} k (R - R_e)^2 \]  \hspace{1cm} (2.8)

Solving the Schrödinger wave equation for the harmonic oscillator potential energy gives the vibrational energy levels, \((E_v)\):

\[ E_v = (v + \frac{1}{2}) \hbar \nu \hspace{1cm} v = 0, 1, 2 \ldots \]  \hspace{1cm} (2.9)

where \(v\) is the vibrational quantum number.

The observed frequency \((\nu)\) and the force constant \((k)\) in Eq. 2.9 are related by the following equation:

\[ \nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{\frac{1}{2}} \mu = \frac{m_A m_B}{m_A + m_B} \]  \hspace{1cm} (2.10)

where \(\mu\) is the reduced mass of the molecule with atoms of mass \(m_A\) and mass \(m_B\).

As IR radiation is typically expressed in wavenumber, it is more convenient to write Eq. 2.9 as:

\[ E_v = (v + \frac{1}{2}) \hbar \tilde{\nu} \hspace{1cm} v = 0, 1, 2 \ldots \]  \hspace{1cm} (2.11)

According to Eq. 2.10, the wavenumber (or frequency) at which a chemical bond within a molecule will absorb IR radiation depends on the reduced mass \((\mu)\) and force constant \((k)\). Chemical bonds with larger force constants (e.g. stiffer bonds) will absorb at higher frequency and molecules with heavy bonds (e.g. large reduced masses) will absorb at lower frequency. The specific selection rule for vibrational transitions is also obtained:

\[ \Delta v = \pm 1 \]  \hspace{1cm} (2.12)

And the change in state from vibrational quantum number, \(v\), to a state with vibrational quantum number \(v + 1\) is:

\[ \Delta E = (v + \frac{3}{2}) \hbar \tilde{\nu} - (v + \frac{1}{2}) \hbar \tilde{\nu} = \hbar \tilde{\nu} \]  \hspace{1cm} (2.13)

At room temperature and below, most molecules will initially be in their vibrational ground state \((v = 0)\). The vibrational transition from \(v = 0\) to \(v = 1\) is called the fundamental mode and is commonly observed within the mid-IR region.

(iii) Vibrational peak positions: anharmonicity and overtones

Fig. 2.5 is not a true representation of a chemical bond as when the bond is stretched sufficiently it will dissociate. In reality, at higher vibrational levels the molecular potential curve deviates
Experimental

Fig. 2.6 Parabolic potential energy of an anharmonic oscillator (blue) with vibrational quantum numbers (v) labelled. The classical harmonic oscillator (red) is shown to highlight how the anharmonic oscillator deviates from the classical harmonic oscillator. $R_e$ is the equilibrium bond length.

from the classical harmonic approximation as the restoring force is no longer proportional to the displacement. Fig. 2.6 shows this anharmonicity and the effect it has on the energy levels which are less widely spaced and expressed by:

$$E_v = (v + \frac{1}{2})\hbar\nu - (v + \frac{1}{2})^2\hbar\nu x_e + \ldots$$

(2.14)

where $x_e$ is the anharmonicity constant.

The fundamental mode has already been described as a transition where $\Delta v = \pm 1$. Anharmonicity leads to a breakdown in the $\Delta v = \pm 1$ vibrational selection rule and can therefore account for weak absorption peaks called overtones corresponding to transitions between $\Delta v = \pm 2, \pm 3, \ldots$. Overtones are mainly observed in the near-IR region although some are also observed in the mid-IR region.

(iv) Polyatomic molecules

The number of fundamental vibrational modes of a polyatomic molecule with N atoms can be predicted by calculating how each atom may move along three perpendicular axes such that:

Non-linear molecules: Number of vibrational modes $= 3N - 6$
Linear molecules: Number of vibrational modes $= 3N - 5$
2.1 Spectroscopy

As each atom in a molecule can move along any three perpendicular axes, the total number of displacements of a polyatomic molecule containing N atoms is 3N. Translational motion accounts for three displacements and rotational motion for another three displacements, hence for non-linear molecules, $3N - 6$. For linear molecules only 2 displacements account for rotation as no rotation exists around the bond axis, hence for linear molecules, $3N - 5$. However, the number of normal modes is not necessarily equivalent to the number of observed IR vibrational transitions. For example, the linear molecule of CO$_2$ will have 4 fundamental modes. However, only three of these modes are classified as IR active in which a change in dipole moment is experienced upon vibration. The $\nu_1$ fundamental mode, or the symmetric stretch, is IR inactive as no change in dipole moment is experienced upon vibration. The IR active $\nu_3$ fundamental mode of CO$_2$ is labelled in Fig. 2.2. CO$_2$ also has a degenerate $\nu_2$ fundamental mode at $\sim 660$ cm$^{-1}$, but due to the limitations of the experimental set-up which are described in Section 2.4.4 mid-IR spectra at < 800 cm$^{-1}$ could not be obtained.

(v) Other vibrational modes of polyatomic molecules

The origin of the fundamental modes and overtones have been described above. However, not all IR absorption features are explained by these modes. Other modes include:

- Combination modes: when two or more fundamental modes are simultaneously excited.

- Fermi resonance: when two vibrational modes of similar energy and the same symmetry are present, usually a fundamental and a weaker overtone or combination mode. A splitting within the vibrational mode is observed and intensity from the more intense mode (e.g. fundamental) is shared with the weaker mode (e.g. overtone or combination mode) which results in two strong absorption bands.

(vi) Fourier Transform IR spectrometer

The Fourier Transform IR (FTIR) spectrometer is the most widely used IR spectrometer and a schematic of a FTIR spectrometer is shown in Fig. 2.7. Typically, FTIR spectrometers will consist of a source, interferometer, a sample compartment, a detector and a computer. FTIR spectrometers are based around a Michelson interferometer which is shown in Fig. 2.7. A Michelson interferometer consists of a beam splitter, a fixed mirror and a movable mirror. IR radiation from the source is collimated onto the beam splitter which transmits half of the IR radiation to the fixed mirror and reflects the other half to the movable mirror. Both mirrors then reflect the IR radiation back to the beam splitter where it is recombined and half of the radiation is passed through the sample to the detector. The rest of the recombined radiation
Experimental

**Fig. 2.7** A schematic diagram of an FTIR spectrometer including the Michelson interferometer. Adapted from Ojeda and Dittrich.\(^{166}\)

is reflected back to the source. The moveable mirror allows a path length difference to be introduced causing constructive and destructive interference. After passing through the sample, an interferogram is obtained. A Fourier transform (a mathematical process) is applied to the interferograms to convert them into constituent frequencies and produce a recognisable IR spectrum. A FTIR spectrometer was used to obtain all mid-IR spectroscopic results and the specific set-up is discussed in Section 2.4.4.
2.1 Spectroscopy

2.1.2 Ultraviolet spectroscopy

UV spectroscopy can identify the electronic transitions that occur within a molecule and is sometimes called electronic spectroscopy. Fig. 2.8 shows an example UV spectrum of CO$_2$ ice deposited at 20 K. A UV spectrum is simply a plot of UV radiation intensity versus the wavelength (or energy). In Fig. 2.8 the x-axis is plotted in wavelength with units of nanometres (nm) which is how all UV spectroscopic results in this thesis will be displayed. However, as mentioned earlier it is also typical to use energy on the x-axis in units of eV. Similar to IR spectroscopy, the y-axis is in absorbance. According to the modified Beer-Lambert Law the absorbance (A) is proportional to the number density (n) of the sample:

$$A = \sigma nl$$  \hspace{1cm} (2.15)

where $l$ is the optical path length or thickness of the sample and $\sigma$ is photoabsorption cross section which is constant for a particular molecule at a specific wavelength.

In this thesis, the reference to VUV radiation or VUV spectroscopy will refer to the the region of UV radiation from 120–340 nm and the associated absorption. Strictly speaking this encompasses several subregions of the UV as shown in Fig. 2.1.

(i) Absorption of UV radiation

When a molecule absorbs UV radiation a valence electron is exited from a lower energy level to a higher energy level in what is referred to as an electronic transition. Fig. 2.9 shows examples of the different electronic transitions which can occur in molecules. The labels $\sigma$, $\pi$ and $n$ on
the energy levels in Fig. 2.9 refer to different molecular orbitals which are present in molecules. Transitions such as $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ are not allowed due to the difference in the symmetry of the molecular orbitals. To understand the labelling and the difference in molecular orbital symmetry, a brief introduction to molecular orbital (MO) theory is given below.

(ii) Molecular Orbital theory

MO theory is a method of describing the electronic structure of molecules using quantum mechanics and builds upon the idea of atomic orbitals (AO). An orbital is an area around an atom or molecule where there is a high probability of finding electrons. Heisenberg’s Uncertainty Principle states that the precise location and momentum of an electron in an atom or molecule is impossible to define. Orbitals are usually depicted as three-dimensional shapes which are governed by the vibrational quantum numbers: $n$ (principal), $l$ (orbital angular momentum), $m_l$ (magnetic) and $s$ (spin).

Fig. 2.10 shows the formation of $\sigma$ MOs from s and p AOs and $\pi$ MOs from p AOs. When the AOs are in-phase they will interfere constructively and the electron density will be highest between the nuclei of the two atoms. Bonding MOs will form and they will have a lower energy level than the respective AOs as less energy is required to hold the atoms together if electrons occupy this bonding MO. However, if the AOs are out-of-phase they will interfere destructively and the electron density will be low between the nuclei of the atoms. Antibonding MOs will form and they will have a higher energy level than the respective AOs. More energy is required to overcome the repulsion between the nuclei and hold the atoms together if electrons occupy this antibonding MO.

The orientation of the AOs also dictates what type of bonds will form and this is also shown in Fig. 2.10. For example, two s-orbitals which are spherically shaped can only overlap in
2.1 Spectroscopy

Fig. 2.10 Formation of $\sigma$ molecular orbitals (MOs) from s and p atomic orbitals (AOs) and $\pi$ MOs from p AOs.

one way and therefore will only form a $\sigma$-orbital. However, p-orbitals have a double lobe structure pointing along the same axis. If two p-orbitals were to interact, there are two possible orientations in which it might occur: head-on or side-on overlap. Where head-on overlap occurs a $\sigma$-orbital is formed, but if side-on overlap occurs then a $\pi$-orbital is formed.

Non-bonding orbitals can also form and are usually found with energy between the bonding and antibonding orbitals. Electrons which occupy n-orbitals do not participate in the bonding of the molecules and are the equivalent of lone pairs of electrons in valence bond theory (which is not discussed here).
(iii) Vibrational progressions and the Franck-Condon Principle

It is implied from Fig. 2.9 that an electronic transition will result in a single discrete line, but Fig. 2.8 shows that broad features are obtained instead. When an electronic transition occurs the energy required for electronic excitation can also cause vibrational excitation in a process referred to as a vibronic transition. The intensity and shape of a vibronic transition or progression can be explained by the Franck-Condon Principle. The Franck-Condon Principle states that as the nuclei are significantly more massive than the electrons, then an electronic transition will take place faster than the nuclei can respond. Therefore, only vertical transitions from a lower energy state to a higher energy state will occur.

Fig. 2.11 Diagram of the Franck-Condon Principle and examples of the different outcomes of transitions between the ground states ($R''_e$) and excited states ($R'_e$) of different internuclear distances. Example of the same bond length ($R'_e \approx R''_e$), a slightly longer bond length when excited ($R'_e > R''_e$) and an even longer bond length when excited ($R'_e >> R''_e$). Adapted from Banwell.\textsuperscript{164}
2.1 Spectroscopy

When a molecule is excited the intermolecular bond length may remain the same or it may increase in length. Fig. 2.11 shows the molecular potential energy diagrams of an upper energy level with the same bond length ($R'_{e} \simeq R''_{e}$), a slightly longer bond length ($R'_{e} > R''_{e}$) and even longer bond length ($R'_{e} >> R''_{e}$). Anything associated with the lower energy state is labelled with a double prime (e.g. lower energy state equilibrium bond length, $R''_{e}$) and the excited state is labelled with a single prime (e.g. excited energy state equilibrium bond length, $R'_{e}$). For simplicity, the vibronic transition is viewed as going from the ground state in the lower energy level to the ground state in the excited energy level. According to the Franck-Condon Principle the internuclear distance will not change upon excitation therefore a vertical transition occurs. If the bond length between the states does not change ($R'_{e} \simeq R''_{e}$), then the strongest transition is from $v''_{0}$ to $v'_{0}$ with some probability of finding electrons in the nearby transitions. This is shown in Fig. 2.11 (i) where the transition can be referred to in the format $(v', v'')$ which in this case is a (0,0) transition and the shape of the vibronic transition is also shown.

If the excited state has a slightly longer bond length than the lower energy state ($R'_{e} > R''_{e}$) as depicted in Fig. 2.11 (ii) then the (2,0) is the strongest transition. For an even longer bond length ($R'_{e} >> R''_{e}$) a continuum feature occurs where no discrete lines are observed. At room temperature the vibrational structure can be resolved in the gas phase, but not for liquid and solid samples and a broad feature is usually observed. However, for low temperatures vibrational structure can be observed in solids as shown in Fig. 2.8. At low temperatures almost all the electrons in a molecule will be in the ground state. As the temperature increases the presence of ‘hot bands’, each with similar wavelength, also increases causing the spectra to lose fine structure due to averaging. A hot band is a vibrational transition from one excited vibrational state to another excited vibrational state.

(iv) Electronic Transitions in the UV range

Fig. 2.12 shows a schematic diagram of the wavelength or energy regions in which different electronic transitions may occur. Electrons which reside in the $\sigma$ bonding MOs are closer to the nuclei and so require more energy to excite. Electrons residing in the $\pi$-bonding and n-bonding MOs are further away from the nucleus and therefore require less energy to excite.

(v) UV Spectrometer

A schematic diagram of a single beam dispersive UV spectrometer is shown in Fig. 2.13. Typically, an UV spectrometer will consist of a UV light source, a monochromator, a sample compartment, a detector and a computer. Light from the UV light source passes through the entrance slit of the monochromator which narrows the beam of light to a usable working size.
**Experimental**

**Fig. 2.12** Schematic diagram of the different electronic transitions which can occur when molecules absorb UV to visible radiation. Adapted from Banwell. 164

**Fig. 2.13** Schematic diagram of a single beam dispersive UV spectrometer.
2.2 Radiation processing with an electron gun

The diffraction grating disperses the polychromatic light and the desired wavelength is selected by changing the exit slit. This dispersed light then passes through the sample to a detector to produce a UV spectrometer.

Below 200 nm, in the VUV and EUV region, as shown in Fig 2.12, almost all of the UV light is strongly absorbed by oxygen and nitrogen in the Earth’s atmosphere and requires vacuum equipment to take measurements. Most commercially available UV spectrometers will therefore have a lower wavelength limit of approximately 200 nm. Hence almost all $\sigma \rightarrow \sigma^*$ transitions cannot be observed using commercial UV spectrometers. A synchrotron light source facility is usually required to access the VUV region. A detailed description of the synchrotron light source used for experiments in this thesis is described in Section 2.4.4.

2.2 Radiation processing with an electron gun

Fig. 2.14 Schematic diagram of an electron gun.

Radiation chemistry was defined in Section 1.3.2 as being characterised by the production of secondary electrons due to the absorption of ionising radiation to induce chemical change. Sources of ionising radiation in the ISM medium included high energy particles such as cosmic rays or high energy photons from YSOs.

In this thesis an electron gun is used to produce electrons to mimic secondary electrons which form when cosmic rays interact with interstellar ice. One cosmic ray is estimated to release $\sim 10^4$ secondary electrons.\textsuperscript{153} A schematic of an electron gun is shown in Fig. 2.14. An electron gun consists of a thermionic emitter such as a hot cathode which emits electrons upon heating. The electrons then pass through a specially shaped electrode called a grid which has a negative bias to control the flow of electrons. One or more anodes then accelerates the beam of electrons by applying a more positive bias and the electron beam is then focussed by passing the beam through a focussing anode. The details of the electron gun used in this thesis are given in Section 2.4.5.
2.3 Ice structure

If molecules (or atoms) collide onto a cold surface (T < 10 K) then the sticking probability will be very high and the molecules will adsorb to the surface. At such low temperatures once the molecules have collided they will not have enough energy to diffuse or rotate. The random way in which the molecules collide onto the cold surface means that the ice film will grow with a non-crystalline or ‘amorphous’ structure. The structure of a non-crystalline ice is depicted in Fig. 2.15 (i) where no long range order across the ice film is obtained. This is assumed to be the case for the majority of interstellar ice found in molecular clouds where the temperature is approximately 10 K. For the experiments performed in this thesis, the lowest temperature at which the substrate can be held is 20 K, and in most cases this will result in formation of a non-crystalline ice.

Thermal processing of non-crystalline ice can allow the molecules to rearrange to form a crystalline ice. The structure of a crystalline ice is depicted in Fig. 2.15 (iii) where long range order across the ice film is obtained. A crystalline ice can also be achieved by using higher deposition temperatures so that the molecules have enough energy to align upon physisorption.

There is also a structure between non-crystalline and crystalline called polycrystalline and this is depicted in Fig. 2.15 (ii). Polycrystalline ice is more ordered than non-crystalline ice, but less ordered than crystalline ice and is characterised by crystallites. Crystallites are small regions of the ice film where the molecules are aligned, but randomly aligned with respect to other crystallites. Grain boundaries are formed between the crystallites which can affect the reactivity of interstellar ices through increased molecular transport as discussed in Section 1.5.2. Polycrystalline ice can form by depositing at a temperature between the non-crystalline and crystalline temperatures. It can also form when a non-crystalline ice has extensive intermolecular bonding which can prevent the alignment of molecules upon thermal processing e.g. intermolecular H-bonding in NH$_3$.

Traditionally, the crystallography of a material would be determined using X-ray crystallography or neutron diffraction. However, the low temperature deposition requirement for
forming a non-crystalline ice generally excludes these methods. Therefore, changes within spectroscopic measurements are used to indicate phase changes. For example, broad peaks for the mid-IR vibrational modes are expected in non-crystalline ice because of the broader statistical distribution of bond lengths due to the disordered orientation of molecules. On the other hand, crystalline solids do possess long-range order and so they have a narrower statistical distribution of bond lengths. This results in the mid-IR vibrational modes narrowing when compared to the vibrational modes of a non-crystalline solid. Splitting of vibrational modes in some crystalline solids is also expected due to Davydov splitting (factor-group splitting) which arises ‘due to the presence of more than one interacting equivalent molecular entity in the unit cell’ \(^{168}\) and therefore cannot be present in non-crystalline solids. Changes in the electronic transitions and Davydov splitting are also observed in UV spectra upon phase change.\(^ {115,169,170}\)

### 2.4 Experimental system and procedure

To grow and systematically study binary mixtures of CO\(_2\) and NH\(_3\) interstellar ice analogues the physical conditions of the interstellar medium were simulated in the laboratory. The Portable Astrochemistry Chamber (PAC) based at The Open University was designed by Dawes\(^ {171}\) to provide low pressure and low temperature conditions in which interstellar ice analogues can be formed whilst maintaining portability. It has undergone several modifications from the original design and the latest set up is described below.

#### 2.4.1 The Portable Astrochemistry Chamber

A schematic diagram of the Portable Astrochemistry Chamber (PAC) is shown in Fig. 2.16. The main chamber is a stainless steel, spherical cube (Kimball Physics MCF275-SC600-A) with an internal diameter of 66 mm. A total of six ConFlat (CF) 40 ports, one on each face, is located on the chamber. The turbomolecular pump (Leybold TURBOVAC TMP 151) is attached to the bottom CF40 flange via a CF40-to-CF100 adaptor. The turbomolecular pump is backed by a two-stage oil rotary vane pump (Leybold TRIVAC D4B). Mounted on the opposite side of the chamber is the two-stage closed cycle helium cryostat (Sumitomo DE-202B) which is supplied by a helium compressor (Sumitomo HC-4E). The cryostat is housed in a stainless steel extension piece attached to a rotary feedthrough (MDC ERMTG 275) which is mounted onto the chamber via a CF40-to-CF100 adaptor. The substrate holder (oxygen-free high conductivity copper, Goodfellow) is attached to the cold head of the cryostat so that the substrate is held centrally in the chamber. A Kapton flexible resistive heater (Omega) is attached to the substrate holder. Also attached to the substrate holder is a silicon diode temperature sensor (Lake Shore...
Fig. 2.16 Schematic diagram of the Portable Astrochemistry Chamber (PAC).
2.4 Experimental system and procedure

Cryosensors DT-670B-SD) connected via 4 manganin wires and positioned as close to the substrate as possible for substrate temperature measurements. The wires of the heater and silicon diode sensor connect to an external temperature controller via a 10-pin CF16 electrical feedthrough. The differentially pumped rotary manipulator allows the substrate holder to be rotated as required. One of the CF40 flanges on the side of the chamber has a stainless steel T-piece attached which houses the electron gun (Kimball Physics FRA-2X1-5549). Also attached to this T-piece is a combination gauge (Leybold IONIVAC ITR 90) which can read pressure to as low as $5 \times 10^{-10}$ mbar. The gas line is attached on the opposite CF40 port to the T-piece and is described in detail in Section 2.4.2. Windows are attached to the other two CF40 ports on the chamber, which are not depicted in Fig. 2.16, to seal the chamber. The windows are made from a transmitting material which depends on the spectroscopic technique being used: zinc selenide (ZnSe) for IR spectroscopy and magnesium fluoride (MgF$_2$) for UV spectroscopy. The material of the substrate is also dependent on the spectroscopic technique being used: ZnSe for IR spectroscopy and MgF$_2$ for UV spectroscopy.

2.4.2 Gas dosing line

The interstellar ice analogues were grown by physical vapour deposition. Fig. 2.17 shows a schematic diagram of the gas line. The gas inlet into the PAC is composed of a 6 mm diameter stainless steel tube welded into the centre of a CF40 flange which is attached to the PAC chamber. The design of this gas inlet allows for direct gas deposition with the inlet nozzle and substrate (at normal incidence) between 2–3 cm in distance. This means that the majority of the molecular gas which enters the PAC will form a molecular ice film. The rate of gas intake is regulated by the high precision leak valve (Kurt J. Lesker VZLVM29) which is connected to the gas inlet via a CF40 flange. This high precision leak valve is connected to a stainless steel T-piece via another CF40 flange which acts as a mixing reservoir. Attached to this mixing reservoir T-piece is a Baratron capacitance manometer (MKS MK 524). A CF40 flange with a 6 mm diameter stainless steel tube is attached to the other side of the T-piece and has an ON/OFF valve situated on the stainless steel tube. The rest of the gas line is composed of all metal Swagelok pieces. The gas cylinders or lecture bottles of CO$_2$ (99.8%, BOC) and NH$_3$ (99.96%, ARGO International Ltd) are isolated from the gas line via ON/OFF valves and the flow of gas is regulated with needle valves. The entire gas line is pumped by a two-stage oil rotary vane pump (Leybold TRIVAC D4B) and can reach pressures of $2 \times 10^{-2}$ mbar. When the gas reservoir is closed, the pirani gauge located near the rotary pump is used to determine the pressure in the gas line.
Fig. 2.17 Schematic diagram of the gas dosing line.
2.4 Experimental system and procedure

2.4.3 Ice growth and thickness measurements

The ice films were grown by physical vapour deposition of the pure or premixed gas onto the substrate which is at \( \sim 20 \) K. The substrate was rotated so that it was at normal incidence to the gas inlet nozzle. During deposition the pressure in the PAC is regulated between \( 1-1.2 \times 10^{-7} \) mbar via the high precision leak valve and \textit{in situ} laser measurements are taken to determine the ice thickness.

![Figure 2.18 Schematic diagram of thin film interference caused by the optical path length difference for light reflected from the vacuum-ice film surface and the ice film-substrate surface. The refractive index of the vacuum \( (n_1) \), the refractive index of ice \( (n_2) \), the angle of incidence of monochromatic light \( (\theta_1) \), the angle of the refracted monochromatic light \( (\theta_2) \) and the thickness of ice \( d_{\text{ice}} \) are labelled.](image)

When monochromatic light (e.g. HeNe laser with a fixed wavelength of \( \lambda_0 = 632.8 \) nm) is shone onto an ice film, the light can be reflected from the vacuum-ice film surface or the ice film-substrate surface as shown in Fig. 2.18. Interference patterns arise due to the constructive and destructive interference of the reflected light and the thickness of the ice can be acquired. The HeNe laser beam is positioned into the chamber through a modified CF40 flange. This modified CF40 flange also serves as the gas nozzle inlet which is positioned in the centre of the flange. Fig. 2.19 shows a photograph of this modified CF40 flange. Two CF16 ports were welded onto the CF40 flange at an angle of 20° and CaF\(_2\) windows were attached to seal the chamber. The HeNe laser beam is positioned so that it reflects off the centre of the substrate within the PAC and the reflected beam is measured with a photodiode which is attached to the other CF16 port.

When the ice film growth commences, variation in the voltage signal from the reflected HeNe beam is observed. Fig 2.20 shows an example of the voltage change for the growth of a
Experimental

**Fig. 2.19** Photograph of the modified CF40 flange which is used for laser reflection measurements. The gas nozzle inlet, CF16 ports for laser reflection and modified CF40 flange are labelled.

CO$_2$:NH$_3$ binary ice mixture in a 1:10 ratio. The interference pattern is fitted in Fig. 2.20 with the following equation:

$$y = y_0 + A \sin \left( \pi \frac{x - x_c}{w} \right)$$  \hspace{1cm} (2.16)

where $y_0$ is the y-offset, $x_c$ is the phase shift, $A$ is the amplitude and $w$ is the half period.

From the amplitude ($A$) which was obtained from the fit (Eq. 2.16), the refractive index of the ice ($n_2$) can be estimated from the following equation:

$$n_2 = \frac{y_0 + A}{y_0 - A}$$  \hspace{1cm} (2.17)

Using Snell’s Law ($n_1 \sin \theta_1 = n_2 \sin \theta_2$) the angle of the refracted beam ($\theta_2$) can be calculated:

$$\theta_2 = \sin^{-1} \left( \frac{n_1 \sin \theta_1}{n_2} \right)$$  \hspace{1cm} (2.18)

where $n_1$ is the refractive index of the vacuum ($n_1=1$), $\theta_1$ is the angle of incidence of the HeNe laser ($\theta = 20^\circ$) and $n_2$ the refractive index of the ice which was obtained in Eq. 2.17.

The thickness of the ice per constructive interference fringe ($d_{fringe}$) can then be calculated using the following equation:

$$d_{fringe} = \frac{\lambda_0}{2n_2 \cos \theta_2}$$  \hspace{1cm} (2.19)
2.4 Experimental system and procedure

Fig. 2.20 In situ laser interferometry voltage measurements against deposition time. The raw data (blue dots) is fitted with Eq. 2.16 (red line). From the fit the y-offset ($y_0$), phase shift ($\phi$), half period ($w$) and amplitude ($A$) are obtained.

While all ices used in this thesis produced at least one complete interference fringe, however, as observed in Fig. 2.20 the number of constructive interference fringes is not an integer value. Therefore, deposition rate ($r$) is calculated using the period ($2w$):

$$ r = \frac{d_{fringe}}{2w} \quad (2.20) $$

Then using the deposition time ($t$), the ice thickness ($d_{ice}$) can be obtained:

$$ d_{ice} = rt \quad (2.21) $$

2.4.4 Monitoring changes within the ices

In situ mid-IR and VUV spectroscopy was used to monitor changes within the interstellar ice analogues. In both cases the spectroscopic measurements were carried out in transmission mode where the IR or UV beam passed through the sample and the transmitting substrate to a detector. Transmission mode provides more details about the bulk properties rather than the surface properties of the ice sample, although some information about the surface of the ice sample can be obtained.
Experimental

Ice thickness adjustment for a sample at \(45^\circ\) with respect to the IR or UV beam

All the mid-IR and VUV spectra were taken with the substrate at a \(45^\circ\) angle with respect to the IR beam. The oblique angle of the substrate to the IR beam meant that both irradiation and collection of the IR spectrum could be obtained without further rotation of the substrate.

\[ d_{\text{ice}} \]

(i) IR or UV beam at normal incidence to substrate

(ii) IR or UV beam at \(45^\circ\) with respect to the to substrate

Fig. 2.21 Schematic diagram showing the different thickness of the ice when the substrate is at a \(45^\circ\) with respect to the IR or UV beam compared to normal incidence. Thickness was calculated using Eq. 2.21 for the ice with the substrate at normal to the IR or UV beam. Eq. 2.21 was used to calculate the difference when the substrate was at \(45^\circ\) with respect to the IR or UV beam.

The ice thickness \((d_{\text{ice}})\) was calculated in Eq. 2.21 and when the substrate is at normal with respect to the IR or UV beam this provides the correct thickness as shown in Fig. 2.21 (i). Fig. 2.21 (ii) shows that when the substrate is positioned so that it is at \(45^\circ\) angle the IR or UV beam passes through a thicker ice sample due to the angle of the substrate. The thickness of the ice can be adjusted accordingly using trigonometry based on the fact that a value for \(d_{\text{ice}}\) and the value of the \(\theta_{\text{substrate}}\) are known. The new thickness of the ice \((d_{\text{ice}45})\) is given below:

\[
d_{\text{ice45}} = \frac{d_{\text{ice}}}{\sin(\theta_{\text{substrate}})} \quad \text{where } \theta_{\text{substrate}} = 45
\] (2.22)
2.4 Experimental system and procedure

The thickness of the ices can be found in Table A.2 Appendix A. Throughout this thesis, unless stated otherwise, where different mixtures are compared with each other in a figure they will be normalised to a specific thickness. The normalisation values can also be found in Table A.2.

**FTIR Spectroscopy**

For the mid-IR spectroscopic studies presented in Chapters 3 and 4, a Nicolet Nexus 670 FTIR spectrometer with an external mercury cadmium telluride (MCT) detector was used to carry out FTIR spectroscopy at The Open University. For mid-IR spectroscopy a KBr beamsplitter with a MCT-A detector was used which has an operating spectral range from 7400–600 cm$^{-1}$. The IR beam exits the spectrometer through the external beam port and enters the PAC via a ZnSe window. It then passes through the sample and/or substrate to another ZnSe window where it exits the PAC. From there it is collimated onto a parabolic mirror which focusses and reflects the IR beam into the MCT detector. The IR beam path from the spectrometer to the MCT detector is shown in Fig. 2.22. The entire IR beam path, apart from the PAC which was under vacuum, was purged with compressed air to remove as much atmospheric H$_2$O and CO$_2$ contaminants. A combination of the KBr beamsplitter, the MCT-A detector and ZnSe windows and substrate sets a lower wavenumber limit of 800 cm$^{-1}$. The maximum wavenumber used in the work described in this thesis was 4000 cm$^{-1}$.

The Nicolet Nexus 670 spectrometer is a single beam spectrometer, therefore a background spectrum is required before the start of each experiment. If the purge is kept constant throughout
the experiment then no atmospheric contamination should be observed in the IR spectrum of the sample after the background has been subtracted. The background scan also subtracts any features due to the substrate.

All the IR spectra were taken with the substrate at a 45° angle with respect to the IR beam. All background spectra were scanned from 4000–800 cm\(^{-1}\) for a total of 512 scans to improve the signal to noise. All sample spectra were scanned from 4000–800 cm\(^{-1}\) for a total of 128 scans. All mid-IR spectra throughout this thesis had a resolution of 1 cm\(^{-1}\).

The electron irradiation experiments were performed at several intervals for a total of 30 min. After each interval the irradiation was stopped and an IR spectrum was obtained. The oblique angle of the substrate to the IR beam meant that both irradiation and collection of the IR spectrum could be obtained without further rotation of the substrate. However, after the initial deposition each experiment also had one IR spectrum taken at normal incidence so that the ratio of the mixture could be determined from literature constants which are predominantly taken at a normal incidence.

Determining the ratios of the binary mixtures using FTIR spectroscopy

Molecules which readily form intermolecular hydrogen-bonds (e.g. NH\(_3\)) are known to stick to the walls of the gas dosing line. Therefore, the partial pressure ratios used for mixing in the gas dosing line did not necessarily reflect the actual mixture deposited on the substrate. To overcome this discrepancy the ratios of the binary mixtures were determined from the IR spectrum once the ice mixture had been deposited via the column densities of CO\(_2\) and NH\(_3\).

The equation to calculate the column density was first presented as Eq. 1.1. As the IR spectra throughout this thesis are presented in absorbance (log scale) it needs to be converted to optical depth (In scale) through multiplication of \(ln(10)\):

\[
N_i = \frac{\int Abs(\tilde{\nu})d\tilde{\nu}}{A_i} \times ln(10)
\]

(2.23)

where \(\int Abs(\tilde{\nu})d\tilde{\nu}\) corresponds to the area of the absorption peak for a specific vibrational mode, \(A_i = \int \sigma(\tilde{\nu})d\tilde{\nu}\) which is the integrated band strength of the specific vibrational mode which is constant and obtained from the literature. In the literature the column density is derived from the optical depth and so \(ln(10)\) was used to convert absorbance into optical depth.

To determine the CO\(_2\) column density the \(\nu_3\) fundamental vibrational mode near 2340 cm\(^{-1}\) was integrated and an A-value of \(7.6 \times 10^{-17}\) cm molecule\(^{-1}\) was used.\(^{124}\) To determine the NH\(_3\) column density the \(\nu_2\) fundamental mode near 1070 cm\(^{-1}\) was integrated and an A-value of \(1.63 \times 10^{-17}\) cm molecule\(^{-1}\) was used.\(^{124}\) The ratios were then determined from the column densities of CO\(_2\) and NH\(_3\). The A-values introduce a \(\pm 20\%\) uncertainty into the
ratio calculation which was due to the integration boundaries and the subtraction of the baseline. However, this uncertainty will produce a systematic shift in the results of this thesis and as such, will not affect the relative trends observed due to the ratio of the ice. The column density for CO$_2$ and NH$_3$ of each experiment can be found in Table A.1 of Appendix A.

**UV Spectroscopy**

The VUV spectroscopic studies presented in Chapters 5 and 6 were conducted in Denmark using the ASTRID2 (Aarhus STorage RIng in Denmark 2) synchrotron radiation source facility at the Institute for Storage Ring Facilities at the University of Aarhus.

Synchrotron radiation source facilities provide access to synchrotron radiation which is electromagnetic radiation emitted when charged particles are accelerated along a curved trajectory by a magnetic field at speeds close to the speed of light. Fig. 2.23 shows a schematic of the main components of a synchrotron radiation source. The charged particle, typically an electron, is accelerated in a linear accelerator (linac) using an electric field until energies of $\sim$MeV are obtained. The electrons then enter the booster where they are further accelerated to energies of $\sim$GeV using a magnetic field and follow a curved trajectory via bending magnets. The electrons are then transferred to the storage ring where they can be further accelerated using radio frequency electric fields if required. The synchrotron energy emitted is directed into beamlines. The beamline contains optics which is designed to extract the desired wavelength of light.

![Fig. 2.23 Top-view schematic diagram of the main components of a synchrotron radiation source facility. Adapted from Mobilio and Boscherini.](image)
Experimental

More specifically the AU-UV beamline is operated with the high energy grating (2000 grooves/mm laminar type) which has been optimised for high resolution between 100–350 nm. The exit slit is translated depending on the wavelength region under investigation in order to maintain the correct focus and attain high wavelength resolution. The desired wavelength range of UV radiation exits the beamline via an exit slit and enters the PAC via a LiF window. It then passes through the sample and/or substrate to a MgF\(_2\) window where the UV radiation exits the PAC. The photomultiplier tube (PMT) detector is attached to the PAC via a short T-piece which forms a small gap between the PMT detector and the PAC. For measurements below 200 nm this gap is evacuated via the use of a scroll pump to prevent strong absorption of UV light by oxygen in this region. For measurements above 200 nm air is let in to allow the oxygen to absorb higher orders of light ensuring artefact free spectra. The UV beam path from the end of the AU-UV beamline to the PMT detector is shown in Fig. 2.24. The MgF\(_2\) window sets a lower wavelength limit of 120 nm and an upper wavelength limit of 340 nm was set by the high energy grating. The UV flux is sufficiently low enough to prevent multiphoton excitation and photochemical reactions from occurring within the interstellar ice analogues on experimental timescales.

2.4.5 Electron gun

A Kimball Physics FRA-2X1-5549 electron gun was used to irradiate the interstellar ice analogues. The beam energy is independently adjustable from 5 eV to 1 keV and the beam
current is also independently adjustable from 1 nA to 400 µA. The electron gun was set to an energy of 1 keV and a beam current of 10 µA for all electron irradiation experiments.

To ensure that there were no substrate effects when the interstellar ice analogues were irradiated with electrons, the penetration depth of the electrons was calculated using the CASINO model. CASINO calculates the trajectories of electrons within a solid using a Monte Carlo method. For details on how CASINO calculates the electron trajectories within a solid, see Drouin et al.\textsuperscript{173} The trajectories of electrons and, hence the penetration depth within a solid, depend on the user defined energy of the electrons, the density and composition of the solid and the angle of the electron beam with respect to the sample. Table A.4 in Appendix A lists the penetration depth and values used in the simulations. Electrons were calculated as having a penetration depth of < 84 nm which was less than any of the interstellar ice analogue thickness.

All the interstellar ice analogues were irradiated in intervals cumulating to a total 30 min. After each interval a spectrum was taken. More irradiation intervals and therefore more spectra were acquired during the mid-IR spectroscopic studies than the VUV spectroscopic studies due to time limitations at the synchrotron facility. After each irradiation interval a mid-IR or VUV spectrum was taken. The irradiation time was converted to electron fluence. The electron fluence ($\Phi$) corresponds to the total number of electrons per unit area with which the interstellar ice analogue is irradiated and is calculated from Eq. 2.24. It is dependent on the irradiation time (t), electron beam current (I) and area of the interstellar ice being irradiated (A).

$$\Phi = \frac{t \times I}{e \times A}$$ (2.24)

where $e$ is the absolute elementary charge of an electron ($1.602 \times 10^{-19}$ C).

All interstellar ice analogues were irradiated for a total of 30 min with 1 keV electrons which corresponds to a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The electron irradiation intervals can be found in Table A.3 in Appendix A.

2.4.6 Experimental procedure

Fig. 2.25 shows a summary of the experimental procedure used for the experiments in this thesis and a detailed description is given below.

(i) When the base temperature ($\sim$20 K) and base pressure (low $10^{-9}$ mbar) was achieved, background spectra were at normal incidence and a 45° angle.
Fig. 2.25 Summary of the various stages of experimental procedure. Labels (i)–(viii) are described in the text.
2.4 Experimental system and procedure

(ii) The substrate was rotated such that it was at normal incidence to the gas inlet nozzle. The ice film was grown by physical vapour deposition of pure or premixed gas onto the cold substrate with in situ laser measurements which were used to determine the ice thickness.

(iii) The substrate was then rotated to normal incidence so that a spectrum of the deposition at normal incidence was taken. This was used to determine the ratio of the ice mixture.

(iv) The substrate was then rotated to 45° and another spectrum was taken.

(v) If electron irradiation experiments were performed then irradiation for a set time interval was taken. If no irradiation was performed then steps (v) and (vi) were skipped.

(vi) After irradiation, a spectrum was taken of the ice. Steps (v) and (vi) were performed until the total desired time of irradiation was obtained.

(vii) The ice was then left for 1 hour to allow the radical species formed to relax within the ice. The ice sample was then warmed up to a set temperature.

(viii) A spectrum of the warmed ice sample was taken. Steps (vii) and (viii) were repeated at set intervals until desorption of the ice was achieved.

Full details of all the experiments performed in this thesis can be found in Table A.5 for the mid-IR spectroscopic study and Table A.6 for the VUV spectroscopic study in Appendix A.

2.4.7 Experimental limitations

There are several limitations associated with the PAC which are described below along with possible implications:

- The base pressure of the PAC is \( \sim 1 \times 10^{-9} \) mbar, therefore the only major contaminant is \( \mathrm{H}_2 \) which does not freeze onto the substrate even at 20 K. As this system cannot be baked then trace amounts of \( \mathrm{H}_2\mathrm{O} \) may also be present, but not detected in the spectroscopic techniques used in this thesis.

- The base temperature of the PAC is 20 K. Temperatures in molecular clouds are initially between 10–20 K. Radicals formed from irradiation of the interstellar ice analogue are already relatively mobile at 20 K compared to 10 K. The mobility of radicals contributes to chemical reactions so irradiation of interstellar ice analogues at 10 K may present different results. Therefore, the results in this thesis are representative of interstellar ices at 20 K.
Experimental

- Due to the requirement of the PAC to be portable, there are a limited number of CF flanges on the PAC. This means that only one monitoring technique can be used at a time e.g. mid-IR spectroscopy and VUV spectrometry. However, the portable nature of the PAC means that the experimental conditions are exactly the same so the mid-IR and VUV spectroscopic results are comparable.

- The deposition rate in experiments is considerably faster than in ISM and this may mean the morphology of the interstellar ice analogue is different from that of interstellar ice where deposition can occur over thousands of years.

2.5 Summary

This chapter covered the theoretical background to IR and UV spectroscopy, the different ice morphologies that may be encountered in the ISM and in experiments and how energetic processing is conducted. A detailed description of the experimental apparatus is given along with the methods for determining the ice thickness, CO₂ and NH₃ ratio and the penetration depth of the electrons. Finally, an experimental procedure is described and the limitations of the experimental set-up along with potential implications are given.

The results of the mid-IR spectroscopic study on the unirradiated binary mixtures of CO₂ and NH₃ are presented in Chapter 3 and the results of the electron irradiation study is given in Chapter 4. The results of the VUV spectroscopic study on the unirradiated binary mixtures of CO₂ and NH₃ are given in Chapter 5 and the results of the electron irradiation study is given in Chapter 6.
Chapter 3

Thermal processing of CO₂:NH₃ interstellar ice analogues: a mid-IR spectroscopic study

This chapter presents the results of a systematic, mid-IR spectroscopic study of the thermal processing of CO₂:NH₃ interstellar ice analogues as a function of deposition mixing ratio using mid-IR spectroscopy. Molecular synthesis was induced in the interstellar ice analogues upon thermal processing to form ammonium carbamate and carbamic acid. These results are discussed and compared to previous results reported in the literature. New observations include differences in crystallinity of both CO₂ and NH₃ within the mixtures as a function of deposition mixing ratio. A new formation pathway for carbamic acid is proposed.

3.1 Introduction

One of the motivations behind the work of this thesis is to the need to gain a comprehensive understanding of the influence of experimental parameters on interstellar ice analogues. As discussed in Section 1.3 most astrochemical laboratory experiments have not systematically investigated the influence of experimental parameters in an extensive manner. Binary mixtures of CO₂ and NH₃ were chosen for several reasons as stated in Section 1.6. As two of the most abundant molecules observed in interstellar ice, combined CO₂ and NH₃ contain the four most common elements to life. This binary mixture has also been the subject of several previous studies including thermal processing studies which provides a benchmark to justify the systematic approach of this thesis. These previous experiments are described in Section 3.1.1.
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To understand the influence of the deposition mixture on the interstellar ice, pure CO$_2$ ice and pure NH$_3$ ice were characterised as described in Sections 3.2 and 3.3, respectively. Characterisation of the CO$_2$:NH$_3$ interstellar ice analogues at 20 K are presented and discussed in Section 3.4.1. The thermal processing results of the CO$_2$:NH$_3$ interstellar ice analogues in terms of overall changes with the mid-IR spectra are presented in Section 3.4.2. Residues of the CO$_2$:NH$_3$ mixtures at 150 and 200 K are presented in Section 3.4.3 with a discussion on how the mid-IR vibrational modes are assigned in order to identify the thermal products. Section 3.5 discusses and compares the thermal processing results of this chapter with previous studies. Finally, the results of this systematic investigation of the thermal processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio are summarised in Section 3.6.

### 3.1.1 Previous studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>CO$_2$:NH$_3$ ratio</th>
<th>Observation technique</th>
<th>$T_{\text{deposition}}$ (K)</th>
<th>$T_{\text{processing}}$ (K)</th>
<th>Main products (&amp; $T_{\text{formation}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frasco$^{162}$</td>
<td>Various$^a$</td>
<td>IR</td>
<td>195</td>
<td>248</td>
<td>non-crystalline AC (195 K) &amp; crystalline AC (248 K)</td>
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<td>Hisatsune$^{163}$</td>
<td>1:3$^a$</td>
<td>IR</td>
<td>83</td>
<td>193</td>
<td>(NH$_3$)CO$_2$ (113-143 K) &amp; AC (193 K)</td>
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<td>Bossa et al.$^{94}$</td>
<td>1:1$^b$</td>
<td>IR &amp; MS</td>
<td>10</td>
<td>80</td>
<td>AC &amp; CA dimer, ~1:1 ratio (80 K)</td>
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<tr>
<td>Bertin et al.$^{141}$</td>
<td>1:1$^c$</td>
<td>HREEL &amp; IR</td>
<td>10</td>
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<td>AC &amp; CA (140 K)</td>
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<tr>
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<td>160</td>
<td>AC &amp; CA dimer (160 K)</td>
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<tr>
<td>Rodríguez-Lazcano et al.$^{140}$</td>
<td>1:1, 1:2, 1:3$^c$</td>
<td>IR</td>
<td>15</td>
<td>15</td>
<td>AC &amp; CA (140–220 K)</td>
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<tr>
<td>Noble et al.$^{95}$</td>
<td>Various$^c$</td>
<td>IR &amp; MS</td>
<td>70–90</td>
<td>150–225</td>
<td>AC and CA dimer (150–225 K)</td>
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</tbody>
</table>

$^a$ ratios derived from partial pressures of the mixture in the gas line, $^b$ method of determining ratio not specified, $^c$ ratios derived from column density, AC = ammonium carbamate, CA = carbamic acid

Several previous studies on the thermal processing of CO$_2$:NH$_3$ interstellar ice analogues have already been mentioned in Section 1.5.2. These studies are summarised in Table 3.1 and an overview is given below.
Binary CO$_2$:NH$_3$ mixtures were first studied by Frasco in 1964.\textsuperscript{162} Frasco deposited a CO$_2$:NH$_3$ mixture at 195 K and observed a reaction. The product was assigned as ammonium carbamate (NH$_2$COONH$_4$) in a non-crystalline or ‘amorphous’ state. Thermal processing to 248 K induced changes in the mid-IR vibrational modes and these changes were assigned as a phase transition of ammonium carbamate from non-crystalline to crystalline. Frasco also deposited the mixture at $\sim$80 K, but no reaction was observed.

The assignments of non-crystalline and crystalline ammonium carbamate by Frasco were challenged by Hitsatsune in 1983.\textsuperscript{163} Using a different deposition temperature to Frasco, Hitsatsune deposited a mixture of CO$_2$ and NH$_3$ at 83 K, which was 112 K lower than the deposition temperature used by Frasco. A reaction occurred between 113–144 K and the product was assigned to the unstable precursor complex of (NH$_3$)$_2$CO$_2$. More changes were observed in the mid-IR vibrational modes during thermal processing to 193 K. Hitsatsune explained that these changes were a result of a proton transfer within the (NH$_3$)$_2$CO$_2$ complex which led to the formation of crystalline ammonium carbamate.

In 2008, Bossa \textit{et al.} deposited CO$_2$:NH$_3$ mixtures at 10 K and observed the formation of a CO$_2$:NH$_3$ molecular complex.\textsuperscript{94} Ammonium carbamate and carbamic acid dimer in a 1:1 ratio were identified upon thermal processing to temperatures higher than 80 K. Further thermal processing to 230 K resulted in the desorption of ammonium carbamate which was observed via mass spectrometry to spontaneously decompose into CO$_2$ and NH$_3$. Whereas, carbamic acid only partially decomposed upon desorption at 260 K.

In the first of three studies on CO$_2$ and NH$_3$ ice mixtures published in 2014, Lv \textit{et al.} investigated both the thermal and energetic processing of this mixture.\textsuperscript{143} Thermal processing of the ice mixture deposited at 16 K agreed with the identification of ammonium carbamate and carbamic acid dimer made by Bossa \textit{et al.}\textsuperscript{94} The energetic processing results are described in Section 4.1.1.

In a study motivated by the stoichiometric ratios of CO$_2$:NH$_3$ mixtures, Rodríguez-Lazcano \textit{et al.} deposited different ratios at 15 K.\textsuperscript{140} Ammonium carbamate and carbamic acid were formed upon thermal processing, although the dimeric form of carbamic acid which was previously assigned by Bossa \textit{et al.} was questioned.\textsuperscript{94} Theoretical calculations were used to try and determine the form of carbamic acid present. In their conclusion, Rodríguez-Lazcano \textit{et al.} stated that while the peak at $\sim$1700 cm$^{-1}$ was due to carbamic acid, the preference for a monomeric or dimeric form could not be made.

In the most recent study published in 2014, Noble \textit{et al.} investigated the chemical kinetics of the thermal processing of CO$_2$ and NH$_3$ between 70-80 K.\textsuperscript{95} No reaction was observed when the mixture had a ratio of CO$_2$ in excess. A high reaction barrier caused the desorption of CO$_2$ before a reaction with NH$_3$ could occur. In contrast, when CO$_2$ and NH$_3$ was in a 1:1 ratio, or
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![Mid-IR spectrum of CO$_2$](image)

**Fig. 3.1** A mid-IR spectrum of pure CO$_2$ deposited at 20 K with vibrational modes labelled.

A ratio with excess NH$_3$, ammonium carbamate formed preferentially at lower temperatures due to a lower reaction barrier compared to carbamic acid. Above 150 K, carbamic acid formed through conversion of ammonium carbamate to carbamic acid.

The experimental conditions, processing type and main products formed in the aforementioned literature studies are summarised in Table 3.1.

### 3.2 Pure CO$_2$ ice

Before investigating CO$_2$:NH$_3$ interstellar ice analogues, a pure CO$_2$ ice analogue and a pure NH$_3$ ice analogue were characterised using mid-IR spectroscopy so that a comparison could be made between the pure ices and the mixtures. The results of pure CO$_2$ ice are presented in this section.

As a reminder, all experiments were conducted with the substrate at a 45° angle with respect to the IR beam. Collection of the mid-IR spectra and the thermal processing of the interstellar ice analogues could then be acquired without rotating the sample. From previous experiments, CO$_2$ is known to have longitudinal optical (LO) – transverse optical (TO) phonon splitting features in the $\nu_3$ and $\nu_2$ fundamental vibrational modes when mid-IR spectra are measured at an oblique angle. Phonons are quantised vibrational motions in which a
lattice of atoms or molecules oscillates uniformly at a single frequency. Optical phonons are out-of-phase movements of the atoms or molecules within the lattice. In IR spectroscopy, optical phonons can propagate in parallel (longitudinal) or perpendicular (transverse) to the IR beam. At oblique angles to the substrate, the mid-IR beam has an electric field with both parallel and perpendicular components and LO phonons can also be observed.

An example of a mid-IR spectrum of pure \( \text{CO}_2 \) taken with the substrate at a 45° angle with respect to the IR beam is shown in Fig. 3.1. The following main vibrational modes of \( \text{CO}_2 \) were observed:

(i) \( \nu_1 + \nu_3 \) combination mode at 3709 cm\(^{-1}\)
(ii) \( 2\nu_2 + \nu_3 \) combination mode at 3601 cm\(^{-1}\)
(iii) \( \nu_3 \) fundamental asymmetric stretch with LO-TO splitting at 2380 and 2345 cm\(^{-1}\)
(iv) \( \nu_3 \) fundamental asymmetric stretch due to \( ^{13}\text{CO}_2 \) at 2283 cm\(^{-1}\)

The \( \nu_2 \) fundamental bending mode with LO-TO splitting at 676 and 658 cm\(^{-1}\), respectively was not observed. This was due to the combined limitations of the MCT detector, the ZnSe windows and the ZnSe substrate which were used as part of the experimental system which was discussed in Section 2.4.7.

### 3.2.1 Thermal processing

After deposition at 20 K, the pure \( \text{CO}_2 \) ice was thermally processed until desorption at 100 K. Thermally induced changes within the \( \text{CO}_2 \) mid-IR spectra were observed and are shown in detail in Fig 3.2. Fig. 3.2 (i) shows that the combination modes, \( \nu_1 + \nu_3 \) and \( 2\nu_2 + \nu_3 \), increased in intensity until \( \sim 80 \) K and then decreased in intensity due to the onset of desorption of \( \text{CO}_2 \) ice. This trend was also observed in the \( ^{13}\text{CO}_2 \) \( \nu_3 \) vibrational mode in Fig. 3.2 (ii). The \( ^{13}\text{CO}_2 \) \( \nu_3 \) vibrational mode also red shifted gradually during the thermal processing. Fig. 3.2 (iii) shows the LO-TO splitting of the \( \nu_3 \) vibrational mode where the LO mode shifted position and a shoulder formed between 50–60 K.

### 3.2.2 Discussion

As explained in Section 2.3, when an ice restructures from a non-crystalline to crystalline structure, narrowing and/or splitting of the mid-IR vibrational modes are expected. Mid-IR vibrational modes are sensitive to the environment in which they residue. Therefore, the
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![Mid-IR spectra of pure CO$_2$ deposited at 20 K and thermally processed to desorption at 100 K, (i) $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes, (ii) $^{13}$CO$_2$ $\nu_3$ mode and (iii) $\nu_3$ fundamental mode. Vertical dashed lines represent the vibrational mode position at 20 K. Spectra are offset on the y-axis for clarity.](image)

**Fig. 3.2**
3.2 Pure CO$_2$ ice

![Mid-IR spectra of the thermal processing of a ‘thick’ CO$_2$ ice which shows the Fermi resonance features of $\nu_1$ fundamental mode and $2\nu_2$ overtone. Spectra are offset on the y-axis for clarity.](image)

Fig. 3.3 Mid-IR spectra of the thermal processing of a ‘thick’ CO$_2$ ice which shows the Fermi resonance features of $\nu_1$ fundamental mode and $2\nu_2$ overtone. Spectra are offset on the y-axis for clarity.

orientation of molecules within a solid and their corresponding intermolecular interactions will determine the shape and width of the vibrational mode.

No obvious changes in the mid-IR spectra from broad to narrow vibrational peaks were observed in Fig. 3.2. However, it can be difficult to determine whether an ice is in a non-crystalline or crystalline structure. For example, there is still debate in the literature as to whether a double peak observed for the $\nu_2$ vibrational mode of CO$_2$ is indicative of crystalline CO$_2$ ice. Gerakines & Hudson stated that even at 10 K, if the deposition rate was fast, then a crystalline ice would be deposited. Baratta & Palumbo argued that the observation of a double peak did not necessarily represent crystalline CO$_2$ ice. Rather, suppression of the double peak feature was observed when small amounts of H$_2$O or CH$_3$OH were added to the system. The authors tentatively assigned the cause of this feature to the formation of CO$_2$ dimers, of which the formation of these dimers was disrupted in the presence of H$_2$O and CH$_3$OH. Baratta & Palumbo argued that Gerakines & Hudson did not observe this double peak as Gerakines & Hudson reported ‘residual H$_2$O from the CO$_2$ reagents and possibly from the vacuum system’. In the CO$_2$ ice shown in Fig. 3.1 the $\nu_2$ vibrational mode of CO$_2$ was not observed due to the limitations of the experimental set up used in this thesis, as stated in Section 2.4.7. However, this debate within the literature highlights the complex nature of assigning the phase of CO$_2$ ice. Even if the $\nu_2$ vibrational mode could be observed from
experiments in this thesis, the angle of the substrate would give rise to LO-TO splitting of the \( \nu_2 \) vibrational mode which would further complicate the interpretation.\(^{176}\)

According to Escribano et al., non-crystalline CO\(_2\) ice could be identified from the presence of a shoulder on the \( \nu_3 \) TO phonon mode at 2328 cm\(^{-1}\).\(^{175}\) Escribano et al. observed the disappearance of this peak at \( \sim 25 \) K which was attributed to the crystallisation of CO\(_2\) ice. However, this shoulder was assigned as a CO\(_2\) dimer by Sivaraman et al.\(^{145}\) in a ‘slipped’ structure based on work by Nxumalo et al.\(^{179}\) As shown in Fig. 3.2 (iii) this shoulder at 2328 cm\(^{-1}\) was present until desorption of the CO\(_2\) ice. As the temperature increased, the ‘amorphous’ shoulder described by Escribano et al. resolved and narrowed. However, Escribano et al. used a resolution of 2 cm\(^{-1}\), whereas all experiments in this thesis were measured at a resolution of 1 cm\(^{-1}\), which may explain the difference in the results obtained by Escribano et al. did not observe this. Therefore, this shoulder was more likely to be due to the CO\(_2\) dimers described by Sivaraman et al.\(^{145}\) than a reference to non-crystalline CO\(_2\) ice.

Several studies have suggested that the presence of the Fermi resonance feature of the \( \nu_1 \) fundamental mode and \( 2\nu_2 \) overtone near 1384 and 1278 cm\(^{-1}\), respectively, will indicate non-crystalline ice.\(^{180,145,177,178}\) As mentioned in Section 2.1.1, when two vibrational modes of similar energy and the same symmetry are present, a splitting of the vibrational modes is observed. Intensity from the stronger vibrational mode is shared with the weaker vibrational mode which enhances it in a phenomenon known as Fermi resonance. As there was no change in dipole moment, the \( \nu_1 \) fundamental mode is IR forbidden in ordered CO\(_2\) (gas-phase or crystalline solid) and so no Fermi resonance was observed. However, non-crystalline CO\(_2\) would lead to a reduction in the symmetry of the CO\(_2\) and therefore ‘activate’ the \( \nu_1 \) vibrational mode. This breakdown in symmetry allowed what is traditionally thought of as IR forbidden modes to be observed and this phenomenon has been observed in other non-crystalline molecules.\(^{181}\) Therefore, the disappearance of the Fermi resonance features should indicate a phase change from non-crystalline to crystalline ice.

As mentioned in Section 3.2.1, a shoulder appeared on the \( \nu_3 \) LO mode between 50–60 K at 2375 cm\(^{-1}\) and a small red shift was observed in the main peak (\( \sim 1 \) cm\(^{-1}\)). As the Fermi resonance feature was very weak, a thicker CO\(_2\) ice than the one shown in Fig 3.2 was required to be able to observe it.\(^{178}\) Fig. 3.3 shows a CO\(_2\) ice with a thickness of a 658 nm, which is \( \sim \times 3 \) thicker than the CO\(_2\) ice shown in Fig. 3.2. Fermi resonance features were present and disappeared between 60–70 K which was at a similar temperature to the shoulder which appeared on the \( \nu_3 \) LO phonon mode.

However, the presence of phonons indicates a crystal lattice and therefore an ordered structure. Indeed the study by Cooke et al. where CO\(_2\) ice is deposited at 27 K refers to CO\(_2\) as crystalline.\(^{176}\) Therefore, it is suggested due to the presence of Fermi features along with
phonons that the CO$_2$ ice deposited at 20 K was probably polycrystalline and undergoes a phase change to a crystalline structure between 50—60 K.

### 3.3 Pure NH$_3$ ice

![Mid-IR spectrum of pure NH$_3$](image_url)

**Fig. 3.4** A mid-IR spectrum of pure NH$_3$ deposited at 20 K with vibrational modes labelled.

The oblique angle of the substrate with respect to mid-IR beam allows the observation of LO and TO phonons in CO$_2$ ice deposited at 20 K. However, no LO or TO phonons were expected for NH$_3$ ice deposited at 20 K. Phonons only arise when a crystal lattice is present and NH$_3$ ice is known to have a non-crystalline structure at 20 K.\textsuperscript{167,182}

An example of a mid-IR spectrum of pure NH$_3$ taken with the substrate at a 45° angle with respect to the IR beam is shown in Fig. 3.4. The following main vibrational modes of NH$_3$ were observed:

(i) $\nu_3$ fundamental asymmetric stretch at 3377 cm$^{-1}$

(ii) $2\nu_4$ overtone at 3294 cm$^{-1}$

(iii) $\nu_1$ fundamental symmetric stretch at 3213 cm$^{-1}$

(iv) $\nu_4 + \nu_L$ combination mode at 1883 cm$^{-1}$ where $\nu_L$ refers to a lattice mode
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(v) $\nu_4$ asymmetric deformation at 1626 cm$^{-1}$

(vi) $\nu_2$ symmetric deformation (‘umbrella mode’) at 1073 cm$^{-1}$

3.3.1 Thermal processing

Fig. 3.5 Mid-IR spectra of pure NH$_3$ deposited at 20 K and thermally processed until desorption at 120 K, (i) $\nu_3$, $2\nu_4$ and $\nu_1$ modes, (ii) $\nu_4 + \nu_L$ and $\nu_4$ and (iii) $\nu_2$ mode. Vertical dashed lines represent the vibrational modes position at 20 K. Spectra are offset on the y-axis for clarity.

After deposition at 20 K the pure NH$_3$ ice was thermally processed until desorption at 120 K. Thermally induced changes within the NH$_3$ spectra were observed and are shown in
3.3 Pure NH$_3$ ice

detail in Fig. 3.5. Fig. 3.5 (i) shows the $\nu_3$, $2\nu_4$ and $\nu_1$ modes and (iii) shows the $\nu_2$ mode. The start of a phase change was observed via the splitting of the $\nu_3$ and $\nu_2$ vibrational modes between 50–60 K with the final changes observed by 90 K. The $\nu_2$ mode split into three features at 1097, 1077 and 1060 cm$^{-1}$. When the sample was warmed from 80–100 K the splitting feature at 1077 cm$^{-1}$ sharpened. The $\nu_3$ band narrowed and split with another, weaker feature observed at 3365 cm$^{-1}$. The broad $\nu_4 + \nu_L$ combination mode shown in 3.5 (ii) sharpened and blue shifted to 1906 cm$^{-1}$ between 60–70 K. Fig. 3.5 (ii) also shows that a complex splitting of the $\nu_4$ vibrational mode along with a blue shift to 1652 cm$^{-1}$ occurred between 60–70 K. These new splitting features appeared on the red wing of $\nu_4$ mode at 1595, 1480 and 1354 cm$^{-1}$ and are assigned as $\nu_2 + \nu_L$ combination modes.

3.3.2 Discussion

There has been considerable debate within the literature about whether NH$_3$ contains a metastable phase and over the assignment of a cubic crystalline phase.$^{183–186,167,182}$ In Fig. 3.5, the onset of a phase transition was observed between 50–60 K which was in agreement with the crystallisation temperature of 57 K stated by Zheng and Kaiser.$^{182}$ However, Zheng and Kaiser stated that there was a dramatic change at this temperature. Fig. 3.5 shows that the change observed between 50–60 K was subtle, with shoulders appearing on the $\nu_3$ and $\nu_2$ vibrational modes. A more significant change across all of the vibrational modes was observed between 60–70 K which was in agreement with a study by Dawes et al.$^{167}$ Dawes et al. stated that a change in phase began at 65 K and was completed by 75 K. An explanation for the discrepancy between the different temperatures was given by Zheng and Kaiser who also investigated the effect of H$_2$O contamination within the ice system. They observed that the crystallisation temperature increased from 57 to 65 K upon the addition of 1 % H$_2$O. While it is possible that there was a slight H$_2$O contamination which was otherwise undetected in the mid-IR spectra, the increase in temperature was much slower in the study by Zheng and Kaiser. This may have given the NH$_3$ molecules more time to rearrange into a more ordered structure. Dawes et al. suggested that a polycrystalline structure rather than a cubic crystalline structure occurred when NH$_3$ was deposited below 50 K and then annealed to 65 K. As depicted in Fig. 2.15 in Section 2.3, polycrystalline solids are solids which contain regions of ordered molecules, or crystallites, which are randomly arranged with respect to each other. Polycrystalline solids are therefore more ordered than non-crystalline solids, but less ordered than crystalline solids. Dawes et al. observed ‘Random fluctuations in the relative intensities of the $\nu_2$ splitting] components as a new sample is prepared each time’.$^{167}$ This would explain the differences observed between the $\nu_2$ splitting pattern intensities between Zheng and Kaiser, Dawes et al. and the results obtained in Fig. 3.5. According to Dawes et al. a perfect crystalline...
could not form in NH₃ ice deposited below 50 K when thermally processed. Steric effects experienced from the randomly arranged H-bonding network of the NH₃ molecules in the non-crystalline structure was suggested as preventing the complete phase transition to a crystalline structure.

### 3.4 Binary mixtures of CO₂:NH₃

As discussed in Section 2.4.4, the ratios of the mixtures were calculated from the CO₂ and NH₃ column densities which were derived from the ν₃ vibrational mode and the ν₂ vibrational mode, respectively. The ratios were determined from mid-IR spectra recorded at a normal incidence to the substrate so that no LO-TO splitting was present. The following CO₂:NH₃ ratios were studied: 3:1, 2:1, 1:1, 1:3 and 1:10.

#### 3.4.1 Deposition at 20 K

Fig. 3.6 shows the mid-IR spectra of CO₂:NH₃ mixtures (3:1, 2:1, 1:1, 1:3 & 1:10) compared with pure CO₂ and pure NH₃ all deposited at 20 K. The band assignments are given in Table 3.2. Two new features were observed in Fig. 3.6 and are marked with dashed lines. The first feature at 3417 cm⁻¹ was present in all ratios except the 1:3 and 1:10 ratios and the second feature at 3253 cm⁻¹ was observed in all ratios except 1:10. From Fig. 3.6 there was a noticeable shift in position of the vibrational mode of the mixtures compared to the respective pure ice vibrational modes. This shift in vibrational mode is better viewed by calculating the difference between the pure ice vibrational mode and the ice mixture vibrational mode (Δν) as shown in Eq. 3.1:

\[
\Delta \tilde{\nu} = \tilde{\nu}_{\text{pure ice}} - \tilde{\nu}_{\text{mixed ice}}
\]

where \(\tilde{\nu}_{\text{pure ice}}\) is the position of a vibrational mode for the pure ice and \(\tilde{\nu}_{\text{mixed ice}}\) is the position of the same vibrational mode, but for the mixed ice. A positive \(\Delta \tilde{\nu}\) value indicates that the vibrational mode has been red shifted and a negative \(\Delta \tilde{\nu}\) value indicated that the vibrational mode has blue shifted. To plot the \(\Delta \tilde{\nu}\) against the deposition mixing ratio, the deposition mixing ratio of each mixture was calculated as a fraction using Eq. 3.2:

\[
\text{Ratio} = \frac{N_{CO_2}}{N_{NH_3}}
\]

where \(N_{CO_2}\) is the column density of CO₂ and \(N_{NH_3}\) is the column density of NH₃ which were obtained from Table A.1 in Appendix A.
Fig. 3.6 Mid-IR spectra of CO$_2$:NH$_3$ mixtures at 20 K compared with 1:0 (pure CO$_2$) and 0:1 (pure NH$_3$). Dashed lines represent new features which formed upon deposition. Spectra are offset on the y-axis for clarity. All spectra are normalised to a thickness of 300 nm. Band assignments are given in Table 3.2.
Table 3.2 Band assignments and positions of the vibrational modes of pure CO$_2$ ice, pure NH$_3$ ice and unirradiated CO$_2$:NH$_3$ mixtures at 20 K. Refs. (a) Gerakines et al.,$^{133}$ (b) Cooke et al.,$^{176}$ (c) Bossa et al.,$^{94}$ (d) Reding and Hornig.$^{187}$

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<tr>
<td>NH$_3$</td>
<td>$v_3$</td>
<td>N–H asym. Stretch</td>
<td>d</td>
<td>3375</td>
<td>3372</td>
<td>3381</td>
<td>3384</td>
<td>3385</td>
<td>3377</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2v_4$</td>
<td>overtone</td>
<td>d</td>
<td>3299</td>
<td>3303</td>
<td>3313</td>
<td>3313</td>
<td>3313</td>
<td>3294</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v_1$</td>
<td>N–H sym. Stretch</td>
<td>d</td>
<td>3221</td>
<td>3223</td>
<td>3221</td>
<td>3217</td>
<td>3215</td>
<td>3213</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v_4 + v_L$</td>
<td>combination</td>
<td>d</td>
<td>1872</td>
<td>1872</td>
<td>1883</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v_4$</td>
<td>deformation</td>
<td>d</td>
<td>1631</td>
<td>1630</td>
<td>1630</td>
<td>1629</td>
<td>1626</td>
<td>1626</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v_2$</td>
<td>umbrella</td>
<td>d</td>
<td>1066</td>
<td>1067</td>
<td>1069</td>
<td>1071</td>
<td>1073</td>
<td>1073</td>
<td></td>
</tr>
</tbody>
</table>

$^{sh}$ shoulder, asym. = asymmetric, sym. = symmetric
The change in wavenumber (Δν) for CO₂ against the mixing ratio fraction is plotted in Fig. 3.7. It shows that all the CO₂ modes red shifted compared to pure CO₂ vibrational modes. As more NH₃ was added to the mixture (i.e. CO₂/NH₃ ratio decreased), a gradual increase in the red shift of the vibrational modes was observed. Apart from the shift in the vibrational modes, broadening of the peak shapes of the ν₁ + ν₃ and 2ν₂ + ν₃ combination modes, and the ν₃ fundamental mode of ¹³CO₂ in the mixtures compared to the vibrational modes of pure CO₂ was observed. LO-TO splitting of the ν₃ fundamental mode was observed in all the ratios except the 1:10 ratio where CO₂ was most dilute and 1:3 ratio where a shoulder was observed. No vibrational mode of the CO₂ dimer at 2328 cm⁻¹ was observed in any of the mixtures.

![Graph showing the change in wavenumber for CO₂ and NH₃](image)

**Fig. 3.7** A scatter plot of the difference in position of a vibrational mode of pure CO₂ with the same vibrational mode of the CO₂:NH₃ mixture.

The Δν for NH₃ against the mixing ratio fraction is plotted in Fig. 3.8. In contrast to the CO₂ vibrational modes where a red shift for all vibrational modes was observed, only the ν₂ mode of NH₃ red shifted. The 2ν₄, ν₄, ν₂ vibrational modes blue shifted and the ν₃ mode was red shifted in the 1:10 and 1:3 ratio, but it blue shifted for the 1:1, 2:1 and 3:1 ratios. Apart from the shift in the vibrational modes, all of the NH₃ vibrational modes narrowed compared to pure NH₃ ice.
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Fig. 3.8 A scatter plot of the difference in position of a vibrational mode of pure NH$_3$ with the same vibrational mode of the CO$_2$:NH$_3$ mixture.

Discussion

The different positions of the same vibrational modes between the mixtures and the pure ices can provide valuable information about the CO$_2$:NH$_3$ mixtures. The following discussion section is split into the following:

(i) Observation of two new absorption features near 3417 and 3253 cm$^{-1}$

(ii) Narrowing of the NH$_3$ vibrational modes

(iii) Broadening of the CO$_2$ vibrational modes

(iv) Red shift in the CO$_2$ vibrational modes

(v) Red and blue shifts in NH$_3$ vibrational modes

(i) Two new absorption features near 3417 and 3253 cm$^{-1}$: The two new features observed at 3417 and 3253 cm$^{-1}$ were assigned as a CO$_2$:NH$_3$ molecular complex by Bossa et al. $^{94}$ This complex was described as a non-hydrogen bonding complex wherein the nitrogen atom from NH$_3$ bonded to the carbon atom of CO$_2$ in a ‘T-shaped’ structure as shown in Fig. 3.9. The assignment of the ‘T-shaped’ structure was based on previous studies of the complex in the gas phase $^{188}$ and via quantum calculations. $^{189}$ Other condensed phase studies by Lv
3.4 Binary mixtures of CO$_2$::NH$_3$

![Diagram of CO$_2$::NH$_3$ molecular complex]

**Fig. 3.9** Schematic of the formation of a ‘T-shaped’ CO$_2$::NH$_3$ molecular complex.

*et al.*$^{143}$ and Rodríguez-Lazcano *et al.*$^{140}$ also reported observing this CO$_2$::NH$_3$ complex. Rodríguez-Lazcano *et al.* only reported it for their 1:1 ratio, but closer inspection of their other ratios revealed that the lower frequency (3253 cm$^{-1}$) vibrational mode was also present in their 1:2 ratio. This ‘T-shaped’ CO$_2$::NH$_3$ molecular complex is an adduct of CO$_2$ and NH$_3$. The NH$_3$ molecule can act as a Lewis base where it donates its lone pair of electrons to the empty orbital of the Lewis acid which in this case is CO$_2$. A dative bond is formed between the two molecules and this is depicted in Fig. 3.9.

(ii) Narrowing of the NH$_3$ vibrational modes: The narrowing of the NH$_3$ vibrational modes in the mixtures compared with pure NH$_3$ may be explained by the extensive, intermolecular H-bonding which is present in pure NH$_3$ ice deposited at 20 K. For example, intermolecular H-bonding is known to be a cause of broadening of vibrational modes in mid-IR spectra. Fig. 3.6 shows that the ratios with higher amounts of CO$_2$ also had the narrowest vibrational modes. This suggests that the presence of CO$_2$ disrupted the ability of NH$_3$ to form such extensive, intermolecular bonds which were observed in the pure NH$_3$ ice.

(iii) Broadening of the CO$_2$ vibrational modes: In contrast to the NH$_3$ vibrational modes, the CO$_2$ vibrational modes broadened compared to the pure CO$_2$ vibrational modes. A study by Bernstein *et al.* on solid H$_2$O:CO$_2$ also observed that the CO$_2$ vibrational mode broadened when it was mixed with H$_2$O.$^{190}$ The broadening of the CO$_2$ vibrational modes was described as being due to intermolecular interactions of the CO$_2$ and H$_2$O. The CO$_2$::NH$_3$ molecular complexes were observed in some ratios (e.g. 3:1, 2:1, 1:1), but it is possible that they are present in all ratios. For example, the higher frequency (3417 cm$^{-1}$) CO$_2$::NH$_3$ molecular complex vibrational mode was on the red wing of the intense $\nu_3$ mode. Ratios which had more NH$_3$ had a comparatively intense $\nu_3$ mode compared to ratios with less CO$_2$ which might explain why the vibrational mode at 3417 cm$^{-1}$ was not observed in the 1:3 and 1:10 ratios. The lower frequency mode (3253 cm$^{-1}$) was on the blue wing of the $\nu_1$ mode which was not as intense as the $\nu_3$ fundamental mode where the higher frequency mode was observed. This might explain why the lower frequency mode was observed in the all the ratios except the 1:10 ratio.
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(iv) **Red shift in the CO$_2$ vibrational modes:** A red shift in the CO$_2$ vibrational modes was observed for all ratios as shown in Fig. 3.7. If a dative bond formed in between the CO$_2$ and NH$_3$ molecular complex, as depicted in Fig 3.9, then this would cause a red shift in the vibrational mode of CO$_2$. A red shift can signify an increase in bond length which was observed in the formation of a dative bond in the CO$_2$:NH$_3$ molecular complex.

While the LO-TO splitting of the $\nu_3$ vibrational mode of CO$_2$ red shifted, the LO mode also diminished in ratios where excess NH$_3$ was present. Cooke *et al.* observed a similar effect when they studied a mixture of CO$_2$ with H$_2$O.$^{176}$ They suggested that the H$_2$O was homogeneously mixed with the CO$_2$ leaving no areas of pure CO$_2$. This in turn disrupted the long range dipole interactions of the CO$_2$ preventing the formation of the LO mode at higher concentrations of H$_2$O. A similar behaviour probably occurred within the CO$_2$:NH$_3$ mixtures.

(v) **Red and blue shifts in NH$_3$ vibrational modes:** Intermolecular H-bonding in pure NH$_3$ ice was expected to undergo a lengthening of the N–H bond and a perceived red shift in the vibrational modes. As established earlier, the narrowing in all the NH$_3$ vibrational modes of the mixtures suggested that a less extensive, intermolecular H-bonding network formed in the mixtures due to the presence of CO$_2$. Therefore, it was expected that the vibrational modes of NH$_3$ in the mixtures would blue shift compared to pure NH$_3$ ice as there was less intermolecular H-bonding present. A blue shift was observed for all vibrational modes except $\nu_3$ and $\nu_2$ modes. The $\nu_3$ mode was red shifted in the two lowest CO$_2$/NH$_3$ ratios which were also coincidently the two ratios where the CO$_2$:NH$_3$ molecular complex was not observed at $\sim 3415$ cm$^{-1}$. When the vibrational mode of the CO$_2$:NH$_3$ molecular complex was observed, it coincided with the observed blue shift in the $\nu_3$ mode. This suggests that the switch from red to blue shift of the $\nu_3$ mode could be due to the formation of the CO$_2$:NH$_3$ complex. Furthermore, when ratios had more CO$_2$ present (i.e. at higher CO$_2$/NH$_3$ values) the vibrational modes of the CO$_2$:NH$_3$ molecular complex was more intense and the blue shift was greater. However, at present no explanation can be given for the unexpected red shifts in the vibrational modes of $\nu_2$ and $\nu_3$.

**Summary**

By comparing the vibrational mode positions of the CO$_2$:NH$_3$ ice mixtures with each other and the pure ice equivalent, it was concluded at 20 K the CO$_2$:NH$_3$ ice mixture is thoroughly mixed so that no pockets of pure CO$_2$ or pure NH$_3$ exist. In turn, this also prevents the intermolecular H-bonding network between NH$_3$ molecules forming as extensively at 20 K in the mixtures compared to pure NH$_3$. Vibrational features of a CO$_2$:NH$_3$ molecular complex were observed at 20 K for all the ratios except the 1:10 ratio although this does not necessarily mean that a
3.4 Binary mixtures of CO\textsubscript{2}:NH\textsubscript{3}

CO\textsubscript{2}:NH\textsubscript{3} molecular complex did not form, rather that it was obscured by the intense $\nu_3$ mode of NH\textsubscript{3}.

3.4.2 Thermal processing of binary mixtures of CO\textsubscript{2}:NH\textsubscript{3}

After deposition at 20 K, the CO\textsubscript{2}:NH\textsubscript{3} mixtures were thermally processed and analysed at discrete temperatures, listed in Table A.5, until desorption. Fig. 3.10 shows an example of the thermal processing results of a mixture of CO\textsubscript{2}:NH\textsubscript{3} in a 1:1 ratio. Several interesting changes have been highlighted and labelled and are described below.

(a) The $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes of CO\textsubscript{2} narrowed and blue shifted between 60–70 K.

(b) The $\nu_2$ vibrational mode of NH\textsubscript{3} split between 70–80 K.

(c) Additional absorption features which formed above 80 K in the region 1800–1300 cm\textsuperscript{-1} at 1647, 1623, 1554, 1501(sh) and 1396 cm\textsuperscript{-1}.

(d) A change in the residue spectra occurred between 150–200 K.

In addition to the changes described above, it was observed that CO\textsubscript{2} and NH\textsubscript{3} both desorbed between 100–110 K and the residue material desorbed by $\sim$250 K. The thermal processing spectra for the other ratios can be found in Appendix A where they all have labelling from (a) to (d). The changes described by labels (a) to (d) occurred at different temperatures between the ratios and are summarised in Table 3.3, as well as the desorption temperatures of CO\textsubscript{2} and NH\textsubscript{3}, and the disappearance of the CO\textsubscript{2}:NH\textsubscript{3} complex.

Discussion

The discussion on the thermal processing of CO\textsubscript{2}:NH\textsubscript{3} mixtures is split into the the (i) CO\textsubscript{2} segregation and structure and (ii) NH\textsubscript{3} structure.

(i) Segregation and ice structure CO\textsubscript{2}: A phase change in pure CO\textsubscript{2} ice from a polycrystalline to crystalline structure was suggested to occur between 50–60 K in Section 3.2.2. Therefore the narrowing and blue shift of the CO\textsubscript{2} combination modes between 50–80 K for the CO\textsubscript{2}:NH\textsubscript{3} mixtures could be due to a phase change. However, in the CO\textsubscript{2}:NH\textsubscript{3} mixtures the combination mode of CO\textsubscript{2} red shifted from the pure CO\textsubscript{2} combination modes. The blue shift observed upon thermal processing of the mixture also suggests that the CO\textsubscript{2} combination modes are more characteristic of pure CO\textsubscript{2} ice suggesting segregation of CO\textsubscript{2} and NH\textsubscript{3} within the mixtures.
Fig. 3.10 Mid-IR spectra of an example of the thermal processing results of a 1:1 CO$_2$:NH$_3$ mixture from 20 to 250 K. (a) Evidence of CO$_2$ segregation through the CO$_2$ $\nu_1 + \nu_3$ combination modes; (b) Evidence of phase change in NH$_3$ through the $\nu_2$ mode of NH$_3$; (c) New absorption features which occur after thermal processing to T $>$ 80 K; and (d) Change in residue spectra between 150–200 K. Spectra are offset on the y-axis for clarity.
3.4 Binary mixtures of CO$_2$:NH$_3$

Table 3.3 Summary of the thermal processing of CO$_2$:NH$_3$ mixtures.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>3:1</th>
<th>2:1</th>
<th>1:1</th>
<th>1:3</th>
<th>1:10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CO$_2$ segregation (K)</td>
<td>by 60</td>
<td>50–60</td>
<td>60–70</td>
<td>70–80</td>
<td>70–80</td>
</tr>
<tr>
<td>(b) NH$_3$ phase change (K)</td>
<td>by 60</td>
<td>60–70</td>
<td>70–80</td>
<td>70–80</td>
<td>70–80</td>
</tr>
<tr>
<td>(c) New bands (K)</td>
<td>&gt;90K</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>&gt;80</td>
</tr>
<tr>
<td>New band positions (cm$^{-1}$)</td>
<td>1647, 1620, 1553, 1396</td>
<td>1647, 1623, 1554, 1501$^{sh}$, 1396</td>
<td>1627, 1553, 1501, 1390</td>
<td>1624$^{sh}$, 1554</td>
<td>1506,1389</td>
</tr>
<tr>
<td>CO$_2$ desorbs (K)</td>
<td>90–100</td>
<td>90–100</td>
<td>100–110</td>
<td>100–110</td>
<td>110–120</td>
</tr>
<tr>
<td>NH$_3$ desorbs (K)</td>
<td>100–110</td>
<td>100–110</td>
<td>100–110</td>
<td>100–110</td>
<td>110–120</td>
</tr>
<tr>
<td>(d) Change in residue (K)</td>
<td>100–110</td>
<td>150–200</td>
<td>150–200</td>
<td>170–200</td>
<td>170–200</td>
</tr>
</tbody>
</table>

$^{sh}$ shoulder

Evidence of segregation can also be further observed by looking at the LO-TO splitting of CO$_2$ within the mixtures. Fig. 3.11 shows the LO-TO splitting in the ice mixtures at 70 K. The two grey shaded areas in Fig. 3.11 represent the range in peak positions of the LO and TO modes of the mixtures at 20 K. The LO and TO phonons in the 3:1, 2:1 & 1:1 ratios blue shifted towards the LO and TO phonon position of pure CO$_2$ ice. The LO and TO phonons in these ratios also narrowed in agreement with the peak profiles of pure CO$_2$.

Fig. 3.12 shows the LO-TO splitting of the 1:3 and 1:10 ratios. At 20 K no splitting was observed in the 1:10 ratio and the LO mode appears as a shoulder on the TO mode for the 1:3 ratio. This was due to the thorough mixing of CO$_2$ and NH$_3$ which disrupted the crystal lattice of CO$_2$ as discussed in Section 3.4.1. As the temperature increased, splitting within the LO modes of the 1:3 and 1:10 ratios suggested that when CO$_2$ and NH$_3$ segregated it also underwent a phase change. For the 1:3 and 1:10 ratio where NH$_3$ is in excess, CO$_2$ can be viewed as a defect within an NH$_3$ ice. Whereas, for 3:1 and 2:1 ratios, the NH$_3$ can be viewed as the defect within the CO$_2$ ice. As discussed in Section 3.2.2, pure CO$_2$ ice is suggested as being in a polycrystalline structure at 20 K. In mixtures where NH$_3$ is a defect in the CO$_2$ ice, the evidence of the LO mode suggests that even in these mixtures CO$_2$ retains some degree of a polycrystalline form. Whereas, in the mixtures where the CO$_2$ is a defect in the NH$_3$ ice,
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![Mid-IR spectra of the CO$_2$ LO-TO splitting of the $\nu_3$ fundamental mode in the CO$_2$:NH$_3$ mixtures at 80 K compared with pure CO$_2$. The grey boxes represent the range of the LO and TO modes of the mixtures at 20 K to show the shift in the LO and TO modes at 80 K. Spectra are offset for clarity on the y-axis and normalised to 300 nm.](image)

Fig. 3.11 Mid-IR spectra of the CO$_2$ LO-TO splitting of the $\nu_3$ fundamental mode in the CO$_2$:NH$_3$ mixtures at 80 K compared with pure CO$_2$. The grey boxes represent the range of the LO and TO modes of the mixtures at 20 K to show the shift in the LO and TO modes at 80 K. Spectra are offset for clarity on the y-axis and normalised to 300 nm.

the absence of the LO mode suggests that the CO$_2$ does not retain a polycrystalline structure instead having a non-crystalline form.

While there are no studies on the structure and dynamics of CO$_2$ and NH$_3$ ice mixtures, there have been several studies on H$_2$O and CO$_2$ mixtures. These studies concluded that CO$_2$ segregates out of the H$_2$O ice which was evidenced through the appearance of pure CO$_2$ features. For all the CO$_2$:NH$_3$ ratios, features associated with pure CO$_2$ ice were observed suggesting that the CO$_2$ and NH$_3$ have segregated. For the 1:3 and 1:10 ratios the segregated CO$_2$ ice also appeared to undergo a phase changed from a non-crystalline structure to polycrystalline or crystalline structure. For the other ratios, a polycrystalline form of CO$_2$ was already observed upon deposition at 20 K. A simple, schematic diagram depicting the segregation behaviour of the ratios is shown in Fig. 3.13.

(ii) Ice structure of NH$_3$: Splitting is observed within the $\nu_2$ mode of NH$_3$ upon thermal processing of CO$_2$:NH$_3$ mixtures between 50–80 K as shown in Fig. 3.10 (b). As discussed
3.4 Binary mixtures of CO$_2$:NH$_3$

Fig. 3.12 Mid-IR spectra of the CO$_2$ LO-TO splitting of the $\nu_3$ fundamental mode in the CO$_2$:NH$_3$ of the 1:3 and 1:10 mixtures at 20 K (dashed lines) and 80 K (solid lines). The 1:3 and 1:10 spectra are offset for clarity on the y-axis and normalised to 300 nm.

in Section 3.3.2, the splitting of the $\nu_2$ mode which indicated a phase change in pure NH$_3$ ice. The $\nu_2$ vibrational mode of NH$_3$ in the CO$_2$:NH$_3$ mixtures which were deposited at 20 K and thermally processed to 80 K are shown in Fig. 3.14 and compared with pure NH$_3$ deposited at 20 K and thermally processed to 80 K. As discussed in Section 3.3.2 and in agreement with Dawes et al.,$^{167}$ pure, non-crystalline NH$_3$ ice deposited at 20 K formed a polycrystalline structure upon thermal processing to 70 K as evidenced through the splitting pattern of the $\nu_2$ vibrational mode. However, Fig. 3.14 shows that the splitting pattern of the $\nu_2$ mode of NH$_3$ in the mixtures was different depending on the ratio. Dawes et al. also showed that the deposition temperature affected the splitting pattern of the $\nu_2$ vibrational mode and this was used to describe the structure of NH$_3$ ice. For example, the splitting of the $\nu_2$ into two peaks as observed in the 1:10 and 1:3 ratios was described by Dawes et al. as representing a polycrystalline structure with small crystallites of similar shapes and sizes. The absence of splitting in the $\nu_2$ mode for the 1:1, 2:1 and 3:1 ratios was not evidence against a phase transition of NH$_3$. In fact, Dawes et al. observed that at deposition temperatures above 85 K only one intense peak was present which indicated a cubic crystalline structure. Dawes et al. explained the lack of a cubic crystalline phase in pure NH$_3$ ice deposited at 20 K and thermally processed as a consequence of the random arrangement of the intermolecular H-bonding present in the non-crystalline ice deposited at $\sim$20 K which caused steric hindrance upon thermal processing.
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**Fig. 3.13** Schematic diagram of CO$_2$ segregation upon thermal processing to 80 K. At 20 K the CO$_2$:NH$_3$ mixture is fairly well mixed and depending on the CO$_2$:NH$_3$ ratio, CO$_2$ will be in a polycrystalline form (3:1, 2:1 & 1:1) or a non-crystalline form (1:3 & 1:10). Upon segregation at 80 K all mixtures have CO$_2$ in a polycrystalline structure. Note, CO$_2$ will more likely segregate out into pockets of pure CO$_2$ rather than a distinct divide which is depicted in this diagram.

An explanation for the apparent increase in phase order of NH$_3$ as it was mixed with more CO$_2$ was that the CO$_2$ disrupted the ability of NH$_3$ to create the random intermolecular H-bonds at 20 K. Indeed, this was suggested in Section 3.4.1 as the reason for the narrowing of the NH$_3$ vibrational modes compared with pure NH$_3$ at 20 K. For crystalline features to be observed upon thermal processing, the CO$_2$ and NH$_3$ must segregate so that NH$_3$ can obtain long range order. For mixtures like the 1:10 and 1:3 ratio, the CO$_2$ can be viewed as a defect within the NH$_3$ ice structure. Therefore, NH$_3$ was more likely to have formed some random H-bond networks at 20 K and this would have prevented the formation of cubic crystalline NH$_3$ ice during thermal processing. However, as CO$_2$ was present within these ratios the intermolecular H-bonding network was less established compared to the pure NH$_3$ ice. With less steric hindrance present due to the reduced H-bonding network compared with pure NH$_3$ ice, a more ordered polycrystalline form of NH$_3$ was observed in the 1:3 and 1:10 ratios. In the 3:1 and 2:1 ratios, NH$_3$ can be considered the defect within the CO$_2$ ice. As very few intermolecular H-bonds between the NH$_3$ defects could form at 20 K then a cubic crystalline structure of NH$_3$ formed upon thermal processing within the 2:1 and 3:1 ratios. This is depicted in Fig. 3.15.
Fig. 3.14 Mid-IR spectra of NH$_3$ $\nu_2$ mode in the CO$_2$:NH$_3$ mixtures which were deposited at 20 K and thermally processed to 80 K compared with pure NH$_3$ ice. Spectra are offset on the y-axis for clarity and normalised to 300 nm thickness.
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Fig. 3.15 Schematic diagram of how the morphology of NH$_3$ changed depending on the ratio of the CO$_2$::NH$_3$ mixture (i) pure NH$_3$ (0:1) forms extensive H-bonds at 20 K some of which remain intact upon heating to 80 K so that a polycrystalline structure with crystallites of random shapes and sizes formed; (ii) CO$_2$::NH$_3$ 1:10 and 1:3 ratios form less extensive H-bonding than pure NH$_3$ at 20 K due to the presence of CO$_2$ and so upon heating to 80 K a polycrystalline with small crystallites of similar sizes formed; and (iii) CO$_2$::NH$_3$ 1:1, 2:1 and 3:1 ratios form even less extensive H-bonding than 1:10, 1:3 and pure NH$_3$ at 20 K due to the presence of CO$_2$ and so upon heating to 80 K a polycrystalline with large crystallites or crystalline structure formed. Partly adapted from Dawes et al. $^{167}$
3.4 Binary mixtures of CO$_2$:NH$_3$

**Summary**

Segregation of CO$_2$ and NH$_3$ occurred in the mixtures upon thermal processing to 50–80 K. A phase change from non-crystalline to polycrystalline or crystalline was observed in CO$_2$ ice in the 1:3 and 1:10 ratios upon thermal processing. For the 3:1, 2:1 and 1:1 ratios, CO$_2$ was already in a polycrystalline structure before thermal processing. A phase change in NH$_3$ for all ratios was observed upon thermal processing. For the 1:3 and 1:10 ratios, NH$_3$ was identified as having a polycrystalline structure with crystallites of random shapes and sizes. NH$_3$ was more ordered in the 1:1, 2:1 and 3:1 ratios and had a polycrystalline structure with crystallites of similar shapes and sizes or a crystalline structure.

**3.4.3 Residues at 150 and 200 K**

Evidence of a reaction occurring within the CO$_2$:NH$_3$ ice was observed at ∼80 K and residue material was present after desorption of CO$_2$ and NH$_3$ for all ratios except the 3:1 ratio. From Fig. 3.10 and Table 3.3, vibrational modes of residue material changed during thermal processing between 150–200 K. From the literature studies summarised in Table 3.1, the predicted composition of the residue material was ammonium carbamate and possibly carbamic acid. Assignments of mixtures or large molecules is difficult using mid-IR spectroscopy, but important for the identification of the residue material. This section is split into predicting the mid-IR spectra of ammonium carbamate and carbamic acid, assigning the CO$_2$:NH$_3$ residue spectra at 150 and 200 K and a summary.

**Predicting the mid-IR spectra of ammonium carbamate and carbamic acid**

Residue material has been observed in all the previous studies described in Section 3.1.1. Table 3.4 shows the different assignments in the literature of the same vibrational mode of residue material of a CO$_2$:NH$_3$ ice mixture at a temperature ∼140 K. The assignments of Noble et al. and Lv et al. are not presented in this table as their assignments were made using the assignments of Bossa et al. Despite the disagreement of the vibrational mode assignments, all of the literature studies identified ammonium carbamate as a product of thermal processing of CO$_2$:NH$_3$ mixtures. In addition, some studies also observed carbamic acid.

By assuming that the products are either ammonium carbamate or carbamic acid and using well established frequency ranges of functional groups for the interpretation of mid-IR, a prediction of the peaks for both molecules can be made. The chemical structure of ammonium carbamate and carbamic acid is shown in Fig. 3.16. Both ammonium carbamate and carbamic acid contain a primary amine group which will result in two N-H stretches (3500–3300 cm$^{-1}$, the asymmetric stretch is higher than the symmetric stretch), a N-H bend
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Table 3.4 Summary of the multiple IR assignments of the same vibrational modes throughout the literature of the thermal processing of CO$_2$:NH$_3$ mixtures.

<table>
<thead>
<tr>
<th>Range (cm$^{-1}$)</th>
<th>Bossa et al.</th>
<th>Hitsatsune et al.</th>
<th>Rodriguez-Lazcano et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>829-833</td>
<td>NH$_2$ wag</td>
<td>CO$_2$ wag</td>
<td>CO$_2$ wag</td>
</tr>
<tr>
<td>1035-1040</td>
<td>NCO$_2$ oop bend</td>
<td>NH$_2$ wag</td>
<td>CO$_2$ sym. str.</td>
</tr>
<tr>
<td>1114-1122</td>
<td>NH$_2$ rock</td>
<td>C – N stretch</td>
<td>NH$_2$ rock</td>
</tr>
<tr>
<td>1261-1265</td>
<td>CO$_2$ wag</td>
<td>NH$_2$ rock</td>
<td>COO$^-$ sym. Stretch</td>
</tr>
<tr>
<td>1397-1404</td>
<td>C – N stretch</td>
<td>NH$_2$ rock</td>
<td>COO$^-$ asym. Stretch</td>
</tr>
<tr>
<td>1445-1451</td>
<td>C – N stretch</td>
<td>NH$_4^+$ bend</td>
<td>COO$^-$ sym. Stretch</td>
</tr>
<tr>
<td>1460-1500</td>
<td>NH$_4^+$ bend</td>
<td>COO$^-$ asym. Stretch</td>
<td>COO$^-$ asym. Stretch</td>
</tr>
<tr>
<td>1623-1628</td>
<td>NH$_2$ wag</td>
<td>COO$^-$ sym. Stretch</td>
<td>COO$^-$ sym. Stretch</td>
</tr>
<tr>
<td>1691-1705</td>
<td>NH$_2$ wag</td>
<td>COO$^-$ asym. Stretch</td>
<td>COO$^-$ asym. Stretch</td>
</tr>
<tr>
<td>2172-2236</td>
<td>NH$_4^+$* bend</td>
<td>COO$^-$ sym. Stretch</td>
<td>COO$^-$ asym. Stretch</td>
</tr>
<tr>
<td>2747-3089</td>
<td>NH$_4^+$* bend</td>
<td>COO$^-$ sym. Stretch</td>
<td>COO$^-$ asym. Stretch</td>
</tr>
<tr>
<td>3140 (broad)</td>
<td>NH$_4^+$* bend</td>
<td>COO$^-$ sym. Stretch</td>
<td>COO$^-$ asym. Stretch</td>
</tr>
<tr>
<td>3415-3475</td>
<td>N – H asym stretch</td>
<td>NH$_4^+$* bend</td>
<td>COO$^-$ sym. Stretch</td>
</tr>
</tbody>
</table>

* = no vibrational mode assigned
asym. = asymmetric
sym. = symmetric
AC = ammonium carbamate, CA = carbamic acid
Fig. 3.16 Chemical structure of ammonium carbamate and carbamic acid with the shared primary amine functional group highlighted in blue.

(1650–1580 cm\(^{-1}\)) and a C-N stretch (1250–1020 cm\(^{-1}\)). Carbamic acid contains a carboxylic acid group with a strong C=O stretch (1720–1706 cm\(^{-1}\), dimer), a broad, intense O-H stretch (3300–2500 cm\(^{-1}\), usually centred on 3000 cm\(^{-1}\)), an O-H bend (1440–1395 cm\(^{-1}\)) and a C–O stretch (1320–1210 cm\(^{-1}\)). Ammonium carbamate contains a carboxylate group with two intense COO\(^–\) stretches, the asymmetric stretch (1650–1540 cm\(^{-1}\)) and the symmetric stretch (1450–1360 cm\(^{-1}\)). Ammonium carbamate also contains an ammonium ion (NH\(_4^+\)) which has several features including a set of overlapping bands in the 3500–2500 cm\(^{-1}\) region (3200, 3000[broad], 3060 & 2860 cm\(^{-1}\)) and a feature near 1450 cm\(^{-1}\).\(^{193}\) This is summarised in Table 3.5 and the group frequencies listed here are for pure, usually crystalline samples which are at room temperature. Therefore, some shifting in the frequency and broadening/narrowing within the vibrational modes is expected and was discussed in Section 2.3. Overlapping broad bands are a problem especially within the O–H/N–H stretching region between 3500–2500 cm\(^{-1}\). Generally N–H stretches produce sharper, but weaker features compared to O–H stretches. The key to interpreting these spectra is to accept that not all the peaks can be identified and to focus on some of the differences between the two molecules. For example, COO\(^–\) stretches can be used to identify whether ammonium carbamate is present and the C–O can be used to identify whether carboxylic acid is present.

Assignment of the CO\(_2\):NH\(_3\) residue spectra at 150 and 200 K

The mid-IR spectra of the 2:1, 1:1, 1:3 and 1:10 ratios at 150 and 200 K are shown in Fig. 3.17. The assignments are shown in Table 3.6 and were made using the reasoning described above.

For residue spectra at 150 K, COO\(^–\) and C–O stretches were identified indicating that both ammonium carbamate and carbamic acid were present. Overall, all the ratios contained a similar number of peaks at 150 K, but some of the relative intensities between the peaks varied depending on the ratio. An example of this variation is the vibrational mode marked...
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**Fig. 3.17** Mid-IR spectra of CO$_2$:NH$_3$ ices thermally processed to 150 K (black traces) and 200 K (coloured traces). The asterisk represents variation in intensity of the vibrational modes depending on the ratio. The 2:1 and 1:1 ratios have been zoomed for clarity. All spectra are normalised to 300 nm thickness.
3.4 Binary mixtures of CO$_2$·NH$_3$

Table 3.5 Summary of the different functional groups present in ammonium carbamate and carbamic acid. Functional groups in bold highlight the differing function groups between ammonium carbamate and carbamic acid.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Range (cm$^{-1}$)</th>
<th>Ammonium carbamate</th>
<th>Carbamic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>N–H stretches (x 2)</td>
<td>3500–3300</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>NH$_4^+$ stretches (x 4)</td>
<td>3500–2500</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>O–H stretch</td>
<td>3300–2500</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>C=O</td>
<td>1720–1706</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>N–H bend</td>
<td>1650–1580</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>COO$^-$ asym. stretch</td>
<td>1650–1540</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>COO$^-$ sym. stretch</td>
<td>1450–1360</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>O–H bend</td>
<td>1440–1395</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>C–O stretch</td>
<td>1320–1210</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>C–N stretch</td>
<td>1250–1020</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

with an asterisk in Fig. 3.17 in the O–H/N–H stretching region near 3200 cm$^{-1}$. In the 2:1 and 1:1 ratio, this vibrational mode was more intense compared to neighbouring peaks at ~3035 and ~2860 cm$^{-1}$, compared to the 1:3 and 1:10 ratios. However, the region between 1800–1300 cm$^{-1}$ remained very similar for all ratios at 150 K.

For residue spectra 200 K, COO$^-$ and C=O stretches were identified indicating that both ammonium carbamate and carbamic acid were present. The vibrational modes changed upon thermal processing from 150 to 200 K. At 200 K, the vibrational modes of the 1:3 and 1:10 ratios were similar. While the 2:1 and 1:1 ratios were also similar to each other there was a difference between the 1:3 & 1:10 ratios and the 1:1 & 2:1 ratios.

Differences were observed in the vibrational modes of the 1:3 and 1:10 ratios as the temperature was increased from 150 to 200 K:

- Vibrational modes between 3800–2500 cm$^{-1}$ decreased in intensity except for the peak at ~3450 cm$^{-1}$ which was more resolved at 200 K.
- The C=O stretch at ~1710 cm$^{-1}$ increased in intensity.
- The N–H bend at 1645 cm$^{-1}$ decreased slightly in intensity.
- The COO$^-$ asymmetric stretch at ~1555 cm$^{-1}$ and COO$^-$ symmetric stretch at ~1405 cm$^{-1}$ also decreased in intensity.
- The NH$_4^+$ mode near 1490 cm$^{-1}$ disappeared and a new mode ‘appeared’ at 1470 cm$^{-1}$. This band was probably present in the spectra at 150 K, but was obscured by the NH$_4^+$ mode near 1490 cm$^{-1}$ and is tentatively assigned as the O–H bend.
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- A new feature was observed as a shoulder on the COO$^-$ symmetric stretch at 1320 cm$^{-1}$ which was tentatively assigned as the C–O stretch due to carbamic acid.

The difference between 150 and 200 K of the vibrational modes of the 2:1 and 1:1 ratios from 150 to 200 K were more pronounced compared to the the 1:3 and 1:10 ratios namely:

- Two vibrational modes disappeared in the 3800–2500 cm$^{-1}$ region at 3335 cm$^{-1}$ and 3036 cm$^{-1}$.
- The C=O stretch at $\sim$1705 cm$^{-1}$ significantly increased in intensity relative to the COO$^-$ stretches which decreased significantly.
- The C–O stretch appeared as a resolved feature rather than a shoulder as observed in 1:3 and 1:10 ratios, which was probably due to the disappearance of the COO$^-$ symmetric stretch.
- The tentatively assigned O–H bend also appeared more resolved due to the disappearance of the COO$^-$ symmetric and most of the asymmetric stretches.

Summary

For the 1:3 and 1:10 ratios, it was concluded that both ammonium carbamate and carbamic acid were present at 150 K and 200 K. Thermal processing from 150 to 200 K converted ammonium carbamate into carbamic acid which was observed via the increase in intensity of C=O stretch and decrease in intensity the COO$^-$ stretches. This assumption was further supported by the appearance of the tentatively assigned C–O stretch and O–H bend. For the 2:1 and 1:1 ratio, both ammonium carbamate and carbamic acid were present at 150 K. Thermal processing from 150 to 200 K showed a larger proportion of the ammonium carbamate was converted to carbamic acid. This was in contrast to the 1:3 and 1:10 ratios which still had a larger amount of ammonium carbamate present.

3.5 Comparison to previous studies

The CO$_2$:NH$_3$ residues at 150 and 200 K were compared to the previous studies which were summarised in Table 3.1. The comparison follows a chronological order commencing with the study by Frasco$^{162}$ and ending with the study by Noble et al.$^{95}$

As the residue spectra of the CO$_2$:NH$_3$ mixtures for all ratios were similar at 150 K in Fig. 3.17, the 1:3 ratio was used to represent all ratios at 150 K and compare with the results of the literature studies. However, the mid-IR spectra of the CO$_2$:NH$_3$ ratios were different at 200 K.
3.5 Comparison to previous studies

Table 3.6 Mid-IR band assignments of CO$_2$:NH$_3$ ices which were thermally processed to 150 and 200 K. No residue was observed for the 3:1 ratio.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>CO$_2$:NH$_3$ at 150 K</th>
<th>CO$_2$:NH$_3$ at 200 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2:1</td>
<td>1:1</td>
</tr>
<tr>
<td>N – H asym stretch</td>
<td>3425</td>
<td>3445</td>
</tr>
<tr>
<td>N – H sym stretch</td>
<td>3335</td>
<td>3338</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>3223</td>
<td>3218</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>3036</td>
<td>3031</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>2854</td>
<td>2869</td>
</tr>
<tr>
<td></td>
<td>2207</td>
<td>2234</td>
</tr>
<tr>
<td>↑ C – O stretch</td>
<td>1718</td>
<td>1705</td>
</tr>
<tr>
<td>N – H bend</td>
<td>1641</td>
<td>1640</td>
</tr>
<tr>
<td></td>
<td>1618</td>
<td>1618</td>
</tr>
<tr>
<td>↓ COO$^-$ asym stretch</td>
<td>1553</td>
<td>1556</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1491</td>
<td>1495</td>
</tr>
<tr>
<td>O – H bend*</td>
<td>1410</td>
<td>1400</td>
</tr>
<tr>
<td>↓ COO$^-$ sym stretch</td>
<td>1335</td>
<td>1332</td>
</tr>
<tr>
<td>↑ C – O stretch*</td>
<td>1115</td>
<td>1120</td>
</tr>
<tr>
<td>C – N stretch</td>
<td>1039</td>
<td>1039</td>
</tr>
<tr>
<td></td>
<td>834</td>
<td>832</td>
</tr>
</tbody>
</table>

* = tentative assignments; asym = asymmetric; sym = symmetric; ↑ = peak intensity increased from 150 to 200 K; ↓ = peak intensity decreased from 150 to 200 K.

in Fig. 3.17. Therefore, the 1:3 ratio at 200 K was chosen to represent the both 1:10 and 1:3 ratios, whilst the 1:1 ratio at 200 K was chosen to represent the both 1:1 and 2:1 ratios.

3.5.1 Frasco and Hitsatsune

Frasco deposited a mixture of CO$_2$ and NH$_3$ at 195 K and assigned the product to ammonium carbamate with a non-crystalline structure (Type 1). Frasco then thermally processed this ice to 248 K and assigned the resulting mid-IR spectra as due to ammonium carbamate in crystalline structure (Type 2).

A comparison of the representative residue spectra at 150 and 200 K from this chapter are compared with the Type 1 and Type 2 residue from Frasco in Fig. 3.18. The 1:3 ratio at 150 K which represented all the ratios was in very good agreement with Frasco Type 1, but not for
Frasco Type 1
Frasco Type 2
1:1 200 K (x 5 zoom)
1:3 200 K
1:3 150 K

Fig. 3.18 Mid-IR spectra of CO$_2$:NH$_3$ mixture in a 1:3 ratio at 150 K (red), a 1:1 ratio (green) and 1:3 (blue) ratio at 200 K compared with literature study by Frasco which are labelled Type 1 and Type 2. Spectra are offset for clarity and normalised to 300 nm. The Frasco Type 1 and Type 2 traces were arbitrarily scaled for best comparison.

Frasco Type 2. In fact none of the ratios agreed with Frasco Type 2. Hitsatsune also reported a similar looking mid-IR spectra, but made different assignments.

A difference between the studies of Frasco and Hitsatsune and this work was the deposition temperature. Frasco deposited his Type 1 mixture at 195 K and the equivalent in the study of Hitsatsune was deposited at 83 K, whereas, the CO$_2$:NH$_3$ mixtures in this thesis were deposited at 20 K. Whether this has affected the mid-IR spectra was not investigated, but may contribute to the differences. Another difference was the absence of a CO$_2$:NH$_3$ molecular complex in the studies by Frasco and Hitsatsune. Thermal processing of CO$_2$:NH$_3$ mixtures showed that the CO$_2$:NH$_3$ complexes disappeared at $\sim$80 K and therefore were unlikely to form at higher deposition temperatures used in Frasco and Hitsatsune.

Frasco identified ammonium carbamate as the only product from the reaction between CO$_2$ and NH$_3$. However, inspection of Frasco Type 1 in Fig. 3.18 shows that there was a peak near 1700 cm$^{-1}$. Peaks near 1700 cm$^{-1}$ were used in Section 3.4.3 as an identifier for carbamic acid and implies that a C=O stretch was present in Frasco Type 1. However, it disappeared in
3.5 Comparison to previous studies

Frasco Type 2 contrary to the results shown in this chapter which showed the growth of the C=O stretch upon thermal processing.

It was concluded that while Frasco Type 1 was almost the same as all the ratios investigated in Fig. 3.17 at 150 K, Frasco Type 2 did not fit any of the ratios used. Whatever process occurred between Frasco’s Type 1 and Type 2 was not the same for the process which occurred between 150 and 200 K for the work presented in this chapter. In larger molecules like ammonium carbamate, especially when mixed with another molecule like carbamic acid, it is also difficult to determine whether it has non-crystalline or crystalline structure. It is difficult to form pure ammonium carbamate under astrophysically relevant conditions and therefore no reference spectra exist for a non-crystalline or crystalline form, so no structural assignment was made.

3.5.2 Bossa et al. and Lv et al.

![Fig. 3.19 Mid-IR spectra of CO$_2$:NH$_3$ mixture in a 1:3 ratio at 150 K (red), a 1:1 ratio (green) and 1:3 (blue) ratio at 200 K compared with Bossa et al. results of ammonium carbamate and carbamic acid dimer (black traces). Spectra are offset for clarity and normalised to a thickness of 300 nm. Bossa et al. traces were arbitrarily scaled for best comparison.](image)

In the study by Bossa et al., the thermal processing products were identified as ammonium carbamate and carbamic acid dimer. A carbamic acid dimer was obtained by subtracting the CO$_2$:NH$_3$ mixed spectrum at 230 K from the spectrum at 140 K. Ammonium carbamate
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was observed by subtracting the carbamic acid dimer from the NH$_3$:CO$_2$ spectrum at 230 K. A comparison of the results of this chapter at 150 and 200 K was made with the ammonium carbamate and carbamic acid spectra obtained by Bossa et al. in Fig. 3.19. The comparison in Fig. 3.19 confirmed that all ratios in this chapter at 150 and 200 K contained a mixture of carbamic acid and ammonium carbamate. At 200 K, the 1:1 ratio at 200 K from this chapter was more similar to the carbamic acid dimer spectra by Bossa et al. The 1:3 ratio at 200 K from this chapter was more similar to the ammonium carbamate spectra by Bossa et al. These results are also in agreement with the thermal processing results obtained in the study by Lv et al.

3.5.3 Rodríguez-Lazcano et al.

Fig. 3.20 Mid-IR spectra of CO$_2$:NH$_3$ mixture in a 1:3 ratio (red) and 1:10 ratio (blue) at 150 K and 200 K compared with Rodríguez-Lazcano et al. 1:3 results (black) at 140 K and 220 K. Spectra are offset for clarity and normalised to 300 nm. The Rodríguez-Lazcano et al. traces were arbitrarily scaled for best comparison.

Fig. 3.20 shows the mid-IR spectra of residue material from the 1:3 ratio acquired in the study by Rodríguez-Lazcano et al. at 140 K compared with the 1:3 and 1:10 ratios in this work. The 1:3 and 1:10 ratios at both 150 and 200 K are in very good agreement with the study by Rodríguez-Lazcano et al. again confirming the presence of ammonium carbamate and carbamic acid in these ratios.
3.5 Comparison to previous studies

3.5.4 Noble et al.

According to a study by Noble et al., ammonium carbamate would form first upon thermal processing to 80 K after deposition at 70 K. Carbamic acid was then formed from ammonium carbamate between 150-225 K. Fig. 3.17 showed evidence of changes within the ratios between 150 and 200 K except the 3:1 ratio. The study by Noble et al. presents the only previous study where excess CO\textsubscript{2} mixtures were investigated and it was observed that ratios with excess CO\textsubscript{2} had no reactivity. This was attributed to the desorption of CO\textsubscript{2} before a reaction could take place because the reaction barriers were too high in CO\textsubscript{2}-rich mixtures. From Table 3.3, the 3:1 ratio had the lowest CO\textsubscript{2} segregation temperature, the lowest NH\textsubscript{3} crystallisation temperature and one of the lowest CO\textsubscript{2} and NH\textsubscript{3} desorption temperatures. It is possible that the low CO\textsubscript{2} segregation and NH\textsubscript{3} phase change temperatures prevented the CO\textsubscript{2} and NH\textsubscript{3} molecules from aligning in the correct orientation for a reaction to happen between CO\textsubscript{2} and NH\textsubscript{3}.

Noble et al. determined that ammonium carbamate forms first at 80 K (C 3.1) followed by carbamic acid between 150–225 K (C 3.2).

\[
2\text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{NH}_4^+\text{NH}_2\text{COO}^- \quad (C\ 3.1)
\]

\[
\text{NH}_4^+\text{NH}_2\text{COO}^- \rightleftharpoons \text{NH}_3 + \text{NH}_2\text{COOH} \quad (C\ 3.2)
\]

From Table 3.6 it was shown that features associated with both ammonium carbamate and carbamic acid formed at \(\sim 80\) K for the 1:1, 1:3 and 1:10 ratio and slightly higher at 90 K for 2:1 ratio. This was in contrast with the study by Noble et al. where no carbamic acid was observed at 80 K. However, the study by Noble et al. deposited the CO\textsubscript{2}:NH\textsubscript{3} mixture at 70 K and a temperature where it was unlikely to form CO\textsubscript{2}:NH\textsubscript{3} molecular complexes. According to Table 3.3, the CO\textsubscript{2}:NH\textsubscript{3} complex disappeared around the same temperature that the new bands in the spectra appeared. This molecular complex or adduct shown in Fig. 3.9 may have undergone internal proton transfer to form a more stable molecule at higher temperatures and hence form carbamic acid, which is depicted in Fig. 3.21. This reaction is the first proposed formation route of carbamic acid at lower temperatures. The thermal processing mid-IR spectra of the ratios in Fig 3.17 showed that the C=O stretch increased in intensity as the COO\textsuperscript{-} stretch decreased in intensity confirming the higher temperature formation route of carbamic acid proposed by Noble et al. The investigation of the COO\textsuperscript{-} stretches showed a maximum intensity was reached by 110 K for the 1:3 and 1:10 ratios and a maximum by 100 K for the 2:1 and 1:1 ratios. These maximum intensity temperatures corresponded with the desorption of CO\textsubscript{2} and NH\textsubscript{3} which agreed with the proposed formation mechanism of ammonium carbamate by Noble et al. whereby CO\textsubscript{2} and NH\textsubscript{3} are required for its formation.
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Fig. 3.21 Schematic diagram of the internal proton transfer of the CO$_2$·NH$_3$ complex to form carbamic acid.

3.5.5 Monomeric or dimeric carbamic acid?

An issue that is debated in the literature is the form of carbamic acid. Bossa et al. stated that carbamic acid was in a dimeric form$^{94}$ while Rodríguez-Lazcano et al. argued that there was not enough spectroscopic evidence to determine if it was in the monomeric or dimeric form.$^{140}$ The C=O stretch observed in the spectra in Fig. 3.17 showed a broad feature. As discussed in Section 3.4.1, broad features are associated with H-bonding which could suggest that carbamic acid formed a dimer. However, as there is no strong evidence to help assign either a monomeric or dimeric form, the form of carbamic acid is left unassigned.

3.6 Discussion and summary

A systematic investigation of the thermal processing of CO$_2$·NH$_3$ interstellar ice analogues as a function of deposition mixing ratio using mid-IR spectroscopy was presented in this chapter and the results are summarised below:

- Vibrational modes of CO$_2$·NH$_3$ molecular complexes were observed for all ratios, except the 1:10, upon deposition at 20 K.

- Thermal processing of CO$_2$·NH$_3$ to temperatures between 50–80 K segregated the CO$_2$ and NH$_3$. A phase change from non-crystalline to polycrystalline or crystalline was observed in the 1:3 and 1:10 ratios at 80 K. For the 3:1, 2:1 and 1:1 ratios the CO$_2$ ice was already in a polycrystalline form at 20 K and no further phase change was observed.

- At 80 K, the crystallisation of NH$_3$ in the mixtures was more ordered than compared with pure NH$_3$, which was attributed to a less extensive intermolecular H-bonding network within the mixtures. Ratios with higher amounts of CO$_2$ (i.e. 3:1 and 2:1) had a more
ordered, cubic crystalline form of NH\textsubscript{3} compared to mixtures with lower amounts of CO\textsubscript{2} (i.e. 1:3 and 1:10) which had a polycrystalline form with crystallites of similar shapes and sizes.

- Formation of new peaks were observed in all ratios when thermally processed to temperatures above 80–90 K except the 3:1 ratio. The COO\textsuperscript{−} stretches of ammonium carbamate and the C=O stretch of carbamic acid were identified from the mid-IR spectra.

- At 150 K, all ratios except the 3:1 ratio contained ammonium carbamate and carbamic acid. At 200 K, all ratios except the 3:1 ratio showed evidence of the conversion of ammonium carbamate to carbamic acid.

- Ammonium carbamate was the major product at temperatures between 80–150 K via the following reaction:

\[
2\text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{NH}_4^+\text{NH}_2\text{COO}^-
\]

- Carbamic acid is a minor product at temperatures between 80–150 K and formed via an internal proton transfer of the CO\textsubscript{2}:NH\textsubscript{3} molecular complex. Above 150 K, ammonium carbamate was converted to carbamic acid.

\[
\text{NH}_4^+\text{NH}_2\text{COO}^- \rightleftharpoons \text{NH}_3 + \text{NH}_2\text{COOH}
\]

Apart from the study by Frasco\textsuperscript{162} and Hisatsune,\textsuperscript{163} the results of the thermal processing of CO\textsubscript{2}:NH\textsubscript{3} mixtures as a function of mixing ratio agree well with the previous studies. Few details are given about the experimental apparatus used in the study of Frasco\textsuperscript{162} and Hisatsune,\textsuperscript{163} but it does not appear to have been conducted under high vacuum conditions. This may be the reason why different results are found for Frasco and Hisatsune. For the other literature studies, the experimental apparatus used is similar to that of the PAC which was described in Section 2.4.1 (e.g. minimum high vacuum conditions).

The residue spectra of the 1:3 and 1:10 ratio shown in Fig 3.17 formed the most intense residue spectra suggesting that more ammonium carbamate and carbamic acid were formed. Interestingly, CO\textsubscript{2} in both of these ratios experienced a phase change from non-crystalline to crystalline (or polycrystalline) when the mixture segregated upon thermal processing. The NH\textsubscript{3} in both of these ratios also changed from a non-crystalline to polycrystalline structure with crystallites of random shapes or sizes. As discussed in Section 1.5.2 the morphology of the interstellar ice analogues is thought to be important in the reactivity of interstellar ice analogues.\textsuperscript{160} A phase change in the other ratios only occurs in the NH\textsubscript{3} ice upon segregation of the mixture. While it could be a coincidence that the 1:3 and 1:10 ratios, where both CO\textsubscript{2}...
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and NH$_3$ change phase upon thermal processing are also the ratios with the larger residues. It may also be due to increased mobility of the molecules within the interstellar ice analogues allowing more molecules to react.

A major motivation behind this thesis was to understand how different experimental parameters affect the interstellar ice analogue. While the experimental ice analogue parameter under investigation in this thesis is the mixing ratio, comparison to a different deposition temperature can also be made. Noble et al. used a higher deposition temperature than the deposition temperatures in this chapter and the deposition temperature affected the formation of carbamic acid at $\sim$150 K. In the work presented in this chapter, carbamic acid was observed in the CO$_2$:NH$_3$ mixtures which were deposited at 20 K and thermally processed to 150 K. Whereas, in the study by Noble et al. no carbamic acid was observed until after 150 K. In the study by Noble et al. no CO$_2$:NH$_3$ molecular complexes were observed at the higher deposition temperatures whereas in this work CO$_2$:NH$_3$ molecular complexes were observed at the deposition temperature of 20 K. This difference led to the suggestion that carbamic acid forms in small amounts from a proton transfer reaction as depicted in Fig. 3.21 demonstrating the need to comprehensively investigate all experimental parameters.

Now that a systematic investigation of the thermal processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio using mid-IR spectroscopy has been conducted, Chapter 4 will present the results of the investigation of radiation processing. A comparison will be made of the thermal processing results shown in this chapter with the radiation results presented in the next chapter.
Chapter 4

Electron and thermal processing of 
CO$_2$:NH$_3$ interstellar ice analogues: a 
mid-IR spectroscopic study

This chapter presents the results of a systematic, mid-IR spectroscopic study of the electron processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio. Molecular synthesis was induced in the interstellar ice analogues upon electron processing to form small identifiable products such as CO, OCN$^-$ and larger products with identifiable function groups such as C=O stretches. This chapter also presents the subsequent systematic, mid-IR spectroscopic study of the thermal processing of the electron processed CO$_2$:NH$_3$ interstellar ice analogues. Further molecular synthesis was induced in the interstellar ice analogues upon thermal processing. These results are discussed and compared to the thermal processing study presented in Chapter 3 and to previous studies reported in the literature.

4.1 Introduction

The need to gain a comprehensive understanding of the influence of experimental parameters on interstellar ice analogues is one of the motivations behind this thesis. It stems from a lack of comprehensive studies into the influence of discrete experimental parameters on interstellar ice analogues. Radiation processed binary mixtures of CO$_2$ and NH$_3$ are a good example of where individual experimental parameters have not been systematically studied although there have been several previous studies reported in the literature. In the following section previous work is described and experimental conditions in these earlier experiments defined to allow closer comparison with the results presented in this thesis.
4.1.1 Literature studies

Several previous studies of the energetic and subsequent thermal processing of CO$_2$:NH$_3$ interstellar ice analogues have been reported in Section 3.1.1, these are summarised in Table 4.1 and discussed below.

In 2008, Bossa et al. studied both the thermal and energetic (VUV) processing of CO$_2$ and NH$_3$ mixtures deposited at 10 K and the thermal processing results were summarised in Table 3.1. Ammonium carbamate and carbamic acid dimer were identified as products from VUV processing of the CO$_2$ and NH$_3$ mixture. The ratio of ammonium carbamate and carbamic acid was 1:28 after VUV processing and subsequent thermal processing, compared to the 1:1 ratio obtained from just thermal processing. Three additional molecules were also identified from the mid-IR spectra: CO, OCN$^-$ and ammonium formate (HCOONH$_4$).

Bertin et al. studied the low energy electron irradiation of a CO$_2$ and NH$_3$ ice mixture at 10 K. They concluded that only neutral carbamic acid was formed at 10 K after energetic processing with low energy electrons. Thermal processing to 140 K was required to form ammonium carbamate.

Jheeta et al. also deposited a mixture of CO$_2$ and NH$_3$ at low temperatures (30 K) and identified ammonium carbamate as a product upon energetic processing with 1 keV electrons. Carbamic acid was not identified post irradiation or during the thermal processing of the ice mixture to 254 K.

Lv et al. also studied both the thermal and energetic processing of CO$_2$ and NH$_3$ ice mixtures and the thermal processing results were summarised in Table 3.1. Energetic processing with 144 keV S$^{9+}$ ions at 16 K formed the previously unobserved product of N$_2$O, along with previously observed CO, OCN$^-$, ammonium formate and carbamic acid dimer. However, no ammonium carbamate was identified at 16 K and no subsequent thermal processing was presented.

4.2 Pure CO$_2$ ice

In order to interpret the results of electron irradiation of the ice mixture it is also necessary to study the products formed from the irradiation of pure ices of the two constituent species CO$_2$ and NH$_3$. The results of the electron processing of pure CO$_2$ ice deposited at 20 K and the subsequent thermal processing are presented in this section.
<table>
<thead>
<tr>
<th>Reference</th>
<th>CO$_2$:NH$_3$ ratio</th>
<th>Observation technique</th>
<th>$T_{deposition}$ (K)</th>
<th>Processing (fluence, cm$^{-2}$)</th>
<th>$T_{processing}$ (K)</th>
<th>Main products (&amp; $T_{formation}$)</th>
</tr>
</thead>
</table>
| Bossa et al.
143 | 1:1$^b$ | IR & MS | 10 | VUV photons ($4.3 \times 10^{19}$) | 10 | CA dimer, AF, OCN$^-$, CO & AC (10 K) |
| Bertin et al.
141 | 1:1$^a$ | HREEL & IR | 10 | Electrons, 9–20 eV (typically few $10^{14}$) | 10 | CA (10 K) |
| Jheeta et al.
142 | 1:1$^c$ | IR | 30 | Electrons, 1 keV ($4.6 \times 10^{17}$)$^d$ | 30 | NH$_4^+$, OCN$^-$, CO, & AC (30 K) |
| Lv et al.
143 | 1:1, 0.75:1$^a$ | IR | 16 | S$_9^+$ ions (144 keV) ([1.3 & 6.8] $\times 10^{14}$) | 16 | N$_2$O, OCN$^-$, CA dimer & AF (16 K) |

$^a$ ratios derived from partial pressures of the mixture in the gas line, $^b$ method of determining ratio not specified, $^c$ ratios derived from column density, $^d$ fluence not explicitly stated, but calculated from values given in text, AC = ammonium carbamate, CA = carbamic acid, AF = ammonium formate
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4.2.1 Electron irradiation at 20 K

As mentioned in Section 2.4.5 the electron irradiation of the interstellar ice analogues was not continuous. Rather, the ice was irradiated for specified time intervals, which are listed in Table A.5, and a mid-IR spectrum was collected after each irradiation period. Fig. 4.1 shows the mid-IR spectra of pure CO$_2$ ice which was irradiated with 1 keV electrons at several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^{-}$ cm$^{-2}$. Fig. 4.1 (i) shows that the combination modes, $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$, decreased in intensity as the fluence increased. This was probably a combination of sputtering due to the angle of the substrate and the dissociation of CO$_2$, and was discussed in Section 2.4.5. Fig. 4.1 (ii) shows the LO-TO splitting of the $^{12}$CO$_2$ $\nu_3$ fundamental mode; (iii) irradiation products CO and CO$_3$ and (iv) irradiation product O$_3$. 

![Fig. 4.1 Mid-IR spectra of pure CO$_2$ deposited at 20 K and irradiated with 1 keV electrons at several intervals for a total fluence of $3.37 \times 10^{15}$ e$^{-}$ cm$^{-2}$, (i) $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes; (ii) LO-TO splitting of the $^{12}$CO$_2$ $\nu_3$ fundamental mode; (iii) irradiation products CO and CO$_3$ and (iv) irradiation product O$_3$.](image-url)
dissociation process. Additionally, a shoulder appeared on the $\nu_3$ TO mode near 2365 cm$^{-1}$ at higher fluence, which is indicated by a dashed line in Fig. 4.1 (ii). Fig. 4.1 (iii) shows the formation of CO at 2140 cm$^{-1}$ and carbon trioxide (CO$_3$) at 2050 cm$^{-1}$. Fig. 4.1 (iv) shows the formation of O$_3$ at 1040 cm$^{-1}$.

**Discussion**

The electron irradiation products of CO$_2$, CO, CO$_3$ and O$_3$, were identified in Fig. 4.1. Previous studies have identified the formation of CO and O atom from direct dissociation of CO$_2$ (C 4.1). The O atom is referred to as a suprathermal or ‘hot’ oxygen because it possesses kinetic energy above the ambient thermal level due to its formation via electron irradiation. A suprathermal oxygen can then either react with more CO$_2$ to form CO$_3$ (C 4.2) or undergo a two-step consecutive reaction to form O$_3$ (C 4.3 and C 4.4). From the presence of O$_3$ it can be inferred that the IR inactive O$_2$ was also formed.

\[
\text{CO}_2 + e^- \rightarrow \text{CO} + \text{O} \quad \text{(C 4.1)}
\]

\[
\text{O} + \text{CO}_2 \rightarrow \text{CO}_3 \quad \text{(C 4.2)}
\]

\[
\text{O} + \text{O} \rightarrow \text{O}_2 \quad \text{(C 4.3)}
\]

\[
\text{O}_2 + \text{O} \rightarrow \text{O}_3 \quad \text{(C 4.4)}
\]

A shoulder was observed on the TO mode near 2366 cm$^{-1}$. The formation of this shoulder may be explained by small defects within the CO$_2$ ice, caused by the irradiation products, which disrupt the long range interactions of CO$_2$ ice and hence, the LO-TO splitting. In a study by Cooke *et al.* the sensitivity of the CO$_2$ LO mode was investigated by irradiating CO$_2$ ice with VUV photons to a total fluence of $1.38 \times 10^{19}$ photons cm$^{-2}$. Splitting within the LO mode was observed and it was hypothesised that the splitting was caused by inhomogeneous mixing of the bulk CO$_2$ ice and the irradiation products. The shoulder observed in Fig. 4.1 is in agreement with the irradiation study by Cooke *et al.* at lower fluence where only a shoulder was observed also near 2366 cm$^{-1}$.

### 4.2.2 Destruction curve of CO$_2$ and growth curves of CO, CO$_3$ and O$_3$

The peak area of CO in Fig. 4.1 (iii) appeared to grow as the electron fluence increased, whereas, CO$_3$ appeared to reach a maximum. Fig. 4.1 (iv) showed that the peak area of O$_3$ also appeared to grow as the fluence increased. The peak area of these molecules can be converted
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to column density ($N_i$) using Eq. 2.23 which was first shown in Chapter 2 and is shown below as a reminder.

$$N_i = \frac{\int Abs(\tilde{\nu})d\tilde{\nu}}{A_i} \times \ln(10)$$

where $\int Abs(\tilde{\nu})d\tilde{\nu}$ corresponds to the area of the absorption peak for a specific vibrational mode, $A_i = \int \sigma(\tilde{\nu})d\tilde{\nu}$ which is the integrated band strength of the specific vibrational mode which is constant and obtained from the literature.

**Table 4.2** Integration range and A-values used to obtain column densities of CO$_2$, CO, CO$_3$ and O$_3$ formed from electron processing of pure CO$_2$ ice at 20 K.

<table>
<thead>
<tr>
<th>Species</th>
<th>Integrated range (cm$^{-1}$)</th>
<th>A-value (cm molecule$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ ($v_1 + v_3$)</td>
<td>3700–3718</td>
<td>$1.8 \times 10^{-18}$</td>
</tr>
<tr>
<td>CO</td>
<td>2128–2155</td>
<td>$1.12 \times 10^{-17}$</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>2035–2055</td>
<td>$8.9 \times 10^{-17}$</td>
</tr>
<tr>
<td>O$_3$</td>
<td>1035–1050</td>
<td>$1.4 \times 10^{-17}$</td>
</tr>
</tbody>
</table>

The integrated range and A-values used to obtain the column densities are shown in Table 4.2. Fig. 4.2 shows the growth curves of CO, CO$_3$ and O$_3$ and the destruction curve of the $v_1 + v_3$ vibrational mode of CO$_2$. The kinetic fits and mechanisms which governed these growth curves are discussed below.

**Fitting rate equations**

Qualitatively from Fig. 4.2 there appeared to be two types of growth (or destruction). Up to about $1 \times 10^{15}$ e$^{-}$ cm$^{-2}$ a faster growth (or destruction) was observed followed by a slower growth or destruction. According to previous studies the dissociation of CO$_2$ can be fitted using a first order rate equation and the formation of CO, CO$_3$ and O$_3$ can be fitted using the first order rate equation, Eq. 4.2.

$$N_{(CO_2)} = Ae^{-\sigma_{des}\phi} \quad (4.1)$$

where $N_{(CO_2)}$ is the column density of CO$_2$, A is the asymptotic value, $\sigma_{des}$ is the CO$_2$ destruction cross section and $\phi$ is the electron fluence in e$^{-}$ cm$^{-2}$.

$$N_{(CO, CO_3 \text{ or } O_3)} = B(1 - e^{-\sigma_{form}\phi}) \quad (4.2)$$

where $N_{(CO, CO_3 \text{ or } O_3)}$ is the column density of CO, CO$_3$ or O$_3$, B is the asymptotic value, $\sigma_{form}$ is the CO formation cross section and $\phi$ is the electron fluence in e$^{-}$ cm$^{-2}$. 
4.2 Pure CO₂ ice

![Graphs showing data for CO₂, CO, CO₃, and O₃](image)

**Fig. 4.2** Destruction curve of (i) CO₂ ν₁ + ν₃ combination mode and growth curves of (ii) CO; (iii) CO₃ and (iv) O₃. The lines connecting the scatter points are for guidance only.

**Table 4.3** Results of the pseudo first order fit from eqn 4.2 of the destruction curve of CO₂.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>A (×10¹⁶)</th>
<th>σ₁des (×10⁻¹⁶ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>50.2 ± 0.3</td>
<td>0.053 ± 0.004</td>
</tr>
</tbody>
</table>

The models described in Eq. 4.1 and 4.2 were fitted to the experimental data using the curve_fi t function from the scipy.optimize library of Python which is a nonlinear least-squares fitter. The curve_fi t function returns the best fit parameters from Eq. 4.1 (e.g. A and σ₁des) or Eq. 4.2 (e.g. B₂ and σ₁form) and also the corresponding covariance matrix. A one standard deviation of the optimal parameter values was then calculated by finding the square root of the diagonal components of the returned covariance matrix.

These fits are shown in Fig. 4.3 as solid black lines with the area of the upper and lower bounds (one standard deviations) shaded in grey. The fitting parameters for the destruction of CO₂ are shown in Table 4.3 and for the formation of CO, CO₃ and O₃ in Table 4.4. However, as previously mentioned, the visual inspection showed that there appeared to be two regimes to the destruction or growth of the species. This was confirmed by the poor fits represented shown in Fig. 4.3. As two regimes were identified by visual inspection, then the sum of two first order equations were fitted to the experimental data to obtain a better fit. The CO₂ destruction curve was fitted using equation 4.3 and the CO, CO₃ and O₃ growth curves were fitted using equation...
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Fig. 4.3 Destruction curve of (i) CO$_2$, and growth curves (ii) CO, (iii) CO$_3$, and (iv) O$_3$. The fits represent the initial fits and were obtained using Equation 4.1 for (i) and Equation 4.2 for (ii), (iii) and (iv). The shaded grey area represents the upper and lower bounds of the fit.
### 4.4 Results of the pseudo first order fit from eqn 4.2 of the growth curves of CO₂ irradiation products: CO, CO₃, and O₃.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>B (×10^{16})</th>
<th>σ₁form (×10^{-16} cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>5.5 ± 0.1</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>CO₃</td>
<td>0.069 ± 0.001</td>
<td>16.5 ± 1.9</td>
</tr>
<tr>
<td>O₃</td>
<td>0.69 ± 0.01</td>
<td>5.6 ± 0.5</td>
</tr>
</tbody>
</table>

And the CO growth curve was fitted using the following equation:

\[ N_{(CO)} = B_1 (1 - e^{-\sigma_{1form} \phi}) + B_2 (1 - e^{-\sigma_{2form} \phi}) \]  
\[ (4.4) \]

where \( A_1, A_2, B_1 \), and \( B_2 \) are asymptotic values, \( \sigma_{1des} \) and \( \sigma_{2des} \) are the destruction cross sections of the two regimes, \( \sigma_{1form} \) and \( \sigma_{2form} \) are the formation cross sections of the two regimes.

The results of the two-phase exponential fits are shown in Fig. 4.4 where the solid black lines represent the fits and the area of upper and lower bounds are shaded in grey. Again, the models described in Eq. 4.3 and 4.4 were fitted to the experimental data using the curve_fit function from the scipy.optimize library of Python and a one standard deviation of the optimal parameter values was calculated. The upper and lower bounds were derived from the one standard deviation of the parameters shown in Table 4.5 and 4.6.

The fitting parameters for the destruction of CO₂ are shown in Table 4.5 and for the formation of CO, CO₃, and O₃ in Table 4.6. The fits for the destruction of CO₂ and formation of CO are much better in Fig. 4.4 (i) and (ii) respectively compared to Fig. 4.3 (i) and (ii) suggesting that there are two different rates of destruction of CO₂ and two different rates for the formation of CO.

Fig. 4.4 (iii) shows the formation curve of CO₃ does not fit well to the two-phase exponential fits of Eq. 4.4 where the upper and lower limits are extremely large. Above fluences of \( \sim 1.2 \times 10^{15} \text{ e}^- \text{ cm}^{-2} \) the column density of CO₃ decreased implying there were competitive formation and destruction processes taking place, which would explain why the fit to the model in Eq. 4.4 did not converge. Destruction of CO₃ has been observed in past studies to form CO₂ and O through the following reaction:

\[ \text{CO}_3 + e^- \rightarrow \text{CO}_2 + \text{O} \]  
\[ (C4.5) \]
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Fig. 4.4 Growth curves of (i) CO$_2$, (ii) CO, (iii) CO$_3$ and (iv) O$_3$. The fits represent the ‘best’ fits and were obtained using Equation 4.3 for (i) and Equation 4.4 for (ii), (iii) and (iv). The shaded grey area represents the upper and lower bounds of the fit.
4.2 Pure CO₂ ice

The formation and destruction of CO₃ is complex and the fitting of the rate equations is beyond this thesis. However, the formation curve of O₃ in Fig. 4.4 (iv) generally appears to fit the two-phase exponential fits of Eq. 4.4.

Discussion

The major products observed in the mid-IR spectra of the electron irradiation of CO₂ are CO, CO₃ and O₃. The destruction of CO₂ and the formation of CO and O₃ can be fitted reasonably well with a two phase exponential first order rate equation. A relative fast and slow destruction cross section exists for CO₂ indicating two different destruction regimes. Initial electron irradiation will destroy CO₂ molecules at a relatively fast rate. However, formation of CO₃ and its subsequent destruction will form CO₂ (C 4.5) therefore giving rise to the two different destruction regimes. The relative fast and slow formation rates of CO and O₃ may be explained as follows. As more CO₂ is formed then more CO can be formed which explains why the formation of CO does not plateau. As more CO forms then more O₃ can form via reactions C 4.3 and C 4.4 and similar to CO no plateau was observed in O₃ growth curve.

Comparing the studies which suggested that the destruction of CO₂ and the formation of CO were of first order, it was noted that they used much lower fluences. If the study by Bennett et al. ¹⁹⁴ is used as an example, as they also used electrons to irradiate CO₂ ice, the total fluence used was ~6 × 10¹⁴ e⁻ cm⁻². To compare it to the fluence used in Fig. 4.3, the first irradiation interval corresponded to a fluence of ~1 × 10¹⁵ e⁻ cm⁻², almost twice as large as the total fluence used by Bennett et al. It may be that at lower fluences the formation rate is first order.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>B₁ (×10¹⁶)</th>
<th>σ₁des (×10⁻¹⁶ cm²)</th>
<th>B₂ (×10¹⁶)</th>
<th>σ₂des (×10⁻¹⁶ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>30.36 ± 0.076</td>
<td>1.30 ± 0.064</td>
<td>3.00 ± 0.091</td>
<td>11.79 ± 0.67</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>B₁ (×10¹⁶)</th>
<th>σ₁form (×10⁻¹⁶ cm²)</th>
<th>B₂ (×10¹⁶)</th>
<th>σ₂form (×10⁻¹⁶ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>3.00 ± 0.08</td>
<td>1.30 ± 0.06</td>
<td>3.00 ± 0.09</td>
<td>11.8 ± 0.7</td>
</tr>
<tr>
<td>CO₃</td>
<td>0.069 ± 0.001</td>
<td>16 ± 2</td>
<td>0 ± 2</td>
<td>-10 ± 30000</td>
</tr>
<tr>
<td>O₃</td>
<td>0.53 ± 0.04</td>
<td>9 ± 1</td>
<td>0.23 ± 0.03</td>
<td>1.0 ± 0.3</td>
</tr>
</tbody>
</table>
Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a mid-IR spectroscopic study

Fig. 4.5 Mid-IR spectra of pure CO$_2$ after irradiation with 1 keV electrons at 20 K and subsequent thermal processing to desorption at 100 K. (i) $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes; (ii) $^{12}$CO$_2$ $\nu_3$ fundamental mode; (iii) CO and CO$_3$ and (iv) O$_3$.

4.2.3 Thermal processing of CO$_2$ ice after electron irradiation at 20 K

After electron processing at 20 K, the CO$_2$ ice was thermally processed to desorption at 100 K. Fig. 4.5 (i) shows that the combination modes, $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$, remained at the same intensity until $\sim$80 K and then decreased in intensity at onset of the desorption of CO$_2$ ice. Fig. 4.5 (ii) shows that the TO mode of the $\nu_3$ vibrational mode increased slightly in intensity until the onset of desorption at 90 K. Fig. 4.5 (iii) shows that a small blue shift occurred in the CO peak between 20–30 K. Also, both CO and CO$_3$ desorbed between 80–90 K. Fig. 4.5 (iv) shows that the profile of O$_3$ changed as the CO$_2$ ice was thermally processed before it desorbed between 80–90 K.
Fig. 4.6 shows the peak area of (i) CO$_2$, (ii) CO, (iii) CO$_3$ and O$_3$ as a function of thermal processing from 20 to 100 K. The peak areas are shown rather than the column density as the A-values are known to change as a function of temperature which was discussed in Section 1.5.1. The peak area of CO$_2$ in Fig. 4.6 (i) remained constant until 90 K where it decreased to almost zero. This suggested that CO$_2$ started desorbing between 80–90 K and was completely desorbed by 100 K. Fig. 4.6 (ii) shows that the peak area of CO remained relatively constant between 20–50 K. Between 50–60 K the peak area decreased from 0.25 to 0.11 cm$^2$. Between 60–80 K the peak area of CO decreased gradually until desorption at 100 K. The peak area of CO$_3$ in Fig. 4.6 (iii) remained constant until 50 K whereupon it decreased from an average value of 0.025 to 0.017 cm$^2$. Between 60–80 K, the peak area of CO$_3$ decreased gradually to 0.011 cm$^2$, whereupon it decreased to 0.002 cm$^2$ between 80–90 K. Fig. 4.6 (iv) shows that the peak area of O$_3$ decreased slowly between 20–50 K from a value of 0.46 to 0.42 cm$^2$. The peak area of O$_3$ then decreased more rapidly between 60–100 K.
Discussion and Summary

Pure CO desorbs between 28–36 K depending on the original deposition temperature of the CO ice. However, from the thermal processing curve of CO shown in Fig. 4.6 (ii) CO formed from the electron processing of CO₂ ice was still present at higher temperatures. Temperature programmed desorption - mass spectrometry experiments on irradiated CO₂ ice by Bahr & Baragiola and Martín-Doménech et al. both showed a broad desorption peak near 50 K. This temperature coincides with the first decrease in peak area observed in the Fig. 4.6 (ii). According to Bahr & Baragiola this desorption peak was due to CO molecules trapped in the pores of the CO₂ ice matrix. Additional desorption peaks for CO were also observed at the desorption temperature of the CO₂ in both studies and attributed to small amounts of CO remaining trapped within the CO₂ ice. The thermal processing curve for CO shown in Fig. 4.6 was in agreement with Bahr & Baragiola as the peak area decreased to approximately zero between 80–90 K which was identified as the onset of CO₂ desorption.

The warm up curve of CO₃ shown in Fig. 4.6 (ii) followed a similar trend to CO whereby CO₃ molecules were likely entrapped within the CO₂ ice matrix. Similar to CO, the peak area of CO₃ decreased between 50–60 K.

The desorption temperature of O₃ formed from O₂ ices is ~62 K. However, from Fig. 4.6 (iv) O₃ formed in CO₂ ice was present until desorption of CO₂. This was in agreement with a study by Sivaraman et al. where CO₂ ice was irradiated with with low energy ions. Sivaraman et al. also noted that thermal processing decreased the column density of O₃. In contrast, the column density of O₃ formed from pure O₂ increased with thermal processing until ~40 K. Similar to CO and CO₃, O₃ fully desorbed at the same temperature as CO₂ suggesting entrapment within the CO₂ matrix.

A tentative phase change from polycrystalline to crystalline was suggested to occur between 50–60 K for thermally processed CO₂ in Section 3.2. The first decrease in peak area observed for CO and CO₃ was also between 50–60 K. This may be due to the CO₂ ice attempting to restructure which allowed some entrapped CO and CO₃ to be released which is sometimes referred to as ‘volcano’ desorption. However, a phase change of electron and thermally processed CO₂ was probably prevented due to the presence of the irradiation products which acted as defects within the crystal lattice.

A feature at 2328 cm⁻¹, which was tentatively assigned to CO₂ dimers disappeared after electron processing in agreement with previous studies and did not reappear during thermal processing. This suggested that the electron irradiation of the CO₂ ice disrupted the formation of CO₂ dimers, which is in contrast to the unirradiated ice system.

Both CO₂ which was thermally processed and CO₂ which was electron and thermally processed desorbed by 100 K. The unirradiated CO₂ had a phase change from polycrystalline
4.3 Pure NH$_3$ ice: electron irradiated ice system

Table 4.7 Summary of the thermal processing result from Chapter 3 and electron and thermal processing results of this chapter CO$_2$ ice.

<table>
<thead>
<tr>
<th></th>
<th>Thermally processed CO$_2$</th>
<th>Electron and thermally processed CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase change (K)</td>
<td>50–60</td>
<td>2140, 2050, 1040</td>
</tr>
<tr>
<td>Irradiation features (cm$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desorption of irradiation features (K)</td>
<td>80–90</td>
<td></td>
</tr>
<tr>
<td>Desorption of CO$_2$ (K)</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

to crystalline between 50–60 K, but no phase change was observed for the electron processed CO$_2$ ice. A summary of both thermally processed CO$_2$ and electron and thermally processed CO$_2$ is given in Table 4.7.

4.3 Pure NH$_3$ ice: electron irradiated ice system

The results of electron irradiation of pure NH$_3$ ice deposited at 20 K and subsequent thermal processing are presented in this section.

4.3.1 Electron irradiation at 20 K

Fig. 4.7 shows the electron irradiation of pure NH$_3$ ice with 1 keV electrons at several intervals cumulating in a total fluence of 3.37 $\times$ 10$^{15}$ e$^{-}$ cm$^{-2}$. Fig. 4.7 (i) shows the $\nu_3$, 2$\nu_4$ and $\nu_1$ vibrational modes, (iii) shows the $\nu_4 + \nu_L$, $\nu_4$ and $\nu_2$ vibrational modes. These vibrational modes decreased in intensity as fluence increased which was probably due to a combined sputtering and dissociation process. Fig. 4.7 (ii) shows the red wing of the $\nu_1$ vibrational mode where two new features were observed and the assignment is discussed below. Fig. 4.7 (iv) shows the red wing of the $\nu_2$ vibrational mode where an additional feature was observed and again the assignment is discussed below.

Discussion

The new bands associated with the electron irradiation of NH$_3$ were less distinct than the electron irradiation products of CO$_2$ as they appeared on the shoulders of the intense vibrational modes of pure NH$_3$. This makes it difficult to assign these IR peaks without first considering the possible reactions that may occur. NH$_3$ can dissociate into either an amino radical (NH$_2$) and a H atom (C 4.6) or, an imidogen radical (NH) and molecular hydrogen (H$_2$) (C 4.7).
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Fig. 4.7 Mid-IR spectra of pure NH$_3$ deposited at 20 K and irradiated with 1 keV electrons at several intervals for a total fluence of $3.37 \times 10^{16}$ e$^-$ cm$^{-2}$. (i) $\nu_3$, $2\nu_4$ and $\nu_1$ vibrational modes; (ii) new features between 3200–2400 cm$^{-1}$; (iii) $\nu_4 + \nu_L$ mode, $\nu_4$ and $\nu_2$ fundamental mode and (iv) NH$_2$. Dashed lines represent the new features associated with irradiation.
4.3 Pure NH₃ ice: electron irradiated ice system

$$\text{NH}_3 \xrightarrow{e^-} \text{NH}_2 + \text{H} \quad \text{(C 4.6)}$$

$$\text{NH}_3 \xrightarrow{e^-} \text{NH} + \text{H}_2 \quad \text{(C 4.7)}$$

According to the literature¹⁹⁹,¹³³ a vibrational mode due to NH₂ should be present near 1500 cm⁻¹ which was observed in Fig. 4.7 (iv). Martín-Doménech et al.¹³⁵ identify a peak near 3100 cm⁻¹ as the NH radical based off assignments by Rosengren & Pimentel.²⁰⁰ However, Rosengren & Pimentel actually assigned this peak to diimide (N₂H₂) which was also assigned as N₂H₂ by Zheng et al. via unreported theoretical calculations.²⁰¹ According to Zheng et al. N₂H₂ can be formed in a multi-step reaction. Two amino radicals can recombine to form internally excited hydrazine ([N₂H₄]*) (C 4.8) which can decompose into N₂H₂ and H₂ (C 4.9).

$$2\text{NH}_2 \rightarrow [\text{N}_2\text{H}_4] \cdot \quad \text{(C 4.8)}$$

$$[\text{N}_2\text{H}_4] \cdot \rightarrow \text{N}_2\text{H}_2 + \text{H}_2 \quad \text{(C 4.9)}$$

Zheng et al. observed a broad irradiation feature near 2800 cm⁻¹ similar to the feature observed in Fig. 4.7 (ii). They assigned this to isodiazene (H₂NN) based off a matrix isolation study of H₂NN by Sylwester & Dervan.²⁰² However, this assignment came from the irradiation of carbamoyl azide (CH₂N₄O) and the band near 2800 cm⁻¹ was not specifically identified as being due to isodiazene. Due to the ambiguity in the assignment of this mode in the literature, this peak will remain unassigned.

4.3.2 Thermal processing after electron processing at 20 K

After electron processing at 20 K, the NH₃ ice was thermally processed to desorption at 120 K. Fig. 4.8 (i) shows the ν₃, 2ν₄ and ν₁ modes, (iii) shows the ν₄ + ν₂ and ν₄ vibrational modes and (iv) ν₂ vibrational mode. All of these vibrational modes narrowed or split between 60–70 K indicating the onset of a phase change. Fig. 4.8 (ii) shows that the irradiation product at ~3030 cm⁻¹ desorbed between 60–70 K. Irradiation products at ~2800 and ~1500 cm⁻¹ desorbed by 120 K.

4.3.3 Comparison of the warm up of NH₃: unirradiated vs electron irradiated

A phase change was observed between 60—70 K for the electron processed NH₃ ice which was similar to the thermally processed NH₃ ice shown in Section 3.5. The ν₂ vibrational mode in the electron processed study had a different splitting pattern intensity compared with the
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**Fig. 4.8** Mid-IR spectra of pure NH$_3$ after electron irradiation with 1 keV electrons for a total fluence of \(3.37 \times 10^{15}\) e$^{-}$ cm$^{-2}$ at 20 K and subsequent thermal processing until desorption at 130 K. (i) \(\nu_3\), \(2\nu_4\) and \(\nu_1\) modes; (ii) new features between 3200–2400 cm$^{-1}$; (iii) \(\nu_4\) fundamental mode (iv) \(\nu_2\) fundamental mode. Dashed line represent the vibrational mode or irradiation feature at 20 K.

thermally processed study. A more pronounced shoulder was observed at 1117 cm$^{-1}$ in the electron processed spectra, along with a slight red shift for the 1096 cm$^{-1}$ feature. A larger red shift (~8 cm$^{-1}$) was observed for the 1077 cm$^{-1}$ feature and the intensity ratio between the 1077 and 1060 cm$^{-1}$ features reversed so that the feature at 1077 cm$^{-1}$ was more intense than the feature at 1060 cm$^{-1}$. This could either be the ‘random fluctuations’ described by Dawes et al.\(^{167}\) or an effect caused by the impact of electron irradiation on the structure of the ice. The electron processed NH$_3$ ice fully desorbed by 130 K about 10 K higher than that of thermally processed NH$_3$ ice. As the ice was only 10 nm thicker, this was not a thickness effect and therefore was probably a result of electron processing. A summary of the thermally processed and electron and thermally processed NH$_3$ ice is given in Table 4.8.
4.4 Mid-IR results of electron processed mixtures of CO$_2$:NH$_3$

**Table 4.8** Summary of the thermal processed results of NH$_3$ ice from Chapter 3 and electron and thermal processed results of NH$_3$ ice from this chapter.

<table>
<thead>
<tr>
<th></th>
<th>Thermal processing NH$_3$</th>
<th>Electron and thermal processing NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase change (K)</td>
<td>50–60</td>
<td>60–70</td>
</tr>
<tr>
<td>Irradiation features (cm$^{-1}$)</td>
<td>$\sim 3030$, $\sim 2800$, $\sim 1500$</td>
<td></td>
</tr>
<tr>
<td>Desorption of irradiation features (K)</td>
<td>70, 120, 120</td>
<td></td>
</tr>
<tr>
<td>Desorption (K)</td>
<td>120</td>
<td>130</td>
</tr>
</tbody>
</table>

4.4 Mid-IR results of electron processed mixtures of CO$_2$:NH$_3$

The results of electron irradiation of several different ratios of CO$_2$ and NH$_3$ mixtures deposited at 20 K and subsequent thermal processing are presented in this section.

4.4.1 Deposition at 20 K

The following ratios were studied in the electron irradiation ice experiments: 4:1, 2:1, 1:1, 1:2, 1:5, and 1:10. These ratios are close to but not exactly the same as the ratios used in the thermal processing study in Chapter 3 and this was due to practical difficulties during gas mixing. A 4:1 ratio was obtained for this electron processing study which was similar to the 3:1 ratio obtained in the thermal processing study in Chapter 3. Ratios of 1:2 and 1:5 obtained for this electron processing study were similar to the 1:3 ratio obtained in the control study shown in Chapter 3.

As the same general trends were observed in the ratios used in this chapter and for the thermal processing ratios used in Chapter 3, then no detailed description of the deposition spectra is required. The higher frequency vibrational mode of the CO$_2$:NH$_3$ molecular complex near 3415 cm$^{-1}$ was observed in the additional 4:1 and 1:2 ratio but not the additional 1:5 ratio. The lower frequency CO$_2$:NH$_3$ molecular complex near 3250 cm$^{-1}$ was observed in all additional ratios. Fig. B.5 shows deposition spectra of the CO$_2$:NH$_3$ mixtures at 20 K and the band assignments are shown in Table B.1.

4.4.2 Electron irradiation at 20 K

After deposition at 20 K, the CO$_2$:NH$_3$ mixtures were processed with 1 KeV electron at several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The exact intervals are given in Table A.5. Fig. 3.10 shows an example of the electron processing results of a mixture of CO$_2$:NH$_3$ in a 1:1 ratio. Several interesting changes have been highlighted and labelled and are summarised below.
Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a mid-IR spectroscopic study

(a) Decrease in intensity of the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes of CO$_2$ as the electron fluence increased.

(b) Formation of a shoulder on the blue wing of the $\nu_3$ mode of NH$_3$.

(c) Decrease in intensity of the $\nu_3$ vibrational modes of NH$_3$ as the electron fluence increased.

(d) Decrease in intensity of the $2\nu_4$ vibrational modes of NH$_3$ as the electron fluence increased.

(e) Decrease in intensity of the $\nu_1$ vibrational modes of NH$_3$ as the electron fluence increased.

(f) Formation of a shoulder on the red wing of the $\nu_3$ mode of NH$_3$.

(g) Formation of a feature near 2800 cm$^{-1}$.

(h) Formation of electron irradiation product OCN$^-$ at $\sim$2170 cm$^{-1}$.

(i) Formation of electron irradiation product CO at $\sim$2140 cm$^{-1}$.

(j) Formation of a C=O stretch at $\sim$1720 cm$^{-1}$.

(k) Formation of several new features within the region 1750–1250 cm$^{-1}$ at 1585, 1484, 1342, 1297 cm$^{-1}$.

The spectra of the other ratios can be found in Appendix B. Most of the ratios contained all the features which were labelled in Fig. 4.9 except for the following. The 1:10 ratio did not appear to contain labelled features (j) or (k) which were due to CO and a C=O stretch, respectively. The 4:1 ratio did not appear to contain labelled features (g) or (i) which were due to a broad peak forming near 2800 cm$^{-1}$ and OCN$^-$, respectively.

4.4.3 New absorption peaks between 1750–1250 cm$^{-1}$ formed during electron processing at 20 K

Several new features were observed between 1750–1250 cm$^{-1}$ during electron processing at 20 K for all ratios and are shown in Fig. 4.10 at a fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$ for comparison. Table 4.9 lists the positions of new features observed and gives some tentative assignments using the same method as described in Section 3.4.3.

Two C=O stretches were observed for all ratios except the 1:10 ratio but this may be due to the intense $\nu_4$ vibrational mode obscuring them. The observation of two C=O stretches may suggest that two types of molecules containing C=O stretches formed. The N–H bend was not observed in the 4:1 and 2:1 ratios and neither was the COO$^-$ asymmetric stretch. A broad
Fig. 4.9 Mid-IR spectra of an example irradiation with 1 keV electrons of a CO$_2$:NH$_3$ mixture in a 1:1 ratio for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$ with the top of the CO$_2$ $v_3$ mode cut off for clarity. Labels a–n are discussed in the text.
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![Graph showing mid-IR spectra of CO$_2$:NH$_3$ mixtures]  

**Fig. 4.10** Mid-IR spectra of CO$_2$:NH$_3$ mixtures irradiated with 1 keV electrons at a fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. Dashed lines represent the formation of new features. Spectra are normalised to a thickness of 300 nm and offset on the y-axis for clarity.

A feature that is tentatively identified as NH$_4^+$ was observed in all ratios as was the C–O stretch. The COO$^-$ symmetric stretch was identified in the ratios with excess NH$_3$ only (i.e. 1:2, 1:5, 1:10). An unassigned peak near 1340 cm$^{-1}$ was observed in all ratios. In addition, Table 4.9 lists the positions of an unassigned feature near 2239 cm$^{-1}$, OCN$^-$, CO and HCN.

**Discussion**

Previous studies of energetically processed CO$_2$:NH$_3$ ice mixtures have identified ammonium formate, (NH$_4^+$[HCOO$^-$])$^{94,143}$ ammonium carbamate$^{94,141–143}$ and carbamic acid$^{94,141,143}$ as products which formed during energetic processing at low temperatures (< 30 K).

The formation of ammonium formate was proposed by Bossa *et al.* to form from several reactions.$^{94}$ First, formic acid (HCOOH) was formed when H atoms (formed during the dissociation of NH$_3$ e.g. C 4.6 and C 4.7) reacted with a CO$_2$ molecule (C 4.10). Proton transfer between HCOOH and NH$_3$ could then form ammonium formate (C 4.11).

$$\text{CO}_2 + 2\text{H} \rightarrow \text{HCOOH} \quad \text{(C 4.10)}$$

$$\text{HCOOH} + \text{NH}_3 \rightarrow \text{NH}_4^+\text{HCOO}^- \quad \text{(C 4.11)}$$
4.4 Mid-IR results of electron processed mixtures of CO$_2$::NH$_3$

Table 4.9 Summary of the new peaks formed between 1750–1250 cm$^{-1}$ after the CO$_2$::NH$_3$ ice mixture was irradiated with 1 keV electrons for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Ratio 4:1</th>
<th>Ratio 2:1</th>
<th>Ratio 1:1</th>
<th>Ratio 1:2</th>
<th>Ratio 1:5</th>
<th>Ratio 1:10</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCN$^-$</td>
<td>2239</td>
<td>2238</td>
<td>2239</td>
<td>2242</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2169</td>
<td>2168</td>
<td>2170</td>
<td>2168</td>
<td>2163</td>
<td>2159</td>
</tr>
<tr>
<td>HCN</td>
<td>2141</td>
<td>2140</td>
<td>2140</td>
<td>2140</td>
<td>2140</td>
<td>2138</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>2090</td>
<td>2092</td>
<td>2092</td>
<td>2091</td>
<td>2096</td>
<td>2091</td>
</tr>
<tr>
<td>N-H bend</td>
<td>1723</td>
<td>1716</td>
<td>1718</td>
<td>1715$^{sh}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COO$^-$ asym. stretch</td>
<td>1692$^{sh}$</td>
<td>1693$^{sh}$</td>
<td>1690</td>
<td>1690</td>
<td>1692$^{sh}$</td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1584$^{sh}$</td>
<td>1589$^{sh}$</td>
<td>1582</td>
<td>1582</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COO$^-$</td>
<td>1487</td>
<td>1481</td>
<td>1483</td>
<td>1502</td>
<td>1503</td>
<td>1500</td>
</tr>
<tr>
<td>C-O stretch</td>
<td>1342</td>
<td>1348</td>
<td>1341</td>
<td>1340</td>
<td>1343</td>
<td>1342</td>
</tr>
<tr>
<td></td>
<td>1303</td>
<td>1303</td>
<td>1305</td>
<td>1302</td>
<td>1298</td>
<td></td>
</tr>
</tbody>
</table>

Bossa et al. did not observe formic acid and suggested that this was due to the rapid proton transfer observed in C 4.11. The presence of two C=O stretches in Fig. 4.10 suggested that two types of molecules have formed with C=O stretches. One of these C=O stretches could be due to formic acid. In order to form ammonium formate, more NH$_3$ molecules were required than CO$_2$ molecules. This might explain why no C=O stretches were observed in the 1:10 ratio. If carbamic acid was formed immediately after electron processing, then it would also be expected that ammonium carbamate would form in a proton transfer reaction (C 4.12) in NH$_3$ dominated mixtures.

\[
\text{H}_2\text{NCOOH} + \text{NH}_3 \longrightarrow \text{NH}_4^+\text{NH}_2\text{COO}^-(C 4.12)
\]

Again, the 4:1 and 2:1 ratios as shown Fig. 4.10 have no COO$^-$ stretches suggesting that ammonium carbamate or ammonium formate do not form after electron irradiation at 20 K. However, both ratios do have NH$_4^+$ stretches which might be due to NH$_4^+$ formed alongside OCN$^-$. The formation of carbamic acid was proposed by Bossa et al. as a reaction between a H atom and CO$_2$ which formed COOH (C 4.13). COOH could then react with NH$_2$ to form carbamic acid (C 4.14).

\[
\text{CO}_2 + \text{H} \longrightarrow \text{COOH} (C 4.13)
\]

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$$\text{COOH} + \text{NH}_2 \rightarrow \text{H}_2\text{NCOOH} \quad (\text{C}4.14)$$

While it is very difficult to assign molecules from the Fig. 4.10 due to overlapping features the proposed mechanisms for ammonium formate (C 4.11) and ammonium carbamate (C 4.12) may explain why COO$^-$ stretches were observed in the ratios with higher amounts of NH$_3$ (i.e. 1:2, 1:3 & 1:5). To form both ammonium formate and ammonium carbamate in reactions C 4.11 and C 4.12, respectively, more NH$_3$ molecules are required compared to the formation of the respective acid. The presence of two C=O stretches may be due to formic acid and carbamic acid and these C=O stretches were stronger in ratios which were more CO$_2$ rich (i.e. 4:1, 2:1 and 1:1). These CO$_2$ rich ratios were also the ratios in which the COO$^-$ stretches were either absent or very weak.

Regardless of the tentative assignments of these peaks at 20 K there is a clear difference between the 4:1 and 1:10 ratios demonstrating that the deposition mixing ratio influences the formation of products which form from electron processing of CO$_2$:NH$_3$ mixtures at 20 K.

### 4.4.4 Formation of CO and OCN$^-$ during electron processing at 20 K

Fig. 4.11 shows the mid-IR spectra of OCN$^-$ and CO absorption features at a fluence of (i) $1.12 \times 10^{15}$, (ii) $2.25 \times 10^{15}$ and (iii) $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. There is a clear dependence on the
deposition mixing ratio of the CO$_2$:NH$_3$ ice and the amount of CO and OCN$^-$ formed. This ratio dependence is better viewed as growth curves. However, as the CO and OCN$^-$ absorption features overlapped it was difficult to obtain the peak area for each molecule. The purpose of the growth curves of CO and OCN$^-$ was to get a relative comparison between the ratios and so a simple approach was taken in order to calculate the peak areas of CO and OCN$^-$ and is described below.

**Growth curves**

![Growth curves diagram](image)

**Fig. 4.12** Example integration area of CO and OCN$^-$ for a 1:2 ratio at a fluence of $2.25 \times 10^{15}$ e$^{-}$ cm$^{-2}$. The total integration area is between 2120–2220 cm$^{-1}$.

Fig. 4.12 shows the formation of OCN$^-$ and CO from a 1:2 CO$_2$:NH$_3$ interstellar ice analogue at a fluence of $2.25 \times 10^{15}$ e$^{-}$ cm$^{-2}$. CO and OCN$^-$ overlap and need to be separated to find the areas of the CO peak and OCN$^-$ peak. While Gaussian functions can be fitted to the CO and OCN$^-$ peaks, as the purpose of the growth curves of CO and OCN$^-$ was to get a relative comparison a simpler, quicker approach is taken.

All the CO$_2$:NH$_3$ mixtures were integrated between 2120–2220 cm$^{-1}$ to obtain an overall area of the CO and OCN$^-$ peaks. A mid-point of the overlapping CO and OCN$^-$ features was identified as shown in Fig. 4.12 and depended on the ratio and electron fluence. For the 1:2 ratio at a fluence of $2.25 \times 10^{15}$ e$^{-}$ cm$^{-2}$ shown in Fig. 4.12 this mid-point was at 2150 cm$^{-1}$. The area of the peak between 2120–2150 cm$^{-1}$ was calculated and taken as the peak area of CO. The peak area between 2150–2220 cm$^{-1}$ was calculated and taken as the peak area of OCN$^-$. In order to check the validity of this approach Gaussian functions were fitted to the CO and OCN$^-$ peaks of the 1:2 CO$_2$:NH$_3$ interstellar ice analogue at a fluence of $2.25 \times 10^{15}$ e$^{-}$ cm$^{-2}$. The CO area determined by the Gaussian function was 0.0738 cm$^{-2}$ and the CO area determined by the simple approach was 0.090 cm$^{-2}$. The OCN$^-$ area determined by the
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Gaussian function was 0.180 cm$^{-2}$ and the OCN$^-$ area determined by the simple approach was 0.176 cm$^{-2}$. While the simple approach does overestimate the CO area it will be a systematic error for all CO areas and as only a relative comparison is required the simple approach is used.

Fig. 4.13 shows the growth curve of CO for all ratios which were processed with 1 keV electrons to a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The 4:1, 2:1 and 1:1 ratios were fitted with the same two-phase first order kinetic equations (Eq. 4.4) used in Section 4.2 for pure CO$_2$ ice. The 1:5 and 1:10 ratios were best fitted with just one first order rate equation (Eq. 4.2). The highest amount of CO was observed in the 4:1 ratio which is the ratio with the most CO$_2$. The 1:10 ratio formed the least amount of CO and is also the ratio with the least CO$_2$. As CO forms from the direct dissociation of CO$_2$, this ratio dependence was expected.

Fig. 4.14 shows the growth curves of OCN$^-$ for all ratios which were processed with 1 keV electrons to a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. All ratios were best fitted with just one first order rate equation (4.2). The highest amount of OCN$^-$ was observed in the 1:5 ratio and the lowest amount of OCN$^-$ was formed in the 4:1 ratio. This suggests a more complex formation mechanism is associated with the formation of OCN$^-$ which is discussed below.
4.4 Mid-IR results of electron processed mixtures of CO$_2$::NH$_3$

**Fig. 4.14** Growth curves of OCN$^-$ for ratios 4:1, 2:1, 1:1, 1:2, 1:5 and 1:10. The fits were obtained using equation 4.2 for all ratios. Curves are normalised to thickness of 300 nm.

**Discussion**

CO forms directly from the dissociation of CO$_2$ upon energetic processing with electrons (C 4.1). Whereas the formation of OCN$^-$ involves several steps$^{94,142}$. CO, formed from the dissociation of CO$_2$, can recombine with an NH$_2$ radical which was formed in C 4.6 to form isocyanic acid (HNCO) (C 4.15) which can then undergo a proton transfer reaction with NH$_3$ to form OCN$^-$ and NH$_4^+$ (C 4.16).

\[
\text{NH}_2 + \text{CO} \rightarrow \text{HNCO} + \text{H} \quad \text{(C 4.15)}
\]

\[
\text{HNCO} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{OCN}^- \quad \text{(C 4.16)}
\]

The highest amount of OCN$^-$ was observed for the 1:5 ratio followed by the 2:1 and then the 1:10 ratio. This is a real effect and not an observed effect caused by normalisation of the growth curves. To form OCN$^-$, two molecules of NH$_3$ to every one molecule of CO is required. Therefore, it is expected that the 4:1 ratio would produce little OCN$^-$ as would the 2:1 ratio. Very little CO was formed for 1:10 ratio which may explain why less OCN$^-$ was formed. However, why the 1:5 ratio was favoured over the 1:2 for forming the most OCN$^-$ is unknown.
As previously observed in Fig. 4.11 the position of OCN$^-$ shifted depending on the CO$_2$:NH$_3$ mixture and so each mid-point was individual to the mixing ratio. Fig. 4.15 shows the position of OCN$^-$ as a function of the mixing ratio. The OCN$^-$ position shifted to lower wavenumbers when the environment it formed in was more polar (i.e. a higher amount of NH$_3$ present within the ratio).

4.4.5 Thermal processing after electron processing at 20 K

After electron processing at 20 K, the CO$_2$:NH$_3$ mixtures were thermally processed at intervals which are given in Table A.5. Fig. 4.16 shows an example of the thermal processing results of a mixture of CO$_2$:NH$_3$ in a 1:1 ratio which was processed with 1 keV electrons at 20 K. Several interesting changes have been highlighted and labelled and are described below:

(a) The $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes of CO$_2$ narrowed and blue shifted between 60–70 K.

(b) The $\nu_2$ vibrational mode of NH$_3$ split between 60–70 K.

(c) The irradiation features highlighted in Fig. 4.9 as labels (k) and (l), resolved and increased in intensity above 90 K.

(d) The CO peak area decreased as the temperature increased until desorption between 130–150 K. Whereas, the OCN$^-$ peak area increased until it reached a maximum $\sim$130 K and then decreased until desorption between 248–296 K.
4.4 Mid-IR results of electron processed mixtures of CO$_2$ and NH$_3$.

Fig. 4.16 Mid-IR spectra of an example thermal processing of a 1:1 CO$_2$:NH$_3$ mixture after electron irradiation for a total electron fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$ at 20 K with the top of the CO$_2$ $v_3$ mode cut off for clarity. Boxes labelled (a)–(e) are discussed in the text.
A change in the residue spectra occurred between 150–200 K.

The thermal processing spectra for the other ratios can be found in Appendix B where they are all labelled (a)–(e). For the different CO$_2$:NH$_3$ ratios, the changes which are labelled (a)–(e) were observed at different temperatures and are summarised in Table 3.3, as well as the desorption temperatures of CO$_2$, NH$_3$, CO, and OCN$^-$, and the disappearance of the CO$_2$:NH$_3$ molecular complex.

Fig. 4.17 shows the peak areas of CO and OCN$^-$ as a function of temperature during the warm up of the CO$_2$:NH$_3$ mixtures after electron irradiation at 20 K. From Fig. 4.17 in all ratios the peak area of OCN$^-$ increased during the warm up of the ice mixtures before desorption at 300 K, whereas, the peak area of CO decreased as the temperature increased. The mechanism behind the increase in OCN$^-$ is discussed below.

**Discussion**

This section is split into the following: (i) Segregation and ice structure of CO$_2$, (ii) Ice structure of NH$_3$ and (iii) Effects of thermal processing on OCN$^-$. 

(i) **Segregation and ice structure of CO$_2$**: A narrowing and blue shift in the position of the CO$_2$ vibrational modes for all ratios was observed between 40–80 K. This was attributed to the CO$_2$ segregation which was also observed in the thermal processing study presented in Section 3.4.2. Again further evidence of this segregation was found upon closer inspection of the LO-TO splitting of the $\nu_3$ mode of CO$_2$ at 80 K. Fig. 4.18 shows the LO-TO splitting in the ice mixtures at 80 K. The two grey shaded areas in Fig. 4.18 represent the range in peak positions of the LO and TO modes of the mixtures at 20 K. The LO and TO phonons in the 4:1, 2:1 & 1:1 ratios blue shifted towards the LO and TO phonon position of pure CO$_2$ ice. The LO and TO phonons in these ratios also narrowed in agreement with the peak profiles of pure CO$_2$.

Fig. 3.12 shows the LO-TO splitting of the 1:2, 1:5 and 1:10 ratios. At 20 K no splitting was observed in the 1:10 ratio and the LO mode appears as a shoulder on the TO mode for the 1:2 and 1:5 ratios. This was due to the thorough mixing of CO$_2$ and NH$_3$ which disrupted the crystal lattice of CO$_2$ as discussed in Section 3.4.1. As the temperature increased, splitting within the LO modes of the 1:2, 1:5 and 1:10 ratios suggested that when CO$_2$ and NH$_3$ segregated it changed phase. The same argument as used for the thermal processing results in Section 3.4.2 can be applied for the 1:2, 1:5 and 1:10 ratio where NH$_3$ is in excess, CO$_2$ can be viewed as a defect within an NH$_3$ ice. Whereas, for 4:1 and 2:1 ratios, the NH$_3$ can be viewed as the defect within the CO$_2$ ice. Similar to the thermal processing study in Section 3.4.2, the mixtures where NH$_3$ is a defect in the CO$_2$ ice (i.e. 4:1, 2:1) and the 1:1 ratio retained some degree of a polycrystalline form. Whereas, in the mixtures where the CO$_2$ is a defect in the
4.4 Mid-IR results of electron processed mixtures of CO$_2$:NH$_3$

Fig. 4.17 Thermal growth curves of CO and OCN$^-$ peak area against temperature during the thermal processing of the electron irradiated CO$_2$:NH$_3$ ice mixtures. Lines connecting the scatter points are for guidance only. Curves are normalised to thickness of 300 nm.

NH$_3$ ice (i.e. 1:2, 1:5 and 1:10), the absence of the LO mode suggests that the CO$_2$ does not retain a polycrystalline instead having a non-crystalline form.

For the 1:2, 1:5 and 1:10 ratios the segregated CO$_2$ ice also appeared to undergo a phase change from a non-crystalline structure to polycrystalline or crystalline structure. For the other ratios, a polycrystalline form of CO$_2$ was already observed upon deposition at 20 K. These results are similar to the thermal processing study presented in Section 3.2 which depicted the segregation and ice structure behaviour in Fig. 3.13.

(ii) Ice structure of NH$_3$: Again, the NH$_3$ $\nu_3$ mode revealed the difference in the phase of NH$_3$ between the ratios. This is shown in Fig. 4.19 which shows the $\nu_3$ vibrational mode of NH$_3$ in the CO$_2$:NH$_3$ mixtures compared with pure NH$_3$ ice. The 1:10, 1:5 and 1:2 ratios
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![Fig. 4.18 Mid-IR spectra of the CO$_2$ LO and TO $\nu_3$ modes of the CO$_2$:NH$_3$ mixtures at 80 K compared with pure CO$_2$. The grey boxes represent the range of the LO and TO modes of the mixtures at 20 K to show the shift in the LO and TO modes at 80 K. Spectra are offset for clarity on the y-axis and normalised to a thickness of 300 nm.](image)

showed a polycrystalline structure with small crystallites of similar sizes, which is similar to the thermal processing mixtures which were shown in Fig. 3.11. The lack of splitting in the 1:1, 2:1 and 4:1 ratios corresponded to an increase in structural order of NH$_3$ and followed the same trend as the thermally processed mixtures where, ratios with more CO$_2$ had a more ordered NH$_3$ ice. This was attributed to a less extensive H-bonding network which formed between the NH$_3$ molecules in the mixtures compared to pure NH$_3$ ice, which was even less in mixtures where CO$_2$ was in excess. Steric hindrance was lowered and so when the CO$_2$ ice segregated out of the NH$_3$ ice, a more ordered form of NH$_3$ was observed.

(iii) Effects of thermal processing on OCN$^-$: The peak areas of OCN$^-$ for all the ratios shown in Fig. 4.17 increased as the temperature was increased. The formation of OCN$^-$ during electron irradiation at 20 K was suggested to have occurred via proton transfer between NH$_3$ and isocyanic acid (C 4.15). Previous studies which have investigated the formation of OCN$^-$ via thermal processing of HNCO and NH$_3$ have also proposed this mechanism. These studies noted that at low temperatures (< 20 K) the formation of OCN$^-$ was initiated by kinetic energy formed from the deposition of the ice mixture. The reaction which occurred
4.4 Mid-IR results of electron processed mixtures of CO$_2$:NH$_3$

![Graph showing mid-IR results of electron processed mixtures of CO$_2$:NH$_3$.](image)

**Fig. 4.19** Mid-IR spectra of NH$_3$ $\nu_2$ mode in the CO$_2$:NH$_3$ mixtures deposited and electron processed at 20 K, and thermally processed to 80 K compared with pure NH$_3$. Spectra are offset on the y-axis for clarity and normalised to a thickness of 300 nm.

During thermal processing of the ice mixture was attributed to the increased mobility of the NH$_3$ molecules. Therefore, the increase in peak area of OCN$^-$ was expected.

### 4.4.6 Residue spectra after electron irradiation at 20 K and warmed to 150 and 200 K.

Fig. 4.20 shows the residue material for the electron and thermal processed CO$_2$:NH$_3$ mixtures at 150 and 200 K. The same method described in Section 3.4.3 for assigning the mid-IR spectra was used in the assignment of the irradiated mixtures at 150 and 200 K. The assignments for Fig. 4.20 are given in Table 4.11.

Except for the 4:1 ratio, the residue spectra of all the other ratios at 150 K have COO$^-$ and C–O stretches indicating that both ammonium carbamate and carbamic acid were present. The same residues are observed at 200K except for the 4:1. Except for the 4:1 ratio, the residue spectra of all the other ratios at 200 K have COO$^-$ and C=O stretches indicating that both ammonium carbamate and carbamic acid were present.

The residue spectra at 150 K for the 4:1 ratio was significantly less than the other ratios and was scaled $\times$3. The 4:1 ratio also had a different spectra profile compared to the other ratios. For example, the N–H asymmetric stretch near 3451 cm$^{-1}$ was not observed. In addition,
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Table 4.10 Summary of the thermal processing of CO$_2$:NH$_3$ ice mixtures which were previously irradiated with 1 keV electrons at 20 K for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$

<table>
<thead>
<tr>
<th></th>
<th>4:1</th>
<th>2:1</th>
<th>1:1</th>
<th>1:2</th>
<th>1:5</th>
<th>1:10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CO$_2$ segregation (K)</td>
<td>30–40</td>
<td>50–60</td>
<td>60–70</td>
<td>60–70</td>
<td>70–80</td>
<td>70–80</td>
</tr>
<tr>
<td>(b) NH$_3$ crystallites (K)</td>
<td>30–40</td>
<td>60–70</td>
<td>60–70</td>
<td>70–80</td>
<td>70–80</td>
<td>70–80</td>
</tr>
<tr>
<td>(c) New bands (K)</td>
<td>&gt;90</td>
<td>&gt;90</td>
<td>&gt;90</td>
<td>&gt;90</td>
<td>&gt;90</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Disappearance of CO$_2$:NH$_3$ complex (K)</td>
<td>60–70</td>
<td>60–70</td>
<td>60–70</td>
<td>70–80</td>
<td>70–80</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ desorbs (K)</td>
<td>90–100</td>
<td>131–150</td>
<td>130–150</td>
<td>130–150</td>
<td>130–150</td>
<td>130–150</td>
</tr>
<tr>
<td>NH$_3$ desorbs (K)</td>
<td>90–100</td>
<td>100–110</td>
<td>110–120</td>
<td>110–120</td>
<td>130–150</td>
<td>130–150</td>
</tr>
<tr>
<td>CO desorbs (K)</td>
<td>90–100</td>
<td>131–150</td>
<td>130–150</td>
<td>130–150</td>
<td>80–90</td>
<td>80–90</td>
</tr>
</tbody>
</table>

the strong COO$^-$ symmetric stretch feature, which was observed in all the other ratios as a resolved feature, was only observed as a shoulder in the 4:1 ratio.

Again the residue spectra at 200 K was similar for all ratios, except the 4:1 ratio. The 4:1 ratio was repeated to ensure that this was not an anomalous result. Except in the 4:1 ratio, the N–H asymmetric stretch near 3451 cm$^{-1}$ resolved upon thermal processing from 150 to 200 K in all ratios. The C–O stretch near 1700 cm$^{-1}$ increased in intensity and a C–O stretch appeared. The NH$_4^+$ mode near 1490 cm$^{-1}$ decreased and an O–H bend appeared near 1470 cm$^{-1}$. For the 4:1 ratio at 200 K, the N–H bend increased in intensity, the COO$^-$ asymmetric stretch disappeared and the C–O stretch appeared.

4.5 Discussion

From Section 4.4.6, ammonium carbamate and carbamic acid were identified at 150 K for all ratios except for the 4:1 ratio. The formation of carbamic acid increased upon warming to 200 K which was observed through the growth of C=O and C–O stretches in all ratios including the 4:1 ratio. A corresponding decrease in the COO$^-$ stretches was also observed. This trend is similar to the thermally processed ice mixtures which were discussed in Section 3.4.3. One difference between the thermal processing results of Section 3.4.3 and the electron and thermal processing results presented here was the observation of a residue in the irradiated 4:1 ratio. No residue was observed for the thermally processed 3:1 ratio which was in agreement with the literature study by Noble et al.$^{95}$
Fig. 4.20 Mid-IR spectra of CO$_2$:NH$_3$ ices after electron irradiation at 20 K and warmed to 150 K (black traces) and 200 K (coloured traces). Key vibrational modes are labelled. The spectra are offset on the y-axis for clarity and normalised to a thickness of 300 nm.
### Table 4.11 Mid-IR band assignments of the vibrational modes of CO$_2$:NH$_3$ ices which have been irradiated with electrons at 20 K and then thermally processed to 150 and 200 K.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>CO$_2$:NH$_3$ at 150 K</th>
<th>CO$_2$:NH$_3$ at 200 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4:1  2:1  1:1  1:2  1:5  1:10</td>
<td>4:1  2:1  1:1  1:2  1:5  1:10</td>
</tr>
<tr>
<td>N – H asym stretch</td>
<td>3451$^{sh}$ 3428$^{sh}$ 3428$^{sh}$ 3435$^{sh}$ 3452$^{sh}$</td>
<td>3430 3452 3435 3429 3439</td>
</tr>
<tr>
<td>N – H sym stretch</td>
<td>3375$^{sh}$ 3322 3321 3332 3378 3378</td>
<td>3322 3324 3224 3330 3328</td>
</tr>
<tr>
<td></td>
<td>3214 3219 3215 3217 3218 3218</td>
<td>3212 3212 3210 3214 3216 3216</td>
</tr>
<tr>
<td></td>
<td>3064 3045 3045 3038 3038 3041</td>
<td>3020 3026 3030 3030 3031 3031</td>
</tr>
<tr>
<td>O – H stretch</td>
<td>2905$^{sh}$ 2858 2872 2870 2848 2843 2892$^{sh}$ 2874 2857 2859 2844 2875</td>
<td>2276 2215$^{sh}$ 2163</td>
</tr>
<tr>
<td>OCN$^-$</td>
<td>2169 2168 2168 2167 2164 2163</td>
<td>2168 2167 2167 2165 2164 1935</td>
</tr>
<tr>
<td></td>
<td>1919 1944 1931 1951 2017</td>
<td>1882 1926 1902 1917 1947</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>1701$^{sh}$ 1705 1692 1696 1696 1695 1692 1704 1692 1696 1697 1690</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1683 1634</td>
<td>1684 1632</td>
</tr>
<tr>
<td>N – H bend</td>
<td>1622 1621 1620 1627 1626 1613 1631 1620 1618 1622</td>
<td>1471 1475 1467 1471 1487 1483</td>
</tr>
<tr>
<td>COO$^-$ sym stretch</td>
<td>1583$^{sh}$ 1550 1548 1547 1548</td>
<td>1578 1548 1547 1546 1547</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1490 1490 1491 1500 1497</td>
<td>1471 1475 1467 1471 1487 1483</td>
</tr>
<tr>
<td>O – H bend</td>
<td></td>
<td>1448</td>
</tr>
<tr>
<td>COO$^-$ asym stretch</td>
<td>1371 1397 1394 1397 1396 1399</td>
<td>1331 1296$^{sh}$ 1291$^{sh}$ 1310$^{sh}$ 1307$^{sh}$ 1312$^{sh}$</td>
</tr>
<tr>
<td>C – O stretch$^*$</td>
<td>1120 1113 1116 1117 1117 1117 1122 1114 1115 1116 1118 1117</td>
<td></td>
</tr>
<tr>
<td>C – N stretch</td>
<td>1040 1037 1036 1036 1036 1040 1033 1034 1035 1039</td>
<td>830 828 829 829 829 827</td>
</tr>
</tbody>
</table>

* C – N stretch
4.5 Discussion

In previous CO$_2$:NH$_3$ studies summarised in Table 4.1, Bossa et al.,$^{94}$ Bertin et al.,$^{141}$ Jheeta et al.$^{142}$ and Lv et al.$^{143}$ studied the energetic processing of CO$_2$:NH$_3$ ices. As residue mid-IR spectra from the energetic processing of the CO$_2$:NH$_3$ ice mixtures was only shown in Bossa et al. and Jheeta et al. then only a comparison can be made with these two studies.

Jheeta et al. irradiated a 1:1 CO$_2$:NH$_3$ ice with 1 keV electrons at 30 K for a total fluence of 4.6 \times 10^{17}$ e$^{-}\text{cm}^{-2}$. The 1:1 ratio at 150 and 200 K and the 4:1 ratio at 200 K are compared against Jheeta et al. results at 254 K in Fig. 4.21. The dashed line at at 1700 cm$^{-1}$ represents the C=O stretch which is an indicator of carbamic acid. It is clear that the C=O stretch was present in mid-IR spectra obtained from the study by Jheeta et al., but no mention or assignment of carbamic acid was made in their study. The electron and thermally processed 1:1 ratio at 200 K from this chapter was in agreement with Jheeta et al., but the 4:1 ratio was not in agreement. In the study by Jheeta et al., they compared their results against Frasco unirradiated spectra (Type 1)$^{162}$ even though the study by Frasco had not been energetically processed. Similar results were obtained which suggests a thermally induced reaction pathway is still responsible for the formation of ammonium carbamate and carbamic acid from energetic and thermal processed ices.

![Mid-IR spectra of CO$_2$:NH$_3$ mixture in a 1:1 ratio at 150 K (blue) and 200 K (turquoise) and 4:1 at 150 K (green) and 200 K (purple) compared with Jheeta et al. results (black)$^{142}$. Spectra are offset for clarity and normalised to 300 nm. Jheeta et al. traces were arbitrarily scaled for best comparison.](image)

Fig. 4.21 Mid-IR spectra of CO$_2$:NH$_3$ mixture in a 1:1 ratio at 150 K (blue) and 200 K (turquoise) and 4:1 at 150 K (green) and 200 K (purple) compared with Jheeta et al. results (black)$^{142}$. Spectra are offset for clarity and normalised to 300 nm. Jheeta et al. traces were arbitrarily scaled for best comparison.

The lack of the strong COO$^{-}$ stretches present in the 4:1 ratio suggested that ammonium carbamate, if it was present was only present in trace amounts. Therefore a comparison of Bossa et al. carbamic acid dimer spectrum was made with the 4:1 ratio at 150 and 200 K in Fig.
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4.22. While similarities existed between the spectra it is not enough to confirm carbamic acid. For example, the N-H asymmetric stretch near 3500 cm$^{-1}$ was present in Bossa et al results, but was missing in the 4:1 ratio at both 150 and 200 K. Additionally, the 4:1 ratio at 150 K did not appear to have the strong C=O stretch.

![Fig. 4.22 Mid-IR spectra of CO$_2$:NH$_3$ mixture in a 4:1 ratio at 150 K (dark blue) and 200 K (turquoise) compared with Bossa et al. carbamic acid dimer spectra (light blue). Spectra are offset for clarity and normalised to a thickness 300 nm. The Frasco Type 1 and Type 2 traces were arbitrarily scaled for best comparison.](#)

Fig. 4.23 shows the comparison of the thermally processed and electron and thermally processed spectra of the 2:1, 1:1 and 1:10 ratios at 150 K. Apart from the presence of OCN$^-$ in the electron processed ratios, the 1:1 and 1:10 ratios were similar in both appearance and intensity. Although it is noted that the irradiated 1:1 ratio had a more pronounced C–O stretch. The thermal processed 2:1 ratio was much less intense than the electron processed 2:1 ratio, with the spectra of the thermal processed 2:1 mixture shown as a ×5 zoom in Fig. 4.23. Therefore, the formation of ammonium carbamate and carbamic acid in the 1:1 and 1:10 ratios had a similar formation mechanism producing similar amounts of the products regardless of whether it was electron processed. On the other hand, electron processing appeared to be significant in the 2:1 ratio in terms of intensity. This may be due to the fact that the desorption temperature of CO$_2$ in the electron processed mixture was between 130–150 K, almost twice as high as the thermal processed system. This suggests that the mechanism governing the formation of ammonium carbamate and carbamic acid at 150 K is still a thermal processing mechanism rather than an electron induced mechanism. However, electron processing of the
Fig. 4.23 Comparison of the thermal processed and electron and thermal processed CO$_2$:NH$_3$ 2:1, 1:1 and 1:10 ratios at 150 K. $u$ refers to the unirradiated mixture (black traces) and $i$ refers to the irradiated mixture (coloured traces). Spectra are offset for clarity and normalised to a thickness 300 nm.

CO$_2$:NH$_3$ ice mixtures appeared to entrap CO$_2$ to a much higher temperature than observed in the thermally processed system which allowed more product to be formed.

Fig. 4.24 shows the comparison of the thermally processed and electron and thermal processed spectra of the 2:1, 1:1 and 1:10 ratios at 200 K. For the 1:10 ratio the mid-IR spectra for both the thermally processed and electron and thermal processed residues were similar in appearance and intensity apart from the presence of OCN$^-$ in the electron processed ratios. The C=O and C–O stretches were less intense in the electron and thermally processed ice. This suggested that carbamic acid formation at higher temperatures was not as efficient in the electron and thermal processed ice. There is also a clear difference in the 1:1 and 2:1 thermally processed and electron and thermal processed residues. Again, features associated with carbamic acid are not as intense in the electron processed residues. In fact, the thermally processed 1:1 and 2:1 ratios showed evidence of conversion of ammonium carbamate to carbamic acid, whereas, the electron and thermal processed 1:1 and 2:1 ratios did not. It could be that this conversion happened at higher temperatures therefore this was investigated in Fig. 4.25. However, this does not appear to be the case and the COO$^-$ stretches of ammonium carbamate were still present at 250 K.

The conversion of ammonium carbamate to carbamic acid at higher temperatures was essentially a decomposition of ammonium carbamate into carbamic acid and a NH$_3$ molecule. When the equilibrium was disrupted at higher temperatures then the formation of carbamic acid occurred. Therefore, something in the electron and thermal processed system was stabilising...
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Fig. 4.24 Comparison of the unirradiated and irradiated CO\textsubscript{2}:NH\textsubscript{3} 2:1, 1:1 and 1:10 ratios at 200 K. \textit{u} refers to the unirradiated mixture (black traces) and \textit{i} refers to the irradiated mixture (coloured traces). Spectra are offset for clarity and normalised to a thickness of 300 nm.

the ammonium carbamate. The only obvious difference is the presence of OCN\textsuperscript{−} in the electron and thermal processed ratios. However, whether this prevents the formation of carbamic acid is not known.

4.6 Summary

A systematic investigation of the electron and thermal processing of CO\textsubscript{2}:NH\textsubscript{3} interstellar ice analogues as a function of deposition mixing ratio using mid-IR spectroscopy was presented in this chapter and the results are summarised below:

- CO\textsubscript{2}:NH\textsubscript{3} molecular complexes were formed upon deposition at 20 K for all ratios except the 1:10.
- Formation of new peaks were observed in all ratios after irradiation with electrons. While the identification of the new peaks was difficult to make, there was a clear difference in the 4:1 and 1:10 spectra suggesting that the molecules formed were dependent on the initial mixing ratio.
- The amount of CO and OCN\textsuperscript{−} was dependent of the initial mixing ratio with the 4:1 ratio having the highest amount of CO and the 1:5 ratio having the highest amount of OCN\textsuperscript{−}.
Fig. 4.25 Comparison of the unirradiated and irradiated CO$_2$:NH$_3$ 2:1, 1:1 and 1:10 ratios at 250 K. $u$ refers to the unirradiated mixture (black traces) and $i$ refers to the irradiated mixture (coloured traces). Spectra are offset for clarity and normalised to a thickness of 300 nm.

- Upon warming, CO$_2$ segregated from the NH$_3$ between 30–80 K depending on the ratio. No crystallisation of the CO$_2$ was observed in the 4:1, 2:1 and 1:1 ratios, but was observed in the 1:2, 1:5 and 1:10 ratios at 80 K.

- The crystallisation of NH$_3$ in the mixtures was more ordered than compared with pure NH$_3$, which was attributed to a less extensive H-bonding network within the mixtures. Ratios with higher amounts of CO$_2$ (i.e. 4:1 and 2:1) had a more ordered, cubic crystalline form of NH$_3$ compared to mixtures with lower amounts of CO$_2$ (i.e. 1:2, 1:5 and 1:10) which had a polycrystalline form with crystallites of similar sizes.

- At 150 K, all ratios except 4:1 contained ammonium carbamate and carbamic acid. At 200 K, all ratios except 4:1 showed evidence of ammonium carbamate converting to carbamic acid.

- For all ratios except the 4:1 ratio, CO$_2$ desorbed between 130–150 K which was higher than the unirradiated CO$_2$.

- For all ratios, except the 4:1 ratio, ammonium carbamate and carbamic acid were present at 150 K.

- For all ratios, except the 4:1 ratio, conversion of ammonium carbamate to carbamic acid between 150–200 K was not observed, unlike the thermally processed mixtures.
For all ratios OCN$^-$ desorbed when the residue desorbed.

The 4:1 ratio at 150 and 200 K is clearly different to the rest of the ratios. Carbamic acid, if present, was not believed to be the major product as characteristic N–H stretches are not present. This ratio was repeated to ensure that this was not an anomalous result.

The systematic, mid-IR spectroscopic investigation into both thermal processing and radiation and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio using mid-IR spectroscopy has been conducted. Chapter 5 will present the systematic, VUV spectroscopic investigation into thermal processing of CO$_2$:NH$_3$ interstellar ice mixtures.
Chapter 5

Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

This chapter presents the first, systematic, VUV spectroscopic study of the thermal processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio. Thermally induced changes were observed in the VUV spectra and tentative assignments of ammonium carbamate and carbamic acid are made which were aided by the mid-IR results presented in Chapter 3. Scattering tails obtained from the VUV spectra offered new information on the coverage of the CO$_2$:NH$_3$ ices which can not be obtained by mid-IR spectroscopy.

5.1 Introduction

VUV spectroscopy is still an underexploited technique in regards to its application for the study of solid phase molecular films. VUV spectroscopy provides an additional, non-destructive \textit{in situ} technique to analyse interstellar ice analogues when complemented with mid-IR studies. Compared to mid-IR spectroscopy, VUV spectroscopy is not limited to molecules which experience a change in their dipole moment and as such, small homonuclear molecules such as O$_2$ and N$_2$ can be observed.\textsuperscript{114,204} In addition, molecules which have weak mid-IR band strengths may have large VUV photoabsorption cross sections.\textsuperscript{205,170}

Few VUV spectroscopic studies have investigated interstellar ice analogue mixtures\textsuperscript{205,170,206} and the work presented in this chapter is the first systematic VUV investigation of CO$_2$ and NH$_3$ ice mixtures. As no studies of CO$_2$ and NH$_3$ mixtures exist in the literature, the literature of CO$_2$ and NH$_3$ is therefore limited to the pure ices deposited at or below 20 K.\textsuperscript{114,167,207,204}
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With the unique capability of being able to carry out both mid-IR and VUV spectroscopy investigations under the same experimental conditions, the complementary mid-IR spectroscopic results of CO$_2$:NH$_3$ binary mixtures discussed in Chapters 3 and 4 will be used to help interpret the VUV spectroscopic results (and vice versa).

5.2 Pure CO$_2$

An example of a VUV spectrum of pure CO$_2$ ice deposited at 20 K and taken with the substrate at a 45° angle with respect to the UV beam is shown in Fig. 5.1. Two electronic transitions were observed:

(i) $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition centred around 125 nm with vibrational structure

(ii) $^1\Delta_u \leftarrow ^1\Sigma_g^+$ transition centred around 143 nm

The $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition exhibited vibrational structure which was assigned in Table 5.1. The vibrational structure band positions agreed with a previous high resolution study by Mason et al.\textsuperscript{114} and 11 out of the 12 vibrational bands reported in Mason et al. were observed. The unobserved band was at 121.32 nm is near the experimental limit of detection as described in Section 2.1.2.

![Figure 5.1](image.png)

**Fig. 5.1** A VUV spectrum of CO$_2$ ice deposited at 20 K with the electronic transitions labelled.
5.2 Pure CO$_2$

5.2.1 Thermal processing

After deposition at 20 K, the CO$_2$ ice was thermally processed until desorption at 100 K. Thermally induced changes within the VUV spectrum of CO$_2$ ice were observed are shown in Fig 5.2. Both the $1\Pi_g \leftarrow 1\Sigma^+_g$ and the $1\Delta_u \leftarrow 1\Sigma^+_g$ transitions were observed in the spectra at 70 and 80 K. However, several differences from the deposited temperature at 20 K were observed and are summarised below.

- A small blue shift in the vibrational structure was observed for the $1\Pi_g \leftarrow 1\Sigma^+_g$ transition at 70 and 80 K and the positions are listed in Table 5.1.
- The $1\Delta_u \leftarrow 1\Sigma^+_g$ transition centred around 141 nm blue shifted from the deposition spectrum at 20 K by $\sim$2 nm.
- The $1\Delta_u \leftarrow 1\Sigma^+_g$ transition exhibited vibrational structure at 70 and 80 K which was not observed at 20 K and is listed in Table 5.1.
- An increase in the baseline, so that a non-zero baseline was observed for CO$_2$ ice appeared at 80 K and the vibrational structure of the $1\Delta_u \leftarrow 1\Sigma^+_g$ transition appeared more defined at 70 K compared to 80 K.

5.2.2 Discussion

The lowest energy electronic transition observed is the $1\Delta_u \leftarrow 1\Sigma^+_g$ transition which results from the promotion of an electron from the $2\pi_u$ MO to the $1\pi_g$ MO. The second absorption band observed is the $1\Pi_g \leftarrow 1\Sigma^+_g$ resulting from a promotion of an electron in the $1\Sigma_g$ MO to the $3s\sigma_g$ orbital which is a Rydberg or Rydberg-valence state.\textsuperscript{114} A Rydberg state is ‘An electronic state that arises by the excitation of a valence electron to a diffuse atomic-like orbital’.\textsuperscript{208}

The ground state of CO$_2$, $X 1\Sigma^+_g$, has a linear geometry with an inversion centre which is referred to as a $D_{\infty h}$ point group in molecular symmetry. However, the lower energy valence excited states of CO$_2$ are known to have a bent geometry which is referred to as a $C_{2v}$ point group. Vibrational structure exhibited on the electronic transition of the $1\Pi_g \leftarrow 1\Sigma^+_g$ shown in Fig. 5.1 also lends further evidence to a bent geometry in the $1\Pi_g \leftarrow 1\Sigma^+_g$. The average separation between the vibrational structure corresponds to 618 cm$^{-1}$ which was of a similar value to the $\nu_2$ bending vibration mode of CO$_2$.

Upon thermal processing to 70 and 80 K, vibrational structure was observed for the $1\Delta_u \leftarrow 1\Sigma^+_g$ transition which was not previously observed at 20 K. However, gas phase CO$_2$ has extensive vibrational structure on the $1\Delta_u \leftarrow 1\Sigma^+_g$ transition.\textsuperscript{209} In a study by Holtom et al.,\textsuperscript{210}
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Fig. 5.2 VUV spectra of pure CO$_2$ deposited at 20 K and thermally processed to 70 and 80 K with electronic transitions labelled. Desorption occurred at 100 K, but the spectrum is not shown here.

sulphur dioxide (SO$_2$) ice was investigated using VUV spectroscopy. Non-crystalline SO$_2$ ice at 25 K had no vibrational structure present. However, crystalline SO$_2$ ice formed either through thermal processing of the non-crystalline ice or from deposition at higher temperatures displayed vibrational structure. The loss of vibrational structure in non-crystalline phase may be explained by the broadening of the vibrational structure due to the random distribution of the bond lengths. A phase change to the crystalline structure reduces this broadening and so vibrational structure is observed. The appearance of vibrational structure $^1\Delta_u \leftarrow ^1\Sigma_g^+$ transition at 70 and 80 K may been an indication of a phase change from polycrystalline to crystalline CO$_2$ ice. Mid-IR spectra of pure CO$_2$ ice presented in Section 3.2 suggested that CO$_2$ underwent a phase change between 50–60 K. Additionally, small shifts in the vibrational structure of $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition may also indicate a phase change.

5.3 Pure NH$_3$

An example of a VUV spectrum of pure NH$_3$ ice deposited at 20 K and taken with the substrate at a 45° angle with respect to the IR beam is shown in Fig. 5.3. Two broad electronic transitions were observed:
Table 5.1 Band positions of the vibrational structure of the $^1\Pi_g \leftarrow ^1\Sigma^+_g$ and $^1\Delta_u \leftarrow ^1\Sigma^+_g$ transitions of CO$_2$ ice at 20, 70 and 80 K. The difference between 20 to 80 K is given for the $^1\Pi_g \leftarrow ^1\Sigma^+_g$ transition.

<table>
<thead>
<tr>
<th>Difference</th>
<th>Band position (nm)</th>
<th>Difference 20–80 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Pi_g \leftarrow ^1\Sigma^+_g$</td>
<td>122.00 122.10 122.40 0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>123.05 123.10 123.10 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>124.00 124.10 124.15 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>125.00 125.05 125.05 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>126.00 126.00 126.00 0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>126.85 127.00 127.05 0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127.85 128.00 128.00 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>128.90 129.00 129.00 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>130.00 130.00 130.00 0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>131.00 131.00 131.05 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>131.95 132.00 132.10 0.15</td>
<td></td>
</tr>
<tr>
<td>$^1\Delta_u \leftarrow ^1\Sigma^+_g$</td>
<td>140.00 140.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>141.80 141.70</td>
<td></td>
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<tr>
<td></td>
<td>143.50</td>
<td></td>
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<td></td>
<td>144.70 144.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>147.60 147.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150.70 150.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>154.40 155.00</td>
<td></td>
</tr>
</tbody>
</table>

(i) A transition centred around 127 nm

(ii) The $\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$ transition centred around 176 nm

The transition centred around 127 nm has been tentatively assigned to the $\tilde{B} \leftarrow \tilde{X}$ molecular transition by Cruz-Diaz et al. 207

5.3.1 Thermal processing

After deposition at 20 K, the NH$_3$ ice was thermally processed until desorption at 120 K. Thermally induced changes within the VUV spectra of the NH$_3$ ice were observed and are shown in Fig. 5.4. Both the unassigned transition centred around 127 nm and the $\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$ transition were observed in the thermal processing spectra. Upon thermal processing to 70 K, the $\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$ transition transformed or split so that a peak maximum was observed at 170 nm with shoulders observed at 162 and 179 nm.
Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

Fig. 5.3 A VUV spectrum of NH$_3$ ice deposited at 20 K with the electronic transitions labelled.

5.3.2 Discussion

The lowest energy electronic transition observed in Fig. 5.3 is the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'_1$ transition which results from the promotion an electron from the $1a_2''$ MO to the $3sa'_1$ MO which is a mixed Rydberg-valence state.\textsuperscript{167} The ground state of NH$_3$, $\tilde{X}^1A'_1$, has a pyramidal geometry centre which is referred to as a $C_3v$ point group in molecular symmetry. However, the $\tilde{A}^1A''$ state has a planar symmetry with a $D_{3h}$ point group.

The second transition was not specifically assigned in previous literature studies.\textsuperscript{167,207} However, Cruz-Diaz et al. suggest that it was due to the $\tilde{B} \leftarrow \tilde{X}$ electronic transition. However, in the gas phase the next absorption band observed is due to two overlapping electronic transitions: the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A'_1$ and $\tilde{C}^1A' \leftarrow \tilde{X}^1A'_1$.\textsuperscript{211} These two states are optically forbidden and become allowed by magnetic dipole and electric quadrupole selection rules, respectively. As these features are weak in the gas phase spectra they are unlikely to be more intense than the $A$ state in the solid phase spectra. The next optically allowed states are the D and E states which are intense in the gas phase.\textsuperscript{211} This band in the solid phase could therefore be overlapping contribution from B, C, D and E states. However, it is not possible to assign the solid-phase spectra without theoretical calculations as the bands do not exhibit any vibrational structure, unlike the complex spectra in the gas phase. As such, no definitive assignment of this band can be made in the solid phase.
5.4 Binary mixtures of CO$_2$:NH$_3$

5.4.1 Determining the ratios

As very few VUV spectroscopic studies have investigated interstellar ice analogue mixtures, there is no established protocol for determining the ratio from the VUV spectra. As discussed in Section 2.4.4 there were discrepancies between the partial pressures used to mix the gases or vapours in the gas line and the deposited ice mixtures. For the binary mixtures of the mid-IR spectroscopic investigations presented in Chapters 3 and 4, the column densities of specific vibrational modes were calculated and these values were used to determine the mixing ratio.
Thermal processing of CO\textsubscript{2}:NH\textsubscript{3} interstellar ice analogues: a VUV spectroscopic study

For VUV spectroscopy, the ratios of the CO\textsubscript{2} and NH\textsubscript{3} mixtures were approximated by mathematically adding the VUV spectrum of a pure NH\textsubscript{3} ice and a pure CO\textsubscript{2} ice, analysing the residual and iterating until a best fit was found. A detailed explanation on how the ratios of the VUV spectra were calculated using this approximation is given below:

1. A VUV spectrum of pure CO\textsubscript{2} ice and a VUV spectrum of pure NH\textsubscript{3} ice were normalised to a thickness of 200 nm.
2. The pure spectrum of CO\textsubscript{2} ice and the pure spectrum of NH\textsubscript{3} ice were mathematically added together.
3. The mathematical spectrum was then fitted to a spectrum of a CO\textsubscript{2}:NH\textsubscript{3} mixture and the residual was analysed.
4. The best fit was obtained through an iterative process which brought the sum of the positive and negative components of the residual closest to zero. The best fit residual contained both positive and negative components due to shifts in the electronic transition positions and changes in the widths of the electronic transitions.
5. From the best fit the CO\textsubscript{2} and NH\textsubscript{3} components were extracted which were given as fractional value of the normalised CO\textsubscript{2} and NH\textsubscript{3} from step 1. The ratio of the CO\textsubscript{2}:NH\textsubscript{3} mixture was determined from these fractions.

An example of this method is shown in Fig. 5.5 for the 4:1 ratio. A ratio of approximately 4:1 was expected for this mixture as the partial pressures of CO\textsubscript{2} and NH\textsubscript{3} used to mix this ratio were the same as the partial pressures which were used in the mid-IR experiments. A 3:1 ratio was obtained for the unirradiated mixture (Chapter 3) and 4:1 ratio was obtained for the irradiated mixture (Chapter 4). The other ratios obtained for the unirradiated VUV spectroscopic study were a 2:1 and 1:3 ratio.

5.4.2 Deposition at 20 K

Fig. 5.6 shows the VUV spectra of CO\textsubscript{2} and NH\textsubscript{3} mixtures in a 4:1, 2:1 and 1:3 ratios compared with pure NH\textsubscript{3} and pure CO\textsubscript{2} all deposited at 20 K and normalised to a thickness of 200 nm. The following differences compared to pure CO\textsubscript{2} and pure NH\textsubscript{3} were observed:

- The position of the $^{1}\Pi_{g} \leftrightarrow ^{1}\Sigma_{g}^{+}$ electronic transition of CO\textsubscript{2} was red shifted in the 4:1 and 2:1 mixtures compared with pure CO\textsubscript{2} but such a shift was not observed for the 1:3 ratio.
Fig. 5.5 Method for determining the ratio of a CO$_2$:NH$_3$ mixture from a VUV spectrum. (i) VUV spectra of CO$_2$ and NH$_3$ are normalised to the same thickness of 200 nm (red = CO$_2$, blue = NH$_3$) and then mathematically added together (black). (ii) The first fit (black dashed) is the mathematical spectrum from (i) which is fitted to the raw data (green) and the first fit residual is analysed. The best fit (black solid) was obtained through an iterative process which brought the positive and negative components of the residual closest to zero and is shown in the best fit residual. (iii) The CO$_2$ and NH$_3$ components which make up the best fit can be extracted. In this case the CO$_2$ component (red dashed) is $\times 1.002$ that of the normalised CO$_2$ spectrum and the NH$_3$ component (blue dashed) is $\times 0.23$ that of the normalised NH$_3$ spectrum so an approximate CO$_2$:NH$_3$ ratio of 4:1 was obtained.
Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

- The vibrational structure observed in the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of pure CO$_2$ in Section 5.2 was not observed in the 4:1 and 2:1 mixtures at 20 K. The intense, unassigned electronic transition of NH$_3$ centred around 127 nm obscured the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition in the 1:3 ratio.

- A new band centred around 140 nm for the 4:1 ratio and centred around 139 nm for the 2:1 ratio was observed, but no band was observed in the 1:3 ratio.

- The $^3\Pi'' \leftarrow ^3\Sigma_1^+$ transition of NH$_3$ was present in all mixtures and a small blue shift was observed compared with pure NH$_3$ ice for the 2:1 and 4:1 ratios.

![VUV spectra of CO$_2$ and NH$_3$ binary mixtures](image)

Fig. 5.6 VUV spectra of CO$_2$ and NH$_3$ binary mixtures in a 4:1, 2:1 and 1:3 ratio compared with pure CO$_2$ and pure NH$_3$. The dashed line highlights a new feature at 140 nm for the 4:1 and 2:1 ratios. The spectra have been normalised to a thickness of 200 nm.

Discussion

A new peak was observed at $\sim$140 nm in the CO$_2$:NH$_3$ binary mixtures of the 4:1 and 2:1 ratios, but not the 1:3 ratio. The mid-IR spectra of CO$_2$:NH$_3$ binary mixtures from Section 3.4.1 showed the formation of a CO$_2$:NH$_3$ molecular complex formed for all ratios except the 1:10 ratio. The CO$_2$:NH$_3$ molecular complex forms a dative bond between the C atom and the N atom with the ammonia. The electron distribution is shared between the two molecules...
5.4 Binary mixtures of CO$_2$:NH$_3$

essentially and the complex can be thought of as a ‘new’ molecule and so an electronic transition can occur. Therefore the new peak observed at $\sim$140 nm in the 4:1 and 2:1 ratios is tentatively assigned as being due to the CO$_2$:NH$_3$ as no other reaction occurred at 20 K. The $\sim$140 nm peak in the 1:3 ratio is probably obscured by the intense $\tilde{A}^1A_2^\prime\prime \leftarrow \tilde{X}^1A_1^\prime$ transition of NH$_3$.

5.4.3 Thermal processing

Fig. 5.7 shows the thermal processing spectra of a CO$_2$ and NH$_3$ mixture in a 4:1 ratio from 20 to 200 K. The following thermally induced changes were observed:

- Pure CO$_2$ ice deposited at 20 K has vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition which was not observed in the 4:1 ratio at 20 K. However, upon thermal processing vibrational structure of the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ was observed between 70–80 K and the assignments are shown in Table 5.2.

- CO$_2$ desorbed by 90 K, which was observed through the disappearance of the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition.

- At 90 K the $\tilde{A}^1A_2^\prime\prime \leftarrow \tilde{X}^1A_1^\prime$ transition of NH$_3$ broadened and blue shifted.

Fig. 5.8 shows the thermal processing spectra of a CO$_2$ and NH$_3$ mixture in a 2:1 ratio from 20 to 250 K. The following thermally induced changes were observed:

- Overall, the intensity of the spectra increased until 90 K before it then decreased.

- Pure CO$_2$ ice deposited at 20 K has vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition which was not observed in the 2:1 ratio at 20 K. However, upon thermal processing vibrational structure of the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ was observed between 60–70 K and the assignments are shown in Table 5.2.

- CO$_2$ desorbed by 90 K, which was observed through the disappearance of the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition.

- The $\tilde{A}^1A_2^\prime\prime \leftarrow \tilde{X}^1A_1^\prime$ transition of NH$_3$ blue shifted as the temperature was increased until 100 K.

- New bands were observed at 100 K indicating the formation of new molecules.

Fig. 5.9 shows the thermal processing spectra of a CO$_2$ and NH$_3$ mixture in a 1:3 ratio. The following thermally induced changes were observed:
Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

Fig. 5.7 VUV spectra of a CO$_2$ and NH$_3$ ice mixture in a 4:1 ratio deposited at 20 K and thermally processed to 200 K. The inset shows a zoom of the region between 120–135 nm.
5.4 Binary mixtures of CO$_2$:NH$_3$

Fig. 5.8 VUV spectra of a CO$_2$ and NH$_3$ ice mixture in a 2:1 ratio deposited at 20 K and thermally processed to 200 K. The inset shows a zoom of the region between 120–135 nm.
Fig. 5.9 VUV spectra of a CO$_2$ and NH$_3$ ice mixture in a 1:3 ratio deposited at 20 K and thermally processed to 250 K. The inset shows a zoom of the region between 120–135 nm.
• Very weak vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ was observed during the thermal processing between 70–80 K.

• The desorption of CO$_2$ could not be identified from the VUV spectra as the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition was obscured by the intense unassigned NH$_3$ transition.

• The $\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$ transition of NH$_3$ blue shifted as the temperature increased and a shoulder was observed at 194 nm at 90 K.

Table 5.2 Band positions of the vibrational structure of the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of the mixtures at 80 K compared with pure CO$_2$ at 80 K.

<table>
<thead>
<tr>
<th>Band position (nm)</th>
<th>Pure CO$_2$</th>
<th>4:1</th>
<th>2:1</th>
<th>1:3</th>
</tr>
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<tr>
<td>122.40</td>
<td>123.10</td>
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<td>125.05</td>
<td>125.20</td>
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<td>126.00</td>
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<td>131.05</td>
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<tr>
<td>132.10</td>
<td></td>
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</tbody>
</table>

Discussion

(i) Vibrational structure of CO$_2$ in the binary mixtures: The $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ in the CO$_2$:NH$_3$ mixtures does not have the vibrational structure which was associated with pure CO$_2$ ice at 20 K. As described in Section 2.1.2 vibrational or vibronic structure arises because the energy required for an electronic excitation also induces vibrational excitation. The shape and intensity of the vibrational features are governed by the Franck-Condon Principle. The lack of vibrational structure in the CO$_2$:NH$_3$ mixtures at 20 K was probably due to inhomogeneous broadening which was caused by the mixing of the CO$_2$ and NH$_3$. Mid-IR spectroscopic results from Chapters 3 and 4 have already shown that CO$_2$ and NH$_3$ are thoroughly mixed via the LO-TO splitting pattern shown in Fig. 3.11 in Section 3.4.1. Segregation of CO$_2$ and NH$_3$ was observed between 60–80 K in the mid-IR spectroscopic study shown in Section 3.4.2. This was also the temperature at which the vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ was
Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

observed for the 4:1 and 2:1 ratios. More specifically vibrational structure was observed for the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ in the 4:1 mixture between 70–80 K and between 60–70 K for the 2:1 ratio. These temperatures were similar to the segregation temperatures shown in Table 3.3 from the mid-IR study. Therefore, the absence and then appearance of vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ is a clear indicator of segregation of the CO$_2$ and NH$_3$ ice.

(ii) Crystallisation of NH$_3$ in the binary mixtures: According to mid-IR spectroscopic results shown in Chapter 3, NH$_3$ in a mixture of CO$_2$ and NH$_3$ will undergo a phase change between 60–80 K. For the mid-IR spectroscopic results, the splitting pattern of the $\nu_2$ vibrational mode of NH$_3$ indicated what type of phase the NH$_3$ formed upon thermal processing of the mixture. These results were summarised in Fig. 3.15 and it was concluded that the ratios with the highest amount of CO$_2$ formed the most ordered phase, either a polycrystalline phase with large crystallites or a crystalline phase.

In the study by Dawes et al., the morphology of NH$_3$ deposited at different temperatures and then thermally processed was investigated using both mid-IR and VUV spectroscopy. Wannier exciton peaks were observed at $\sim$194 nm on the $\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$ transition of NH$_3$ for some NH$_3$ ices depending on the morphology. It was hypothesised that the appearance of a Wannier exciton peak would be most prominent in ice where many grain boundaries were present. This would be ices which had a polycrystalline structure with crystallites of similar shapes and sizes, which according to the mid-IR results in Chapter 3, would be CO$_2$:NH$_3$ mixtures with ratios of 1:10 and 1:3.

A shoulder was observed at 194 nm of the $\tilde{A}^1A''_2 \leftarrow \tilde{X}^1A'_1$ transition of NH$_3$ for the 1:3 ratio and is shown in Fig. 5.10 compared with the 4:1 and 2:1 ratios where no shoulder was observed. This shoulder is assigned as a Wannier exciton peak. An exciton is a the bound state of an electron-hole pair which is capable of migrating. A Wannier exciton refers to an exciton which has a large dielectric constant. Observation of a Wannier exciton requires an ice with many grain boundaries which would reflect a polycrystalline structure with small crystallites of similar shapes and sizes. The 2:1 and 4:1 ratios which were described as having either a polycrystalline structure with large crystallites or a crystalline structure from the mid-IR spectroscopic results. Consequently there would be fewer grain boundaries present within the ices and therefore, it is less likely that a Wannier exciton peak would be present in these ratios.

In the study by Dawes et al. the exciton peak was much more pronounced for pure NH$_3$ ice deposited at 75 and 100 K compared to the exciton peak observed in the 1:3 ratio as shown in Fig. 5.11. Mid-IR spectroscopic results in Chapter 3 show that CO$_2$ and NH$_3$ have segregated by 90 K leaving areas of pure CO$_2$ and pure NH$_3$. In the study by Dawes et al., for the pure NH$_3$ ice deposited at 75 and 100 K, where an exciton peak was observed there are many grain boundaries. However, for the CO$_2$:NH$_3$ mixtures shown in this chapter
5.4 Binary mixtures of CO$_2$:NH$_3$

![Graph showing VUV spectra](image)

**Fig. 5.10** VUV spectra of the Wannier exciton peak at 194 nm of the 1:3 ratio (orange) compared against the 4:1 (blue), 2:1 (green) and 0:1 (black) CO$_2$:NH$_3$ ratios at 90 K. The shaded region indicates the area of the Wannier exciton peak. All spectra are normalised to a thickness of 200 nm.

The regions of segregated NH$_3$ are interspersed between regions of segregated CO$_2$ ice so are fewer NH$_3$-NH$_3$ grain boundaries. Furthermore, the presence of CO$_2$ during deposition at 20 K disturbed the pre-defined H-bonding between the NH$_3$ molecules, which increased crystallinity and crystallite formation in the NH$_3$ upon segregation. Note, the exciton peak was not observed in samples which were deposited at low temperatures and then annealed. The exciton peak was therefore weaker in the 1:3 mixture compared to the pure NH$_3$ ice deposited at 75 and 100 K in the study by Dawes *et al.*

5.4.4 Residue spectra at 150 and 200 K

**Fig. 5.12** shows the VUV spectra of the 4:1, 2:1 and 1:3 ratios at 150 and 200 K. The spectral profile of the 4:1, 2:1 and 1:3 ratios at 150 K were similar although the 1:3 ratio had a more defined peak at 154 nm. At 200 K the spectral profile again looked similar for the 4:1, 2:1 and 1:3 ratios. The peak at 154 nm decreased and a well defined peak was present at 172 nm for the 4:1 and 2:1 ratio and at 170 nm for the 1:3 ratio.

**Discussion**

In Chapter 3, ammonium carbamate and carbamic acid were identified at 150 K for all the ratios apart from the 3:1 ratio. Ammonium cabramate and carbamic acid were also identified at 200 K with evidence of ammonium carbamate converting to carbamic acid. This was observed
Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

Fig. 5.11 VUV spectra of the Wannier exciton peak at 194 nm of the 1:3 ratio (orange) compared against NH$_3$ deposited at 75 K (black dash) and 100 K (black dot dash) from Dawes et al.\textsuperscript{167} The shaded region indicates the area of the Wannier excition peak. All spectra are normalised to a thickness of 200 nm.

through the decrease in COO$^-$ stretches associated with ammonium carbamate and through the increase in C=O and C–O stretches associated with carbamic acid. For the VUV spectra at 150 K presented in Fig. 6.14 all ratios had a peak at $\sim$150 nm which decreased upon thermal processing to 200 nm. Using the evidence that ammonium carbamate converts to carbamic acid upon thermal processing from 150–200 K from the results in Chapter 3 this peak is tentatively assigned as an electronic transition of ammonium carbamate. The shoulder at 170 nm resolved into a peak upon thermal processing from 150 to 200 K and this is tentatively assigned as an electronic transition due to carbamic acid.

A noticeable difference between the mid-IR and VUV residue spectra is the presence of a residue for the VUV 4:1 ratio. The mid-IR 3:1 ratio from Chapter 3 showed no residue when observed with mid-IR spectroscopy. However, a residue material might have been present but in trace amounts that could not be observed using mid-IR spectroscopy. For example, in studies by Dawes et al.\textsuperscript{205} and James et al.\textsuperscript{170} VUV spectroscopy was used to study benzene mixtures with H$_2$O and CO$_2$, respectively. In these studies the comparatively high VUV photoabsorption cross sections of benzene compared to H$_2$O or CO$_2$ were exploited. This was in contrast to the mid-IR band strength (A-value) where H$_2$O or CO$_2$ band strengths were much larger compared to benzene. Therefore, it is possible that the products, ammonium carbamate and carbamic acid, have relatively large VUV photoabsorption cross sections which makes them easier to observe using VUV spectroscopy compared to mid-IR spectroscopy.

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5.4 Binary mixtures of CO$_2$:NH$_3$

![Graph showing absorbance vs wavelength](image)

**Fig. 5.12** VUV residue spectra of CO$_2$ and NH$_3$ mixtures in a 4:1, 2:1 and 1:3 ratio at 150 and 200 K. The dash dot line highlights a feature at 152 nm and the dashed line highlights a feature at 170 nm. The spectra are normalised to a thickness of 200 nm and offset on the y-axis for clarity.

### 5.4.5 Summary

The presence (or absence) of vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ was used as an indicator of segregation. Comparison of the residue spectra at 150 and 200 K with the mid-IR results presented in Chapter 3 allowed tentative assignments of the electronic transitions of ammonium carbamate and carbamic acid. A summary of the thermal processing results is given in Table 5.3.

**Table 5.3** A summary of the products formed after thermal processing of the 4:1, 2:1 and 1:3 CO$_2$:NH$_3$ binary mixtures.

<table>
<thead>
<tr>
<th></th>
<th>4:1</th>
<th>2:1</th>
<th>1:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibrational structure on $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$</td>
<td>20–70</td>
<td>50–60</td>
<td>70–80</td>
</tr>
<tr>
<td>Exciton peak</td>
<td>✗</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>✓ (90 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residue at 150 K</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Residue at 200 K</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
5.5 Scattering tails during the thermal processing of the binary mixtures

![Diagram](image)

**Fig. 5.13** Schematic diagram showing the different types of ice surface topography. Scattering tails in the VUV spectra are observed where the surface of the ice is not uniformly smooth. (i) uniformly smooth; (ii) uniform sized clumps or particles and (iii) random sized clumps or particles.

If the surface of the ice is not uniformly smooth then scattering tails can be observed in the VUV spectra. Sometimes the surface topography of the ice will be rough possessing a clumpy structure as shown in Fig. 5.13. These clumps, which are referred to as particles throughout this thesis, can scatter the light causing a scattering tail to be observed. For example, Fig. 5.14 shows the thermal processing VUV spectra from 200–340 nm of pure NH₃ ice after deposition at 20 K. Scattering tails are present at 20, 70, 80 and 90 K.

![Graph](image)

**Fig. 5.14** VUV spectra of pure NH₃ ice deposited at 20 K and thermally processed. The VUV spectra shows the region between 200–340 nm which highlights the Rayleigh scattering tails.

Specifically these are Rayleigh scattering tails as the particle size is less than $\lambda/10$ and the intensity of scattered light ($I_s$) is proportional $\lambda^{-4}$. This dependency is derived from the Rayleigh scattering cross section ($\sigma_{Ray}$) which for a single scatterer is given by:
5.5 Scattering tails during the thermal processing of the binary mixtures

\[ \sigma_{\text{Ray}} = \left( \frac{128\pi^5}{3} \right) \left( \frac{m^2 - 1}{m^2 + 2} \right)^2 \left( \frac{r^6}{\lambda^4} \right) \] (5.1)

where \( m \) is the relative refractive index of the particle to the surrounding medium and \( r \) is the particle size.

A simple Rayleigh model can be fitted to the VUV absorption spectra at \( \lambda > 215 \text{ nm} \), where the only contribution to the loss of intensity in \( I_t \) is due to scattering for the majority of VUV spectra. As a reminder, the absorbance (A) is derived from the Beer-Lambert Law (Eq. 2.5) and is given below:

\[ A = \log \left( \frac{I_0(\lambda)}{I_t(\lambda)} \right) \]

By treating the transmitted intensity \( (I_t) \) as equal to the incident intensity \( (I_0) \) minus \( I_s \), \( (I_t = I_0 - I_s) \), Eq. 2.5 can be rewritten as:

\[ A = \log \left( \frac{1}{1-I_s} \right) \] (5.2)

The scattered intensity \( I_s \) is proportional to the scattering cross section given in Eq. 5.1. As \( I_s \) is proportional to \( \lambda^{-4} \), then:

\[ A = \log \left( \frac{I_0}{I_0 - c\lambda^{-4}} \right) \] (5.3)

where \( c \) is a constant of proportionality and is dependent on the particle size \( (r) \), the refractive index \( (m) \) as shown by Eq. 5.1 and also the number density of scatterers \( (N) \) present within the sample.

Fig. 5.15 shows an example of the process used to fit the Rayleigh Model (Eq. 5.3) of pure NH\(_3\) ice which was deposited at 20 K and thermally processed to 90 K. From the fit the constant of proportionality was obtained as \( c = (1.63 \pm 0.001) \times 10^8 \). As this quantity is dimensionless it is better expressed as a percentage change in the constant of proportionality of the processed ice relative to the constant of proportionality at deposition \( (\Delta c) \):

\[ \Delta c = \left( \frac{c_p - c_{\text{dep}}}{c_{\text{dep}}} \right) \times 100 \] (5.4)

where \( c_p \) is the constant of proportionality of the processed interstellar ice analogue and \( c_{\text{dep}} \) is the constant of proportionality of interstellar ice analogue at 20 K.

Therefore, the Rayleigh scattering fit of the pure NH\(_3\) ice shown in Fig. 5.3 which was deposited at 20 K and thermally processed to 90 K had a change in the constant of proportionality relative to the constant of proportionality at deposition \( (\Delta c) \) equal to 98% which meant that
Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

**Fig. 5.15** Example of a Rayleigh scattering fit to the tail ($\lambda \text{>} 200$ nm) of pure NH$_3$ which was deposited at 20 K and thermally processed to 80 K.

The constant of proportionality at 90 K was 98% larger than the constant of proportionality at deposition (20 K).

### 5.5.1 Pure NH$_3$

Table 5.4 shows the results of the Rayleigh scattering model for pure NH$_3$ deposited at 20 K and thermally processed. As the temperature increased the $\Delta c$ value increased until it reached a maximum at 90 K before it decreased to values lower than the initial deposition value.

**Table 5.4** Results of the Rayleigh scattering model fits (Eq. 5.3) for pure, NH$_3$ ice.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$c \times 10^8$</th>
<th>$\Delta c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.823 ± 0.007</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>1.53 ± 0.01</td>
<td>85</td>
</tr>
<tr>
<td>80</td>
<td>1.63 ± 0.01</td>
<td>98</td>
</tr>
<tr>
<td>90</td>
<td>2.15 ± 0.01</td>
<td>162</td>
</tr>
<tr>
<td>100</td>
<td>0.298 ± 0.005</td>
<td>-64</td>
</tr>
<tr>
<td>110</td>
<td>0.66 ± 0.02</td>
<td>-19</td>
</tr>
<tr>
<td>120</td>
<td>0.53 ± 0.01</td>
<td>-36</td>
</tr>
</tbody>
</table>
5.5 Scattering tails during the thermal processing of the binary mixtures

5.5.2 CO$_2$:NH$_3$ 4:1 mixture

Table 5.5 shows the results of the Rayleigh scattering model for a 4:1 mixture of CO$_2$ and NH$_3$ ice deposited at 20 K and thermally processed. During thermal processing the $\Delta c$ value spiked at 90 K, with another smaller spike at 150 K.

Table 5.5 Results of the Rayleigh scattering model fits (Eq. 5.3) for 4:1 CO$_2$:NH$_3$ mixture.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$c \times 10^7$</th>
<th>$\Delta c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.51 ± 0.12</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>1.94 ± 0.16</td>
<td>284</td>
</tr>
<tr>
<td>80</td>
<td>1.98 ± 0.15</td>
<td>291</td>
</tr>
<tr>
<td>90</td>
<td>11.0 ± 0.28</td>
<td>2068</td>
</tr>
<tr>
<td>100</td>
<td>3.84 ± 0.08</td>
<td>660</td>
</tr>
<tr>
<td>120</td>
<td>5.34 ± 0.11</td>
<td>957</td>
</tr>
<tr>
<td>150</td>
<td>2.04 ± 0.08</td>
<td>303</td>
</tr>
<tr>
<td>200</td>
<td>1.59 ± 0.04</td>
<td>215</td>
</tr>
</tbody>
</table>

5.5.3 CO$_2$:NH$_3$ 2:1 mixture

Table 5.6 shows the results of the Rayleigh scattering model for a 2:1 mixture of CO$_2$ and NH$_3$ ice deposited at 20 K and thermally processed. Similar to the 4:1 ratio, the $\Delta c$ value spiked at 90 K, but no further spikes were observed.

Table 5.6 Results of the Rayleigh scattering model fits (Eq. 5.3) for unirradiated, 2:1 CO$_2$:NH$_3$ mixture.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$c \times 10^7$</th>
<th>$\Delta c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.08 ± 0.26</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>1.29 ± 0.27</td>
<td>50</td>
</tr>
<tr>
<td>60</td>
<td>3.05 ± 0.33</td>
<td>155</td>
</tr>
<tr>
<td>70</td>
<td>2.14 ± 0.34</td>
<td>-9</td>
</tr>
<tr>
<td>80</td>
<td>2.92 ± 0.31</td>
<td>-36</td>
</tr>
<tr>
<td>90</td>
<td>12.8 ± 0.38</td>
<td>784</td>
</tr>
<tr>
<td>100</td>
<td>1.37 ± 0.13</td>
<td>-17</td>
</tr>
<tr>
<td>120</td>
<td>1.06 ± 0.05</td>
<td>-27</td>
</tr>
<tr>
<td>150</td>
<td>1.08 ± 0.06</td>
<td>-25</td>
</tr>
<tr>
<td>200</td>
<td>1.13 ± 0.06</td>
<td>-22</td>
</tr>
<tr>
<td>250</td>
<td>0.49 ± 0.09</td>
<td>-69</td>
</tr>
</tbody>
</table>
Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

5.5.4 CO$_2$:NH$_3$ 1:3 mixture

Table 5.7 shows the results of the Rayleigh scattering model for a 1:3 mixture of CO$_2$ and NH$_3$ ice deposited at 20 K and thermally processed. Similar to the 4:1 and 2:1 ratios a spike in the $\Delta c$ value was observed at 90 K.

Table 5.7 Results of the Rayleigh scattering model fits (Eq. 5.3) for unirradiated, 1:3 CO$_2$:NH$_3$ mixture.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>c ($\times 10^7$)</th>
<th>$\Delta c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.40 ± 0.21</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>5.06 ± 0.55</td>
<td>261</td>
</tr>
<tr>
<td>80</td>
<td>6.96 ± 0.39</td>
<td>397</td>
</tr>
<tr>
<td>90</td>
<td>10.6 ± 0.37</td>
<td>659</td>
</tr>
<tr>
<td>100</td>
<td>8.40 ± 0.41</td>
<td>499</td>
</tr>
<tr>
<td>120</td>
<td>8.44 ± 0.12</td>
<td>503</td>
</tr>
<tr>
<td>150</td>
<td>9.26 ± 0.18</td>
<td>442</td>
</tr>
<tr>
<td>200</td>
<td>7.60 ± 0.11</td>
<td>315</td>
</tr>
</tbody>
</table>

5.5.5 Discussion

Rayleigh scattering tails with an intensity proportional to $\lambda^{-4}$ were fitted to all the mixtures and pure NH$_3$. The presence of particles indicated that both pure NH$_3$ and the mixtures do not cover the substrate as uniformly smooth films and instead formed a rough ice with ‘clumps’ on the surface. This probably arises due to the non-wetting behaviour of NH$_3$, investigated previously on Au and amorphous water substrates. Single peaks from temperature programmed desorption studies indicated that multilayers formed due to the preference of NH$_3$ to bind to neighbouring molecules rather than the substrate. While CO$_2$ ice is also known to exhibit non-wetting behaviour at low coverages, eventually CO$_2$ will cover the entire substrate in a uniform film, with a smooth surface or particles that are outside of the Rayleigh regime and no Rayleigh scattering tails could be fitted using Eq. 5.3 for CO$_2$ ice.

As recalled from Chapter 3 the crystallisation temperature of NH$_3$ within the mixtures was dependent upon the ratio. A spike in the $\Delta c$ value at 90 K was observed in all mixtures and pure NH$_3$ ice and is a strong indication of molecular rearrangement and macroscopic change of morphology which is most likely due to crystallisation. Upon crystallisation pure NH$_3$ ice went from a non-crystalline to polycrystalline structure with crystallites of random shapes and sizes. The 4:1 and 2:1 ratios went from a non-crystalline to polycrystalline structure with crystallites of similar sizes and the 1:3 ratio formed a polycrystalline structure with large crystallites or a crystalline structure. Regardless of whether the crystallites are random shapes and sizes or
similar sizes, the segregation of CO$_2$ from the mixture and the formation of crystallites would increase the number of particles present within the ice and hence, the $\Delta c$ value. The decrease in the $\Delta c$ value above 90 K may indicate macroscopic surface reconstruction and smoothing of the surface. Desorption of NH$_3$ or thermal reaction could also contribute to the decrease in the $\Delta c$ value.

![Graph](image)

**Fig. 5.16** A comparison of $\Delta c$ for each CO$_2$:NH$_3$ mixture (bottom panel) and pure NH$_3$ (top panel) against temperature. $\Delta c$ values are normalised to a thickness of 200 nm.

## 5.6 Summary

A systematic investigation of the thermal processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio using VUV spectroscopy was presented in this chapter and the results are summarised below:

- Pure CO$_2$ has vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition when deposited at 20 K which was not observed in the mixtures when deposited at 20 K. However, when the mixtures were thermally processed to the CO$_2$ segregation temperatures which were determined from the mid-IR results of Chapter 3 (60–90 K), vibrational structure was once again observed.
Thermal processing of CO\textsubscript{2}:NH\textsubscript{3} interstellar ice analogues: a VUV spectroscopic study

- A Wannier exciton peak was observed in the 1:3 ratio when thermally processed to 90 K indicating a phase change. Wannier exciton peaks require the presence of grain boundaries to form and the 1:3 ratio has the most grain boundaries at 90 K with its polycrystalline structure with crystallites of similar shapes and sizes.

- The 4:1 ratio formed a residue at 150 and 200 K in contrast to the mid-IR spectroscopic results of Chapter 3 which may be due to the residue molecules having comparably large VUV photoabsorption cross sections and relatively weak IR integrated band strengths.

- Ammonium carbamate to carbamic acid conversion may be observed through the disappearance of a peak at $\sim$150 nm upon thermal processing from 150 to 200 K and the formation of a peak at $\sim$170 nm. However, at best these are tentative assignments and will remain so until pure ammonium carbamate and carbamic acid are characterised using VUV spectroscopy.

- Rayleigh scattering tails were fitted to pure NH\textsubscript{3} and all of the mixtures at 20 K and for majority of the thermal processing spectra. Pure NH\textsubscript{3} does not form a uniformly smooth ice and instead forms a rough ice with clumps on the surface as do mixtures of CO\textsubscript{2} and NH\textsubscript{3}. For all the mixtures and pure NH\textsubscript{3} ice these clumps remained similar in the number of scatterers and/or size throughout thermal processing up to 90 K, whereupon the $\Delta c$ value spiked for all mixtures and pure NH\textsubscript{3} ice.

Now that a systematic investigation of the thermal processing of CO\textsubscript{2}:NH\textsubscript{3} interstellar ice analogues as a function of deposition mixing ratio using VUV spectroscopy has been conducted, Chapter 6 will present the results of the investigation of radiation processing. A comparison will be made of the thermal processing results shown in this chapter with the radiation results presented in the next chapter.
Chapter 6

Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

This chapter presents the first, systematic, VUV spectroscopic study of the electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio. Electron induced molecular synthesis at 20 K showed the formation of CO for all ratios and O$_3$ for a CO$_2$-rich ratio. The tentative assignments of ammonium carbamate and carbamic acid made in Chapter 5 were further refined by results provided in this chapter. Again scattering tails obtained from the VUV spectra offered new information on the coverage of the CO$_2$:NH$_3$ ices which cannot be obtained by mid-IR spectroscopy.

6.1 Introduction

Few VUV spectroscopic studies have investigated interstellar ice analogue mixtures and even fewer studies have investigated the energetic processing of these mixtures. The work presented in this chapter is the first systematic VUV investigation of electron processed CO$_2$ and NH$_3$ ice mixtures. Interpretation of the results in this chapter rely on the results of the mid-IR spectroscopic study in Chapters 3 and 4 and the VUV spectroscopic thermal processing results of Chapter 5.

The results of electron and thermal processing of pure CO$_2$ is presented in Section 6.2 and of pure NH$_3$ in Section 6.3. Section 6.4 presents the electron and thermal processing of CO$_2$:NH$_3$ binary mixtures and Section 6.5 shows the Rayleigh scattering tail fits. Finally a summary of the results in this chapter is given in Section 6.6.
6.2 Pure CO$_2$

A VUV spectrum of CO$_2$ deposited at 20 K is shown in Fig. 5.1 with the labelled electronic transitions. The results of the electron processing of pure CO$_2$ ice deposited at 20 K and the subsequent thermal processing are presented in this section.

6.2.1 Electron processing

As mentioned in Section 2.4.5 the electron processing of the interstellar ice analogues was not continuous. Rather, the ice was irradiated for a specified time intervals, which are listed in Table A.6, and after each irradiation period a VUV spectrum was collected. Fig. 6.1 shows the VUV spectra of pure CO$_2$ deposited at 20 K and irradiated with 1 keV electrons at several intervals for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. Two new transitions were observed upon electron processing:

- An intense vibrational progression centred around 147 nm due to the $\Lambda^1 \Pi \leftarrow \Sigma^+ \times 1 \Sigma^+$ transition of CO\textsuperscript{212,214}. Table 6.1 shows the assignment of the CO vibrational progression.

- A broad Hartley Band of O$_3$ centred around 258 nm\textsuperscript{213,214}

<table>
<thead>
<tr>
<th>v', v''</th>
<th>Band position (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,0</td>
<td>132.20</td>
</tr>
<tr>
<td>7,0</td>
<td>134.55</td>
</tr>
<tr>
<td>6,0</td>
<td>136.85</td>
</tr>
<tr>
<td>5,0</td>
<td>139.50</td>
</tr>
<tr>
<td>4,0</td>
<td>142.10</td>
</tr>
<tr>
<td>3,0</td>
<td>144.75</td>
</tr>
<tr>
<td>2,0</td>
<td>147.95</td>
</tr>
<tr>
<td>1,0</td>
<td>151.25</td>
</tr>
<tr>
<td>0,0</td>
<td>155.00</td>
</tr>
</tbody>
</table>

6.2.2 Thermal processing

After processing with 1 keV electrons, the CO$_2$ ice was thermally processed until desorption. Fig. 6.2 shows the thermal processing VUV spectra of pure CO$_2$ after electron irradiation at
6.2 Pure CO$_2$

20 K. The A$^1\Pi \leftarrow X^1\Sigma^+$ transition of CO decreased in intensity as the temperature increased until 90 K where it desorbed. The Hartley Band of O$_3$ decreased in intensity as the temperature increased and desorbed between 80–90 K. The $\Pi_g \leftarrow \Sigma_g^+$ of CO$_2$ transition increased in intensity until 80 K. A non-zero baseline was observed at 80 K.

6.2.3 Discussion

Ozone

Formation of O$_3$ was observed in the mid-IR spectroscopic results of electron irradiated pure CO$_2$ ice in Section 4.2. The formation of O$_3$ from CO$_2$ deposited at 5.5 K has been observed using UV-vis spectroscopy by Jones et al. which was irradiated using 5 keV electrons.$^{214}$ During this study it was observed that O$_3$ formed from CO$_2$ ice had a similar spectral profile to O$_3$ formed from O$_2$ ice.

A phase change from non-crystalline to crystalline O$_3$ was observed in both mid-IR$^{198}$ and VUV$^{213}$ spectroscopic studies between 47 and 55 K. A phase change in O$_3$, which was formed from VUV processing of O$_2$ ice, was observed through changes in electronic transitions at $\lambda < 170$ nm.$^{213}$ However, Fig. 6.2 shows that electronic transitions from both CO$_2$ and CO obscured any electronic transitions of O$_3$ at $\lambda < 170$ nm and hence, observation of a phase change. However, from the mid-IR spectroscopic results shown in Fig. 4.5, it was confirmed that a phase change occurred which corroborated existing literature.$^{197}$

The Hartley band of O$_3$ disappeared upon thermal processing to 90 K in agreement with the mid-IR results presented in Section 4.2 and a mid-IR study by Sivaraman et al.$^{213}$ However, Sivaraman et al. observed other VUV electronic transitions of O$_3$ above 90 K and the absence of the Hartley band was given as the ‘reduction in O$_3$ concentration due to its loss of O$_3$ molecules by sublimation’.$^{213}$ For the electron processing of CO$_2$, if O$_3$ was entrapped within the CO$_2$ ice above 80 K it was not observable in either the mid-IR or VUV results obtained in this thesis. However, mass spectrometric results obtained from a study by Jones et al. show that O$_3$ remains entrapped in CO$_2$ until desorption at 100 K.$^{214}$

Vibrational structure on $^1\Delta_u \leftarrow ^1\Sigma_g^+$ transition

Thermal processing of CO$_2$ ice showed vibrational structure on the $^1\Delta_u \leftarrow ^1\Sigma_g^+$ transition formed between 70–80 K in Section 5.2. It was tentatively assigned as an indicator of a phase change in CO$_2$ from a polycrystalline to crystalline structure. No vibrational structure on the $^1\Delta_u \leftarrow ^1\Sigma_g^+$ transition was observed during thermal processing of the electron processed CO$_2$ ice due to the intense A$^1\Pi \leftarrow X^1\Sigma^+$ transition of CO in the region 130–170 nm.
Fig. 6.1 VUV spectra of pure CO$_2$ ice irradiated with 1 keV electrons at several intervals for a total fluence of $3.37 \times 10^{15}$ e$^{-}$ cm$^{-2}$. The top inset shows a zoomed region of the $\Pi_g \leftarrow \Sigma^+_g$ of CO$_2$ and the $A^1\Pi \leftarrow X^1\Sigma^+$ transition of CO. The bottom inset shows a zoomed region of the Hartley Band of O$_3$. 

The figure shows the absorbance spectra of CO$_2$ and CO as a function of wavelength. The absorbance scales are shown in the insets, with absorbance values ranging from 0.0 to 0.9 for the CO$_2$ spectra and from 0.0 to 0.03 for CO. The fluence values for each spectrum are indicated in the legend: 0, 1.12, 2.25, and 3.37.
Fig. 6.2 VUV spectra of pure CO$_2$ ice irradiated with 1 keV electrons for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$ and then thermally processed until desorption. The top inset shows a zoomed region of the $\Pi_g \leftarrow \Sigma_g^+$ of CO$_2$ and the $A^1\Pi \leftarrow X^1\Sigma^+$ transition of CO. The bottom inset shows a zoomed region of the Hartley Band of O$_3$. 

\[ \text{Absorbance} \]

\[ \text{Wavelength (nm)} \]
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Fig. 6.3 VUV spectra of pure NH$_3$ ice irradiated with 1 keV electrons at several intervals for a total fluence of $3.37 \times 10^{15}$ e$^-\text{cm}^{-2}$.

6.3 Pure NH$_3$

A VUV spectrum of NH$_3$ deposited at 20 K is shown in Fig. 5.3 with the labelled electronic transition. The results of electron processing of pure NH$_3$ ice deposited at 20 K and the subsequent thermal processing are presented in this section.

6.3.1 Electron processing at 20 K and subsequent thermal processing

As mentioned in Section 2.4.5 electron processing of the interstellar ice analogues was not continuous. Rather, the ice was irradiated for specific time intervals, which are listed in Table A.6, and a VUV spectrum was collected after each irradiation period. Fig. 6.3 shows the VUV spectra of pure NH$_3$ deposited at 20 K and processed with 1 keV electrons for a total fluence of $3.37 \times 10^{15}$ e$^-\text{cm}^{-2}$. A new transition was observed at 150 nm upon electron processing. The intensity of the NH$_3$ electronic transitions decreased probably due to dissociation and sputtering of the NH$_3$ ice. A pronounced scattering tail appeared after and persisted throughout electron irradiation.

After processing with 1 keV electrons, the NH$_3$ ice was thermally processed until desorption. Fig. 6.4 shows the thermal processing VUV spectra of pure NH$_3$ after electron irradiation at
The new irradiation product transition at 150 nm in Fig. 6.3 was quite intense which was in contrast to the equivalent mid-IR spectra in Fig. 4.7. In Fig. 4.7 only weak irradiation features were present on the wings of the intense, pure NH$_3$ vibrational modes. However, identification of the VUV electronic transition at 150 nm is still difficult as no VUV spectroscopic studies exist on the irradiation of NH$_3$ ice within the literature. It is suggested that this feature may be due to hydrazine (N$_2$H$_4$), which although it was not observed in the mid-IR results of Section 4.3, has been detected through a temperature programmed desorption-mass spectrometry study.\textsuperscript{152}

### 6.4 Binary mixtures

The ratios of the binary mixtures for the electron irradiated system were determined using the same method as described in Section 5.4.1 and the following CO$_2$:NH$_3$ ratios were obtained:

![VUV spectra of pure NH$_3$ ice irradiated with 1 keV electrons for a total fluence of 3.37 \times 10^{15} \text{ e}^- \text{ cm}^{-2} and then subsequently thermally processed until desorption.](image-url)
4:1, 2:1 and 1:3. The deposition spectra of these ratios can be found in Fig. B.16 of Appendix B.

### 6.4.1 Electron processing 20 K

Fig. 6.5 shows the VUV spectra of a CO$_2$:NH$_3$ mixture in a 4:1 ratio which was processed with 1 keV electrons at several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The formation of CO was observed through the intense $A^1\Pi \leftarrow X^1\Sigma^+$ transition and the formation of O$_3$ was observed through the Hartley Band. As the fluence increased, the intensity of the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'_1$ transition of NH$_3$ decreased.

Fig. 6.6 shows the VUV spectra of a CO$_2$:NH$_3$ mixture in a 2:1 ratio which was processed with 1 keV electrons at several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The formation of CO was observed through the intense $A^1\Pi \leftarrow X^1\Sigma^+$ transition, but no formation of O$_3$ was observed. As the fluence increased, the intensity of the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'_1$ transition of NH$_3$ decreased.

Fig. 6.7 shows the VUV spectra of a CO$_2$:NH$_3$ mixture in a 1:3 ratio which was processed with 1 keV electrons at several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The formation of CO was observed through the $A^1\Pi \leftarrow X^1\Sigma^+$ transition. No formation of O$_3$ was observed. As the fluence increased, the intensity of the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'_1$ transition of NH$_3$ decreased.

A comparison of the electron processed mixtures at a fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$ is shown in Fig. 6.8. The intensity of the $A^1\Pi \leftarrow X^1\Sigma^+$ transition of CO was much weaker in the 1:3 ratio compared to the 4:1 and 2:1 ratios.

### Discussion and Summary

The formation of O$_3$ in the 4:1 ratio was not previously observed in the mid-IR results in Chapter 4. Fig. 6.9 shows that the relatively strong $v_2$ vibrational mode of NH$_3$ obscured the weak $v_3$ mode of O$_3$ in the 4:1 ratio after irradiation with 1 keV electrons for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. Interestingly residue mid-IR and VUV spectra of the 4:1 ratio at 150 and 200 K were different to the other ratios. Whether this was specifically due to O$_3$ formation is not known, but a ratio with a relatively large excess of CO$_2$ facilitated the formation of O$_3$ which was inhibited in the other mixtures.

A summary of the electron processing products of the CO$_2$:NH$_3$ mixtures is given in Table 6.2. The formation of CO after electron processing was observed in all ratios and the 4:1 ratio also formed O$_3$. 

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Fig. 6.5 VUV spectra of a NH$_3$ and CO$_2$ mixture in a 4:1 ratio irradiated with 1 keV electrons at 20 K for several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The top inset shows a zoomed region of the $\Pi_g \leftrightarrow \Sigma_g^+$ of CO$_2$ and the $A^1\Pi \leftrightarrow X^1\Sigma^+$ transition of CO. The bottom inset shows a zoomed region of the Hartley Band of O$_3$. 
Fig. 6.6 VUV spectra of a NH$_3$ and CO$_2$ mixture in a 2:1 ratio irradiated with 1 keV electrons at 20 K for several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The inset shows a zoomed region of the $\Pi_g \leftarrow \Sigma_g^+$ of CO$_2$ and the $A^1\Pi \leftarrow X^1\Sigma^+$ transition of CO.
Fig. 6.7 VUV spectra of a NH₃ and CO₂ mixture in a 1:3 ratio irradiated with 1 keV electrons at 20 K for several intervals cumulating in a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The inset shows a zoomed region of the $\Pi_g \leftrightarrow \Sigma_g^+$ of CO₂ and the $A^1\Pi \leftrightarrow X^1\Sigma^+$ transition of CO.
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**Fig. 6.8** VUV spectra of a CO$_2$:NH$_3$ mixtures in a 4:1, 2:1 and 1:3 ratio irradiated with 1 keV electrons at a fluence of $3.37 \times 10^{15} \text{ e}^\text{−} \text{ cm}^{-2}$. The inset shows a zoomed region of the $\Pi_g \leftarrow \Sigma_g^+$ of CO$_2$ and the $\tilde{A}^1\Pi \leftarrow \tilde{X}^1\Sigma^+$ transition of CO.

### 6.4.2 Thermal processing after electron processing at 20 K

After electron irradiation at 20 K the mixtures were thermally processed to 250 K. Fig. 6.10 shows the thermal processing of the 4:1 ratio. The following thermally induced changes were observed:

- Pure CO$_2$ ice deposited at 20 K has vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition which was not observed in the 4:1 ratio at 20 K. However, after thermal processing to 70 K, vibrational structure of the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ was observed.

- CO$_2$ desorbed between 90–100 K, which was observed through the disappearance of the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ transition.

- CO and O$_3$ which formed from the electron irradiation of the mixture desorbed between 80 and 90 K.
Fig. 6.9 A mid-IR spectrum of the $\nu_2$ vibrational mode of NH$_3$ of a 4:1 CO$_2$:NH$_3$ mixture which was deposited at 20 K and irradiated with 1 keV electrons for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The grey shaded area shows where the $\nu_3$ vibrational mode of O$_3$ should be present, but is obscured by the $\nu_2$ vibrational mode of NH$_3$.

Table 6.2 A summary of the products formed from 1 keV electron irradiation of a 4:1, 2:1 and 1:3 CO$_2$:NH$_3$ binary mixtures.

<table>
<thead>
<tr>
<th>CO$_2$:NH$_3$ ratio</th>
<th>CO intensity</th>
<th>O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>Strong</td>
<td>✓</td>
</tr>
<tr>
<td>4:1</td>
<td>Strong</td>
<td>✓</td>
</tr>
<tr>
<td>1:1</td>
<td>Strong</td>
<td>✗</td>
</tr>
<tr>
<td>1:3</td>
<td>Weak</td>
<td>✗</td>
</tr>
</tbody>
</table>

- A new band centred around 205 nm formed by 110 K and increased in intensity until it reached a maximum at 150 K before it decreased in intensity until desorption by 250 K.

Fig. 6.11 shows the thermal processing of the 1:1 ratio after electron irradiation. The following thermally induced changes were observed:

- Pure CO$_2$ ice deposited at 20 K has vibrational structure on the $^{1}\Pi_g \leftarrow ^1\Sigma_g^+$ transition which was not observed in the 2:1 ratio at 20 K. However, upon thermal processing to 70 K vibrational structure of the $^{1}\Pi_g \leftarrow ^1\Sigma_g^+$ transition of CO$_2$ appeared.

- CO$_2$ desorbed between 90–100 K, which was observed through the disappearance of the $^{1}\Pi_g \leftarrow ^1\Sigma_g^+$ transition.
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Fig. 6.10 The thermal processing VUV spectra of a NH$_3$ and CO$_2$ mixture in a 4:1 ratio which was irradiated with 1 keV electrons at 20 K for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The top inset shows a zoomed region of the $\Pi_g \rightarrow \Sigma^+_g$ of CO$_2$ and the $A^1\Pi \rightarrow X^1\Sigma^+$ transition of CO. The bottom inset shows a zoomed region of the Hartley Band of O$_3$.
Fig. 6.11 The thermal processing VUV spectra of a NH₃ and CO₂ mixture in a 2:1 ratio which was irradiated with 1 keV electrons at 20 K for a total fluence of $3.37 \times 10^{15}$ e⁻ cm⁻². The inset shows a zoomed region of the $\Pi_g \leftarrow \Sigma_g^+$ of CO₂ and the $A^1\Pi \leftarrow X^1\Sigma^+$ transition of CO.
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- CO which formed from the electron irradiation of the mixture desorbed between 120 and 150 K.

- A new band centred around 205 nm formed by 110 K and increased in intensity until it reached a maximum at 150 K before it decreased in intensity until desorption by 250 K.

- Vibrational structure was present on the transition centred around 145 nm at 150 K, but was not due to A$^1\Pi \leftarrow X^1\Sigma^+$ transition of CO as this desorbed by 150 K.

After electron irradiation at 20 K the mixtures were thermally processed to 250 K. Fig. 6.12 shows the thermal processing of the 1:4 ratio. The following thermally induced changes were observed:

- Pure CO$_2$ ice deposited at 20 K has vibrational structure on the $^1\Pi_g \leftarrow ^1\Sigma^+_g$ transition which was not observed in the 2:1 ratio at 20 K. However, unlike the 4:1 and 2:1 ratio, even during thermal processing no vibrational structure of the $\Pi_g \leftarrow \Sigma^+_g$ transition of CO$_2$ was observed.

- CO$_2$ desorbed between 90–100 K, which was observed through the disappearance of the $^1\Pi_g \leftarrow ^1\Sigma^+_g$ transition.

- CO which formed from the electron irradiation of the mixture desorbed between 120 and 150 K.

- A new band centred around 205 nm formed by 110 K and increased in intensity until it reached a maximum at 150 K before it decreased in intensity until desorption by 250 K.

- Vibrational structure was present on the transition centred around 145 nm at 150 K, but was not due to A$^1\Pi \leftarrow X^1\Sigma^+$ transition of CO as this desorbed by 150 K.

A summary of the thermal processing results of the electron processed CO$_2$:NH$_3$ mixtures is given in Table 6.3.

Discussion

Entrapment of O$_3$ in a CO$_2$ matrix was observed by Jones et al. until desorption of CO$_2$ at 100 K.\textsuperscript{214} However, while the Hartley band of O$_3$ disappeared between 80–90 K in Fig 6.10 this does not necessarily mean that all of the O$_3$ desorbed from the CO$_2$:NH$_3$ ice mixture. In section 6.2.3 a study by Sivaraman on O$_3$ formed from pure O$_2$ was discussed. The Hartley band was observed to disappear before other electronic transitions associated with O$_3$ disappeared. These other electronic transitions of O$_3$ were obscured by other electronic transitions in the mixtures.
Fig. 6.12. The thermal processing VUV spectra of a NH$_3$ and CO$_2$ mixture in a 1:3 ratio which was irradiated with 1 keV electrons at 20 K for a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The inset shows a zoomed region of the $\Pi_g \leftarrow \Sigma_g^+$ of CO$_2$ and the A$^1\Pi \leftarrow X^1\Sigma^+$ transition of CO.
Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

Table 6.3 Summary of the electron irradiation and subsequent thermal processing of the CO$_2$:NH$_3$ mixtures.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>4:1</th>
<th>2:1</th>
<th>1:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of vibrational structure on the $\Pi_g \leftarrow \Sigma_g^+$ transition of CO$_2$ (K)</td>
<td>70</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Desorption of CO (K)</td>
<td>80–90</td>
<td>120–150</td>
<td>120–150</td>
</tr>
<tr>
<td>Desorption of O$_3$ (K)</td>
<td>80–90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desorption of CO$_2$ (K)</td>
<td>90–100</td>
<td>90–100</td>
<td></td>
</tr>
<tr>
<td>Formation of vibrational structure on the transition centred around 145 nm (K)</td>
<td>150</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

As entrapment of O$_3$ occurred within a pure CO$_2$ ice until desorption of CO$_2$, it is likely that O$_3$ was also entrapped with a CO$_2$:NH$_3$ ice mixture until CO$_2$ desorbed between 90–100 K.

An exciton peak was observed upon thermal processing to 90 K in the unirradiated thermal processed mixture of the 1:3 ratio of CO$_2$:NH$_3$ in Fig. 5.10. Fig 6.13 shows that no exciton peak was observed in any of the irradiated mixtures. As discussed in Section 5.4.3 Wannier exciton peaks require an ice containing crystallites with many grain boundaries to form. It stands to reason that the formation of products from the electron irradiation of CO$_2$:NH$_3$ mixtures sufficiently disrupted the crystallite network and their associated grain boundaries, preventing the propagation of a Wannier exciton in NH$_3$.

6.4.3 Residue spectra at 150 and 200 K

Fig. 6.14 shows the VUV spectra of the 4:1, 2:1 and 1:3 ratios at 150 and 200 K. The 4:1 residue spectra at 150 and 200 K was similar in spectral profile with a distinct electronic transition at 205 nm. Between 120–175 nm the intensity of the residue decreased between 150 and 200 K. The 2:1 residue spectra at 150 K had vibrational structure centred around a transition at 145 nm. This transition disappeared upon thermal processing to 200 K. The 1:3 residue spectra at 150 K and 200 K was similar in profile retaining the vibrational structure on the transition centred at 145 nm.

Comparison with thermal processed CO$_2$:NH$_3$ mixtures

Fig. 6.15 shows the comparison of the thermal processed and electron and thermal processed residues at 150 K. The following differences were observed:
6.4 Binary mixtures

Fig. 6.13 VUV spectra of the region where a Wannier exciton peak should form at 194 nm. The electron processed CO$_2$:NH$_3$ mixtures 4:1 (blue), 2:1 (green) and 1:3 (orange) were compared against the electron processed 0:1 (black) ratio, when thermally processed to 90 K. The shaded region indicates the area where the Wannier exciton peak would be observed. All spectra are normalised to a thickness of 200 nm.

- The electron processed residues were more intense compared with the thermal processed residues which was in agreement with the mid-IR results.

- The electron and thermal processed 4:1, 2:1 and 1:3 ratios all lacked the feature at 175 nm which was observed for the equivalent thermal processed binary mixtures.

- The electron and thermal 4:1 ratio also had a feature centred around 205 nm which was not observed in the 4:1 thermally processed ice which was not irradiated.

Fig. 6.16 shows the comparison of the thermal processed and electron and thermal processed residues at 200 K. The following differences were observed:

- The electron processed residues were more intense compared with the thermal processed residues which was in agreement with the mid-IR results.

- The electron and thermal processed 4:1, 2:1 and 1:3 ratios all lacked a feature at 175 nm which was observed for the equivalent thermal processed binary mixtures.

- The electron and thermal 4:1 ratio also had a feature centred around 205 nm which was not observed in the 4:1 thermally processed ice.
Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

![Graph showing VUV residue spectra of CO$_2$ and NH$_3$ mixtures in a 4:1, 2:1 and 1:3 ratio after electron processing at 20 K and subsequent thermal processing to 150 K and 200 K.](image)

**Fig. 6.14** VUV residue spectra of CO$_2$ and NH$_3$ mixtures in a 4:1, 2:1 and 1:3 ratio after electron processing at 20 K and subsequent thermal processing to 150 K and 200 K.

**Interpretation of the residue spectra**

The mid-IR systematic investigation of the thermal processing of CO$_2$:NH$_3$ interstellar ice analogues in Chapter 4 identified conversion of ammonium carbamate to carbamic acid for all the ratios investigated (Chapter 4 electron processed mid-IR ratios: 2:1, 1:1, 1:2, 1:5, 1:10) except for the 4:1 ratio. The conversion of ammonium carbamate to carbamic acid was hindered when compared to the thermal processing results of Chapter 3. The mid-IR electron and thermal processed 4:1 ratio showed no evidence of the strong COO$^-$ or C=O stretches associated with ammonium carbamate and carbamic acid, respectively.

Tentative assignments of electronic transitions observed in the thermally processed residue spectra were proposed in Section 5.4.4. The transition at $\sim$150 nm was tentatively assigned as being due to ammonium carbamate and the transition at $\sim$170 nm was tentatively assigned as being due to carbamic acid.

Using the mid-IR results of the electron processed binary mixtures in Chapter 4 which concluded that the conversion from ammonium carbamate to carbamic acid between 150–200 K was hindered in the electron and thermal processed mixtures. The residue spectra at 200 K for the electron irradiated mixtures should still be dominated by ammonium carbamate compared to the unirradiated residues and this comparison is shown in Fig. 6.16. A lack of an observed
transition at $\sim 170$ nm of the electron processed 2:1 and 1:3 residues further supports the assignment of carbamic acid being responsible for the transition at $\sim 170$ nm. Small amounts of carbamic acid was probably present within the 2:1 and 1:3 residues, but obscured by the ammonium carbamate transition at $\sim 150$ nm. The absence of a transition at $\sim 170$ nm in the electron and thermal processed 4:1 ratio confirms the mid-IR results of Chapter 4 which showed no evidence of the formation of carbamic acid. In this case there is no ammonium carbamate transition at $\sim 150$ nm which could be obscuring a peak at $\sim 170$ nm.

The electron and thermal processed residue spectra of all mixtures at 200 K contained a transition at $\sim 150$ nm. This transition was tentatively assigned as being due to ammonium carbamate. However, no strong COO$^-$ stretches in the mid-IR 4:1 residues were present which suggested that ammonium carbamate was not present in this mixture. However, if this transition was due to NH$_4^+$ ion of ammonium carbamate then it could be that the 4:1 residue contained an NH$_4^+$ ion. However, it is still a mystery as to what the counterion to the ammonium ion is in the 4:1 electron processed ratio. From the mid-IR results it is unlikely to contain a COO$^-$ group as these were not present in the mid-IR results.
Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

![Graph showing VUV residue spectra comparison](image)

**Fig. 6.16** Comparison of VUV residue spectra at 200 K of unirradiated residues (u prefix) of CO$_2$ and NH$_3$ mixtures and electron irradiated (i prefix) at 20 K and subsequent thermal processing to 200 K residues. Dashed lines at 152 nm and 170 nm highlight features present.

### 6.4.4 Summary

Electron and thermal processing of the CO$_2$:NH$_3$ 4:1 ratio formed a new band near 205 nm at 110 K which was not observed in any of the other ratios. O$_3$ was also formed in this mixture, but for none of the other mixtures. The presence of O$_3$ may have directly influenced the formation of the different residue material through active participation in a reaction or indirectly influenced the formation of the residue by inhibiting particular reaction pathways present in the other ratios.

### 6.5 Scattering tails in the electron irradiated binary mixtures

The Rayleigh scattering tails were fitted in the same way as described in Section 5.5. Rayleigh scattering tails were fitted to all of the electron and thermal processed VUV spectra except for CO$_2$ which exhibits no Rayleigh scattering tails and the results are described below.
6.5 Scattering tails in the electron irradiated binary mixtures

Pure NH$_3$

Table 6.4 shows the results of the Rayleigh scattering model for pure NH$_3$ ice deposited at 20 K, processed with 1 keV electrons for a total fluence of $3.37 \times 10^{15} \text{ e}^{-} \text{ cm}^{-2}$ and thermally processed. An increase in the $\Delta c$ value was observed after electron processing to a fluence of $3.37 \times 10^{15} \text{ e}^{-} \text{ cm}^{-2}$ and remained relatively constant throughout thermal processing.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Fluence ($\times 10^{15} \text{ e}^{-} \text{ cm}^{-2}$)</th>
<th>$c (\times 10^{8})$</th>
<th>$\Delta c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>0.61 $\pm$ 0.04</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1.12</td>
<td>1.85 $\pm$ 0.03</td>
<td>204</td>
</tr>
<tr>
<td>20</td>
<td>2.24</td>
<td>2.13 $\pm$ 0.03</td>
<td>250</td>
</tr>
<tr>
<td>20</td>
<td>3.37</td>
<td>2.31 $\pm$ 0.02</td>
<td>279</td>
</tr>
<tr>
<td>70</td>
<td>3.37</td>
<td>2.22 $\pm$ 0.02</td>
<td>265</td>
</tr>
<tr>
<td>80</td>
<td>3.37</td>
<td>2.29 $\pm$ 0.02</td>
<td>276</td>
</tr>
<tr>
<td>90</td>
<td>3.37</td>
<td>2.30 $\pm$ 0.02</td>
<td>278</td>
</tr>
<tr>
<td>100</td>
<td>3.37</td>
<td>2.32 $\pm$ 0.02</td>
<td>281</td>
</tr>
<tr>
<td>120</td>
<td>3.37</td>
<td>2.21 $\pm$ 0.02</td>
<td>263</td>
</tr>
<tr>
<td>150</td>
<td>3.37</td>
<td>2.01 $\pm$ 0.04</td>
<td>231</td>
</tr>
<tr>
<td>200</td>
<td>3.37</td>
<td>1.97 $\pm$ 0.02</td>
<td>223</td>
</tr>
</tbody>
</table>

CO$_2$:NH$_3$ 4:1 mixture

Table 6.5 shows the results of the Rayleigh scattering model for a 4:1 mixture of CO$_2$ and NH$_3$ ice deposited at 20 K, processed with 1 keV electrons for a total fluence of $3.37 \times 10^{15} \text{ e}^{-} \text{ cm}^{-2}$ and thermally processed. The 4:1 ratio has a feature on the Rayleigh scattering tail centred around 205 nm which was subtracted from the spectra before fitting with Eq. 5.3 to prevent the feature from skewing the results. An initial increase in the $\Delta c$ value was observed after the first irradiation interval at a fluence of $1.12 \times 10^{15} \text{ e}^{-} \text{ cm}^{-2}$ before it decreased slightly for successive irradiation intervals. During thermal processing the $\Delta c$ value increased slightly at 70 K and decreased sharply at 90 K. The $\Delta c$ value then increased steadily until 120 K before it decreased again.

CO$_2$:NH$_3$ 2:1 mixture

Table 6.6 shows the results of the Rayleigh scattering model for a 2:1 mixture of CO$_2$ and NH$_3$ ice deposited at 20 K, processed with 1 keV electrons for a total fluence of $3.37 \times 10^{15} \text{ e}^{-} \text{ cm}^{-2}$ and thermally processed. The $\Delta c$ value increased throughout electron processing at 20 K.
Electron and thermal processing of CO\textsubscript{2}:NH\textsubscript{3} interstellar ice analogues: a VUV spectroscopic study

Table 6.5 Results of the Rayleigh scattering model fits (Eq. 5.3) for electron irradiated, 4:1 CO\textsubscript{2}:NH\textsubscript{3} mixture.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Fluence ($\times10^{15}$ e$^{-}$ cm$^{-2}$)</th>
<th>c ($\times10^{7}$)</th>
<th>$\Delta$c</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>0.733 ± 0.10</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1.12</td>
<td>10.3 ± 0.12</td>
<td>1302</td>
</tr>
<tr>
<td>20</td>
<td>2.24</td>
<td>8.65 ± 0.09</td>
<td>1080</td>
</tr>
<tr>
<td>20</td>
<td>3.37</td>
<td>7.83 ± 0.09</td>
<td>968</td>
</tr>
<tr>
<td>70</td>
<td>3.37</td>
<td>9.16 ± 0.10</td>
<td>1149</td>
</tr>
<tr>
<td>80</td>
<td>3.37</td>
<td>8.64 ± 0.16</td>
<td>1078</td>
</tr>
<tr>
<td>90</td>
<td>3.37</td>
<td>4.74 ± 0.14</td>
<td>547</td>
</tr>
<tr>
<td>100</td>
<td>3.37</td>
<td>5.23 ± 0.17</td>
<td>613</td>
</tr>
<tr>
<td>110</td>
<td>3.37</td>
<td>5.65 ± 0.19</td>
<td>671</td>
</tr>
<tr>
<td>120</td>
<td>3.37</td>
<td>6.19 ± 0.19</td>
<td>745</td>
</tr>
<tr>
<td>150</td>
<td>3.37</td>
<td>5.93 ± 0.22</td>
<td>709</td>
</tr>
<tr>
<td>200</td>
<td>3.37</td>
<td>4.03 ± 0.15</td>
<td>449</td>
</tr>
</tbody>
</table>

Similarly to the 4:1 ratio, during thermal processing the $\Delta$c value increased slightly at 70 K, but dissimilarly to the 4:1 ratio, the $\Delta$c value of the 2:1 ratio generally decreased after 70 K.

CO\textsubscript{2}:NH\textsubscript{3} 1:3 mixture

Table 6.7 shows the results of the Rayleigh scattering model for a 1:3 mixture of CO\textsubscript{2} and NH\textsubscript{3} ice deposited at 20 K, processed with 1 keV electrons for a total fluence of $3.37 \times 10^{15}$ e$^{-}$ cm$^{-2}$ and thermally processed. The $\Delta$c value increased with electron processing to a fluence of $2.24 \times 10^{15}$ e$^{-}$ cm$^{-2}$ before it decreased during the last electron irradiation interval. Similarly to pure NH\textsubscript{3} ice, the $\Delta$c value remained relatively constant throughout thermal processing.

Discussion

The $\Delta$c value for all CO\textsubscript{2}:NH\textsubscript{3} mixtures and pure NH\textsubscript{3} were higher after electron processing to a fluence of $3.37 \times 10^{15}$ e$^{-}$ cm$^{-2}$ than at deposition. Molecular dissociation and the formation of new products due to electron processing of the samples appeared to disrupt the ice structure. Although generally, through mid-IR studies, it was assumed that the change in ice morphology was thermally induced, the VUV scattering results indicate direct evidence that, as well as inducing chemical changes, pre-thermal electron irradiation also caused macroscopic changes in ice structure and morphology. A slight decrease in the $\Delta$c value during irradiation of the pure NH\textsubscript{3}, the 4:1 and 1:3 CO\textsubscript{2}:NH\textsubscript{3} mixtures was probably due to a combination of sputtering and reactions of the dissociated molecular fragments. Sputtering of the ice would lead to a
6.5 Scattering tails in the electron irradiated binary mixtures

Table 6.6 Results of the Rayleigh scattering model fits (Eq. 5.3) for electron irradiated, 2:1 CO$_2$:NH$_3$ mixture.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Fluence ($\times 10^{15}$ e$^-$ cm$^{-2}$)</th>
<th>c ($\times 10^7$)</th>
<th>$\Delta c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>0.80 ± 0.33</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1.12</td>
<td>4.97 ± 0.14</td>
<td>517</td>
</tr>
<tr>
<td>20</td>
<td>2.24</td>
<td>6.34 ± 0.12</td>
<td>689</td>
</tr>
<tr>
<td>20</td>
<td>3.37</td>
<td>7.24 ± 0.13</td>
<td>800</td>
</tr>
<tr>
<td>70</td>
<td>3.37</td>
<td>9.03 ± 0.13</td>
<td>1022</td>
</tr>
<tr>
<td>80</td>
<td>3.37</td>
<td>7.81 ± 0.16</td>
<td>871</td>
</tr>
<tr>
<td>90</td>
<td>3.37</td>
<td>6.88 ± 0.09</td>
<td>755</td>
</tr>
<tr>
<td>100</td>
<td>3.37</td>
<td>7.26 ± 0.12</td>
<td>803</td>
</tr>
<tr>
<td>110</td>
<td>3.37</td>
<td>7.07 ± 0.12</td>
<td>779</td>
</tr>
<tr>
<td>120</td>
<td>3.37</td>
<td>6.67 ± 0.12</td>
<td>729</td>
</tr>
<tr>
<td>150</td>
<td>3.37</td>
<td>6.48 ± 0.16</td>
<td>705</td>
</tr>
<tr>
<td>200</td>
<td>3.37</td>
<td>5.42 ± 0.18</td>
<td>574</td>
</tr>
</tbody>
</table>

decrease in the number of scatterers which $\Delta c$ is dependent upon and hence a decrease in $\Delta c$ value. Reaction of the dissociated fragments could lead to less scatterers present within the ice which would also decrease the $\Delta c$ value.

Interestingly, during thermal processing no spike in the $\Delta c$ value was observed for the mixtures or the pure NH$_3$ ice unlike the thermally processed ices presented in Chapter 5 where a spike was observed at 90 K for all mixtures and pure NH$_3$ ice. This spike in the $\Delta c$ value was attributed to the crystallisation of NH$_3$. The lack of a spike in the electron processed mixtures and pure NH$_3$ does not necessarily mean that crystallisation of NH$_3$ did not occur. In fact the mid-IR results from Chapter 4 confirmed that the NH$_3$ within the mixtures or the pure ice did crystallise. As the clumps form at the surface of the ice, the observed Rayleigh scattering tails were due to the surface properties rather than the bulk properties. During irradiation electrons can only penetrate to a finite depth (see Table A.4) and it is assumed that the majority of the NH$_3$ molecules at the surface were dissociated. While NH$_3$ molecules in the bulk of the ice crystallised during thermal processing, the bulk ice properties did not contribute to the Rayleigh scattering tails which were dependent on the layers of ice closest to the surface. Molecular rearrangement from crystallisation is therefore not observed and so no spike in the $\Delta c$ occurred.

The NH$_3$ rich mixture (1:3 ratio) followed a very similar trend to pure NH$_3$ ice whereby after an initial increase in the $\Delta c$ value due to electron processing the $\Delta c$ value remained at a similar value throughout thermal processing. This was not the case for the 4:1 ratio which had a significant decrease in the $\Delta c$ value at 90 K nor, to a lesser extent, for the 1:2 ratio. It is difficult to ascribe a reason for the this difference as the $\Delta c$ value is dependent on several
Table 6.7 Results of the Rayleigh scattering model fits (Eq. 5.3) for electron irradiated, 1:3 CO$_2$:NH$_3$ mixture.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Fluence ($\times 10^{15}$ e$^-$ cm$^{-2}$)</th>
<th>c ($\times 10^8$)</th>
<th>$\Delta c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>0.50 ± 0.27</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1.12</td>
<td>1.60 ± 0.16</td>
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</tr>
<tr>
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<td>1.67 ± 0.19</td>
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<tr>
<td>200</td>
<td>3.37</td>
<td>1.55 ± 0.02</td>
<td>210</td>
</tr>
</tbody>
</table>

... things (e.g. number of scatterers, refractive index of the ice and particle size). However, one possible explanation could be the onset of desorption of irradiation products at 90 K causing the observed decrease in the $\Delta c$ value. CO, which is an irradiation product observed in all the mixtures, started desorbing around 90 K and the largest amount was observed in the 4:1 ratio, followed by the 2:1 ratio with very little observed in the 1:3 ratio.

6.6 Summary of the electron irradiated CO$_2$:NH$_3$ mixtures

A systematic investigation of the electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of deposition mixing ratio using VUV spectroscopy was presented in this chapter and the results are summarised below:

- Formation of O$_3$ was observed in the 4:1 ratio after electron irradiation at 20 K, but not in any of the other ratios.
- For the 2:1 and 1:3 ratios no significant change was observed upon thermal processing from 150 to 200 K. In the unirradiated residues a peak at 175 nm was observed at 150 and 200 K and tentatively assigned as being due to carbamic acid. If the peak at 175 nm was due to carbamic acid then no observation of the 175 nm peak in the electron irradiated residues is in agreement with the mid-IR results. Mid-IR results showed no conversion of ammonium carbamate to carbamic acid.
6.6 Summary of the electron irradiated CO$_2$:NH$_3$ mixtures

![Graph showing the comparison of Δc for electron processed 4:1, 2:1 and 1:1 CO$_2$:NH$_3$ mixture and pure NH$_3$ against temperature. Two points are shown at 20 K for each ratio. The point marked with a black cross hair indicates the Δc at deposition and the point marked with a white cross hair indicates the Δc after 3.37 x 10$^{15}$ e$^-$ cm$^{-2}$. Δc values are normalised to a thickness of 200 nm.](image)

**Fig. 6.17** A comparison of Δc for electron processed 4:1, 2:1 and 1:1 CO$_2$:NH$_3$ mixture and pure NH$_3$ against temperature. Two points are shown at 20 K for each ratio. The point marked with a black cross hair indicates the Δc at deposition and the point marked with a white cross hair indicates the Δc after 3.37 x 10$^{15}$ e$^-$ cm$^{-2}$. Δc values are normalised to a thickness of 200 nm.

- The feature at 150 nm is tentatively assigned as being due to ammonium ions. In the case of the 2:1 and 1:3 ratio the source of ammonium ions in likely due to ammonium carbamate.

- In agreement with the mid-IR results, the electron irradiated 4:1 ratio residue spectra at 150 and 200 K were different to the 2:1 and 1:3 residue spectra at 150 and 200 K. The peak at 150 nm which was tentatively assigned as being due to NH$_4^+$ ions was present in the 4:1 ratio which might imply that part of the residue is composed of ammonium ions.

- Rayleigh scattering tails were fitted to pure NH$_3$ and all of the mixtures at 20 K and for majority of the thermal processing spectra. Pure NH$_3$ does not form a uniformly smooth ice and instead forms a rough ice with clumps on the surface as do mixtures of CO$_2$ and NH$_3$. Overall, electron processing increased the Δc value probably due to the increase in scatterers from the dissociation of the CO$_2$ and NH$_3$ molecules demonstrating that electron irradiation not only induces chemical changes but also physical changes within the ices.

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This chapter completes the aim of this thesis to systematically investigate the thermal and radiation processing (via electron processing) of a CO$_2$:NH$_3$ binary ice system as a function of deposition mixing ratio using mid-IR and VUV spectroscopy. The next chapter, will discuss the implication of the results of Chapters 3, 4, 6 and this chapter in a wider astrochemical context. The next chapter will also provide suggestions for future work and concluding comments.
Chapter 7

Implications of a systematic study on CO$_2$:NH$_3$ mixtures

7.1 Introduction

Understanding how experimental parameters influence an interstellar ice analogue is important for gaining a comprehensive understanding of molecular synthesis in interstellar ice. However, very few astrochemical laboratory experiments have comprehensively investigated the influence of a single parameter. The aim of this thesis was to systematically investigate thermal and radiation processing of one binary ice system as a function of deposition mixing ratio. Thermal processing represents the thermal gradient observed in interstellar ices around YSOs as well as the thermal evolution of ices during the star formation process. Radiation processing was mimicked by using an electron gun to simulate the secondary electrons which are released when a cosmic ray passes through interstellar ice. A CO$_2$:NH$_3$ binary ice system was used to demonstrate that even simple binary ice systems where experimental parameters are investigated systematically will provide much more information on the ice system. Such an ice system has been the subject of several previous thermal processing\textsuperscript{162,163,94,140,95} and several energetic processing studies.\textsuperscript{94,141–143} Furthermore, CO$_2$ and NH$_3$ are two of the most abundant observed molecules in interstellar ices and when combined they contain the four most common elements to life. The work presented and discussed in this thesis is the first comprehensive study of both thermal and radiation processing of the CO$_2$:NH$_3$ binary ice as a function of mixing ratio, using a combination of two complementary \textit{in situ} spectroscopic techniques.

A summary of the results from Chapters, 3, 4, 5 and 6 are given in Section 7.2 and the implications on astrochemical experiments are given in Section 7.3. The implications for astrophysical observations is given in Section 7.4 and for astrochemical models in Section
7.5. A brief overview of ongoing and future work is presented in Section 7.6 and concluding remarks for this thesis are given in Section 7.7.

7.2 Summary of results

7.2.1 Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a mid-IR spectroscopic study

Mid-IR results of the thermal processing of several ratios (3:1, 2:1, 1:1, 1:3, 1:10) of CO$_2$:NH$_3$ ice mixtures deposited at 20 K were presented in Chapter 3. From previous literature experiments it was established that ammonium carbamate and carbamic acid formed from the thermal processing of CO$_2$ and NH$_3$ binary mixture deposited at $\sim$20 K$^{94,140,143}$ or 70 K.$^{95}$ For CO$_2$:NH$_3$ mixtures with excess NH$_3$ deposited at 20 K, both ammonium carbamate and carbamic acid were observed at 140 and 200 K.$^{140}$ However, for CO$_2$:NH$_3$ mixtures with excess NH$_3$ deposited at 70 K only ammonium carbamate was observed at 150 K. Carbamic acid and ammonium carbamate were observed after thermal processing to 200 K.

In agreement with previous results reported in the literature the results presented in Chapter 3 of the thermal processing of CO$_2$:NH$_3$ mixtures deposited at 20 K demonstrated the formation of both ammonium carbamate and carbamic acid. The additional results obtained from this systematic mid-IR study of thermally processed CO$_2$:NH$_3$ mixtures are summarised below:

- Due to the angle of the substrate with respect to the IR beam both LO and TO modes of the $\nu_2$ fundamental mode of CO$_2$ were observed. The splitting pattern of the LO and TO modes of CO$_2$ at 20 K suggested that the CO$_2$:NH$_3$ mixtures were thoroughly mixed. Segregation of the CO$_2$:NH$_3$ was observed upon thermal processing to 50–80 K.

- The LO-TO splitting pattern suggested that CO$_2$ crystallised in the 1:3 and 1:10 ratio, but not for the 3:1, 2:1 and 1:1 ratios at $\sim$80 K.

- A phase change in NH$_3$ was observed for all mixtures above 80 K. The mixtures appeared to form a more ordered phase of NH$_3$ compared to thermal processing of pure NH$_3$ ice. The NH$_3$ in the excess CO$_2$ ratios (3:1 and 2:1) appeared more ordered compared to the other ratios (1:1, 1:3 and 1:10) which themselves were more ordered than pure NH$_3$ ice. This difference was attributed to the extent of the intermolecular H-bonds of NH$_3$ which formed upon deposition of the CO$_2$:NH$_3$ mixtures at 20 K.
7.2 Summary of results

- No thermal processing reaction was observed for the 3:1 ratio using mid-IR spectroscopy which was due to the lack of sensitivity of mid-IR spectroscopy. However, complementary VUV studies showed that a reaction did occur.

- A tentative formation route for carbamic acid was proposed when CO$_2$:NH$_3$ mixtures were deposited at 20 K and subsequently processed to 150 K: the CO$_2$:NH$_3$ complex formed at 20 K undergoes a proton transfer reaction to form carbamic acid.

7.2.2 Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a mid-IR spectroscopic study

Mid-IR results of several ratios (4:1, 2:1, 1:1, 1:2, 1:5, 1:10) of CO$_2$:NH$_3$ mixtures deposited at 20 K, irradiated with 1 keV electrons at 20 K and subsequently thermally processed were presented in Chapter 4. From previous experiments reported in the literature it has been suggested that the formation of ammonium carbamate, ammonium formate, carbamic acid, CO and OCN$^-$ are formed after energetic processing with VUV photons at 10 K. It was also suggested that irradiation with low energy electrons (9 eV) formed ammonium carbamate, OCN$^-$, CO and NH$_4^+$ ions at 30 K. Experiments involving ion bombardment of S$^{9+}$ ions suggested that N$_2$O, OCN$^-$, CO and ammonium formate formed at 16 K. Previous experiments appear to have been conducted using a 1:1 ratio CO$_2$:NH$_3$ mixture for the energetic processing and with only one study using another ratio (0.75:1) with no remarks about a ratio dependency of irradiation products formed.

In agreement with previous experiments the formation of CO and OCN$^-$ were observed after electron irradiation of the ice mixtures at 20 K. However, identification of larger molecules was difficult due to the overlapping vibrational modes of NH$_3$ and several electron irradiation products in the region of 1750–1250 cm$^{-1}$. The additional results obtained from this mid-IR systematic study of electron irradiated CO$_2$:NH$_3$ mixtures and subsequent thermal processing are summarised below:

- Although it was not possible to identify the molecules which formed after electron irradiation at 20 K, a ratio dependency on the irradiation peaks was observed. For example, the 1:10 had peaks associated with COO$^-$ stretches, whereas the 4:1 ratio did not.

- There was a ratio dependency on the amount of CO and OCN$^-$ formed from electron irradiation after a total fluence of $3.37 \times 10^{15}$ e$^-$ cm$^{-2}$. The ratio with the highest amount of CO formed was the 4:1 ratio and the ratio with the highest amount of OCN$^-$ formed was the 1:5 ratio.
Implications of a systematic study on CO$_2$:NH$_3$ mixtures

- Similar to the unirradiated results presented in Chapter 3, the degree of phase change of NH$_3$ was dependent on the mixing ratio.

- The products formed in the 4:1 ratio after electron irradiation at 20 K and thermal processing to 150 and 200 K were significantly different to the other ratios. There was no evidence of ammonium carbamate and carbamic acid which were observed for all the other ratios.

- Except for the 4:1 ratio, all the ratios formed ammonium carbamate and carbamic acid after electron irradiation at 20 K and thermal processing to 150 K. However, thermal processing to 200 K did not induce the thermal conversion to carbamic acid as observed in the thermal processing study presented in Chapter 3. The only obvious difference was the presence of OCN$^-$ in the electron and thermal processed residues compared to the thermal processed residues. However, whether the presence of OCN$^-$ prevented the conversion is not known.

7.2.3 Thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

VUV spectra of CO$_2$:NH$_3$ mixtures in three ratios (4:1, 2:1 and 1:3) deposited at 20 K and thermally processed were presented in Chapter 5. No previous VUV spectroscopic studies exist of CO$_2$:NH$_3$ mixtures, therefore the VUV spectra presented in Chapter 5 were new and the interpretation relied on the mid-IR results presented in Chapter 3. The results of this systematic VUV study of CO$_2$:NH$_3$ mixtures are summarised below:

- Vibrational structure associated with the $\Pi_g \leftarrow \Sigma_g^+$ transition of pure CO$_2$ was not observed in mixtures of CO$_2$ and NH$_3$ at 20 K. However, upon thermal processing the vibrational structure was observed for the 2:1 and 1:3 ratios when CO$_2$ and NH$_3$ segregated around 80 K.

- Changes within the VUV spectra when thermally processed from 150 to 200 K, such as the decrease in intensity of an electron transition $\sim$150 nm and increase in peak intensity at $\sim$170 nm, were indicative of the thermal conversion of ammonium carbamate to carbamic acid. The transition at $\sim$150 K was tentatively assigned as due to ammonium carbamate and a transition at $\sim$170 nm was tentatively assigned as carbamic acid.

- A thermal reaction was observed for the 4:1 ratio, but was not observed in the analogous mid-IR results presented in Chapter 3. This was probably due to the better sensitivity of VUV spectroscopy in observing the residue molecules.
7.2 Summary of results

- Rayleigh scattering tails suggested that both pure NH$_3$ and CO$_2$:NH$_3$ mixtures did not form a smooth ice during deposition and instead formed ice layers with a rough surface topography. Changes in the scattering tail parameter observed during thermal processing were consistent with phase changes observed in the spectra (e.g. spike in the $\Delta c$ value around 90 K), indicating global morphological changes in the ice samples.

7.2.4 Electron and thermal processing of CO$_2$:NH$_3$ interstellar ice analogues: a VUV spectroscopic study

VUV spectra of CO$_2$:NH$_3$ mixtures in three ratios (4:1, 2:1 and 1:3) deposited at 20 K and subsequently irradiated with electrons at 20 K and thermally processed were presented in Chapter 6. Again no previous VUV spectroscopic studies exist on energetically processed CO$_2$:NH$_3$ mixtures. The results of this systematic VUV study of electron irradiated CO$_2$:NH$_3$ mixtures and subsequent thermal processing are summarised below:

- The formation of O$_3$ was observed in the 4:1 ratio. This was not possible with mid-IR spectroscopy as the $\nu_2$ mode of NH$_3$ obscured it. This highlights the complementary information which can be obtained by performing VUV spectroscopic studies.

- After electron irradiation at 20 K and subsequent thermal processing, the 4:1 residue was significantly different to the 2:1 and 1:3 ratio which was in agreement with the mid-IR results presented in Chapter 4. A distinctive transition $\sim$205 nm formed although it remains unassigned.

- Again, Rayleigh scattering tails suggested that both pure NH$_3$ and CO$_2$:NH$_3$ mixtures did not form a smooth ice during deposition and instead formed ice layers with a rough surface topography. In addition the Rayleigh scattering tails showed that electron processing not only induced chemical changes but it also induced physical change within the ice structure.

7.2.5 Conclusions

While a systematic investigation into the thermal and electron processing of a CO$_2$:NH$_3$ binary ice system as a function of deposition mixing ratio is time consuming in both data acquisition and interpretation, the additional information gained, which was summarised in this section demonstrates the advantages of such a coherent and systematic study. This additional information is in spite of the fact that CO$_2$:NH$_3$ interstellar ice analogues have been studied repeatedly by different groups, and highlights the importance and need for a more
systematic and comprehensive approach to carrying out such experiments. To fully understand an interstellar ice analogue system, the way in which astrochemical experiments are conducted must be changed. A comprehensive study, systematically investigating a wider parameter space will aid in a better understanding of the physical and chemical properties of an ice mixture and molecular synthesis in interstellar ice, better interpretations of interstellar ice observations and more accurate data for astrochemical models.

The main conclusions from the systematic investigation into the thermal and electron processing of a CO$_2$:NH$_3$ binary ice system as a function of deposition mixing ratio was that experimental parameters need to be comprehensively investigated. Dependency on the deposition mixing ratio included the degree of phase changes in both CO$_2$ and NH$_3$ during thermal processing (with and without electron processing) and the formation of ammonium carbamate and carbamic acid after electron and thermal processing.

### 7.3 Implications for Astrochemical Laboratory Experiments

As summarised in Section 7.2, a substantial amount of new information was acquired from the systematic investigations of the thermal and electron processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of mixing ratio. But what are the implications for future astrochemical laboratory experiments?

In contrast to the thermally processed CO$_2$:NH$_3$ mixtures, the deposition mixing ratio had a significant impact on the formation of electron processed products at 20 K and the subsequent thermally induced products. As none of the literature experiments energetically processed the CO$_2$:NH$_3$ ice analogues as a function of deposition mixing ratio, the ratio dependence on product formation was not known until now. Knowing that a molecule does not form from one ratio is as important as knowing that it forms from other ratios. Therefore, going forward with astrochemical laboratory experiments the deposition mixing ratio of the interstellar ice should always be investigated thoroughly to understand whether product formation is uniform across all ratios or specific to a particular ratio. The deposition ratio is but one experimental parameter which must be investigated in order to understand the influence of experimental parameters on interstellar ice analogues.

The advantages of a combined mid-IR and VUV study of interstellar ice analogues was also demonstrated. The thermal processing of CO$_2$:NH$_3$ interstellar ice analogues using mid-IR spectroscopy in Chapter 3 suggested that no reaction occurred in a 3:1 ratio. However, thermal processing of CO$_2$:NH$_3$ interstellar ice analogues using VUV spectroscopy in Chapter 4 showed
that a reaction did occur in a 4:1 ratio (similar to the mid-IR 3:1 ratio) demonstrating that mid-IR spectroscopy was not sensitive enough to detect this reaction. Yet, interpretation of this VUV spectroscopic result was only possible with the mid-IR spectroscopic study. Therefore, demonstrating the strengths of a combined analysis study of interstellar ice analogues.

7.4 Implications for Astrophysical Observations

How can the results of this thesis be applied to astrophysical observations? The formation routes of ammonium carbamate and carbamic acid are summarised in a schematic diagram in Fig. 7.1. The heating rate of an interstellar ice and the thickness can affect the desorption of molecules into the gas phase. Due to the long time scales associated with astrophysical environments, interstellar ice will desorb at much lower temperatures compared to laboratory interstellar ice analogues. If observations of an interstellar ice revealed vibrational modes commensurate with ammonium carbamate and an astrophysical temperature of \( \sim 200 \text{ K} \), then using Fig 7.1 it might be inferred that the \( \text{CO}_2: \text{NH}_3 \) ice mixture had been subjected to energetic processing and thermal processing. If the ice had undergone thermal processing only, then carbamic acid would be observed as well at astrophysical equivalent temperature of \( \sim 200 \text{ K} \). If an observation of an interstellar ice had vibrational features of both ammonium carbamate and carbamic acid, then it might be inferred that the interstellar ice had undergone thermal processing to astrophysical equivalent temperature of \( \sim 150 \text{ K} \) and may also have been energetically processed.

Needless to say, binary mixtures of \( \text{CO}_2 \) and \( \text{NH}_3 \) are not representative of the multicomponent interstellar ice compositions, but it provides an example of how the knowledge acquired from systematic experiments may be used to infer energetic and thermal histories of interstellar ice.

At present, interstellar ice observations do not provide high enough resolution or sensitivity to detect complex features associated with ammonium carbamate and carbamic acid, but this will change with the commissioning of JWST in 2021. As first discussed in Section 1.2, JWST will cover a wavelength range of 0.6–28.5 \( \mu \text{m} \) making it ideal for interstellar ice observations. The increased angular resolution of JWST will allow mapping of different thermal and radiation environments of star-forming region providing snapshots of ice evolution on an unprecedented scale. In fact the Early Release Science proposal ‘IceAge: Chemical evolution of ices during star formation’ described in Section 1.2 was granted time to use JWST and intends to map the ice evolution over different star forming regions. Before the commissioning of JWST, a logical step instead would be to observe and map ammonium carbamate and carbamic acid in the gas phase with (sub)mm astronomy for example using the Atacama Large Millimeter/submillimeter
Implications of a systematic study on CO$_2$:NH$_3$ mixtures

Fig. 7.1 Summary of formation routes for ammonium carbamate and carbamic acid from Chapters 3, 4, 5, 6
7.5 Implications for Astrochemical Models

Array (ALMA). Unfortunately, ammonium carbamate and carbamic acid do not thermally desorb intact, instead decomposing into CO$_2$ and NH$_3$.$^{94}$

Observational time on telescopes such as the future JWST is limited and being able to direct or target specific areas for the detection of specific molecules is vital. If the results summarised in Fig. 7.1 are taken as an example then if gas phase maps of CO$_2$ and NH$_3$ existed and there were regions of high amounts of NH$_3$ compared to CO$_2$, then searching for the COO$^-$ vibrational features of ammonium carbamate in interstellar ices would be advised.

7.5 Implications for Astrochemical Models

As mentioned in Section 1.4, the majority of gas-grain models that incorporate a large network of chemical reactions will use the rate-equation model. In the rate-equation model, the gas and gas-grain phase chemical kinetics are described by ordinary differential equations and the chemical kinetic data is obtained from laboratory data. While rate constants were not derived for the electron irradiation products of CO and OCN$^-$, growth curves were presented in Fig. 4.13 and 4.14, respectively. The growth curves clearly show a ratio dependency on the formation cross sections and the type of formation growth (e.g. first order, consecutive). Rate-equation models therefore need to include the dependency of formation cross section on experimental parameters like the mixing ratio. Rate-equation models also need to address that product formation is not universal across all deposition mixing ratios.

7.6 Ongoing and future work

When first designing the work programme to be undertaken in this PhD it was planned to systematically investigate thermal and energetic processing of three binary mixtures as a function of mixing ratio. Three molecules from the binary ice system could then be studied in a ternary mixture. Data collection for the systematic study into thermal and energetic processing of CO$_2$:CH$_3$OH and CH$_3$OH:NH$_3$ mixtures as a function of mixing ratio were also planned. However, as evidenced throughout this thesis, a substantial amount of new information from only one binary mixture was obtained through a systematic investigation.

As the data has already been acquired, the next logical step after this thesis would be to analyse the CO$_2$:CH$_3$OH and CH$_3$OH:NH$_3$ mixtures and this is described in Section 7.6.1. However, another and maybe more prudent investigation would be systematically investigate the effect of other experimental parameters of the CO$_2$:NH$_3$ binary ice and this is discussed in Section 7.6.2.
**Implications of a systematic study on CO$_2$:NH$_3$ mixtures**

### 7.6.1 Binary mixtures CO$_2$:CH$_3$OH and CH$_3$OH:NH$_3$

The results in this thesis can be used to target areas of analysis of the CO$_2$:CH$_3$OH and CH$_3$OH:NH$_3$ binary mixtures. For example, from results in this thesis some key questions to ask include:

1. Does the deposition mixing ratio affect the degree of phase change within the molecules?
2. What is the degree of mixing between the molecules in the binary mixtures?
3. Is product formation universal over all ratios?

The deposition mixing ratio dependency on the structural phase of CO$_2$ and NH$_3$ was unknown before the systematic investigation into thermal and electron processing of CO$_2$:NH$_3$ interstellar ice analogues as a function of mixing ratio was performed in this thesis.

### 7.6.2 The influence of experimental parameters on the CO$_2$:NH$_3$ binary ice system

As the results of this thesis have characterised the CO$_2$:NH$_3$ binary ice system as a function of mixing ratio, it would now be interesting to explore the effect of different experimental parameters on this system. For example, the thermal processing study presented in Chapter 3 was compared with a literature study by Noble *et al.* who deposited CO$_2$:NH$_3$ analogues between 70–80 K as a function of deposition ratio. The CO$_2$:NH$_3$ ice analogues in Chapter 3 were deposited at 20 K and a difference in product formation was observed. Already, there is evidence that the experimental parameter of deposition temperature on the CO$_2$:NH$_3$ has an effect on at least product formation. A proposal of the following experimental parameters to investigate is given below:

1. Deposition temperature
2. Deposition rate
3. Electron gun energy
4. Electron irradiation temperature
5. Irradiation source e.g. X-rays, ions
7.7 Concluding remarks

The aim of this thesis was to systematically investigate the thermal and electron processing of a CO$_2$:NH$_3$ binary ice system as a function of deposition mixing ratio to demonstrate the need for systematic investigations in astrochemical laboratory experiments. Systematic astrochemical laboratory experiments are time consuming in both data acquisition and interpretation, but this thesis demonstrates the advantages from such a systematic approach. This thesis clearly shows that despite several studies of this simple binary system in the literature, the conclusions of such studies cannot be extrapolated to more realistic ice analogues. Detailed information, otherwise missed through a less systematic approach, can only be extracted via a thorough, systematic study as evidenced by the new and significantly relevant information extracted from the results of this study. These results highlight the need for systematic experiments in regards to astrophysical observations and the potential to use interstellar ices as tracers of the chemical and physical environment. The results also highlight the need for a systematic approach to experiments in order to provide the best data for astrochemical models which can rely heavily upon experimental values.
References


References


References


References


References


References


References


References


References


References


References


Appendix A

Experimental details

A.1 Interstellar ice analogue ratio

The ratios of the CO$_2$:NH$_3$ mixtures in the mid-IR studies shown in Chapters 3 and 4 were calculated from the column densities of the CO$_2$ $\nu_3$ fundamental mode and the NH$_3$ $\nu_2$ fundamental mode. The column densities were calculated using Eq. 2.23. These results are shown in Table A.1.

Table A.1 Column densities of CO$_2$ and NH$_3$ used to calculated the CO$_2$:NH$_3$ ratios of the mid-IR studies shown in Chapters 3 and 4.

<table>
<thead>
<tr>
<th>Chapter</th>
<th>$N_{CO_2}$ ($\times 10^{17}$ molecules cm$^{-2}$)</th>
<th>$N_{NH_3}$($\times 10^{17}$ molecules cm$^{-2}$)</th>
<th>CO$_2$:NH$_3$ ratio</th>
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<td>0.78</td>
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</table>

A.2 Interstellar ice analogue thickness

The thickness of the interstellar ice analogues was originally calculated from Eq. 2.21 from *in situ* laser measurements as described in Section 2.4.3. To adjust for the angle of the substrate at 45° with respect to the IR or UV beam Eq. 2.22 was used. When comparing spectra from different experiments a normalisation factor was used based of the thickness of the ice. These results are shown in Table A.2.
Experimental details

A.3 Electron fluence

The electron fluence was calculated using Eq. 2.24 and the corresponding electron fluences are shown in Table A.3.

A.4 Electron penetration depth

The penetration depth of the 1 keV electrons during irradiation was calculated using the CASINO simulation model described in Section 2.4.5. CASINO requires the density of the material which was obtained for pure CO$_2$ and NH$_3$ ice from the literature. For the mixtures a weighted density was calculated using Eq. A.1. The results are shown in Table A.4.

$$\rho_{\text{mixture}} = (\rho_{\text{NH}_3} \times \%\text{NH}_3) + (\rho_{\text{CO}_2} \times \%\text{CO}_2)$$  \hspace{1cm} (A.1)

where $\rho_{\text{mixture}}$ is the weighted density of the mixture, $\rho_{\text{NH}_3}$ was the density of pure NH$_3$, $\%\text{NH}_3$ was the percentage of NH$_3$ in the mixture, $\rho_{\text{CO}_2}$ was the density of pure CO$_2$ and $\%\text{CO}_2$ was the percentage of CO$_2$ in the mixture.

A.5 Experimental details

Table A.5 shows the deposition temperature $T_{\text{dep}}$, irradiation time interval if applicable and the thermal processing temperatures $\text{process}$ for the mid-IR spectroscopic studies of CO$_2$:$\text{NH}_3$ presented in Chapters 3 and 4. Table A.6 shows the deposition temperature $T_{\text{dep}}$, irradiation time interval if applicable and the thermal processing temperatures $\text{process}$ for the VUV spectroscopic studies of CO$_2$:$\text{NH}_3$ presented in Chapters 5 and 6.
**A.5 Experimental details**

*Table A.2* Ice thickness of all experiments presented in this thesis.

<table>
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<td>1:0 **</td>
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<td>0:1</td>
<td>343</td>
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<td>400</td>
<td>0.75</td>
</tr>
<tr>
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<td>361</td>
<td>424</td>
<td>0.71</td>
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<td>343</td>
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<td>0.74</td>
</tr>
<tr>
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<td>1:0</td>
<td>404</td>
<td>475</td>
<td>0.63</td>
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<td>356</td>
<td>418</td>
<td>0.72</td>
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<tr>
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<td>382</td>
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<tr>
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<td>2:1</td>
<td>361</td>
<td>424</td>
<td>0.71</td>
</tr>
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<td>339</td>
<td>398</td>
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<td>470</td>
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<td>1:5</td>
<td>405</td>
<td>476</td>
<td>0.63</td>
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<td>387</td>
<td>455</td>
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<td>5</td>
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<td>308</td>
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<td>195</td>
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<td>0.87</td>
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<td>4:1</td>
<td>242</td>
<td>284</td>
<td>0.70</td>
</tr>
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<td>2:1</td>
<td>160</td>
<td>188</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>119</td>
<td>140</td>
<td>1.43</td>
</tr>
<tr>
<td>6</td>
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<td>242</td>
<td>284</td>
<td>0.70</td>
</tr>
<tr>
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<td>0:1</td>
<td>101</td>
<td>119</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>4:1</td>
<td>202</td>
<td>237</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>193</td>
<td>227</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>131</td>
<td>154</td>
<td>1.30</td>
</tr>
</tbody>
</table>

* For Chapter 3 and 4 the interstellar ice analogues were normalised to a thickness of 300 nm. For Chapter 5 and 6 the interstellar ice analogues were normalised to a thickness of 200 nm. ** A thick CO$_2$ ice was used to determine the phase at 20 K (see Section 3.2.2 for more details).
Experimental details

Table A.3 Time intervals used during the electron irradiation studies.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Time (s)</th>
<th>Fluence ($\times 10^{15}$ e $^{-}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>0.11</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>0.23</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>0.34</td>
</tr>
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<td>4</td>
<td>240</td>
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<tr>
<td>5</td>
<td>300</td>
<td>0.56</td>
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<tr>
<td>6</td>
<td>360</td>
<td>0.68</td>
</tr>
<tr>
<td>7</td>
<td>420</td>
<td>0.79</td>
</tr>
<tr>
<td>8</td>
<td>480</td>
<td>0.90</td>
</tr>
<tr>
<td>9</td>
<td>540</td>
<td>1.01</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>1.12</td>
</tr>
<tr>
<td>12</td>
<td>720</td>
<td>1.35</td>
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<tr>
<td>14</td>
<td>840</td>
<td>1.57</td>
</tr>
<tr>
<td>16</td>
<td>960</td>
<td>1.80</td>
</tr>
<tr>
<td>18</td>
<td>1080</td>
<td>2.02</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
<td>2.25</td>
</tr>
<tr>
<td>22</td>
<td>1320</td>
<td>2.47</td>
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<td>24</td>
<td>1440</td>
<td>2.70</td>
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<td>26</td>
<td>1560</td>
<td>2.92</td>
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<td>28</td>
<td>1680</td>
<td>3.15</td>
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<tr>
<td>30</td>
<td>1800</td>
<td>3.37</td>
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Table A.4 CASINO calculated penetration depth of 1 keV electrons.

<table>
<thead>
<tr>
<th>Chapter</th>
<th>CO$_2$:NH$_3$ ratio</th>
<th>Density (g cm$^{-3}$)</th>
<th>Penetration depth (nm)</th>
</tr>
</thead>
<tbody>
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<td>4</td>
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<td>1.11</td>
<td>61</td>
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<tr>
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<td>0:1</td>
<td>0.74</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>4:1</td>
<td>1.06</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>1.02</td>
<td>64</td>
</tr>
<tr>
<td></td>
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<td>1:3</td>
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<td>0.86</td>
<td>64</td>
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<td>1:0</td>
<td>1.11</td>
<td>60</td>
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<tr>
<td></td>
<td>0:1</td>
<td>0.74</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>4:1</td>
<td>1.06</td>
<td>55</td>
</tr>
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<td>1:3</td>
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Table A.5 List of experiments for the mid-IR spectroscopic studies in Chapter 3 and 4.

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<tr>
<th>Chapter</th>
<th>CO\textsubscript{2}:NH\textsubscript{3}</th>
<th>T\textsubscript{dep} (K)</th>
<th>Irradiation intervals (s)</th>
<th>T\textsubscript{process} (K)</th>
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</thead>
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<td>20</td>
<td></td>
<td>30, 40, 50, 60, 70, 80, 90, 100, 110, 120</td>
</tr>
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<td>20</td>
<td></td>
<td>60, 70, 80, 90, 100, 110, 120</td>
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<tr>
<td></td>
<td>2:1</td>
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<tr>
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<td>1:0</td>
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<td>0:1</td>
<td>20</td>
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<tr>
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<td>20</td>
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<tr>
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<td>1:1</td>
<td>20</td>
<td>60, 120, 180, 240, 300, 360, 420, 480, 540, 600, 720, 840, 960, 1080, 1200, 1320, 1440, 1560, 1680, 1800</td>
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</tr>
<tr>
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<td>1:10</td>
<td>20</td>
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Table A.6 List of experiments for the VUV spectroscopic studies in Chapter 5 and 6.

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<tr>
<th>Chapter</th>
<th>CO$_2$:NH$_3$</th>
<th>$T_{dep}$ (K)</th>
<th>Irradiation intervals (s)</th>
<th>$T_{process}$ (K)</th>
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</thead>
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<td>20</td>
<td></td>
<td>70, 80, 90</td>
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<tr>
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<td>0:1</td>
<td>20</td>
<td></td>
<td>70, 80, 90, 100, 110, 120</td>
</tr>
<tr>
<td></td>
<td>4:1</td>
<td>20</td>
<td></td>
<td>70, 80, 90, 100, 120, 150, 200, 250</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>20</td>
<td></td>
<td>20, 50, 60, 70, 80, 90, 100, 110, 120, 130, 150, 200, 250</td>
</tr>
<tr>
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<td>1:3</td>
<td>20</td>
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<td>70, 80, 90, 100, 120, 150, 200, 250</td>
</tr>
<tr>
<td>6</td>
<td>1:0</td>
<td>20</td>
<td>600, 1200, 1800</td>
<td>40, 50, 60, 70, 80, 90, 100</td>
</tr>
<tr>
<td></td>
<td>0:1</td>
<td>20</td>
<td>600, 1200, 1800</td>
<td>70, 80, 90, 100, 120, 150, 200</td>
</tr>
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<td>4:1</td>
<td>20</td>
<td>600, 1200, 1800</td>
<td>70, 80, 90, 100, 110, 120, 150, 200, 250</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>20</td>
<td>600, 1200, 1800</td>
<td>70, 80, 90, 100, 110, 120, 150, 200, 250</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>20</td>
<td>600, 1200, 1800</td>
<td>70, 80, 90, 100, 110, 120, 150, 200, 250</td>
</tr>
</tbody>
</table>
Appendix B

Additional mid-IR and VUV spectra

B.1 Chapter 3: Additional thermal processing spectra of CO$_2$:NH$_3$ mixtures from 20–250 K

The mid-IR spectra of the thermal processing of CO$_2$:NH$_3$ mixtures deposited at 20 K have labels (a–d) which were first described in Section 3.4.2 and are repeated here as a reminder:

(i) Two new absorption features near 3417 and 3253 cm$^{-1}$
(ii) Narrowing of the NH$_3$ vibrational modes
(iii) Broadening of the CO$_2$ vibrational modes
(iv) Red shift in the CO$_2$ vibrational modes
(v) Red and blue shifts in NH$_3$ vibrational modes

The mid-IR spectra of the thermal processing of CO$_2$:NH$_3$ for the following ratios 1:10 (Fig. B.4, 1:2 (Fig. 3.10), 2:1 (Fig. B.2) and 3:1 (Fig. B.1) are shown below.

B.2 Chapter 4: Electron and thermal processing of CO$_2$:NH$_3$ mixtures

B.2.1 Deposition spectra

Fig. B.5 shows the mid-IR spectra of CO$_2$:NH$_3$ mixtures (4:1, 2:1, 1:1, 1:2, 1:5 and 1:10) deposited at 20 K which were used in the electron irradiation studies in Chapter 4 and the band assignments and positions of the vibrational modes are shown in Table B.1.
Fig. B.1: Mid-IR spectra of the warm-up of the 3:1 CO$_2$:NH$_3$ mixture to 250 K. Labels (a) and (b) are described in Section 3.4.2. Spectra are offset on the y-axis and zoomed in with part of the CO$_2$ ν$_3$ mode off the scale for clarity.
Fig. B.2. Mid-IR spectra of the warm up of the 2:1 CO$_2$:NH$_3$ mixture to 250 K. Labels (a)–(d) are described in Section 3.4.2. Spectra are offset on the y-axis and zoomed in with part of the CO$_2$ ν$_3$ mode off the scale for clarity.
Fig. B.3 Mid-IR spectra of the warm up of the 1:3 CO$_2$:NH$_3$ mixture to 250 K. Labels (a)–(d) are described in Section 3.4.2. Spectra are offset on the y-axis for clarity.
Fig. B.4 Mid-IR spectra of the warm up of the 1:10 CO\textsubscript{2}:NH\textsubscript{3} mixture to 250 K. Labels (a)–(d) are described in Section 3.4.2. Spectra are offset on the y-axis for clarity.

offset absorbance

0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35

Wavenumber (cm\textsuperscript{-1})

1000
1500
2000
2500
3000
3500

249 K
200 K
170 K
150 K
130 K
120 K
110 K
100 K
90 K
80 K
70 K
60 K
50 K
40 K
30 K
20 K

F.2 Chapter 4: Electron and thermal processing of \text{CO}_2:\text{NH}_3\text{ mixtures}
Fig. B.5 Mid-IR spectra of CO$_2$:NH$_3$ mixtures at 20 K compared with 1:0 (pure CO$_2$) and 0:1 (pure NH$_3$) before electron processing. Spectra are offset on the y-axis for clarity. All spectra are normalised to a thickness of 300 nm. Dashed lines represent new features which formed upon deposition.
### Table B.1

Band assignments and positions of the vibrational modes of pure CO$_2$, pure NH$_3$ and unirradiated CO$_2$:NH$_3$ mixtures deposited at 20 K before irradiation with 1 keV electrons.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Vib. Mode</th>
<th>Assignment</th>
<th>Ref.</th>
<th>Position (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Pure CO$_2$ 4:1 2:1 1:1 1:2 1:5 1:10 Pure NH$_3$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$v_1 + v_3$</td>
<td>combination</td>
<td>a</td>
<td>3709 3703 3702 3701 3700 3698 3698</td>
</tr>
<tr>
<td></td>
<td>$2v_2 + v_3$</td>
<td>combination</td>
<td>a</td>
<td>3601 3596 3595 3594 3593 3592 3591</td>
</tr>
<tr>
<td></td>
<td>$v_3$</td>
<td>C=O asym. stretch (LO)</td>
<td>b</td>
<td>2380 2374 2369 2367 2360$^{sh}$ 2353 (dh)</td>
</tr>
<tr>
<td></td>
<td>$v_3$</td>
<td>C=O asym. stretch (TO)</td>
<td>a, b</td>
<td>2345 2335 2335 2336 2338 2342 2343</td>
</tr>
<tr>
<td>$^{13}$CO$_2$</td>
<td>$v_3$</td>
<td>asym. Stretch</td>
<td>a</td>
<td>2283 2280 2279 2278 2278 2277 2277</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>CO$_2$:NH$_3$ complex</td>
<td>c</td>
<td>3418 3414 3413 3405$^{sh}$</td>
</tr>
<tr>
<td></td>
<td>$v_3$</td>
<td>N–H asym. Stretch</td>
<td>d</td>
<td>3387 3382 3381 3376 3373 3373 3377</td>
</tr>
<tr>
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<td>$2v_4$</td>
<td>overtone</td>
<td>d</td>
<td>3313 3313 3308 3310 3304 3292 3294</td>
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<td></td>
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<td>$v_4 + v_L$</td>
<td>N–H sym. Stretch</td>
<td>d</td>
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<td>$v_4$</td>
<td>deformation</td>
<td>d</td>
<td>1860 1861 1861 1883</td>
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<td></td>
<td>$v_2$</td>
<td>umbrella</td>
<td>d</td>
<td>1062 1068 1067 1067 1072 1073</td>
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</tbody>
</table>

$^{sh}$ shoulder
asym. = asymmetric
sym. = symmetric
Additional mid-IR and VUV spectra

B.2.2 Additional electron processing spectra of CO$_2$:NH$_3$

The mid-IR spectra of the electron processing of CO$_2$:NH$_3$ mixtures deposited at 20 K have labels (a–n) which were first described in Section 4.4.2 and are repeated here as a reminder:

(a) Decrease in intensity of the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes of CO$_2$ as the electron fluence increased.
(b) Formation of a shoulder on the blue wing of the $\nu_3$ mode of NH$_3$.
(c) Decrease in intensity of the $\nu_3$ vibrational modes of NH$_3$ as the electron fluence increased.
(d) Decrease in intensity of the $2\nu_4$ vibrational modes of NH$_3$ as the electron fluence increased.
(e) Decrease in intensity of the $\nu_1$ vibrational modes of NH$_3$ as the electron fluence increased.
(f) Formation of a shoulder on the red wing of the $\nu_3$ mode of NH$_3$.
(g) Formation of a feature near 2800 cm$^{-1}$.
(h) Formation of electron irradiation product OCN$^-$ at $\sim$2170 cm$^{-1}$.
(i) Formation of electron irradiation product CO $\sim$2140 cm$^{-1}$.
(j) Formation of a C=O stretch at $\sim$1720 cm$^{-1}$.
(k) Formation of several new features within the region 1750–1250 cm$^{-1}$ at 1585, 1484, 1342, 1297 cm$^{-1}$.

The mid-IR spectra the electron processing of CO$_2$:NH$_3$ for the following ratios 1:10 (Fig. B.6), 1:5 (Fig. B.7), 1:2 (Fig. B.8), 2:1 (Fig. B.9) and 4:1 (Fig. B.10) are shown below.

B.2.3 Additional thermal processing spectra of electron irradiated CO$_2$:NH$_3$

The mid-IR spectra of the thermal processing of the electron processing of CO$_2$:NH$_3$ mixtures deposited at 20 K have labels (a–e) which were first described in Section 4.4.2 and are repeated here as a reminder:

(a) The $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination modes of CO$_2$ narrowed and blue shifted between 60–70 K.
(b) The $\nu_2$ vibrational mode of NH$_3$ split between 60–70 K.
(e) The irradiation features highlighted in Fig. B.10–B.6 as labels (k) and (l), resolved and increased in intensity above 90 K.

(d) The CO peak area decreased as the temperature increased until desorption between 130–150 K. Whereas, the OCN\(^{-}\) peak area increased until it reached a maximum \(\sim 130\) K and then decreased until desorption between 248–296 K.

(e) A change occurring in the residue material between 150–200 K.

The mid-IR spectra of the thermal processing of the electron processed CO\(_2\):NH\(_3\) for the following ratios 1:10 (Fig. B.11, 1:5 (Fig. B.12), 1:2 (Fig. B.13), 2:1 (Fig. B.14) and 4:1 (Fig. B.15) are shown below.
B.3 Chapter 6: VUV study on electron and thermal processing of CO$_2$:NH$_3$ mixtures

Fig. 5.6 shows the VUV spectra of CO$_2$ and NH$_3$ mixtures in a 4:1, 2:1 and 1:3 ratios.
Fig. B.6 Mid-IR spectra of the 1 keV electron irradiation of a CO$_2$:NH$_3$ mixture in a 1:10 ratio with the top of the CO$_2$ $v_3$ mode cut off for clarity. Labels a–n are discussed in the main text.
Additional mid-IR and VUV spectra

Fig. B.7 Mid-IR spectra of the 1 keV electron irradiation of a CO₂:NH₃ mixture in a 1:5 ratio with the top of the CO₂ ν₃ mode cut off for clarity. Labels a–n are discussed in the main text.
Fig. B.8 Mid-IR spectra of the 1 keV electron irradiation of a CO$_2$-NH$_3$ mixture in a 1:2 ratio with the top of the CO$_2$ $\nu_3$ mode cut off for clarity. Labels a–n are discussed in the main text.
Fig. B.9 Mid-IR spectra of the 1 keV electron irradiation of a CO$_2$:NH$_3$ mixture in a 2:1 ratio with the top of the CO$_2$ $\nu_3$ mode cut off for clarity. Labels a–n are discussed in the main text.
B.3 Chapter 6: VUV study on electron and thermal processing of CO$_2$:NH$_3$ mixtures

![Fig. B.10](image)

Mid-IR spectra of the 1 keV electron irradiation of a CO$_2$:NH$_3$ mixture in a 4:1 ratio with the top of the CO$_2$ ν$_3$ mode cut off for clarity. Labels a–n are discussed in the main text.
Fig. B.11 Mid-IR spectra of an example warm-up of a 1:10 CO$_2$:NH$_3$ mixture after electron irradiation at 20 K with the top of the CO$_2$ $v_3$ mode cut off for clarity. Boxes labelled (a)–(e) are discussed in the main text.
Fig. B.12 Mid-IR spectra of an example warm-up of a 1:5 CO₂:NH₃ mixture after electron irradiation at 20 K with the top of the CO₂ v₃ mode cut off for clarity. Boxes labelled (a)–(e) are discussed in the main text.
Fig. B.13 Mid-IR spectra of an example warm-up of a 1:2 CO₂:NH₃ mixture after electron irradiation at 20 K with the top of the CO₂ ν₃ mode cut off for clarity. Boxes labelled (a)–(e) are discussed in the main text.
Fig. B.14 Mid-IR spectra of an example warm-up of a 2:1 CO$_2$:NH$_3$ mixture after electron irradiation at 20 K with the top of the CO$_2$ $\nu_3$ mode cut off for clarity. Boxes labelled (a)–(e) are discussed in the main text.
Additional mid-IR and VUV spectra

Fig. B.15 Mid-IR spectra of an example warm-up of a 4:1 CO$_2$:NH$_3$ mixture after electron irradiation at 20 K with the top of the CO$_2$ $\nu_3$ mode cut off for clarity. Boxes labelled (a)–(e) are discussed in the main text.
Fig. B.16 VUV spectra of CO$_2$ and NH$_3$ binary mixtures in a 4:1, 2:1 and 1:3 ratio before processing with 1 keV electrons. The dashed highlights a new feature at 140 nm for the 4:1 and 2:1 ratios. The spectra have been normalised to a thickness of 200 nm.
Appendix C

Publications and conference contributions

C.1 Publications

In addition to work presented in this thesis, research for other projects has led to two publications:


C.1.1 Future Publications

The results presented in this thesis will be prepared for two publications in *Phys. Chem. Chem. Phys.* in the following format:

1. Results from Chapters 3 and 5 combining the mid-IR and VUV spectroscopic studies on the thermal processing of CO$_2$:NH$_3$ interstellar ice analogues.

2. Results from Chapters 4 and 6 detailing the combining the mid-IR and VUV spectroscopic studies on the electron processing of CO$_2$:NH$_3$ interstellar ice analogues.
C.2 Research Activities


3. Talk given at the RSC Spectroscopy and Dynamics Group Meeting, University of Nottingham, UK, (2019), ‘Using mid-IR and vacuum-UV spectroscopy to study interstellar ice analogues’.


5. Poster presented at the RSC Astrophysical Chemistry Group Meeting, University of Sheffield, UK (2018) and KIDA2017, University of Bordeaux, France (2017), ‘Using VUV spectroscopy to monitor the formation of benzene derivatives’.


7. Talk given at the Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Brazil, (2017) ‘Experimental Astrochemistry at The Open University’.

C.3 Experiments led as PI

1. AU-UV beamline, ASTRID2 Synchrotron, Denmark: 13 days awarded for the proposal ‘Continuing the systematic VUV studies of electron-irradiated mixtures of CH$_3$OH:NH$_3$ interstellar ice analogues’ for beam time in 2020.

2. AU-UV beamline, ASTRID2 Synchrotron, Denmark: 6.5 days awarded for the proposal ‘Systematic VUV studies of electron-irradiated mixtures of CH$_3$OH:NH$_3$ interstellar ice analogues’ completed 2019.

3. AU-UV beamline, ASTRID2 Synchrotron, Denmark: 6.5 days awarded for the proposal ‘Systematic VUV studies of electron-irradiated, condensed molecular films of CO$_2$:NH$_3$’ completed 2019.