Ozone formation in icy mantles

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Ozone formation in icy mantles

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A Thesis submitted towards a PhD in Physics

Submission date: 29 August 2002
Date of award: 14 January 2009
Abstract

In this thesis the results of a detailed experimental study of the chemistry induced by irradiation of ice mantles by electrons and ions are presented. This research is directed towards gaining a better understanding of the mechanisms by which molecules are synthesised in the InterStellar Medium (ISM) and lunar surfaces.

Several experimental systems were used to simulate the conditions of the ISM and lunar surfaces. Ice mantles were formed on chemically inert substrates under ultrahigh vacuum and at temperatures as low as 11 K. The ice mantles were irradiated using electrons (e\(^-\)), ions (He\(^+\) and D\(^+\)) and protons (H\(^+\)) with energies ranging from keV to MeV. Vacuum UltraViolet (VUV) and InfraRed (IR) spectroscopic techniques were used to probe the ice before and after irradiation to investigate both the ice morphology and to identify any molecular species synthesised during irradiation. Details of the experimental methodology used in the experiments are presented in detail in this thesis.

Several experiments explored the formation of ozone in such ice mantles, since the presence of ozone in any planetary or lunar atmosphere has been suggested as biomarker in the search for life. However recent space missions have revealed ozone on several Saturnian moons and Jupiter’s Ganymede. In this thesis we show that ozone is readily produced abiotically by irradiation of oxygen, carbon dioxide, nitrous oxide and nitrogen dioxide ices. These results have important implications for the use of ozone as a biomarker in the search for life on extraterrestrial planets.

In this thesis the physical and chemical mechanisms leading to ozone formation are discussed and, for the first time, isotopic effects are explored by exploring the synthesis of different isotopomers of ozone in an oxygen ice mixture of 18O\(_2\) and 16O\(_2\). The synthesis of higher nitrogen oxides in nitrous oxide and nitrogen dioxide ices has been observed for the first time.
ACKNOWLEDGEMENTS

All the credit goes to Prof Nigel Mason for offering a place in his group and helping me throughout the course of this research. His support during the entire period enabled me to work with various research laboratories and to make academic contacts around the world.

I would like to thank Prof Hugh Hill and Prof Brian Mitchell of the ISU and University of Rennes-1 for their help in finding me a position with Prof Nigel Mason. It was a great time spent at both the universities during the MSS course and internship.

Starting from my first year I would like to thank our group members, Dr. Anita Dawes, Dr. Philip Holtom and Dr. Mike Davis at the Open University for their support from my first day at the Open University. I would like to thank Prof Ralf Kaiser, Department of Chemistry at the University of Hawaii, for allowing me to work in his laboratory for more than a month to produce papers that contribute towards my thesis. I would like to thank the three Indian scientists, Dr. Minaxi Vinodkumar, Dr. Raja Sekhar and Dr. Chetan Limbachiya. It was in my second year I was able to work with Dr. Raja Sekhar at the Centre for Advanced Technology, BARC – Indore, India. I would like to thank colleagues in Belfast, Prof Bob McCullough, Dr. Adam Hunniford, Mr. Tony Merrigan, in Denmark, Dr. Nyk Jones and Dr. Soren Hoffman.

Also thanks to our new colleagues in the group, Dr. Radmilla Panajotovic, Dr. Sylwia Ptasinska and Mr. Sohan Jheeta. Many thanks to Dr. Marla Moore in Cosmic Ice lab (NASA Goddard Space Flight Centre), Dr. Elisabeth Palumbo, Prof Giovanni Strazzulla, Mr. Daniele Fulvio, Dr. Guiseppe Baratta and Mr. Franco in Catania Astrophysical Observatory.

I would like to thank my friends in Milton Keynes, Mr. Srinivasan Tummala, Mr. Birendra Giri, Ms. Sona Kitzlerova, Mr. Olivier Zanetello and Ms. Evelyn Noyojo. Also many thanks to friends of the Open University cricket club.

Finally, my thanks to my parents (Mr. Sivaraman & Mrs. Jothimani), sister (Mrs. Jeyachitra), niece (Ms. Monisha) and Manima (Mrs. Manonmani) to whom this thesis is dedicated and whose support has been vital.

Bhalamurugan Sivaraman (20-08-2008)
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CHAPTER 1: INTRODUCTION TO ASTROCHEMISTRY

1.1 Introduction

If we are to unravel the mechanisms leading to the chemical evolution of the universe we need to gain a detailed knowledge of the complex chemistry occurring under astronomical conditions (Gerlich and Smith, 2006). Such ‘astrochemistry’ has several distinct differences from that occurring in the terrestrial and industrial environments upon which most chemical studies have concentrated; for example

(i) Due to the low densities encountered in many astronomical regions the chemical time scales may be tens of thousands (or even millions) of years, with simple binary molecular encounters being predominant in the gaseous phase.

(ii) The chemistry may occur at much lower temperatures than those commonly encountered on Earth, e.g. at temperatures as low as a few Kelvin in the interstellar medium thus emphasizing so-called ‘barrierless’ chemical reactions (Kaiser, 2002).

(iii) Chemical species not commonly found on Earth may play a key role in astrochemistry e.g. the molecular ions H$_3^+$ and HeH$^+$ both of which are believed to have played a key role in the first chemical reactions to have ever occurred in the history of the universe.

Obtaining information on the different chemical environments within our universe has relied critically upon the continuing technological advances in observational astronomy and computer modelling combined with a growing experimental programme that seeks to recreate such conditions in the laboratory. However, it has only been in the last two to three decades that our knowledge of the major chemical processes underpinning the chemical evolution in the Universe has developed sufficiently that we may now, with some confidence, propose reasonable hypotheses to describe some of the observational data and explore how chemistry affects
star/planet formation and postulate the role of astrochemistry in the formation of molecules essential to the emergence of life - the latter being a core part of the new scientific discipline of ‘Astrobiology’ upon which much of the ESA and NASA space programmes will be focused in the 21st Century (DesMarais et al, 2003).

Due to the inherent temperature of most of the universe being well below that required for most molecules to ‘freeze’ out onto any suitable surface, icy mantles are found in most regions of the universe (Table 1.1) (DesMarais et al, 2003; Armstrong et al, 2005; Milliken et al, 2005). Thus most planetary and lunar surfaces in our own solar system (Venus and Mercury being the exceptions) contain large amounts of ice. Most of the outer Solar System bodies are covered in ice as are a number of the satellites of Jupiter and Saturn. In particular, Europa has been studied in detail to establish whether it is possible for a subsurface ocean to be present and recent evidence for the presence of ozone (previously thought to be characteristic of bioactivity) has been reported on Saturn’s moons Rhea, Dione and Enceladus and the Jovian moon Ganymede (Noll et al, 1997). Nor should we forget the large number of Kuiper belt (Jewitt & Luu, 2004) objects located beyond Neptune including the recent object, 2003 UB313, whose role as a potential 10th planet is currently the topic of much discussion (Brown, Trujillo & Rabinowitz, 2005). Similarly cometary systems are mainly comprised of ice. Hence ice is the perhaps the most common phase of water in our own Solar system and is likely to be the most common phase in other planetary systems.

Beyond our solar system lie those vast regions of the interstellar medium (ISM), the ‘chemical factories’ for over 150 molecules. It is now apparent that much of the chemistry of the ISM arises from heterogeneous chemistry on icy surfaces of dust grains. For example these icy mantles provide the environment for the formation of molecular hydrogen - the most abundant
molecule in the universe – through the recombination of atomic hydrogen, similarly surface (heterogeneous) chemistry is believed to be responsible for the assembly of more complex molecules e.g. H₂O, H₂S, CH₃OH, OCS, OCN… In addition these mantle ices are always being processed by ultraviolet radiation, cosmic rays or stellar winds (Fraser, McCoustra & Williams, 2002). This processing changes the basic composition of the ices and causes some complex organic refractory residues to form. Indeed in the modern field of astrobiology it is in these regions that the prebiotic material necessary for the origins of life are believed to form (Ellinger et al, 2005).

**TABLE 1.1 Typical Ices found in the Solar System**

<table>
<thead>
<tr>
<th>Planet</th>
<th>Satellite</th>
<th>Ice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jupiter</td>
<td>Io</td>
<td>SO₂, SO₃, H₂S?, H₂O?</td>
</tr>
<tr>
<td></td>
<td>Europa</td>
<td>H₂O, SO₂, CO₂, C₄H₄, XCN, H₂O₂, H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Ganymede</td>
<td>H₂O, SO₂, CO₂, C₄H₄, XCN, O₂, O₃</td>
</tr>
<tr>
<td>Saturn</td>
<td>Enceladus</td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td>Dione</td>
<td>H₂O, C₄H₄O₃</td>
</tr>
<tr>
<td></td>
<td>Rhea</td>
<td>H₂O, C₄H₄O₃</td>
</tr>
<tr>
<td></td>
<td>Titan</td>
<td>H₂O, CH₄, C₂H₆, CO, NH₃</td>
</tr>
<tr>
<td>Neptune</td>
<td>Triton</td>
<td>N₂, CH₄, CO, CO₂, H₂O</td>
</tr>
<tr>
<td>Pluto</td>
<td>Charon</td>
<td>N₂, CH₄, CO, H₂O, NH₃, NH₃ hydrate</td>
</tr>
<tr>
<td>Kuiper Belt objects</td>
<td>Quaoar</td>
<td>H₂O, CH₄, CH₃OH, NH₃, NH₃ hydrate</td>
</tr>
</tbody>
</table>
Therefore, in order to understand much of the chemistry that underpins larger astronomical phenomena, it is essential to probe the physico-chemistry of ice surfaces under astronomical conditions. The physical properties and chemical reactivity of the ice will depend crucially upon the morphology of the ice surface and thus it is necessary to explore how the morphology of astrochemical ices is influenced by their local environment (e.g. temperature and pressure) and the mechanisms by which they are processed.

It is thought that chemistry in the cold regions in the universe might have led to the evolution of life by providing necessary complex molecules so called precursor molecules. So far Earth is the only place that is known to contain an organic life form. Based on these two considerations simple molecules taking an active part in present day Earth's atmosphere have been chosen for study as the first step towards understanding the role of these molecules in cold regions of space. In particular we study the production and stability of Ozone, \( \text{O}_3 \). In this chapter the interstellar and planetary environment are discussed together with importance of studying ozone forming through unique chemistry in the colder regions of space.

1.2 Ices and irradiation environment

1.2.1 Interstellar medium

The interstellar medium, commonly denoted as ISM, is a very active place for molecular synthesis and for the birth of new stars. There are many regions of the ISM in which temperatures range from \( 10^6 \text{K} \) to 10 K. Two types of interstellar clouds are defined according to their physical properties and the chemical constitution, 'diffuse' and 'dense' molecular clouds (Table 1.2).
Diffuse clouds have low density and high temperatures whereas dense molecular clouds have higher density and are the coldest (10 K) region of the ISM.

In the ISM, interstellar dust particles provide the surface for molecules to stick on and accumulate to form ice layers (Figure 1.1). Interstellar dust particles are identified to be made of silicates, graphite, and amorphous carbon or hydrogenated amorphous carbon, with varying sizes from 10 – 30000 Å. To date more than 200 molecules (including isotopic composition) have been identified in the ISM and the list grows with the recent identification of phosphorus containing species. The list of molecules ranges from diatomics to those containing 13 atoms. Relative to hydrogen (H), elements like helium (He), oxygen (O), carbon (C) and nitrogen (N) are found to be most dominant elements in the ISM (Table 1.3). Table 1.4, summarizes all the oxygen containing simple molecules (< 4 atoms) so far identified in the ISM mostly in the dense molecular clouds.

Table 1.2: Typical characteristics of cool interstellar nebulae.

<table>
<thead>
<tr>
<th>Type of nebula</th>
<th>Number density</th>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffuse</td>
<td>0.050</td>
<td>80</td>
<td>5 x 10^{-19}</td>
</tr>
<tr>
<td>Dense</td>
<td>5.000</td>
<td>10</td>
<td>7 x 10^{-18}</td>
</tr>
</tbody>
</table>

Table 1.3: Interstellar abundance of elements relative to hydrogen.

<table>
<thead>
<tr>
<th>Element</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.00</td>
</tr>
<tr>
<td>He</td>
<td>0.09</td>
</tr>
<tr>
<td>O</td>
<td>7 x 10^{-4}</td>
</tr>
<tr>
<td>C</td>
<td>3 x 10^{-4}</td>
</tr>
<tr>
<td>N</td>
<td>9 x 10^{-5}</td>
</tr>
</tbody>
</table>
The production of simple molecules such as O₂ and N₂ on the interstellar dust or grain mantle is restricted due to the abundance of H atoms. When H atoms are consumed in a reaction to form molecular hydrogen during the increase in cloud density then the formation of molecules like O₂ and N₂ are enabled. In regions where H dominates then the production of H dominated species (eg. H₂O, NH₃ and CH₄) is more likely. Apart from reactions that take place by diffusion of molecules or atoms, reactions are also enabled by the action of radiation. For diffuse clouds starlight can induce chemistry but in the case of dense a cloud, which is opaque to starlight, molecules are formed by the energetic cosmic ray particles.

The irradiation of dense clouds by the action of cosmic rays leads to the liberation of electrons due to ionization of molecular hydrogen (Equation 1.1). In a diffuse cloud electrons can be formed by photoionisation (Equation 1.2). Such secondary electrons can then in turn induce chemistry in the ice.

\[ \text{H}_2 + \text{cosmic ray} \rightarrow \text{H}_2^+ + e \]  
\[ \Lambda + hv \rightarrow \Lambda^+ + e \]  

Figure 1.1: Formation of new molecules on cold grain surfaces. (Adapted from Tielens, 2005).
Table 1.4: Summary of simple molecules (<4 atoms), containing oxygen, detected in the ISM. Those given in blue are identified both in gas and solid phase. Parenthesis indicates identification only in the solid phase.

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>Two</th>
<th>Three</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>SO₂</td>
</tr>
<tr>
<td></td>
<td>FeO</td>
<td>C₂O</td>
</tr>
<tr>
<td></td>
<td>HO</td>
<td>CO₂</td>
</tr>
<tr>
<td></td>
<td>NO</td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>(OCN)</td>
</tr>
<tr>
<td></td>
<td>PO</td>
<td>HNO</td>
</tr>
<tr>
<td></td>
<td>SO</td>
<td>OCS</td>
</tr>
<tr>
<td></td>
<td>SiO</td>
<td>N₂O</td>
</tr>
</tbody>
</table>

1.2.2 The Solar system

Our solar system is so far unique, with a ‘habitable zone’ in which life can exist in the presence of liquid water and adequate sunlight both the Earth and Mars are placed in such a ‘habitable zone’ hence there remains great interest in determining whether life ever existed (or indeed exists) on Mars. Recent evidence for the presence of liquid water on the Martian surface in the past has raised the probability of life having once existed on Mars whilst the identification of bacteria (extremophiles) that can survive under extreme conditions on Earth (e.g. extreme cold of the polar regions) suggests that life may survive in inclement conditions of modern Mars.
Furthermore as we explore the solar system other potential habitats for life have been revealed, outside the habitable zone! For example the Saturnian moon, Europa, which may support a subsurface ocean, is believed to be a possible habitat for life. However at present we know little about the chemical conditions on Europa and other planetary moons. Therefore it is necessary to explore such ‘planetary’ chemistry and identify whether it can support the chemical changes that are necessary for making the building blocks of life. The following sections review relevant planetary and satellite surfaces containing molecular ices and discuss the chemical reactions that may occur within them.

**Planets**

The molecules present in the atmospheric layers of any planet take part in reactions that govern the planet’s surface temperature. These molecules are composed of the most abundant cosmic elements listed in Table 1.3. The atmospheric composition of Earth is listed in Table 1.5.

**Table 1.5: Principle constituents of Earth’s atmosphere. (Adapted from Vazquez and Hanslmeier, 2006)**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Composition by volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen ($N_2$)</td>
<td>78.08</td>
</tr>
<tr>
<td>Oxygen ($O_2$)</td>
<td>20.95</td>
</tr>
<tr>
<td>Carbon dioxide ($CO_2$)</td>
<td>0.0375</td>
</tr>
<tr>
<td>Water vapour ($H_2O$)</td>
<td>0.001-4</td>
</tr>
<tr>
<td>Nitrous oxide ($N_2O$)</td>
<td>0.00003</td>
</tr>
<tr>
<td>Ozone ($O_3$)</td>
<td>0.000004</td>
</tr>
</tbody>
</table>

Mars is found to contain molecules that are frozen to the surface of the planet where surface temperatures of 140 -150 K have been recorded. Several probes and rovers have explored Mars in the recent years and so it is most explored planet apart from our own Earth. At present there are three rovers exploring the Martian surface while Mars Express is in orbit around the
planet. Ices in Mars are detected in the polar regions of the planet. CO$_2$ is found to be the main constituent of the Martian ices. Though O$_3$ is observed to be present as an atmospheric constituent the detection of this molecule in the surface ices is unconfirmed. However the presence of the Phoenix lander in the polar regions of the planet may provide us with precise data about the molecular composition in the ice phase. The presence of oxygen isotopes, measured by insitu mass spectrometers in Mars, is almost equal to the amount (ratio of $^{16}$O / $^{18}$O ~ 490) observed on Earth.

The planets Jupiter, Saturn, Uranus and Neptune whilst themselves gas giants with no surfaces on which ice can form have several satellites that dominate the ice chemistry in the solar system. These satellites are discussed in the next section. The last of the solar system objects Pluto (a planetoid) is observed to contain nitrogen, N$_2$, and carbon monoxide, CO, ices.

**Icy satellites**

The icy satellites of Jupiter and Saturn have been found to have surface temperatures ranging from 50 – 70 K depending on the day and night cycle. The Galilean satellites, Europa, Ganymede and Callisto, and the Saturnian satellites, Rhea and Dione (Figure 1.2) are found to contain either molecular oxygen or ozone ice. These satellites are sited within the magnetospheres of their respective planets and so are constantly bombarded by ions (Figure 1-3). Table 1.6, summarizes the relevant molecules found in these icy satellites together with their possible irradiation environment.
Figure 1.2: The satellites of Jupiter (Europa, Ganymede, Callisto) and Saturn (Rhea, Dione). Note figure not to scale. Credit and Source NASA.

Figure 1.3: Energetic ions supply chain for a satellite embedded in a planetary magnetosphere. (Adapted from Johnson 1990).
Table 1.6: Ices present in the planetary / satellite surfaces. Only relevant ices to this work are listed.

<table>
<thead>
<tr>
<th>Object</th>
<th>Detection of Surface Ices (a)</th>
<th>Radiation Particle Environment Energy Flux (eV cm(^{-2}) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(_2)</td>
<td>CO(_2)</td>
</tr>
<tr>
<td>Mars</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Jovian satellites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Europa</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Ganymede</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Callisto</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Saturnian satellites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enceladus</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Dione</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Rhea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hyperion</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Iapetus</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Phoebe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-ring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranian satellites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ariel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neptunian satellites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triton</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Pluto</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

(a) Table of ice data adapted from Roush (2001), and Hibbitts and Szany (2007)  
(b) From Cooper et al. (2001), (c) Richardson (1998), (d) McNutt (1991),  
(e) Thompson et al. (1987), (f) Johnson (1989).

1.3 Chemical reactions in space – In the ice phase

Many chemical reactions (Table 1.6) can occur in the ISM and planetary atmospheres both in the gas and ice phase. The reactions that take place in the gas and ice phase may be quite different
and a very important differentiating factor is the life time of the atom or molecule produced in the reaction.

During impact of energetic particles with molecules in the ice phase, the molecule dissociates contributing atoms for subsequent chemical reactions. These atoms are produced with significant kinetic energies and are therefore no longer in equilibrium with the surrounding molecules in the ice matrix. These atoms are called suprathermal atoms. Such atoms will soon lose all their energy by repeated collision with other molecules or atoms, which results in the production of new molecules. Therefore non-equilibrium chemistry is induced in the ice matrix during irradiation. Unlike the gas phase, atoms that are formed in the ice may be stored in the ice matrix. These atoms gain mobility or enough kinetic energy by thermal energy input, i.e. heating, to move through the ice matrix and form new products. The atoms that diffuse to react by the supply of heat energy are called thermal atoms. The reactions that are induced by the suprathermal and thermal atoms are termed as suprathermal and thermal reactions, respectively. These are the two important forms of reactions that govern the chemistry in the ice phase induced by energetic particles.
Table 1.6: Important astrochemistry reactions and interactions of atoms and molecules.  
(Adapted from Carbo and Ginebreda, 1985 & Fraser et al, 2002).

<table>
<thead>
<tr>
<th>Category</th>
<th>Reaction Type</th>
<th>Equation</th>
</tr>
</thead>
</table>
| 1 | Ion –molecule reactions | (a) Charge transfer: $A^+ + B \rightarrow A + B^+$  
(b) Radiative association: $A^+ + B \rightarrow AB^+ + hv$  
(c) Atom transfer: $A^+ + BC \rightarrow AB^+ + C$  
AB$^+ + C \rightarrow A^+ + BC$ |
| 2 | Electron recombination reactions | (a) Radiative: $A^+ + e^- \rightarrow A + hv$  
(b) Dissociative: $AB^+ + e^- \rightarrow A + B$ |
| 3 | Photochemical reactions | (a) Photodissociation: $AB^+ + hv \rightarrow A^+ + B$  
(b) Photoionization: $A + hv \rightarrow A^+ + e^-$ |
| 4 | Neutral-neutral reactions | (a) Atom transfer: $AB + C \rightarrow A + BC$  
(b) Radiative association: $A + B \rightarrow AB + hv$  
(c) Chemionization: $A + B \rightarrow AB^+ + e^-$ |
| 5 | Three body reactions | (a) Dissociation (Collisional): $AB + M \rightarrow A + B + M$  
(b) Association: $A + B + M \rightarrow AB + M$ |
| 5 | Other reactions | (a) Ion –ion neutralization: $A^+ + B^- \rightarrow AB$  
(b) Negative ion-neutralization: $A^+ + BC \rightarrow AB^- + C$ |
1.4 Probing astrochemistry in the laboratory

In order to understand the chemistry that takes place in the ISM and planetary and satellite surfaces we need to probe them. Apart from sending rovers and landing probes to analyse insitu chemicals it is also possible to simulate the interstellar, planetary / satellite environment in the laboratory. At present there are some experimental limitations in the laboratory for achieving equivalent pressure conditions. Pressure in the laboratory simulations is $10^4$ times higher than the interstellar medium, which indicates a less clean environment. However the chemistry induced by irradiation takes place in the bulk of the ice and this eliminates the effect of contamination in the ices. Temperatures down to 10 K are easily achieved and therefore molecular ices are formed on a substrate. Energetic ions from laboratory irradiation sources are then used to simulate the cosmic rays and other irradiation environments. Non destructive methods, e.g. infrared and mass spectroscopy, are then used to detect the chemical changes induced by irradiation. In this way, observations are supported by laboratory experiments facilitating better understanding of the chemistry and providing data for computing modelling of both the ISM and planetary systems.

1.5 The role of oxygen and ozone in Astrochemistry and Astrobiology

In this thesis we have chosen to concentrate upon the role of oxygen and ozone in ISM and planetary astrochemistry. Table 1.4 listed some of the simplest molecules containing oxygen observed in the ISM whilst recently the Odin satellite revealed the presence of molecular oxygen itself in the interstellar medium (Larsson 2007). Oxygen is believed to be essential to the development of life and may itself be a biomarker (since it is linked to the photosynthesis cycle) therefore it is one of the key molecules in astrobiology studies. However, molecular oxygen is hard to detect since it is infrared inactive in the gas phase therefore the heavier oxygen species, ozone is often used as a probe for presence of molecular oxygen.
1.5.1 Oxygen and ozone

Ozone is believed to be an essential component of any planetary atmosphere capable of sustaining life, hence the detection of ozone in the atmosphere of exoplanets is a major objective of both the Darwin and Terrestrial Planet Finder (TPF) space telescopes (Beichman, Woolf, & Lindensmith 1999; Leger 2000). The observation of an exo-planetary atmosphere containing water, oxygen, carbon dioxide and ozone would then be regarded as strong evidence that the planet can support life - if not the existence of life itself (Angel, Cheng, & Woolf 1986; Burke 1986; Leger et al. 1999; Leger, Pirre, & Marceau 1994). On Earth the development of an oxygen-rich atmosphere is attributed to developing photosynthesis from ocean based plants like algae (Berkner & Marshall 1964). Eventually concentrations of molecular oxygen in the atmosphere were sufficiently high to allow the development of a stratospheric ozone layer by the well known Chapman reactions (1.3) and (1.4).

\[
\text{O}_2(X^3\Sigma_g^-) + \text{hv} \rightarrow \text{O}(^{3}P) + \text{O}(^{3}P) \quad (1.3)
\]

\[
\text{O}(^{3}P) + \text{O}_2(X^3\Sigma_g^-) + \text{M} \rightarrow \text{O}_3(X^1\Pi_A) + \text{M} \quad (1.4)
\]

Ozone is created when solar ultraviolet radiation (\(\lambda < 240 \text{ nm}\)) dissociates oxygen molecules to form atomic oxygen which quickly combines with further oxygen molecules to form ozone via a three body collision. The formation of a stratospheric ozone layer that was thick enough to filter UVA and UVB from the terrestrial surface in turn led to the development of land based flora and eventually fauna. This simple description of the evolution is supported by fossil evidence and therefore - not surprisingly - has been adopted as a generalized mechanism for the evolution of life on other planetary bodies. This in turn has led to the continued support for ozone as an essential biomarker of any habitable world.
The first tentative evidence for the presence of ozone on an extraterrestrial, planetary body was provided by the Mariner 7 spacecraft (Barth & Hord 1971) which revealed ozone in the Martian atmosphere. Subsequent extensive studies by the Mariner 9 spacecraft exposed varying amount of ozone with seasons (Barth et al. 1973). These observations were explained by photolysis of carbon dioxide (CO₂) liberating oxygen atoms which subsequently formed oxygen and ultimately ozone via the Chapman mechanism. The arrival of Mars Express with SPICAM (Spectroscopy for the Investigation of the Characteristics of the Atmosphere of Mars) has provided additional information on ozone in the Martian atmosphere (Bertaux et al. 2000).

The first suggestion of ozone being formed on a planetary moon was provided by (IUE) International Ultraviolet Explorer (Nelson et al. 1987) which suggested the presence of ozone on the surface of Ganymede. This was confirmed by Noll et al. (1996) using the HST (Hubble Space Telescope) Faint Object Spectrograph; the authors report the observation of an absorption feature at 260 nm, a feature they ascribed to the Hartley continuum of ozone. Galileo UVS (Ultraviolet Spectrometer) spectra confirmed the findings and provided the first map of ozone on the surface of Ganymede (Hendrix, Barth, & Hord 1999). Noll et al. (1997) utilized the Space Telescope Imaging Spectrograph (STIS) on HST to make available global, disk-resolved maps of the 260 nm absorption band; this map revealed that the absorption was stronger in the trailing hemisphere. These results were initially controversial since it was not thought possible that ozone could be formed in any atmosphere/ice that was not oxygen rich. However, Noll et al. (1997) reported similar spectroscopic features in the absorption spectra of the Saturnian moons Rhea and Dione. The identification of ozone on moons around two different planets in regions of the solar system with quite distinct solar fluxes and quite different planetary compositions removed the possibility that there were special circumstances unique to Ganymede. Consequently, the process of ozone formation on the water ice-covered moons is apparently more general and not biological in origin - thus ozone may not after all be regarded as a unique biomarker.
1.5.2 Oxygen isotopes

The origin of the oxygen isotopic fractionation ($^{18}$O vs. $^{16}$O) in distinct Solar System molecules such as ozone ($O_3$), water ($H_2O$), carbon monoxide (CO), and carbon dioxide (CO$_2$) has been a topic of experimental and theoretical studies since it was discovered nearly 30 years ago. The study of oxygen isotopic variations is not confined to the Solar System; the first detection of molecular oxygen isotopomer ($^{16}$O$^{18}$O) in the interstellar medium was reported in 1993 (Pagani, Langer, & Castets 1993); current space telescopes (e.g. Spitzer) are capable of developing maps of isotopic variations in star forming regions. The Solar abundances of the oxygen isotopes have been determined to be $^{18}$O/$^{17}$O = 5.5 , $^{16}$O/$^{18}$O = 500, $^{16}$O/$^{17}$O = 2750 (Penzias 1981).

First measured in chondritic meteorites, isotopic enrichments have been found in Martian rocks and are now routinely utilized to identify Martian meteoritic material that is deposited on Earth (Clayton 1993; Clayton et al. 1991). In 1965, Taylor suggested a classification of rocks in the solar system according to their $^{18}$O/$^{16}$O ratio (Taylor et al. 1965). Recently Ozima et al. (Ozima et al. 2007) classified 400 bulk meteorite samples using their oxygen isotopic data and reported the similarity between solar and planetary oxygen. NASA’s ‘Genesis’ and ‘Stardust’ missions were recently launched to measure the proportions of oxygen isotopes in the solar wind and from a comet by collecting (and returning) ‘dust’ samples to the Earth (Burnett 2003; McKeegan et al. 2006). The results from Stardust mission reveals isotopic composition of circumstellar stardust grain dependable on the solar system origin (McKeegan, et al. 2006). Such studies are expected to provide vital information on the chemical origins of our Solar System and may reveal how the different planets were formed (McKeegan, et al. 2006). Oxygen isotopes may also be used to understand the formation of the Earth-Moon system (Spicuzza et al. 2007).
The use of oxygen isotopes can also explain the chemical reactions and pathways followed in forming ozone. The ozone formation process in the gas phase has been studied extensively (Heidenreich III & Thiemens 1983; Morton et al. 1990; Thiemens 2001; Thiemens & Jackson 1988, 1990). Each of the three stable oxygen isotopes (\(^{16}\text{O} / ^{17}\text{O} / ^{18}\text{O}\)) may take part in the Chapman reactions (Equation 1.3 and 1.4) producing a wide range of isotopomers that have since been measured in the terrestrial stratosphere (Krankowsky, Lammerzahl, & Mauersberger 2000; Mauersberger 1987). Kinetic isotope effects and symmetry induced isotopic fractionation suggest different rate constants for equations (1.3) and (1.4) depending on the isotopes involved (Gao & Marcus 2001; Gellene 1996; Janssen & Marcus 2001; Mauersberger et al. 1999). Initially, the isotopomers were thought to form via cyclic ozone intermediate which ring opened to the acyclic form. However, this interpretation has been challenged, and fast isotopic exchange reactions involving \(^{18}\text{O}\) enriched molecular oxygen (\(^{16}\text{O}^{18}\text{O}\)) (Janssen et al. 1999; Larsen, Pedersen, & Sehested 1991) has to be considered as well.

In this thesis we explore the formation of ozone isotopomers in irradiated oxygen ice for the first time to explore some of these reaction channels.

1.5.3 Ozone formation from oxides of nitrogen

Ozone may be formed by irradiation of any oxygen containing compounds with the released oxygen atoms forming molecular oxygen and thence initiating the Chapman reactions. In the gas phase such two (or three) step processes are likely to lead to only small ozone concentrations but in an ice the probability is greatly increased. Accordingly the formation of ozone from ices composed of oxygen containing molecules should be explored. For example does irradiation of \(\text{CO}_2\) ice (as found in the Martian polar ice caps) lead to ozone formation? Similarly irradiation of ice composed of the nitrogen oxides may lead to creation of ozone. Such
abiotic processes if occurring on a planetary surface may then mask any ozone created by biotic driven chemistry. In this thesis we report results on the study of nitrous oxide (N$_2$O) and nitrogen dioxide (NO$_2$) ice.

Nitrous oxide is an important gaseous species in the terrestrial atmosphere (Miller 1954). First detected by Adel in 1938, through its characteristic absorption band at 7.8 µm (Adel 1938), it one of the most important greenhouse gases in the troposphere. In the stratosphere N$_2$O plays a key role in ozone depletion chemistry being a natural source for nitric oxide (NO) that destroys ozone in a catalytic NOx reaction. Significant amounts of N$_2$O are released into the atmosphere as a result of biological activity at Earth’s surface but chemical production of N$_2$O is also possible via the reaction of molecular nitrogen (N$_2$) either with atomic oxygen (O) or with O$_3$ (Harteck & Dondes 1954), however, research has shown that non-biological formation pathways are less significant (Demore & Roper 1962; Goody & Walshaw 1953) than biological. Photo-dissociation reactions of N$_2$O include the production of atomic oxygen and molecular nitrogen and nitric oxide via the following reactions (Bates & Hays 1967):

\[
\begin{align*}
N_2O + hv & \rightarrow N_2 + O (^1D) \text{ or } O (^1S) \quad (\lambda < 337 \text{ nm or } 210 \text{ nm, respectively}) \\
& \rightarrow NO + N (^3S) \quad (\lambda < 250 \text{ nm})
\end{align*}
\]

(1.5) (1.6)

N$_2$O was the third molecule to be detected in space to contain the NO bond therefore demonstrating the universality of basic chemistry that, on Earth at least, led to evolution of life. Significant concentrations of nitrous oxide (a relative fractional abundance of $10^{-9}$ to molecular hydrogen H$_2$) have been observed in the Sgr B2(M) (Ziurys et al. 1994) and is believed (Millar et al. 1991) to have been produced by neutral-neutral reactions involving nitrogen dioxide (NO$_2$).
1.6 Conclusion

In this chapter an introduction to interstellar and planetary / satellite environments has been presented with emphasis on the presence of oxygen bearing species. The importance of laboratory simulations to understand chemical changes induced by irradiation is explained. Although identified in other planetary / satellite surfaces very little information exists about the abiotic formation of ozone and therefore more laboratory simulations are needed. The methodology to perform laboratory simulation and the results of producing ozone from different oxygen containing molecules will be explained in the forthcoming chapters.
CHAPTER 2: MOLECULAR SPECTROSCOPY, IRRADIATION PROCESSES AND PHYSICAL CHEMISTRY

2.1 Introduction

In the search for simple and complex molecules on other planetary and satellite surfaces and in the interstellar medium, ground and space based observations using spectroscopy techniques play an important role. In this thesis we intend to investigate the irradiation of solid ice in the laboratory with the help of ultraviolet (UV) and infrared (IR) spectroscopy techniques. In this chapter we briefly discuss the fundamentals of molecular structure and discuss the basic principles of spectroscopy. We also review the different types of irradiation process and describe how we define the reaction rates used to describe the chemistry of the reactions induced by such irradiation.

2.2 Atomic and molecular structure

Four basic quantum numbers are required to describe the structure of atomic orbitals and the electron occupancy in each orbital. These are the principal (n), orbital (l), magnetic (m) and spin (s) quantum numbers. The Pauli Exclusion Principle states that each energy state can occupy only one e\(^{-}\) in one orbital, therefore when two electrons are present in one orbital they have opposite 'spins'. The spin quantum number (m\(_s\)) has a value +1/2 or -1/2 to denote up and down spin respectively. Depending upon the value of l, the shape of the orbital is determined and orbital is represented symbolically as \(s (l=0), p (l=1), d (l=2), f (l=3)\), etc. The atomic energy levels are denoted by term symbols which describe the total orbital angular momenta of the atom. The term-symbols are given as \(^{2S+1}L_{\text{g}}\), where L is the total orbital angular momentum, S the spin angular momentum and J the total angular momentum.
Atoms combine to form molecules through various bonds such as covalent, ionic and metallic bonds. Molecule electronic orbitals are made up of overlapping atomic orbitals and different molecular orbitals are produced depending upon the way atomic orbitals combine. s and p\textsubscript{x} orbitals which are aligned along the molecular axis form \( \sigma \) orbitals and p\textsubscript{x} and p\textsubscript{y} orbitals which are perpendicular to molecular axis combine to form molecular \( \pi \) orbitals. Such \( \sigma \) and \( \pi \) orbitals show the presence of double or triple bonds in a molecule. For some polyatomic molecules, e.g. CH\textsubscript{4}, hybrid bonds are formed from a combination of one s and three p atomic orbitals to form four molecular \( \sigma \) orbitals. This is termed sp\textsuperscript{3} hybridisation.

Molecular term symbols have a form similar to atomic term symbols being given as

\[ ^{2S+1}A_{\text{g/u}} \]

where \( \Lambda \) shows the total angular momentum described by \( \Sigma, \Pi, \Delta, \Phi \) to represent various orbitals, \( \Omega \) represents the total angular momentum quantum number, g / u represents even and odd parity respectively. Molecular orbitals in homonuclear diatoms are labelled with a parity subscript to denote their behaviour under inversion. Orbitals which keep the same sign are said to have even parity and are labeled with a subscript g for gerade (the German for even) whereas the orbitals which change sign have odd parity (u, ungerade German for odd). Finally, the \( \pm \) superscript represents the behaviour of the molecular wavefunction under reflection. Molecular oxygen has two \( \pi \) electrons with parallel signs and the two orbitals have even parity but behave differently under reflection, the ground state term symbol for oxygen is \( ^3\Sigma^+ \).

When sufficient energy is supplied to an atom or molecule one or more of electrons can be removed. The energy that is required for this process is termed as the 'ionization energy'. The first ionization energy is defined as the amount of energy required to remove the most loosely
bound electron from an atom / molecule. The energy required to remove the inner electrons increases as we move towards the nucleus.

\[ \text{Energy} + \text{Atom/Molecule} \rightarrow \text{Positive ion} + \text{Electron} \]  

(2.1)

2.3 Molecular vibrations

A molecule must change its electric dipole moment during vibration in order to absorb/emit infrared radiation. This is the selection rule for infrared spectroscopy. The dipole moment of the molecule changes if the bond expands and contracts. This occurs in a heteronuclear diatomic molecule but no change in dipole moment will take place in a homonuclear diatomic molecule and will remain zero irrespective of the bond length, so such molecules have no IR spectrum. Rotation of the molecule is also possible, however for the molecular ices discussed in this thesis, rotations are not likely because in the ice phase all molecular rotations are hindered. For a diatomic molecule only one vibration corresponding to either the stretching or compression of the molecule is possible. Therefore a diatomic molecule possesses one degree of freedom to vibrate, however in a polyatomic molecule containing \( N \) atoms the degrees of freedom are \( 3N - 5 \), for a linear molecule, and \( 3N - 6 \) for a non-linear molecule. \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), shown in figure (2.1), are good examples of a triatomic linear and non-linear molecule respectively.

\[
\begin{align*}
\text{Linear} & : \quad \text{O} = \text{C} = \text{O} \\
\text{Non-linear} & : \quad \begin{array}{c}
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\end{align*}
\]

Figure 2.1: Linear and non-linear molecules.
Vibrations can involve either a change in bond length (stretching) or bond angle (bending). CO₂ and H₂O possess three vibrational modes, two of which correspond to stretching motions, and the other corresponding to the bending motion. Stretching can be of two types symmetric and asymmetric stretching. For example CO₂ possesses a carbonyl (C=O) vibration which gives rise to an intense infrared band due to an increase change in the dipole moment, whereas less or smaller changes in the dipole moment will lead to a weak absorption. Symmetric stretching of the CO₂ molecule is infrared inactive because there is no change in the dipole moment (Figure 2.2) whereas the asymmetric stretching is infrared active since, due to the different bond length, a net dipole moment is present in the molecule (Figure 2.2).

![Figure 2.2: Stretching vibrations of carbon dioxide molecule.](image)

The frequency of these vibrations (ν) can be calculated using equation (2.2), where μ is called the reduced mass (Equation 2.3) and k is the force constant derived from Hooke's law. Substituting, c = νλ in equation (2.2), the reciprocal of wavelength will directly give the wavenumber. The reduced mass is obtained by combining the atomic masses of the two elements present in the molecule and is expressed as follows:

$$\nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \tag{2.2}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2.3}$$

where m₁ and m₂ are the masses of the atoms at the ends of the bond. The infrared vibrational band frequency or wavenumber can be found for a triatomic molecule containing two elements. This equation applies to the infrared vibration of a molecule in all the three phases (solid, liquid...
and gas), however normally a slight variation in the frequencies between solid and gas phase is observed due to damping of vibrations in solid phase.

The frequency of vibration for a molecule thus obtained has few complications in the band assignment due to overtone, combination and Fermi resonance bands. Overtone bands in an infrared spectrum are multiples of the fundamental absorption frequency. Assuming evenly spaced energy levels the first overtone will appear as twice the frequency or wavenumber of the fundamental and so on for the second overtone and the rest (Figure 2.3). Combination bands arise when two fundamental bands absorb energy simultaneously. It is normally the sum of the two absorbing frequencies or wavenumbers. When an overtone or a combination band has the same frequency or a similar frequency to a fundamental, two bands appear, split either side of the expected value of about equal intensity. This leads to two bands appearing closed together when only one is expected. This is called the Fermi resonance and the two bands appearing due to this is called the Fermi doublet.

![Energy levels of fundamentals and overtones of infrared bands.](image)

**Figure 2.3: Energy levels of fundamentals and overtones of infrared bands.**

### 2.4 Electronic transitions and dissociation

Due to photon absorption an electron might be excited to other higher electronic states following the selection rules, $\Delta \Lambda = 0, \pm 1$; $\Delta S = 0$; $g \leftrightarrow u$; and, for $\Sigma$ states, $+ \leftrightarrow +/\leftrightarrow -$. The Franck-Condon principle, states that an electronic transition takes place faster than the time taken
for nuclei to respond. There are three possible electronic transitions which eventually lead to the
dissociation of the molecules shown in figure (2.4).

[1] The transition to an excited state where the internuclear separation is greater than the
ground state (Figure 2.4(a)). The total energy of the dissociation products is greater in the upper
state than that in the lower state by an amount $E_{ex}$, called excitation energy. [2] The excited state is
unstable hence no minimum is shown in the figure (2.4(b)). So the molecule dissociates into
products with total excitation energy $E_{ex}$. [3] Predissociation occurs when the two different
excited states, one stable and the other unstable intersect and this has been shown in figure
(2.4(c)).

Figure 2.4: Possible dissociation methods by electronic excitation. (Adapted from
Banwell, 1972). $D''_0$ and $D'_0$ are the dissociation energies of normal and excited states.
2.5 The Born-Oppenheimer approximation

It is impossible to solve the Schrödinger equation for a molecule exactly/analytically and therefore Born-Oppenheimer approximation is adopted. In this approximation the electronic and nuclear motion in molecules can be treated separate due to the large differences between electron and nuclei masses. In this way, the total wave function and energy of a molecule can be expressed as the product and sum of electronic (\(E_e\)), vibrational (\(E_v\)) and rotational (\(E_r\)) wave functions and energies, as given in equations 2.2 and 2.3, respectively. This implies that the electronic (\(\varphi_e\)), vibrational (\(\varphi_v\)) and rotational (\(\varphi_r\)) functions are independent of each other.

\[
\varphi = \varphi_e \times \varphi_v \times \varphi_r \tag{2.4}
\]

\[
E = E_e + E_v + E_r \tag{2.5}
\]

2.6 Morse function

A diatomic molecule can be described in terms of the potential energy (\(E\)) curve of an anharmonic oscillator given by the following 'Morse' function:

\[
E = D_q \left[ 1 - \exp \left( a(r - r_e) \right) \right]^2 \tag{2.6}
\]

where, \(a\) is constant for a particular molecule, \(D_q\) is the dissociation energy, and \(r_e\) is the equilibrium separation or the bond length when the molecule possesses minimum potential energy. Therefore the potential energy of the molecule alters with the bond length between two nuclei (Figure 2.5) and the molecule dissociates at large \(r\). Due to zero-point vibrational energy, the actual dissociation energy is a fraction lower than \(D_q\) evaluated in 2.6.
2.7 The electromagnetic spectrum

To study the energy levels of atoms and dissociation of molecules it is essential to understand the wide electromagnetic spectrum (Table 2.1) from X-rays – ultraviolet - visible - infrared - microwave to radio waves. Various types of radiation can then be defined in terms of their wavelengths or frequencies. The wavelength, \( \lambda \), is defined as the linear distance between successive maxima or minima of a wave, and the frequency, \( \nu \), as the number of waves per second. The product of wavelength and frequency gives the velocity of the radiation, as follows:

\[
\epsilon = \nu \lambda
\]  

(2.7)

where \( \epsilon \) is the velocity of light in vacuum (3.8 x 10^8 m s^{-1}).

The relation between frequency of the electromagnetic radiation and its energy is as follows:

\[
E = b \nu
\]  

(2.8)

where \( b \) is the Planck constant (6.624 x 10^{-34} \text{ J s}).

Therefore,

\[
E = b \epsilon / \lambda
\]  

(2.9)

An atom or molecule that interacts with electromagnetic radiation will gain energy. Therefore, the absorption of electromagnetic radiation at different energies characterizes the change, which takes place with an atom or a molecule. The use of VUV and IR spectroscopy corresponds to the change of electron distribution and change of configuration for a molecule, respectively (Figure 2.6). The change in configuration is due to the change in dipole moment induced by absorption of infrared radiation.
Figure 2.5: The Morse curve: the energy of a diatomic molecule undergoing anharmonic extension (adapted from Banwell, 1972).

Table 2.1: Electromagnetic spectrum.

<table>
<thead>
<tr>
<th>Electromagnetic radiation</th>
<th>Wavelengths</th>
<th>Frequency [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiowaves</td>
<td>100 m – 30 cm</td>
<td>$3 \times 10^6$ - $10^9$</td>
</tr>
<tr>
<td>Microwave</td>
<td>30 cm – 0.3 mm</td>
<td>$10^9$ - $10^{12}$</td>
</tr>
<tr>
<td>Infrared</td>
<td>0.3 mm – 600 nm</td>
<td>$10^{13}$ - $5 \times 10^{14}$</td>
</tr>
<tr>
<td>Visible</td>
<td>600 nm – 400 nm</td>
<td>$5 \times 10^{14}$ - $7.5 \times 10^{14}$</td>
</tr>
<tr>
<td>Near UV</td>
<td>400 nm – 200 nm</td>
<td>$7.5 \times 10^{14}$ - $1.5 \times 10^{15}$</td>
</tr>
<tr>
<td>VUV</td>
<td>200 nm – 10 nm</td>
<td>$1.5 \times 10^{15}$ - $10^{16}$</td>
</tr>
<tr>
<td>X-ray</td>
<td>10 nm – $10^4$ nm</td>
<td>$10^{16}$ - $10^{19}$</td>
</tr>
<tr>
<td>γ-ray</td>
<td>$10^2$ nm – $10^6$ nm</td>
<td>$10^{19}$ - $10^{23}$</td>
</tr>
</tbody>
</table>
2.8 Spectroscopy

Spectroscopy offers an excellent way of studying various energy levels of atoms and molecules. When a sample is irradiated by electromagnetic radiation the transmitted light gives rise to spectral lines which are characteristic of the sample. The main molecular transitions affecting the spectra of the samples are in the order of increasing energy rotational, vibrational and electronic. High energy UV radiation causes electronic transitions, IR radiation gives rise to vibrational excitation and radiation in the microwave range causes rotational excitation.

<table>
<thead>
<tr>
<th>Change of spin</th>
<th>Change of orientation</th>
<th>Change of configuration</th>
<th>Change of electron distribution</th>
<th>Change of electron distribution</th>
<th>Change of nuclear configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiowave</td>
<td>Microwave</td>
<td>Infrared</td>
<td>Visible and ultraviolet</td>
<td>X-ray</td>
<td>γ-ray</td>
</tr>
<tr>
<td>10</td>
<td>10^3</td>
<td>10^5</td>
<td>10^7</td>
<td>10^9</td>
<td></td>
</tr>
</tbody>
</table>

Energy (J mol⁻¹)

Figure 2.6: Molecular processes associated with the electromagnetic spectrum (adapted from Stuart, 2004).

2.8.1 Ultra-violet spectroscopy in the solid phase

Ultraviolet photons with energies of a few electron volts cause transitions of electrons between orbitals within a molecule, e.g. the Lyman-α radiation in atomic hydrogen excitation is associated with an energy transition of 10.2 eV. In molecular systems there are two types of simple electronic excitations, valence and Rydberg transitions. Both of these transitions occur when an electron moves to higher energy orbital, therefore they show similar features.
However a valence transition involves the promotion of an electron to the valence orbital whereas in a Rydberg transition the electron is promoted to an orbital with greater quantum number. In gaseous samples this does not result in a significant difference but in the solid phase with a smaller intermolecular separation, the Rydberg states are more susceptible to perturbation. This results either in a broadening of vibrational fine structure and a small (nearly 0.2 eV) additional blue shift, or the complete suppression of the Rydberg excitation from the electronic spectrum of the ice.

In the solid phase, such as molecular ices, the interaction between molecules can strongly affect the resulting UV spectra. At extremely low temperatures (10 – 30 K) almost all molecular samples solidify into an amorphous or crystalline structure. The spectra of amorphous solid ice displays only the broad electronic transitions. In amorphous structures individual molecules have random orientations and the molecular rotation is suppressed, whereas the vibrational excitations have slightly different energies contributing to an overall broadening effect in the vibrational fine structure. In crystalline ice, molecules are aligned with long range order and little or no broadening of the vibrational fine structure takes place.

2.8.2 Infrared spectroscopy

Modern infrared spectroscopy in this field is based on Fourier Transform InfraRed (FTIR) spectroscopy, which is based on the interference of radiation between two beams to produce an interferogram, which is further processed using a Fourier transform. An interferogram is a signal produced as a function of the change of pathlength between the two beams. A Michelson interferometer is commonly used to obtain an interferogram. This consists of two perpendicular plane mirrors, one of which can travel in a direction perpendicular to the plane. A beamsplitter reflects 50% of the incident radiation from one of the mirrors while 50% will be
transmitted to the other mirror. The two beams reflected from both these mirrors will then recombine and interfere. The reflected beam from the stationary mirror is then 50% reflected back to the source and the rest 50% is transmitted. The emerging beam at 90° to the source is the transmitted beam which is detected in FTIR spectrometry (Figure 2.7). The moving mirror is responsible to produce the optical path difference to obtain a constructive and destructive interference pattern. Two equations of the Fourier transform are used which relate the intensity falling on the detector to the spectral power density at a particular wavenumber.

Figure 2.7: Schematic of a Michelson interferometer.

After recording an infrared spectrum it is important to analyse it by interpreting the information contained in the infrared bands. Group frequencies, wavenumbers corresponding to particular parts of a molecule, will assist in the interpretation of an infrared spectrum. In our experiments a mid infrared spectrum (4000 – 400 cm⁻¹) is used. There are four regions within the
mid infrared range which corresponds to particular types of vibration for a molecule. These are [i] X-H stretching region (4000 - 2500 cm\(^{-1}\)), [ii] triple bond region (2500 - 2000 cm\(^{-1}\)), [iii] double bond region (2000 - 1500 cm\(^{-1}\)) and [iv] the finger print region (1500 - 600 cm\(^{-1}\)). Band positions and modes of vibrations for a molecule can be calculated and compared with the bands that are observed in experimental infrared spectra. In this thesis, already published vibrational band modes and peak positions are used to assign the new bands produced by the respective molecule vibrational modes.

2.9 The Beer – Lambert law

The physical process in which the electromagnetic radiation is absorbed by a sample or material under investigation can be mathematically described in terms of the Beer-Lambert law which relates the amount of light transmitted to the number density of the sample. The ratio of the transmitted and incident electromagnetic radiation is related to the sample concentration and the path length according to the following equation:

\[
\frac{I(\lambda)}{I_0(\lambda)} = \exp (-\alpha c l)
\]

(2.10)

where, \(I(\lambda)\) and \(I_0(\lambda)\) are the transmitted and incident radiation respectively, and \(c\) is the sample concentration, \(l\) is the path length and \(\alpha\) is the absorption cross section. The absorbance \(A\) is equal to the difference between the logarithms of the intensity of the light entering the sample \(I_e\) and the intensity of the light transmitted \(I\) by the sample:

\[
A = \log I_e - \log I = \log \left(\frac{I_e}{I}\right)
\]

(2.11)

and transmittance is defined as:

\[
T = \frac{I}{I_e}
\]

(2.12)
relating equations (2.9) and (2.10) implies:

\[ A = \log \left( \frac{1}{T} \right) = -\log (T) \quad (2.13) \]

Where the transmittance is expressed in terms of percentage then the relationship between absorbance and transmittance given in equation (2.13) is easy to understand when expressed in numbers because both are dimensionless quantities.

2.10 Structure of the molecular ice

Molecules striking a cold surface stick to the surface, therefore molecular ices are formed on the cold surface. The molecular ice present on the surface can either be in the amorphous or in the crystalline phase. From previous experiments (A.Dawes et al, 2007) it is well known that the temperature of the cold surface and the deposition rate of the molecules determines the ice structure being formed. If molecules have sufficient energy and time to rearrange then this re-orientation of the molecules will result in an ordered (crystalline) ice structure. The energy gained by the molecules from the charged particle irradiation also leads to structural changes in the ice. It is also possible for the molecular ice to exhibit both amorphous and crystalline phases. Simultaneously this is possible in an ice mixture containing two different molecules that have different sticking probabilities and mobilities. Small contours of amorphous and crystalline phase will be present in the ice formed over the cold substrate. This can also take place due to the action of energetic particles because of local molecular distortions. Solid ammonia ice is a very good example showing that under different experimental conditions, e.g. varying the deposition temperature and changing the temperature after deposition, the structure of the ices can be very different (Figure 2.8).
Apart from the deposition rate and the effect of energetic particles impinging upon molecular ice, heating will induce mobility of the molecules to rearrange and orientate to form the crystalline phase or, if already in the crystalline phase, then a change from one crystalline structure to another is also likely. This can be shown using oxygen molecular ice as an example and is relevant to this thesis, where O_2 ice below 23.9 K has the crystalline monoclinic structure and heating the O_2 ice above 23.9 K changes it to a rhombohedral crystalline structure. Structural changes will affect the density of the molecular ice, i.e. number of molecules per square centimeter of the substrate is different and therefore, depending on the ice structure, the trapping of atoms or molecules in the ice will change. Also at the time of irradiation by energetic particles differences in ice structure imply that the number of molecules interacting with the irradiation particle changes, which in turn changes the distance that a particle can travel in the ice.

2.11 Irradiation processes

In interstellar and planetary / satellite ices chemical synthesis is carried out by irradiation of the ice by energetic ions by fast electrons and ultraviolet (UV) photons. Star light is a source of UV photons, while cosmic rays and planetary magnetospheres are the two main sources for energetic ions and electrons. In 1963, Wehner et al suggested that particle radiation may have modified the surface materials of planetary bodies or their satellites. Several of these satellites are known to be embedded within their planetary magnetosphere and therefore ion irradiation by their respective planetary magnetosphere is a major source for chemical changes to take place in the icy satellites.

The effects of irradiation are the same for all the three forms of irradiation and are summarized in Table 2.2. The magnitude of this effect differs with the energy and size of the irradiation particle. These two factors determine the penetration and the number of molecule-
irradiation particle interaction. For example the UV photons are known to interact in the ratio of one molecule per photon whereas the energetic ions interact with more than one molecule and also produce secondary electrons. The greater the penetration depth of the irradiation particle, the higher the number of molecular interactions before the particle comes to rest or is chemically captured (Figure 2.9).

Table 2.2: Events initiated by irradiation. (Adapted from Johnson 1990).

<table>
<thead>
<tr>
<th>Event Type</th>
<th>Physical stage $&lt; 10^{-13} \text{ s}$</th>
<th>Physiochemical stage $&lt; 10^{-11} \text{ s}$ (Luminescence $&gt; 10^{-9} \text{ s}$)</th>
<th>Chemical stage $\sim 10^{-6} \text{ s to years}$ (temperature and flux-dependent)</th>
<th>Long-term effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident radiation</td>
<td>Energy absorption</td>
<td>Electronic recombination</td>
<td>Diffusion of radicals</td>
<td>Repair and equilibrium</td>
</tr>
<tr>
<td></td>
<td>Radiation Cascade</td>
<td>Molecular dissociation and rearrangements</td>
<td>Production of new molecules</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electronic energy transfer</td>
<td>Sputtering</td>
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</tr>
</tbody>
</table>

36
Figure 2.8: Structures of solid ammonia at different temperatures (A Dawes et al, 2007; M.P.Davis, 2006).
The irradiating particle often undergoes scattering due to the interaction with molecules losing energy in collisions and therefore eventually comes to rest in the ice. Collisions of the energetic particle with the target can be divided into two types: [i] nuclear (elastic) and [ii] electronic (inelastic), and although both energy losses occur at the same time they are generally treated separately and additively. They are both dependent on the material number density \( n \) and the net energy loss is generally written as follows

\[
\frac{dE}{dx} \approx n (S_n + S_e)
\]

where \( \frac{dE}{dx} \) is referred to the stopping power of the material and \( S_n, S_e \) are referred to as the electronic and nuclear (collisional) stopping cross sections. Electronic stopping dominates for ions with high energy and low atomic number, whereas nuclear stopping dominates for ions with low energy and high atomic number. At higher energies when electronic excitation and ionization events dominate the energy loss, the scattering of the incident particles is small and the stopping can be thought of as continuous. However, for both low incident ion energies, for which nuclear elastic collisions dominate and very high velocities, at which nuclear reactions occur, the deflections need to be incorporated (Johnson 1990).

![Figure 2.9: Schematic diagram of ion irradiation path. (Adapted from Johnson, 1990).](image-url)
Stopping powers are used to calculate the range of ions in a medium or material using modeling computer programs. Computer programs based on the quantum mechanical treatment of ion-atoms collisions are used to calculate the stopping power and range of ions in the molecular ice target. SRIM (Stopping and Range of Ions in Matter) and TRIM (Transport of Ions in Matter) are the two programs used to estimate the stopping power and range of energetic ions in solid molecular ices. The distance travelled by a incident irradiation particle is calculated using continuous slowing-down approximation in which all the particles are assumed to travel the same average distance, called the mean range \( R_m \) given by

\[
R_m = \int_0^E \frac{dE}{(dE/dx)}
\]

(2.15)

![Diagram of energetic particle penetration into an ice sample.](image)

**Figure 2.10:** Energetic particle penetration into an ice sample. \( R \), range of the particle before stopping and \( R_p \) projected range along incident direction (Adapted from Johnson, 1990).

From figure (2.10), the ratio of \( R / R_p \) gives an estimation of the amount of energy deposited into the ice due to deflections. This ratio is relatively high for secondary electrons and ions produced and therefore imply that they cover smaller distances before they come to rest.
Irradiation of molecular ices induces chemical reactions. Generally several new products are found to be present in the ice after irradiation. Production of new molecules might depend on the availability of other new products formed by initial (elementary) reaction steps. This implies that one or several reaction steps, with different reactions rates, can take place and contribute to the synthesis of simple or complex molecules in the ice. Therefore, it is necessary to understand the chemical formation pathways of simple or complex molecules produced.

2.12.1 Chemical kinetics and reaction mechanisms

A reaction of the form given in equation (2.16) can occur through one or more reaction steps through intermediate products. The products obtained are influenced by rate of the reaction (kinetics), the reaction barrier associated with the process and the number of reaction steps (reaction mechanisms / pathways). The reaction rate favouring the formation of the product is dependent both on the reactants and products involved in the reaction and also with the amount of energy released (exothermic) or absorbed (endothermic). The reaction barrier $E_a$ (activation energy) is associated with the reactants necessary to form products. The number of reaction steps that are followed to form a molecule primarily depends on the rate of the reaction and stability or lifetime of the intermediate product.

\[ A + B + C \rightarrow \ldots \rightarrow AB + AC + BC + ABC \]  \hspace{1cm} (2.16)

It is important to note that reaction kinetics expressed mathematically, called the rate equation or rate law (equation 2.17), is used to confirm the reaction mechanisms followed for product formation. The rate equation or rate law, that links the reaction rate with concentrations of the reactants is as follows;
\[
\frac{d[\text{reactant}]}{dt} \propto -k[\text{reactant}]
\] (2.17)

where \( k \) is the rate coefficient or rate constant. The negative sign indicates the decrease in the reactant concentration with time. The reactions can be classified as zero order, first order, second order, pseudo first order and \( n^{th} \) order reactions. In this thesis reactions of pure molecular ices, \( \text{O}_2, \text{CO}_2, \text{N}_2\text{O}, \text{NO}_2 \) and of oxygen-16 and 18 isotopic ice mixtures are studied. The aim was to study the formation of \( \text{O}_3 \) from these pure and mixed ices, therefore the reaction kinetics and mechanisms involving the oxygen atoms and molecules to form \( \text{O}_3 \) is explored.

A reaction containing an extremely large amount of reactants, where increasing the reactant concentration does not affect the product formation, is a zero order reaction. This type of reaction is not likely to happen in a molecular ice due to the changes in the thickness of the ice leading to differences in the molecular formation. If the product formation is dependent on just one of the reactant molecules or atoms then the reaction is said to follow first order reaction kinetics. However, if one of the reactant remains constant and the availability of the other product limits the reaction then it is called a pseudo first order reaction. The feasibility of this reaction is highly likely in our experiments with molecular ices because the availability of the atoms produced by irradiation limits the reaction. When the reaction rate depends on the presence of two reacting species then the reaction is said to undergo second order reaction kinetics.

Single or multi step reactions following one or more of the above mentioned reaction mechanisms might lead to the formation of ozone for a given molecular ice. Indeed to form this molecule it is necessary to have both atomic and molecular oxygen. Therefore for oxygen ice where plenty of molecular oxygen is available and reaction is limited by the availability of atomic oxygen ozone formation can simply follow the pseudo first order reaction. However, in the production of ozone in other molecular ices, e.g. \( \text{CO}_2, \text{N}_2\text{O} \) and \( \text{NO}_2 \), we need to generate oxygen.
molecules from oxygen atoms and then to form ozone by further reactions. This might take place in a two step consecutive reaction, like $A+A \rightarrow AA + A \rightarrow AAA$, where $A$ can be atomic oxygen. This reaction mechanism is also likely to form ozone isotopomers while using isotopic oxygen as one of the reaction constituents. Therefore either one or two step reactions are involved in the production of ozone.

2.13 Conclusion

Molecular structure and spectroscopy relevant to astrochemistry have been discussed. Molecular structure in terms of atomic and molecular orbitals is presented and molecular energy levels are described. The principles of spectroscopy governing the vibrational and electronic transitions are discussed. The role of the electromagnetic spectrum with emphasis on the ultraviolet and infrared wavelengths in obtaining the information embedded from spectroscopic features is documented. Microscopic structures of the molecular ice and the changes in the structures with respect to experimental conditions are explained. The principles of irradiation processes relevant to molecular ices and the effect of such processes are detailed. Finally, the chemical kinetics and reaction mechanisms likely in the formation of ozone are described for the ices studied in this thesis.
CHAPTER 3: EXPERIMENTAL PROCEDURES AND METHODS

3.1 Introduction

In order to understand the reactions leading to the synthesis of new molecules on the surface of an interstellar dust grain or planetary or satellite ice it is necessary to simulate the conditions that prevail in those environments. The temperature recorded in dense clouds in which the interstellar dust grains are present is about 10 K, whereas 50 - 150 K are common surface temperatures on rocky planets and their moons. At such low temperatures molecules will readily condense onto the surface.

In the laboratory experimental focus is on the purity of the ice formed on the substrate and hence pressures of $10^{-11}$ – $10^{-7}$ Torr are necessary to have minimal / no contamination from the H$_2$O or CO$_2$ or other trace gases common in vacuum systems. However we should note that such laboratory simulations still operate at $10^4$ - $10^7$ times greater pressure than that in the interstellar medium (ISM). In the ISM and on planetary lunar surfaces these ices are subject to several irradiation sources ranging from comic rays, energetic magnetospheric particles to solar wind particles, with energies from keV – MeV. In this project we aimed to study the effect of irradiation of ISM / planetary ices as a function of temperature, morphology and types of irradiation. An integrated series of experiments was performed at:

[2] Queens University in Belfast (QUB), UK,
[3] The Institute for Storage rings (ISA), University of Aarhus, Denmark,
[4] The University of Hawaii (UH), USA,
[5] The Cosmic ice lab, NASA Goddard Space Flight Center (GSFC), USA,
[6] Catania Astrophysical Observatory (CAO), University of Catania, Italy.
In this chapter experimental techniques and methods used in different laboratory irradiation environments to irradiate molecular ices will be discussed. Some of techniques such as achieving low pressure, low temperature and gas line construction are common amongst all the laboratories and so they are summarized in a single section. However the irradiation sources and methods for analysing the chemistry that is induced by such irradiation varies with the laboratories and so these are discussed separately. In order to better compare and generalise the experimental setups used at all laboratories, normalized line diagrams of the vacuum chambers are presented.

3.2 Ultra-High Vacuum and low temperature in the laboratory

The common procedures followed in achieving low vacuum and temperature conditions are discussed below. In all of the laboratories vacuum chambers are used in order to create a clean environment for experiments involving molecular ices of thickness ranging from nm - µm scales. Turbo molecular pumps and dry / oil rotary pumps or scroll pumps are used in combination in a process to achieve Ultra High Vacuum (UHV) conditions. The vacuum that is created ranges from $10^{-11}$ to $10^{-7}$ Torr or mbar.

Once UHV is achieved then cryogen, eg. liquid helium, is used to cool down the substrate to 10 – 20 K. In the case of liquid nitrogen only 85 K can be achieved as a base temperature. An alternate source for cryogen is a closed cycle helium refrigeration system that can cool a substrate down to 10 K at the first stage and liquid nitrogen temperatures (85 - 90 K) are achieved at the second stage (Figure 3.1). This closed cycle system is used in the University of Hawaii, the Cosmic ice lab and Catania astrophysical observatory laboratories, whereas liquid helium is used in the rest of the laboratories during this work.
Figure 3.1: The two different systems using helium as the cryogen to bring down the substrate temperature to 10 K.

The temperature is measured on the substrate and heating is also performed very close to the substrate using resistive heaters in all the laboratories. The power used to heat the substrate varies with all the laboratories and in principle a better control of the heating sample is achieved using resistive heaters either for instant or slow heating of the substrate. In this way both the temperature and pressure are maintained as low as possible to simulate planetary, satellite and interstellar conditions and to study the chemistry under these conditions.

3.3 Gas dosing

Ice surface analogues are achieved by depositing molecular gas onto the cold substrate held at low temperatures e.g. 10 K. Preparing the gas line is a process to eliminate contamination of gases other than the desired gas for deposition. Normally the gas line is pumped using a backup pump either a dry rotary or scroll pump. Especially for oxygen dry pumps are used due to safety concerns, since pumping oxygen through oil pumps might trigger an explosion in the hot hydrocarbon oil. The whole gas line is evacuated to a base pressure of $10^{-3}$ mbar.
In the experiments discussed here mostly one molecular gas to form a single molecular ice is used except in the case of oxygen isotopes, where oxygen-16 and oxygen-18 are used. To mix two gases in the 1:1 ratio a gas mixing chamber is used. A line diagram of the gas line is shown in figure 3.2 where a regulator is used to draw small quantities of gas from pressurised gas lecture bottles. This is then passed into the gas cell or the gas mixing chamber. In order to measure the pressure in the gas line a non-ionising pressure gauge is used. These are either a transducer or capacitance type gauges which measures the absolute pressure independent of the gas used. Normally mbar quantities of gas are let in to the gas line before they are opened to the UHV chamber. An all metal UHV leak valve which enables very fine gas leak adjustments in quantities of $10^{-6}$ mbar of gas is used to let the molecular gases into the UHV chamber.

![Figure 3.2: Schematic of the gas line system used for pure molecular gas deposition.](image)
3.4 Gas deposition and molecular ice formation

Once the substrate was cooled down to low temperatures at UHV pressures then gas deposition can be started in order to obtain molecular ice samples on the cold substrate. There are several methods used for gas deposition and these are discussed in the following sub sections.

3.4.1 Background gas deposition

In this method small quantities of gas are allowed into the UHV chamber containing the cold substrate. The gas inlet nozzle is directed towards the walls of the chamber. Therefore gas molecules entering the UHV chamber are dispersed within the boundaries of the chamber inner walls, when these molecules come in contact with the cold substrate they stick on to the surface. In this way a few layers of molecular ice were formed.

In the background deposition method where infrared spectroscopy is used in a transmission mode the substrate required a special design to eliminate molecules that could stick on the “wrong side” of the substrate – that side where irradiation was not performed. Therefore, the unirradiated side of the substrate was covered leaving small opening with an extended conduit for the infrared beam to pass through the ice (Figure 3.3). This combination enabled an even deposition of molecules on the front face but reduces the number of molecules being deposited on the back face of the substrate.

In this method larger quantities of gas are used for a longer time because only a small percentage of the molecules come into contact with the substrate under vacuum conditions, however a uniform ice surface can be obtained by using this method. Gases were deposited using this method in experiments performed at the Catania Astrophysical Observatory.
Figure 3.3: Schematic of the background method for gas deposition and the substrate design used to prevent molecules being deposited on the unirradiated face of the substrate.

3.4.2 Direct gas deposition

Most of the laboratories use this method to obtain molecular ice samples on the substrate. In this method the gas inlet is targeted directly onto the substrate (Figure 3.4). The distance between the inlet nozzle and the substrate is optimized to be within 2 – 3 cm. Also during this type of deposition the substrate is usually placed normal to the inlet nozzle. Therefore those molecules entering the vacuum chamber by opening the gas line-UHV separator valve are directed towards the cold substrate and most of the gas used will form an icy layer over the substrate.

Figure 3.4: Schematic of the direct gas deposition method used in most of the laboratories.
3.4.3 Methods used to quantify gas deposition

Using a gas quantity method

The gas cell or the gas mixing chamber was prepared with a known quantity of gas. The amount of gas in the gas cell ranges from a few to 100 mbar depending on the sensitivity of the pressure gauge used. The quantity of gas in mbar to be deposited is decided before deposition. Deposition is carried out until the required pressure decrease is recorded in the gas cell. This method can only be used during direct deposition. Usually a reservoir of gas is used in order to have a constant flow rate from the gas cell to the UHV chamber. The main advantage of this method is that it is easy to control the deposition rate of a given amount of gas for either slower or faster deposition. It is found that deposition rate also plays a major role in determining the morphology of the ice. It is also necessary to know the ice thickness in an independent way to compare the quantity of molecules let into the chamber and number of molecules forming ice.

Using a pressure and time method

This method is adapted from surface science experiments where $10^{-6}$ Torr quantities of gas deposited in 1 sec corresponds to 1 Langmuir. The Langmuir scale was not used in these experiments. Rather a pressure and time deposition technique was used and the ice thickness was determined using an independent procedure (see section 3.5). In this method a high precision manually operated UHV leak valve that can let in small amounts of gas was used.

The chamber pressure was used as a measurement together with recording the time for deposition. Normally this method is employed in UHV chambers reading base pressures less than $10^{-10}$ Torr. However, in our experiments typically a deposition pressure of $10^{-7}$ Torr was used with deposition time varying from seconds to minutes depending on the thickness of the ice required.
This method has the same advantages as the gas quantity method, explained above, where changing the pressure and the timing for deposition determines either slower or faster deposition. In addition maintaining a constant pressure during deposition ensures a constant flow rate of the gas which eventually relates to a constant deposition rate.

3.5 Monitoring ice thickness

3.5.1 Interference fringes method

A laser beam is used to obtain an interference pattern due to the reflection of light from the ice-vacuum and ice substrate interface. The fringes relate to the thickness of the ice grown on the substrate (Figure 3.5). The deposition can be stopped after reaching the required number of fringes for a desired ice thickness (Equation 3.1). Both of the types of deposition described above can use this technique.

The main advantage of this method is that it is independent of the type of molecular gas that is used to grow molecular ice. When more than one molecular ice experiment needs to be compared with respect to the sample thickness then this technique can be used to produce approximately the same ice thickness just by measuring the number of fringes.

![Figure 3.5: Molecular ice growth on a cold substrate monitored using interference fringes method.](image)
The ice thickness, \( t \), can be determined from

\[ t = \frac{m \lambda}{2n (1 - \sin^2 \theta / n^2)^{1/2}} \] (3.1)

where, \( \lambda \) is the laser wavelength (nm), \( m \) is the number of fringes, \( n \) is the index of refraction and, \( \theta \) is the angle of incidence of the laser beam.

### 3.5.2 Using a real-time infrared spectrum method

This method involves the use of an infrared spectrometer to record an infrared spectrum while depositing gas on to the cold substrate (Figure 3.6). This method can be applied for both types of gas deposition. As the deposition is carried out the number of molecules sticking to the substrate increases such that the recorded IR band strength also increases. Deposition is carried out until the desired band strength of a particular molecule is reached, or until a good and clear infrared spectrum is recorded. Deposition can be carried out until bands appear clearly in the spectrum with less noise and deposition is stopped before the bands reach a saturation limit. The advantage of this method is the online visual of the growth of infrared bands due to icy layer formation. In particular while using a mixture of gases this method is very effective to ensure a good infrared spectrum for analysis. The limitation of this method is that it cannot be used for infrared inactive molecules.

![Infrared band](image)

**Figure 3.6:** Molecular ice growth on a cold substrate monitored using infrared bands.
The ice thickness can be calculated using equation (3.2). This equation can only be used when oscillations are observed in the infrared spectra due to multiple reflections taking place within the ice.

\[ t = \frac{N_{osc}}{2n (\nu_0 - \nu_1)} \]  

(3.2)

where \( t \) is the ice thickness (cm), \( n \) is the index of refraction, \( N_{osc} \) is the number of fringes or oscillations, \((\nu_0 - \nu_1)\) is the wavenumber of the oscillation occurring between \( \nu_0 \) and \( \nu_1 \).

If no oscillations are present in the infrared spectrum then equations (3.3 & 3.4) can be used to calculate the number of molecules in column density \( (N, \text{ molecules per unit area}) \) and then ice thickness, respectively.

\[ N = \frac{\text{Area (in optical depth)}}{A_{\text{molecule}}} \]  

(3.3)

### 3.6 Laboratory irradiation sources

To mimic the irradiation environment from cosmic ray particles and accelerated charged particles from planetary magnetospheres we need to use a wide range of irradiation sources and energies. Therefore electrons and ions at various energy ranges (1 keV - 0.8 MeV) were used in our experiments to study the molecular formation in the ice mimics. In addition we record the photoabsorption spectra using synchrotron radiation (based at the University of Aarhus) to explore the spectroscopy and morphology of ices.

Electrons with 1, 5 and 10 keV energies were used during the experiments at three different laboratories, at The Open University, the University of Hawaii and at the Cosmic ice lab in NASA Goddard, respectively. In all three laboratories a commercial electron gun was used. The electron beam current ranges between a few nA and a few µA.
To irradiate the ices with low energy (1 – 4 keV) ions, eg H\(^+\), He\(^+\) and D\(^+\), experiments were carried out using the Electron Cyclotron Resonance (ECR) ion source based at the Queens University in Belfast. The kinetic energy was different for different ions used, to ensure that the velocity of the ion was kept constant for each type of irradiation, eg for H\(^+\) or D\(^+\) or He\(^+\), the energy of the ion varies from 1 – 3 keV (equation 3.5),

\[
K.E_{\text{(ion)}} = \frac{1}{2}mv^2
\]  

(3.5)

Higher energy irradiation experiments were performed at the Catania Astrophysical Observatory using a commercial ion implanter from DANFYSIK (1080). Protons, H\(^+\), at 200 keV were used in the experiments. This beam line is equipped with ion beam rastering and so the charged particles are implanted over the entire sample surface.

In addition to these sources, MeV proton irradiation was achieved by using a Van der Graff accelerator facility based at the NASA Cosmic ice laboratory. Protons at 1 MeV were generated from the accelerator. A nickel foil is used to separate the accelerator and the experimental chamber section where 0.2 MeV of the beam energy is lost. Therefore, protons at 0.8 MeV reach the substrate.

Finally as a VUV photon source, we used synchrotron irradiation facility based at the University of Aarhus, to record the VUV spectra of molecules in the condensed phase. The UV1 beamline provides low photon energy irradiation over wavelengths ranging from 100 – 700 nm but in these experiments only the 120 - 320 nm range was used.
3.7 Irradiation dose

Since all the irradiation sources were different and a wide range of energies were used to study the chemistry, in order to compare and understand the amount of energy implanted on to the ice by different irradiation sources a common scale has to be used. There are several factors that affect the amount of energy deposited during the irradiation processes including:

[1] the density of the ice sample,
[2] the thickness of the ice sample,
[3] the type of irradiation source (electron, proton or ion),
[4] the energy of the electron, proton or ion used,

From the above list it is clear that parameters involving both ice properties and irradiation source plays a vital role. The contribution from the ice sample is in terms of the stopping power of the ice (see Chapter 2) for a given energy and type of irradiation. The stopping power of a molecular ice for a given density and thickness can be obtained (see section 3.7) for a specified ion and energy. Stopping power is given in eV Å⁻¹ or eV cm² molecule⁻¹. The contribution from irradiation source was in terms of the number of electrons or ions used to irradiate the ice sample per unit area, termed as fluence. Fluence (electrons or ions per unit area) is dependent on the electron or ion beam current (\(I_{\text{sample}}\)), irradiation time (\(t\)) and area of the sample (\(a\)) being irradiated, as given in the following equation:

\[
\text{Fluence (electrons or ions cm}^2\text{)} = t \ (s) \times I_{\text{sample}} \ (\text{A}) / e \ (\text{C}) \times a \ (\text{cm}^2) \quad (3.6)
\]
From the product of stopping power and fluence (equation 3.7) a unit of eV molecule\(^{-1}\) will be obtained and this is termed as dose. The dose is the quantity that gives a common scale to compare different irradiation source.

\[
Dose = \text{Stopping power} \times \text{fluence} \\
= [\text{eV cm}^2 \text{ molecule}^{-1}] \times [\text{electrons or ions cm}^{-2}] = \text{eV molecule}^{-1}. \tag{3.7}
\]

Thus the dosage was determined for each irradiation source used and either 16 or 18 amu is used commonly to obtain dose in eV 16 or 18 amu\(^{-1}\). This is obtained by dividing 16 or 18 amu by the molecular mass of the ice under irradiation. For example equation (3.8) shows oxygen (molecular mass = 32) ice irradiation in terms of dose in eV 16amu\(^{-1}\).

\[
Dose = [\text{eV molecule}^{-1}] \times \frac{16}{32} = \text{eV 16amu}^{-1} \tag{3.8}
\]

To study the formation kinetics of a new molecule formed by irradiation the temporal growth, i.e. the number of molecules vs. time, is used. However, for low energy ions (1-4 keV) the term fluence (ions cm\(^{-2}\)) can be used to determine the production of new molecules in terms of column density (molecules cm\(^{-2}\)) in order to relate the number of ions implanted and new molecules produced in an unit area. Finally to compare irradiation from different sources at different energies on a molecular ice it is imperative to use the irradiation dose.

3.8 Pre-experimental simulations

Before commencing an experimental run in the laboratory, the interaction of charged particles in molecular ices was simulated. For ions, the Stopping and Range of Ions in Matter code (SRIM) or Transport of Ions in Matter code (TRIM) program was used to calculate both the range of ions and total stopping power of the ice. In the case of electrons, a Monte Carlo
Simulation of the electron trajectory in solids (CASINO) can calculate the range of electrons and stopping power and range tables for electrons (ESTAR, web based program) can used to calculate the stopping power of the ice.

This virtual irradiation experiment was made before performing laboratory experiments. [1] If a reactive ion is used, like H+, then the range of the ion can be estimated and the ice thickness can be limited for all the ions to pass through or increased for all the ions to stop in the ice. [2] In the case of high energy proton irradiation, where all protons are stopped at the substrate, an optimum ice thickness can be estimated for a constant value of $S_{\text{tot}}$ (total stopping power) of the ice.

3.8.1 Low energy ions and ion implantation

Using SRIM, the range of ions and stopping power in the O$_2$, CO$_2$, N$_2$O and NO$_2$ ices was calculated before laboratory experiments were performed, for example in the CO$_2$ ice experiments SRIM was used to calculate the ion range in solid CO$_2$ to know the ice thickness required to stop all the ions within the ice. Inputs to run the simulation require an approximate sample density, type of ion, energy, molecular sample and the angle of incidence. The ion energies for H+, D+ and He+ were determined using equation (3.5). Since ions were implanted at an angle of $45^\circ$ normal to the sample, it was necessary to allow for this in determining the ion range in the ice. The following figure (3.7) shows the ion trajectory and range in solid CO$_2$.

The range of ions and stopping power obtained for the CO$_2$ ice and are listed in Table (3.1). Using values from Table 3.1 the sample thickness was selected to be in the order of µm so that all the ions stop within the ice layer. In the case where ion implantation was made, the
stopping power was determined by the ratio of energy implanted and the range of the ion in the ice.

Table 3.1: Range and stopping power of H⁺, D⁺ and He⁺ ions in solid CO₂ calculated using SRIM.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (keV)</th>
<th>Range (Å)</th>
<th>Stopping power (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>1.5</td>
<td>1209</td>
<td>1.75</td>
</tr>
<tr>
<td>D⁺</td>
<td>2.12</td>
<td>810</td>
<td>3.7</td>
</tr>
<tr>
<td>He⁺</td>
<td>3</td>
<td>816</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Figure 3.7: Trajectory and range of [a] H⁺, [b] D⁺ and [c] He⁺ ions in solid CO₂ at an angle of 45° normal to the sample.
3.8.2 High energy protons

For experiments involving high energy ions, e.g. 200 – 800 keV protons, simulations were carried out to determine the optimal ice thickness for all the ions to pass through the ice (Figure 3.8 (a)) and at the same time to achieve good ionization for the entire ice thickness used (Figure 3.8 (b)). Therefore ionization induced in the ice with respect to thickness was used to select the optimal ice thickness required.

Figure 3.8: [a] Range and trajectory of 200 keV H⁺ in oxygen ice. [b] Ionization with respect to target depth.

As explained in the previous section the parameters were assigned and the outcomes of the simulations are shown in figure (3.8 a and b) for an oxygen ice irradiated by 200 keV H⁺. Using results from figure (3.8(b)), a sample thickness of about 1µm was selected for irradiation in our experiments.

For 0.8 MeV proton irradiation, solid CO₂ was used in a simulation to observe the range and stopping power of these highly charged protons. In our laboratory experiment irradiation was carried out at a normal to the ice surface. So during the simulation the angle of incidence was given as 0° degree, whereas in the above two cases the angle of ion incidence was 45°. All the
other parameters were set to be the same for CO$_2$ ices, as given in the previous section, and the results of the simulation are shown in figure (3.9).

Figure 3.9: [a] Range and trajectory of 0.8 MeV H$^+$ in oxygen ice. [b] Ionization with respect to target depth.

In almost all the cases we used 1 – 2 µm thick samples for 0.8 MeV irradiation and so from the above figures we can clearly see that the ions strike the substrate after passing through the ice. From figure (3.9(b)) the ionization induced was almost constant for a 1 – 2 µm thick sample. A slightly different procedure is followed to calculate the stopping power for the ice at higher energies where the ions pass through the ice sample inducing ionization. This procedure is given in Appendix A.

Comparing both the proton irradiation at energies 200 and 800 keV we can conclude from the figures 3.8 and 3.9 that the stopping power for a 200 keV irradiation ($S_{\text{total}} \sim 9 \text{ eV Å}^{-1}$) was higher than for the 800 keV ($S_{\text{total}} \sim 3 \text{ eV Å}^{-1}$) proton irradiation for ice thickness of ~ 1 µm. From equation (3.8, section 3.6), after considering the same number of ions per unit area of the
sample, it is evident that a higher dose is obtained in the sample being irradiated by the 200 keV than the 800 keV protons.

3.8.3 1 – 10 keV electrons

To determine the stopping power and range of electrons in solid ices we can use CASINO to provide the range and ESTAR for both the stopping power and range. This program can estimate the stopping power for a range of energies starting from 0.001 MeV. But in our experiment only 1, 5 and 10 keV electrons were used, and so the values for the range and stopping power were adopted from Lea (1962), given in Table (3.2). Therefore, the ice thickness can be selected for laboratory irradiation experiments using electrons over this energy range.

Table (3.2): Range and energy dissipation of 1-10 keV electrons in a medium of density 1 g cm$^{-3}$. Values taken from Lea (1962).

<table>
<thead>
<tr>
<th>Electron energy (keV)</th>
<th>Energy dissipation (keV / µm)</th>
<th>Range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.33</td>
<td>0.05344</td>
</tr>
<tr>
<td>5</td>
<td>3.872</td>
<td>0.7468</td>
</tr>
<tr>
<td>10</td>
<td>2.298</td>
<td>2.517</td>
</tr>
</tbody>
</table>

3.9 Detecting chemical modifications in the ice

In order to detect the chemical changes induced by the effect of irradiation on a molecular ice a reliable and non destructive detection method needs to be used. Infrared spectroscopy was used as a tool to detect chemical modifications that occur in the ice phase and mass spectrometry was used to analyse the products subliming from the substrate into the gas phase.

3.9.1 Infrared spectrometry

A commercial Fourier Transform InfraRed (FTIR) spectrometer using either the transmission or absorption mode was used to record the infrared spectra of molecules over the Mid-InfraRed (MIR) range, 4000 – 400 cm$^{-1}$. A Michelson interferometer was used to obtain the
interferogram and then by applying a Fast Fourier transform (FFT) mathematical tool a FTIR spectrum is generated. The MIR range with resolutions from 1 to 4 cm\(^{-1}\) was used in all the laboratories where electron, proton and ion irradiation were carried out. A background infrared spectrum of the substrate, kept at low temperature and at UHV, was recorded initially before depositing a molecular gas. After gas deposition the recorded spectrum was ratioed to the background spectrum acquired before deposition.

3.9.2 Mass spectrometry

Mass spectrometer was used in the experiments to record molecules in the gas phase. Gas phase in the vacuum chamber was either due to sputtering of the ice at the time of irradiation or due to ice sublimation during warm-up. A commercial quadrupole mass spectrometer was used in irradiation experiments involving 5 keV electrons performed at University of Hawaii. The quadrupole mass spectrometer used can record 1 – 200 amu.

3.10 Chemical substrates and windows

Our experimental requirements were to have a UHV chamber cooled down to a very low temperature in which molecular ices can be deposited. To probe the chemical properties of the deposited ice both infrared and ultra violet radiation were used. Therefore the UHV chamber must be fitted with infrared or ultra violet radiation transparent windows to allow the beam into the chamber whilst maintaining UHV conditions. Table 3.3, lists the optical properties of the windows that were used in the experiments. Zinc selenide (ZnSe) was used as the substrate material due to good thermal conductivity in comparison with potassium bromide (KBr). In addition ZnSe is chemically inert, whereas KBr is hygroscopic. So KBr was used as the window material except at CAO, where Silicon (Si) was used as a substrate. Therefore all three infrared transmission windows were used as substrate material and out of which only KBr was used as a window material to hold UHV inside the chamber and atmospheric pressure outside the chamber.
For the VUV experiments either magnesium fluoride (MgF₂) or calcium fluoride (CaF₂) was used as a substrate material.

Table 3.3: Transmission range and radiation specific use of the common window materials used in the experiments.

<table>
<thead>
<tr>
<th>Window material</th>
<th>Transmission range (µm)</th>
<th>Use in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc selenide (ZnSe)</td>
<td>0.6 - 21</td>
<td>YES NO</td>
</tr>
<tr>
<td>Potassium bromide (KBr)</td>
<td>0.23 - 25</td>
<td>YES NO</td>
</tr>
<tr>
<td>Calcium fluoride (CaF₂)</td>
<td>0.13 - 10</td>
<td>NO YES</td>
</tr>
<tr>
<td>Magnesium fluoride (MgF₂)</td>
<td>0.12 - 7</td>
<td>NO YES</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>1.2 - 15</td>
<td>YES NO</td>
</tr>
</tbody>
</table>

3.11. Experimental setup and technique

3.11.1. Experimental apparatus at the Open University

The experimental astrochemistry apparatus based at the Open University (OU) can simulate irradiation environments down to temperatures of 20 K and pressures of the order of 10⁻¹⁰ Torr. Figure (3.10), shows a schematic diagram of main chamber (in line diagram) used in the molecular physics laboratory at The Open University.

The chamber has four ports on each side of the stainless steel chamber. One of which is used for the gas inlet, another used for the electron gun and the other two ports placed on either side are used for the infrared beam to pass through. Potassium bromide (KBr) windows are used in order to have an interface between the UHV (10⁻¹⁰ Torr) and atmospheric pressure regions to allow infrared beam to probe the ice (see section 3.9). The Zinc Selenide (ZnSe) substrate used inside the chamber is also infrared transparent. As KBr is hygroscopic and ZnSe is chemically inert the later was chosen for depositing the molecular ices.
Using liquid helium (section 3.2) the ZnSe substrate was cooled down to \(~20\) K. The substrate was then rotated towards the gas inlet which was a metal nozzle that extends into the UHV chamber from the gas line. After deposition the substrate was rotated towards the IR beam to record spectra of the deposited ice sample. Further rotating the substrate to face the electron beam will expose the ice for irradiation, as in figure (3.10). The area of the substrate was about 2 cm\(^2\) and the electron beam spot size at 1 keV was 3-4 mm as given by the electron gun supplier (Kimbal Physics Inc). The substrate was also placed at 45\(^\circ\) angle such that both electron irradiation and IR detection can be performed at the same time. This technique allows the detection and quantification of new molecules with respect to time. Therefore the kinetics of the process can be studied. Using resistive heaters the sample could be heated to any desired temperature above the irradiation temperature and a spectrum recorded. Spectral changes, if any, due to a rise in temperature indicate other chemical changes that take place in the ice. Spectra
recorded at different temperatures while heating the substrate allow the sublimation temperature of the ice to be evaluated. In this way ice sublimation temperatures can be found even without a mass spectrometer. The thickness of the ice was selected such that electrons were stopped at the substrate (Figure 3.11) rather than in the µm thick ice sample (section 3.7.3).

![Figure 3.11: Range (in µm) of 1 keV electron in the ice and ZnSe substrate. Line diagram not to scale.](image)

3.11.2 Experimental methodology to record VUV spectra of astrochemical ices

The same experimental chamber used at the OU was modified for VUV compatibility (Figure 3.12) and used at the ISA storage ring facility based in University of Aarhus, Denmark. In order to modify the chamber to be VUV compatible calcium fluoride (CaF₂) or magnesium fluoride (MgF₂) substrates were used for ice formation and a PhotoMultiplier Tube (PMT) used to record the photons passing through the ice and substrate. The substrate was cooled to temperatures between 20 and 90 K using either liquid helium or liquid nitrogen, and the pressure in the chamber was as low as 2 – 5 x 10⁻⁸ mbar. A background VUV spectrum of the substrate was recorded before each sample deposition and then a molecular ice sample was formed on to the substrate by rotating it to 90° towards gas deposition side. The substrate was then turned towards the VUV source and a spectrum of the ice together with the substrate was recorded.
By subtracting background spectrum recorded before sample deposition, the absorption spectrum of the molecular ice was obtained.

Figure 3.12: Schematic diagram of the modified OU astrochemistry chamber used to record VUV spectra of ices.

Photons pass through the substrate (Figure 3.13) because the substrate used is transparent (see section 3.9) with only a very small fraction being absorbed at VUV wavelengths. A very thick ice sample will result in a complete absorption within the ice, therefore, ice thicknesses in these experiments were only the order of a few nm. A long time period (in minutes) is needed to record a full VUV spectra since it is dependent on the resolution (0.1 – 1 nm) and the scanning wavelength range (120 – 320 nm) used, during this time the temperature had to be kept constant in order to measure the VUV spectra of the ice at a particular temperature.
3.11.3 Experimental methodology for low energy ion irradiation

Low energy (1 – 4 keV) ion (H+, He+, D+) irradiation experiments were performed at the ECR ion source in Queen’s University in Belfast using the OU astrochemistry chamber. The port used for mounting the electron gun in the OU laboratory was used to connect the chamber to the ECR beam line/ion source. The same ZnSe substrate and KBr windows were used in these ion irradiation experiments, since FTIR was used to probe the chemistry induced in the ice due to ion irradiation (Figure 3.14). Experiments performed on the ion beam line concentrated on CO2 ices and so liquid helium was used to achieve temperatures (20 – 30 K) well below the sublimation temperature (80 K) of CO2 ices at UHV pressures of 10^{-8}-10^{-7} mbar.

Using liquid helium (section 3.2) the ZnSe substrate was cooled down to 30 K. The substrate was then rotated towards the gas inlet which was a metal nozzle that extends into the UHV chamber from the gas line. After deposition the substrate was then turned in towards the IR beam to record spectrum of the deposited ice sample. Further rotating the substrate to face the ion beam will expose the ice for irradiation, as in figure 3.14. The area of the substrate was about
2 cm² and the ion beam spot size at 1 - 4 keV was 8 - 10 mm as determined by an aperture just before the ice chamber.

Figure 3.14: Schematic diagram of the OU astrochemistry chamber for experiments involving low energy ions on the ECR ion source at Queens University in Belfast.

The substrate was also placed at 45° such that ion irradiation and IR detection can be performed at the same time. This technique allows the formation of new molecules to be explored with respect to time. Therefore the kinetics of the formation process can be studied.

Using electrical resistive heaters the sample was heated to a desired temperature above the irradiation temperature and a spectrum was recorded. Spectra recorded at different temperatures while heating the substrate determined the sublimation temperature of the ice. The Ice thickness in these experiments was selected using the pre-experimental simulations determined in section (3.7.1) so that the ion is implanted in the first few nm layers of the ice (Figure 3.15).
3.11.4 Experimental methodology used for 5 keV electron irradiation

Electrons at 5 keV were used to irradiate ice samples in a surface scattering machine based at the Department of Chemistry, University of Hawaii (Figure 3.16). A chamber pressure of $10^{-11}$ Torr was achieved during electron irradiation experiments performed at base temperatures of 11 – 30 K. Low temperatures at the substrate were achieved using a closed cycle helium refrigeration system. In this chamber, in addition to the FTIR which is used to probe chemistry in the ice phase, a quadrupole mass spectrometer that can record up to 1 - 200 amu, was used to record molecules that sublime from ice to the gas phase.

A slightly different infrared detection technique was used because the substrate used was a silver mono crystal (Ag). The IR beam was used in an absorption-reflection-absorption mode such that electron irradiation and IR detection can be performed simultaneously. An IR beam from the source was targeted at an angle of 75° whereas the mass spectrometer was fixed at an angle of 45°, both normal to the substrate. After recording a background spectrum, the Ag substrate was turned towards gas deposition and then turned back to record the IR spectrum of
the molecule deposited. 5 keV electrons were fired at normal to the substrate. Table 3.2, was used to select the ice thickness for irradiation experiments using 5 keV electrons, which are stopped at the substrate (Figure 3.17). The mass spectrometer was turned on to record any desorption/sputtering of the deposited species due to irradiation. The combination of the instruments in various angles normal to the substrate enables the detection of new molecules simultaneously during irradiation.

While heating the sample/substrate to higher temperatures after irradiation, the combination of mass spectrometer and FTIR provides valuable information in terms of the chemical changes that takes place in the ice as well as interim desorption of molecules before complete ice sublimation. In such experiments the ice was warmed at a rate of 0.5 K min\(^{-1}\) and so the temperature at which the molecules sublime could be derived both from the mass spectrometer and FTIR data.

![Figure 3.16: Schematic diagram of the surface scattering chamber used for performing 5 keV electron irradiation experiments on molecular ices at University of Hawaii.](image)
Figure 3.17: Range (in µm) of 5 keV electrons in the ice and Ag substrate. Line diagram not to scale.

3.11.5 Experimental methodology used for 0.8 MeV proton and 10 keV electron irradiation

The experimental apparatus that was used to irradiate the molecular ices on a polished aluminium (Al) substrate / mirror using 0.8 MeV and 10 keV electrons was based at the Cosmic ice laboratory at the NASA Goddard Space Flight Center, Greenbelt, USA. The chamber pressure was typically $10^{-7}$ Torr at base temperatures of 10 K, using a closed cycle helium refrigeration system. A slightly modified IR beam passage through the ice sample was used. The IR beam was projected at an acute angle between incident and the reflected beams from the Al substrate.

A solid state laser was focused onto the Al substrate when the gases were allowed in the vacuum chamber to make molecular ice. Interference patterns were obtained due to ice formation upon the Al substrate. From equation (3.1) the number of fringes required to make a desired ice thickness can be obtained. Experiments were normally carried out with µm thick ice samples because proton / electron beams at these energies penetrate several µm.
In all the experiments, pre-experimental simulations (given in section 3.7.2 and 3.7.3) were used to choose the ice thickness, so that either the 0.8 MeV protons or 10 keV electrons were stopped at the substrate (Figure 3.19). IR spectra of the samples were then recorded before irradiation. The Al substrate with the ice was then turned towards the 0.8 MeV proton beam that was produced using a Van de Graff accelerator. Irradiation was carried out at intervals of 0.5, 1, 2, 4, 8, 12 eV 18 amu\(^1\) to record an IR spectra of the ice at various doses. After irradiation the ice was then warmed up using resistive heaters that are mounted close to the Al substrate. Warm-up was carried out at 20 K intervals, unlike the 0.5 K min\(^1\) heating program used in section 3.10.5, and IR spectra were recorded.
3.11.6 Experimental apparatus used for 200 keV proton irradiation

The experimental setup used to irradiate molecular ices by 200 keV protons was based at the Catania Astrophysical Observatory (Figure 3.20). A close cycle helium refrigeration system was used to cool silicon (Si) and potassium bromide (KBr) substrates to 16 K. At low
temperatures the pressure in the chamber was recorded to be $10^7$ Torr. To begin an experiment with a new molecule a Si substrate was used and a number of fringes recorded as the gas was deposited using a laser beam focused onto the substrate (Figure 3.21(a)). The ice thickness required was determined from the pre-experimental simulations (section 3.7.2) the thickness being selected such that irradiation passed through the ice and was stopped at the substrate (Figure 3.21(b)). In contrast to other experiments molecular gas was let into the chamber and directed onto the walls of the chamber rather than towards the substrate. In this way background gas deposition was made, this was to ensure an even ice thickness at the substrate. A total of 5 fringes deposition was carried out and deposition was ceased at regular intervals to record the IR

![Figure 3.20: Schematic diagram of the experimental chamber used for performing 200 keV proton irradiation experiments on molecular ices at the Catania astrophysical observatory.](image)

200 keV protons (from DANFYSIK ion implanter)

IR beam (From source)

Polariser

KBr

Laser

Si or KBr substrate

Molecular gas inlet

IR beam (To detector)
spectrum at a particular ice thickness. Using the procedures given in chapter 4, the ice thickness, density, number of molecules present before irradiation and integrated absorption coefficient values were calculated. IR spectra were also recorded during warm-up of the ice at irregular intervals to know the increase or decrease in the band intensity of a molecule at a given temperature.

Figure 3.21: [a] Laser beam reflectance from the ice-vacuum and ice-Si substrate interface and [b] range in µm for 200 keV protons in the ice and KBr substrate. Line diagram not to scale.
After obtaining the required data for calculating the optical constants for the ice under study, the substrate was changed to KBr. Si was used as a good scale to calibrate temperatures due to the characteristic infrared bands at different temperatures. Therefore, the substrate was changed to KBr for irradiation experiments in order to distinguish new bands appearing from new molecules formed by irradiation and also while warming up the irradiated sample. Gas molecules were deposited onto the KBr substrate until 5 fringes were obtained in the interference spectrum. An IR spectrum was recorded before irradiation. The source for 200 keV protons was from a commercial ion implanter DANFYSIK 1080. The substrate was placed at 45° to both the proton beam and the infrared beam. Irradiation doses range from 0.5 – 26 eV 16amu¹. A raster mode was used for irradiation and so the ice was irradiated evenly. During IR recording a polarizer was used to choose either s or p polarizations of the IR beam to record the weak and strong bands.

3.12 Conclusion

The experimental apparatus and procedures used in the six different laboratories in which experiments were performed are summarised in this chapter. Similarities and differences in the experimental apparatus and procedure used at different labs are discussed. A minimum temperature of 10 K and pressures ranging from 10⁻¹¹ – 10⁻⁷ Torr were achieved. Electrons, protons and ions (D⁺, He⁺) were used as the source of irradiation for energies ranging from 1 keV – 0.8 MeV. Short descriptions of the proton, ion and electron irradiation sources are summarised. A simulation program, such as SRIM, was used to support the laboratory experiments. All the different irradiation sources used can be compared in terms of irradiation dose. The results obtained from using these experimental setups and their corresponding irradiation sources are discussed in detail in the following chapters.
CHAPTER 4: CALCULATION OF ICE PARAMETERS

4.1 Introduction

In order to quantify the results obtained in the irradiation experiments, the physical parameters of the molecular ices need to be known. From TRIM calculations (discussed in chapter 3), using initial approximate values for density and ice thickness, we can estimate the ice thickness \( d \) needed for irradiation experiments involving reactive ions, like \( H^+ \), so it is very important to know and to check the thickness of the ice that we obtained by deposition. To calculate the thickness of the ice, it is necessary to estimate the optical parameters of the ice deposited under such low temperature and pressure conditions. The refractive index \( n \) is the key parameter in estimating the thickness of an ice formed under particular experimental conditions. Knowing \( n \) and measuring the density \( \rho \) of the ice it is possible to estimate the column density (given in molecules cm\(^{-2}\)) and from these determine the integrated absorption coefficient \( A \), given in cm molecule\(^{-1}\)). In this chapter we estimate and present the values of ice density, thickness and absorption coefficient for oxygen, nitrous oxide and nitrogen dioxide.

4.2 Procedure

A laser, operating at a fixed wavelength (543 nm) was used to obtain an interference pattern from the ice grown on a silicon (Si) substrate. A silicon substrate was used for the following reasons: [1] it has a well known refractive index, [2] a good flat optical surface, [3] good thermal conductivity and [4] reflection is only from the front surface (Figure 4.1). The laser beam was projected onto the Si substrate, kept at a low temperature (16 K), while molecules were being deposited on to it. The interference pattern is produced by the laser light reflected from the ice-vacuum and the ice-surface interface. This interference curve (Figure 4.2) and its amplitude contains information on the ice refractive index and thickness. Equation (4.1) relates the
reflectance \((R_r_{\text{polarisation}})\) from the sample, to the complex (real and imaginary part) refractive index of the substrate \((n_s)\) and ice \((n_i)\), the thickness \((d)\) of the ice, the wavelength \((\lambda)\) of the laser used and the angle of incidence \((i)\) of the laser beam.

\[
R_{r_{\text{polarisation}}} = f (n_s, n_i, d, \lambda, i)
\]  

(4.1)

The refractive index of the ice can be derived by knowing that the amplitude of the interference curve depends directly on \(n_i\), since all the other parameters are known. From the experimental interference pattern (Figure 4.2), and using the relation between the parameters in equation (4.1) a theoretical interference curve (Figure 4.3) was obtained with the same amplitude. The flow diagram shown in figure (4.4), explains the procedure followed to calculate the value of \(n_i\) for a given ice (Westley et al 2000).
Figure 4.2: The experimental interference pattern obtained during NO$_2$ ice grown on a Si substrate.

Figure 4.3: Theoretical reflectance curve for NO$_2$ ice.
When the final $n_f$ value is evaluated, a good theoretical fit to the experimental data is obtained. Therefore to calculate the thickness of the ice at the desired point of the ice deposition we need to compare theoretical and experimental interference curves. Since the experimental curve is given in arbitrary units and a slight decrease in the experimental curve with thickness could also be observed due to scattering, in order to compare the curves they must be normalised. In particular the two curves are normalised in a way that the minima are set to zero and the maxima are set to one.

![Flow diagram](image)

**Figure 4.4:** Flow diagram describing the procedure followed in calculating the refractive index of a given ice.
To calculate the thickness of the sample at a particular point in the interference curve the normalised intensity is used as given equation (4.2) and at this value a line is drawn to the normalised theoretical curve obtained (Figure 4.5) such that the intercept will give the thickness \(d\) of the ice at the particular point \(y_{\text{point}}\) of deposition.

\[
y = \frac{y_{\text{point}} - y_{\text{max}}}{y_{\text{max}} - y_{\text{min}}} \tag{4.2}
\]

![Diagram](Image)

**Figure 4.5:** Normalised theoretical curve (black line). Value of \(y\) obtained from equation 4.2 (red line) and the intercept from x-axis (dotted black line) reads the thickness.

In order to obtain the density of the ice the Lorenz-Lorentz relation (4.3) is used. For a given material the Lorenz-Lorentz coefficient, \(L\), is constant for a given wavelength regardless of the material phase or temperature, this quantity is expressed in \(\text{cm}^3 \text{ g}^{-1}\). The value of \(L\) was obtained from the Table 4.1 after substituting the values in equation (4.3).

\[
L = \frac{[(n^2 - 1)]}{(n^2 + 2)} / \varphi \tag{4.3}
\]
Table 4.1: Values of density and refractive index used to calculate the L value of the molecular species considered in this work. The related material phase and temperature is also labelled. (Roux et al, 1980).

<table>
<thead>
<tr>
<th>Molecular species</th>
<th>Phase</th>
<th>Temperature</th>
<th>Density (g cm(^{-3}))</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>ice</td>
<td>20 K</td>
<td>1.22</td>
<td>1.25</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>ice</td>
<td>20 K</td>
<td>0.988</td>
<td>1.27</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>liquid</td>
<td>?</td>
<td>1.45</td>
<td>1.4</td>
</tr>
</tbody>
</table>

In order to derive the density of a given ice with a measured refractive index \(n\), we used the \(\rho\) and \(n\) values of the ice substance available in literature. Once we have determined \(L\), we can use the refractive index that we measured in order to derive the density of the deposited ice through equation 4.3.

From the values of \(d\) and \(\rho\) the column density (molecules cm\(^{-2}\)) is determined using the relationship given in equation (4.4). At the time of deposition infrared spectra are recorded at 0.5, 1, 2, 3.5 and 5 fringes. From the infrared spectra the band area (in optical depth) is measured for every different ice thickness corresponding to the number for fringes. A plot of the band area (in optical depth) against the column density (Figure 4.6) is used to derive the \(A\) (integrated absorption coefficient, cm molecule\(^{-1}\)) value for a given ice from equation (4.5), which is the value of the slope.

\[
\text{Column density} = \left[ \frac{d \rho}{((\text{molecular mass})(1.66 \times 10^{-24}))} \right] \quad (4.4)
\]

\[
A = \frac{\text{Band area (in optical depth)}}{\text{column density}} \quad (4.5)
\]

Once the column density is determined using equation 4.4 the thickness of the ice sample can be calculated using equation 4.6, where \(t\) is the ice thickness (cm), \(N\) is the column density.
(molecules cm⁻²), \( A \) is the absorption coefficient (cm molecule⁻¹), \( M \) is the molecular mass (g), \( N_A \) is the Avogadro number of molecules, \( \rho \) is the ice density (g cm⁻³).

\[
t = N M / N_A \rho
\]  

(4.6)

Figure 4.6: A plot of the band area against the column density for \( \text{N}_2\text{O} \) and the slope of the fit (red line) gives the value of \( A \) in equation (4.5).

4.3 \( \text{O}_2, \text{N}_2\text{O}, \text{NO}_2 \) and \( \text{CO}_2 \)

For the experiments carried out with \( \text{O}_2, \text{N}_2\text{O} \) and \( \text{NO}_2 \) all the values \((n, d, \rho)\) of the ices deposited are computed in the way explained above and are listed in Table 4.2. Since \( \text{O}_2 \) vibrations are not observed in the infrared the \( A \) value for this molecule cannot be determined but for \( \text{N}_2\text{O} \) and \( \text{NO}_2 \) the \( A \) values are listed in Table 4.3 for the three most intense bands. For \( \text{CO}_2 \) ice we used literature value for subsequent analysis, the values of \( A \) and \( \rho \) are very well
known for lower and higher temperature ices. Table 4.4 lists the values for the CO$_2$ ice measured by Gerakines et al (1995) and Wood and Roux (1982).

Table 4.2: Values of $n$, $\rho$, $d$ and column density of O$_2$, N$_2$O and NO$_2$ ices after 5 fringes deposition at 16 K.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Refractive index ($\lambda = 543$ nm)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Thickness ($\mu$m)</th>
<th>Column density (molecule cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>1.32218±0.0010</td>
<td>1.5426</td>
<td>1.0401</td>
<td>3.02x10$^{18}$</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>1.3176±0.00089</td>
<td>1.16</td>
<td>1.047</td>
<td>1.588x10$^{18}$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>1.31645±0.00077</td>
<td>1.1744</td>
<td>1.0515</td>
<td>1.617x10$^{18}$</td>
</tr>
</tbody>
</table>

The difference between the values of density in Table 4.1 and 4.2 were due to the difference in the experimental conditions used, for example like temperature. Table 4.2, gives the values obtained via our experiment whereas values in Table 4.1 from Roux et al (1980) were used to calculate the value of $L$ in order to obtain density of the ice formed under present experimental conditions.

For the NO$_2$ deposited at 60 K the values of $n_f$ and $\rho$ are found to be 1.548 and 1.9 g cm$^{-3}$, respectively in this work. The $\rho$ for NO$_2$ is higher at 60 K compared with the 16 K sample. This shows the difference in the morphology of the ices being irradiated at 16 and 60 K. From Table 4.3, the change in density for the CO$_2$ ice at higher temperature also indicates the morphology change with increase in temperature. For the N$_2$O ice a change in the intensity of the infrared bands corresponding to phase changes with increasing temperature has been reported by Roux et al (1980), therefore the N$_2$O ice also exhibits density changes with respect to temperature. The changes in density and phase for O$_2$ ices with increase in temperature have been studied in detail.
by Frieman and Jodl (2003). Therefore all the ices used in our experiments have changes in
density and morphology corresponding to changes in temperature.

Table 4.3: Values of band intensities at 16 K for the three most intense bands of N$_2$O and
NO$_2$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Band number, cm$^{-1}$</th>
<th>$A$, cm molecule$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>2232</td>
<td>7.47 x 10$^{-17}$</td>
</tr>
<tr>
<td></td>
<td>1275</td>
<td>1.54 x 10$^{-17}$</td>
</tr>
<tr>
<td></td>
<td>2590</td>
<td>1.99 x 10$^{-17}$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>1300</td>
<td>8.92 x 10$^{-17}$</td>
</tr>
<tr>
<td></td>
<td>1750</td>
<td>4.33 x 10$^{-17}$</td>
</tr>
<tr>
<td></td>
<td>1860</td>
<td>1.95 x 10$^{-17}$</td>
</tr>
</tbody>
</table>

Table 4.4: Value of $A$ and $\varphi$ for the CO$_2$ ices. Corresponding temperature is given in
brackets.

<table>
<thead>
<tr>
<th>Density, g cm$^{-3}$ (from Wood et al, 1982)</th>
<th>$A$, cm molecule$^{-1}$ (from Gerakines et al, 1995)</th>
<th>Band position, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.08 (20 K)</td>
<td>7.6 x 10$^{-17}$ (14 K)</td>
<td>2343</td>
</tr>
<tr>
<td></td>
<td>7.4 x 10$^{-17}$ (60 K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.1 x 10$^{-17}$ (14 K)</td>
<td>660, 665</td>
</tr>
<tr>
<td></td>
<td>1.1 x 10$^{-17}$ (60 K)</td>
<td></td>
</tr>
<tr>
<td>1.67 (80 K)</td>
<td>1.4 x 10$^{-18}$ (14 K)</td>
<td>3708</td>
</tr>
<tr>
<td></td>
<td>1.5 x 10$^{-18}$ (60 K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.5 x 10$^{-19}$ (14 K)</td>
<td>3600</td>
</tr>
<tr>
<td></td>
<td>5.5 x 10$^{-19}$ (60 K)</td>
<td></td>
</tr>
</tbody>
</table>
4.4 Conclusion

The values of refractive index, density and thickness of the ice calculated were used to obtain column density and integrated absorption coefficient values which will be used in the following chapters for analysing the results obtained after irradiation by energetic particles. Absorption coefficient values can be obtained directly applied to calculate the column density of the ice from the band area (measured in optical depth). For example, the relative number of ozone molecules formed from nitrogen dioxide ice by proton irradiation can be estimated as presented in chapter 8.
5.1 Introduction

To produce ozone in any solid ice surface it is necessary to have sufficient amounts of molecular oxygen. We therefore began our studies of the irradiation of ices with pure oxygen samples and then with mixture of oxygen isotopes. Baragiola et al. (1999) and Fama et al. (2002) have previously investigated ozone formation in 100 keV proton-irradiated oxygen matrices; Lacombe et al. (1997), using low energy (up to 10 eV) electrons, and Bennett & Kaiser (2005), using 5 keV electrons, have probed ozone formation by electron irradiation of molecular oxygen ices at 10 K. However, very little information exists on the precise mechanisms involved in ozone formation as a function of temperature-dependence which is highly relevant to astrophysical ices. Despite the increasing use of oxygen isotope monitoring as an analytical tool for classification of astronomical material to date there have been few laboratory experiments to explore the isotopic fractionation during chemical synthesis experiments. In the case of ozone isotopomer formation there is a single experiment using water (H\textsubscript{2}\textsuperscript{18}O)-oxygen (\textsuperscript{16}O\textsubscript{2}) mixture irradiated by 5keV electrons to form three isotopomers of ozone are produced (Zheng, Jewitt, & Kaiser 2007).

In this chapter we investigate the formation mechanisms of ozone in oxygen ices and report ozone yields as a function of ice temperature (11 – 30 K) and electron beam current. These data will help us to predict the existence of ozone on solar system bodies. The formation of different isotopomers of ozone by electron irradiation of pure (\textsuperscript{16}O\textsubscript{2}:\textsuperscript{18}O\textsubscript{2}) oxygen ice prepared under astrochemical conditions was also investigated and the formation kinetics of all six O\textsubscript{3} isotopomers was explored. Such results may provide some clues as to the isotopomeric abundances that might be found in solar system ices.
5.2 Pure molecular oxygen (\( O_2 \))

5.2.1 Detecting the phases of molecular oxygen

Solid molecular oxygen exists in three different crystalline phases (Cairns et al, 1965): the \( \alpha O_2 \), monoclinic phase (Barrett et al, 1967), between 0 - 23.9K; the \( \beta O_2 \), rhombohedral phase (Horl, 1982) between 23.9 - 43.6 K; and the \( \gamma O_2 \) phase between 43.6 - 54.4 K. In our experiments, molecular oxygen was deposited for about 300 seconds and at a pressure of \( 1 \times 10^{-7} \) Torr, onto a silver mono crystal substrate kept at 11K. Using the infrared band area of the \( \alpha - O_2 \) and \( \beta - O_2 \) phases of molecular oxygen, an approximate value of the number of molecules in the ice and thickness of the ice before irradiation can be derived using the equation (4.6 in chapter 4) and using the very recent values of \( \Lambda = 5 \times 10^{-21} \) cm molecule \(^1\) (Vandenbussche et al 1999) and ice density 1.54 g cm\(^{-3}\) (Freiman & Jodl 2004). A typical thickness of about 300 ± 30 nm at 11K was prepared under the deposition conditions used.

![Figure 5.1: \( \alpha O_2 \) monoclinic crystalline phase of molecular oxygen observed at 11 K.](image-url)
Under UHV conditions solid O$_2$ films start to sublime (monitored via mass spectrometry) when the sample temperature reaches 28K and most of the oxygen matrix was lost between 36 and 42K (Bennett & Kaiser 2005). Hence, in the present study, only $\alpha$O$_2$ and $\beta$O$_2$ phases were likely to be important. Spectra collected at the base temperature of 11 K show the $\alpha$O$_2$, monoclinic phase (Figure 5.1, Table 5.1) while solid $\beta$-O$_2$ was identified by a spectral signature at 1595 cm$^{-1}$ (A L Smith et al, 1950) and was readily observed in the 30K sample prior to electron irradiation (Figure 5.2). Though oxygen is itself an infrared inactive molecule, due to its induced dipole moment infrared signatures were observed (Figure 5.1 and 5.2).

![Figure 5.2: $\beta$-O$_2$, rhombohedral crystalline phase of molecular oxygen observed at 30K by annealing the sample deposited at 11K.](image)

The density of $\alpha$O$_2$ has been reported to vary between 1.535 – 1.525 g cm$^{-3}$ and of $\beta$O$_2$ between 1.521 – 1.396 g cm$^{-3}$ (Freiman & Jodl, 2004) and a value of 1.495 g cm$^{-3}$ was given by Horl (1962). Therefore the target density was lower at higher temperatures (Figure 5.3).
Figure 5.3: Density changes in \( \alpha \) and \( \beta \) phases of molecular oxygen with respect to temperature. (Adopted from Freiman & Jodl, 2004)

Table 5.1: Infrared band assignments of solid oxygen.

<table>
<thead>
<tr>
<th>O(_2) Vibrational assignment</th>
<th>Wavenumber, cm(^{-1})</th>
<th>Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>1549</td>
<td>O-O stretching (fundamental)</td>
</tr>
<tr>
<td>( \nu_1 + \nu_L )</td>
<td>1614</td>
<td>Fundamental + Lattice mode</td>
</tr>
<tr>
<td>( 2\nu_1 )</td>
<td>3076</td>
<td>Overtone of fundamental</td>
</tr>
</tbody>
</table>
5.2.2 Oxygen dimers in the solid phase

In the solid phase interactions with neighbouring molecules may alter the symmetry of the molecules slightly allowing their fundamental transitions to be infrared active. However VUV spectroscopy is a more useful tool for infrared inactive homonuclear diatomic molecules, like O₂, to study the properties of this molecule in the ice phase. A previous experiment (Mason et al, 2006) has shown the possibility of O₂ dimer formation when molecular O₂ ice was formed by deposition. Figure 5.4, shows the VUV spectra of solid O₂. In our experiments molecular oxygen was deposited at a pressure of 1 x 10⁻⁷ mbar onto a cold CaF₂ window, kept at ≈25 K, for different exposure times (15, 20, 25 and 32 second) and VUV spectra were recorded. The feature peaking at 180 nm was assigned to the (O₂)₂ dimer. The band was very weak when using thin O₂ ice layers but grew in intensity with increased deposition to form a thick O₂ ice (Figure 5.4). This suggests that more O₂ dimers were formed in thicker ice samples, therefore the proportion of dimers and monomers of O₂ vary with the ice thickness.

![Figure 5.4: VUV spectra of solid oxygen at different thicknesses kept at ~25 K.](image)
5.3 Electron irradiation effects

5.3.1. Pure molecular oxygen at 11 K

Electron (5 keV) irradiation experiments were carried out in the Department of Chemistry, University of Hawaii. Molecular oxygen (99.99%) was condensed for 300 seconds at a pressure of $10^{-7}$ Torr at 11 K and the sample thickness was estimated to be $300 \pm 30$ nm (at 11 K). The solid oxygen matrix, maintained at 11 K, was irradiated by 5 keV electrons for about 3600 seconds and at a beam current of 100 nA. Irradiation was followed by isothermal (constant temperature) and warm-up phase. With the onset of irradiation, additional absorption features appeared in our infrared spectra (Figure 5.5). These can be attributed to the ozone molecule ($O_3$).

Out of eleven observed bands reported by Brosset (Brosset et al. 1993) in a study of solid ozone film at 5 K, we observed seven bands at 11 K (Table 5.2). These are $v_1$ (1104 cm$^{-1}$), $v_2$ (702 cm$^{-1}$), $v_3$ (1037 cm$^{-1}$), $2v_3$ (2044 cm$^{-1}$), $3v_3$ (3028 cm$^{-1}$), $v_2 + v_3$ (1721 cm$^{-1}$), and $v_1 + v_3$ (2105 cm$^{-1}$). The positions of all three bands are in excellent agreement with those reported in earlier studies (Bennett & Kaiser 2005; Brewer & Wang 1972; Dyer, Bressler, & Copeland 1997; Schriver-Mazzuoli et al. 1995). The $v_1 + v_2 + v_3$ band (2798 cm$^{-1}$) was also observed during the warm-up phase (Bennett & Kaiser 2005). A detailed inspection of the profile of the $v_3$ band suggests that this feature is in fact a composite structure (Figure 5.6). A deconvolution reveals three absorption bands. The ozone monomer was at 1037 cm$^{-1}$ together with two closely satellite peaks at 1032 cm$^{-1}$ and 1042 cm$^{-1}$; the first one is attributable to the ozone-oxygen complex [$O_3...O$], whereas the latter can be assigned to the ozone dimer [$O_3...O_3$] (Bahou, Schriver-Mazzuoli, & Schriver 2001; Bennett & Kaiser 2005; Chaabouni, Schriver-Mazzuoli, & Schriver 2000b; Schriver-Mazzuoli, et al. 1995). The [$O_3...O$] complex was observed about 200 s after the onset of irradiation. The formation of the ozone dimer, [$O_3...O_3$], was only detectable at longer irradiation times of 1500 seconds.
Table 5.2: Infrared absorption bands of ozone observed in the sample irradiated at 11 K. * absorption frequencies of the \( \text{O}_3 \) monomer taken from Brosset et al (1993) \( ^{\ddagger} \) absorption frequencies of the \( \text{O}_3 \) monomer taken from Brewer & Wang (1972) \( ^{\ddagger} \) absorption frequencies of the \( \text{O}_3 \) monomer in good agreement with Bennett & Kaiser (2005).

<table>
<thead>
<tr>
<th>( \text{O}_3 ) Vibrational Band assignment</th>
<th>( \alpha\text{O}_3 ) Frequency, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>At 5 K(^{\ddagger} )  1108.8</td>
</tr>
</tbody>
</table>

\( \alpha\text{O}_3 \) \( ^{\wedge} \) (at 11K) Frequency, cm\(^{-1}\) Characterization

<table>
<thead>
<tr>
<th>This work</th>
<th>Absorption Coefficient (cm molecule(^{-1}))</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>( \nu_1 )</th>
<th>1104</th>
<th>O-O symmetric stretch</th>
<th>1.8E-19</th>
<th>1.84E-19</th>
</tr>
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<tbody>
<tr>
<td>( \nu_2 )</td>
<td>702</td>
<td>O-O-O bend</td>
<td>7.11E-19</td>
<td>7.11E-19</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>----------------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>1037</td>
<td>O-O asymmetric stretch</td>
<td>1.4 E-17</td>
<td>1.53E-17</td>
</tr>
<tr>
<td>( 2\nu_3 )</td>
<td>2044</td>
<td>Overtone</td>
<td>---</td>
<td>5.80E-20</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>----------------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>( 3\nu_3 )</td>
<td>3028</td>
<td>Overtone</td>
<td>---</td>
<td>1.23E-19</td>
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<tr>
<td>( 2\nu_1 )</td>
<td>2044</td>
<td>Overtone</td>
<td>---</td>
<td>6.01E-20</td>
</tr>
<tr>
<td>( \nu_1 + \nu_2 )</td>
<td>1803.9</td>
<td>Combination band</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 + \nu_3 )</td>
<td>2105</td>
<td>Combination band</td>
<td>2.58E-18</td>
<td>1.30E-18</td>
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<tr>
<td>( \nu_2 + \nu_3 )</td>
<td>1721</td>
<td>Combination band</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>( \nu_2 + 3\nu_3 )</td>
<td>3703.9</td>
<td>Combination band</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 + \nu_2 \nu_3 )</td>
<td>2798</td>
<td>Combination band</td>
<td>3.31E-20</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.5: First four intense bands of $\alpha$O$_3$ at the end of the irradiation period.
Figure 5.6: The $v_3$ band of O$_3$ at the end of irradiation. Deconvolution and curve fitting shows the presence of (O$_3$...O) and (O$_3$...O$_3$).

The infrared spectroscopic detection of ozone, O$_3$, and the accompanying [O$_3$...O] complex (Figure 5.6) suggests that the interaction of the keV electrons with the oxygen molecule leads to a cleavage of the oxygen-oxygen bond forming two oxygen atoms for an electron current of 100 nA. The data propose the formation of oxygen atoms during the keV electron exposure but what was the initial electronic state of the oxygen atoms formed? Cosby (1993) has shown the energetic electrons impinging on solid oxygen can produce oxygen atoms in the electronic ground ($^3$P) and in the first electronically excited ($^1$D) states. At electron energies above 100 eV the dissociation process of an oxygen molecule produces one oxygen atom in its first electronically excited state ($^1$D) and a second oxygen atom in its ground state ($^3$P); a simultaneous production of two ground state oxygen atoms is less favorable. (Cosby 1993) Subsequently, O($^1$D) can undergo intersystem crossing (ISC). In the matrix the lifetime of O($^1$D) varies strongly from 32 s to 780 ms (Mohammed 1990). We can therefore conclude that after the isothermal phase all O($^1$D) atoms
were relaxed to their $^3P$ ground state. The quenching of O($^3D$) to O($^3P$) was expected to be a rapid process due to multiple encounters in the solid state matrix; therefore, the lifetime of electronically excited oxygen atoms was expected to be less than a few µs to 100 ns (Benderskii & Wight 1994; Mohammed 1990; Ning et al. 2000; Turnipseed et al. 1991).

Based on these considerations we propose the following reaction mechanisms to account for the experimental data. Upon interaction of the 5 keV electrons with molecular oxygen two oxygen atoms are formed. During this process, oxygen atoms can be formed with high kinetic energies up to a few eV. These oxygen atoms are not in thermal equilibrium with the surrounding ice and must be classified as suprathermal. If an oxygen atom has enough excess kinetic energy it can escape its formation site in the lattice to react with a neighbouring oxygen molecule forming ozone via equation (5.1). However, in the limiting case, an oxygen atom can also be formed with no excess kinetic energy so that it is 'trapped' in the matrix site.

$$O_2 + O(^3P) \rightarrow O_3 \quad (5.1)$$

The v$_3$ feature can be used to quantify the amount of ozone formed during the irradiation phase, the isothermal phase, and during the warm-up regime. The column density of the ozone may then be estimated utilizing a modified Lambert-Beer law (given in chapter 3) with an absorption coefficient of the v$_3$ fundamental of $1.4 \times 10^{-17}$ cm molecule$^{-1}$ (Smith et al. 1985). Based on this fundamental mode we can extract the temporal evolution of the column density of the ozone molecule (Figure 5.7). By fitting these data to kinetic rate laws we can then extract rate constants and obtain information on the underlying reaction mechanism to form ozone. Considering the proposed reaction mechanism in equation (5.1) we would expect that the temporal evolution of the ozone monomer can be fitted by a pseudo first order equation (5.2).
\[ [O_3](t) = a_i (1 - e^{-kt}) \]  \hspace{1cm} (5.2)

Figure 5.7: Temporal evolution of \( O_3 \) monomer. A pseudo first order reaction mechanism is followed and solid line indicates the fit using equation 5.2. Error within \( \pm 10\% \).

Figure 5.8: Temporal evolution of ozone-oxygen \((O_3\ldots O)\) complex. A pseudo first order reaction mechanism is followed and solid line indicates the fit using equation 5.5. Error within \( \pm 10\% \).
The production of the \((O_3\cdots O)\) molecular complex can be explained from the oxygen bond cleavage in an oxygen dimer \((O_2\cdots O_2)\), following equation 5.4. The \((O_3\cdots O)\) produced contributes to the ozone monomer when the accompanying atomic oxygen leaves the cage due to excess kinetic energy or the molecule itself dissociates to ozone monomer and atomic oxygen during irradiation. The detection of this molecule supports ozone monomer formation, given in equation (5.1), in a mixed oxygen monomer and dimer matrix and also the presence of atomic oxygen during irradiation. The suggested reaction in equation 5.4 to form ozone-oxygen complex leads to the use of equation 5.5 giving, pseudo first order kinetics, that fit the temporal growth of this complex (Figure 5.8).

\[
(O_2\cdots O_2) \rightarrow (O_2\cdots O\cdots O) \rightarrow (O_3\cdots O)
\]  

\[
[(O_3\cdots O)](t) = a_2 (1-e^{-kt})
\]  

Referring to figure 5.6, in an irradiated matrix we also found the presence of ozone dimer \((O_3\cdots O_3)\), only few minutes after irradiation and during the dissociation of the associated \((O_3\cdots O)\). Identification of this molecule suggests additional reactions (equation 5.6(a)) involving atomic and molecular oxygen in the matrix together with molecules formed via equations 5.1 & 5.4. The other possible way to form ozone dimer is by the close proximity of two ozone monomers. The VUV spectra involving pure oxygen ices (section 5.2.2) has shown the presence of oxygen dimers as a function of the ice thickness. As the thickness of the sample is increased the oxygen dimer signature grows more intense indicating more dimer formation. Since the molecular oxygen ice sample used for the electron irradiation is thicker than the sample used to
obtain the VUV spectra the ice matrix has sufficient oxygen dimers to produce ozone dimers by equation 5.6(b).

\[
(O_3...O) + O_2 \rightarrow O_3...O_3 \quad (5.6(a))
\]

\[
(O_2...O_2) + 2O \rightarrow O_3...O_3 \quad (5.6(b))
\]

In an \( O_2 \) sample at 11K, irradiated at the same electron energy (5 keV) but with a different beam current (10nA), (1/10 of the previous irradiation) much less ozone is formed when compared with irradiation using 100 nA beam current. The formation of new molecules using two different currents can be compared in terms of fluence (electrons per square centimeter) on the

![Fluence dependence in the \( O_3 \) production; in an \( O_2 \) sample irradiated at 11 K by 5 keV electrons at two beam currents of 10, 100 nA.](image)

Figure 5.9: Fluence dependence in the \( O_3 \) production; in an \( O_2 \) sample irradiated at 11 K by 5 keV electrons at two beam currents of 10, 100 nA.
sample as shown (Figure 5.9). This shows the direct comparison with the rate of electron implantation and the corresponding amount of molecules produced. The values of rate constants in equation 5.2 & 5.5 are summarized in Table 5.3. From figure 5.9, we observe more ozone production for a given number of electrons implanted for a longer time.

![Graph showing absorbance vs. wavenumber]

**Figure 5.10: Spectra recorded at the end of irradiation in a sample kept at (a) 11K (b) 20K and (c) 30K.**

### 5.3.2 Effect of temperature

In order to understand the effect of ice temperature on the formation of ozone a solid $O_2$ sample was irradiated at 20 and 30K. To prepare the 20 K and 30 K oxygen ice samples the gases were first condensed at 11 K followed by a slow heating of the ice samples at 0.5 K min$^{-1}$ to the desired temperature. The sample thicknesses were 275 ± 30 nm (20 K), and 130 ± 15 nm (30 K). Ice samples were irradiated by electrons at 5 keV with 10 and 100 nA beam currents. The spectra recorded at the end of irradiation for all three temperatures (11, 20 & 30K) show different spectral shapes in the $v_3$ fundamental vibrational region (Figure 5.10). The spectral region 1060 –
1020 cm\(^{-1}\) is known to have the signatures for O\(_3\) monomer, dimer and the ozone oxygen complex (O\(_3\)...O), in an irradiated \(^{16}\)O\(_2\) ice matrix, hence the difference in the spectral shapes indicates that the different amounts of these molecules were formed at different temperatures.

Most importantly the ozone monomer column density increases with irradiation time for all temperatures of 11 K, 20 K, and 30 K. However the ozone monomer column density is highest at the lower temperature (Figure 5.11). The column densities of the [O\(_3\)...O] complex also increase with irradiation up to 24 minutes into the experiment; here, the trend is reversed as compared to the ozone monomer: the actual column density of the [O\(_3\)...O] complex rises as the temperature of the oxygen matrix is increased (Figure 5.12(a)). However as the irradiation time is enhanced even further we can see a sharp drop in the [O\(_3\)...O] complexes; after about 26 minutes, the temporal profile for all temperatures flattens out (Figure 5.12(b)). The integral absorption coefficient of the [O\(_3\)...O] complex is unknown, so we only fit the temporal evolution of the band area. Simultaneously with the descent of the signal from the [O\(_3\)...O] complex at about 24 min, new absorption peaks of the [O\(_3\)...O\(_3\)] complex appear; these absorptions rise in intensity with an increasing electron exposure and more dimers are present at higher temperatures (Figure 5.13). How can these results be explained?
Figure 5.11: Temporal growth of ozone monomer up to the end of irradiation, shown in terms of column density vs. time in minutes for the sample irradiated at electron beam currents (a) 100 nA (b) 10 nA. Solid line are the fits for the pseudo first order reaction kinetics given in equation 5.5. Error within ± 10%.

Figure 5.12: Temporal growth of ozone-oxygen (O₃...O) complex, shown in terms of integrated area vs. time in minutes, for (a) 24 minutes, during irradiation (red line shows the fit using equation 5.5) and (b) 60 minutes, until the end of irradiation. Error within ± 10%.
During the irradiation process, oxygen atoms can be formed with high kinetic energies up to a few eV. These oxygen atoms are not in thermal equilibrium with the surrounding ice and must be classified as suprathermal. If an oxygen atom has enough excess kinetic energy it can escape its formation site in the lattice to react with a neighbouring oxygen molecule forming ozone via equation (5.1). However, in the limiting case, an oxygen atom can also be formed with no excess kinetic energy so that it is 'trapped' in the matrix site. Increasing the temperature from 11 K to 30 K means such atoms gain excess thermal energy. This enhances the mobility of these atoms to migrate. In principle three reaction pathways are open: (i) the oxygen atoms can react back to 'recycle' molecular oxygen, (ii) oxygen migrates to a neighbouring ozone molecule forming a \([O_3\ldots O]\) complex, or (iii) the oxygen atom diffuses to an oxygen molecule reacting via equation (1) to ozone. If pathway (iii) dominates, we would expect an increase of ozone as the temperature rises from 11 K to 30 K. This has clearly not been observed experimentally (Figure 5.11), and so pathway (iii) is not dominant. On the other hand, channel (ii) would result in an increased formation rate of the \([O_3\ldots O]\) complex as the temperature rises from 11 K to 30 K. This correlates nicely with our experimental observation, i.e. an enhanced contribution of the
[O₃...O] complex with rising sample temperature (Figure 5.12). Finally since atomic oxygen can recombine with a neighbouring oxygen atom, pathway (i) would make less oxygen atoms available to form ozone via equation (5.1), and we expect a decreased ozone production as the temperature increases. This is in agreement with the temperature dependent temporal profile of the ozone monomer (Figure 5.11).

Considering the proposed reaction mechanisms for 20, 30K irradiated samples, similar to the 11K sample, we would expect that the temporal evolution of the ozone monomer and of the [O₃...O] complex can be fit by pseudo first order equations 5.2 and 5.5 with the column density of the ozone monomer, [O₃], and the absorption of the ozone – oxygen complex, [(O₃...O)]. The values of the rate constants are summarized in table 5.3. It should be noted that the rate constants are the same order of magnitude for 20, 30K ice as 11K ice. At 10 nA, the rate constants on the formation of the ozone monomer are - within the error limits - identical.

It is important to note the atomic oxygen migration distances at higher temperatures because the availability of these atoms controls the reaction process to form ozone. The migration of atoms opens geminate (equation 5.7) and non-geminate reactions (equation 5.8) of oxygen atoms produced from electron irradiation and so recycles molecular oxygen. To be precise a recombination of two closely lying atoms (geminate recombination), O(³P)...O(³P), obeys first order kinetics (Danilychev & Apkarin, 1993). At temperatures ranging from 10 - 30 K the difference in the mobility of the O atoms (Ning & Qin, 2001) determines if recombination is either geminate or non-geminate.

\[
\begin{align*}
[O(³P)...O(³P)] & \rightarrow O_2 \\
O(³P) + O(³P) & \rightarrow O_2
\end{align*}
\]
Table 5.3: Rate constants and pre-exponential factors for equations 5.2 & 5.5.

<table>
<thead>
<tr>
<th>Electron beam Current, nA</th>
<th>Temperature, K</th>
<th>$k_1$, s$^{-1}$</th>
<th>$a_1$, cm$^2$</th>
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</thead>
<tbody>
<tr>
<td>100</td>
<td>11</td>
<td>(0.48±0.02) x 10$^3$</td>
<td>(2.58±0.05) x 10$^{16}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>(0.7±0.04) x 10$^3$</td>
<td>(1.66±0.04) x 10$^{16}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>(0.39±0.09) x 10$^3$</td>
<td>(1.60±0.02) x 10$^{16}$</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>(0.11±0.05) x 10$^3$</td>
<td>(2.07±0.69) x 10$^{16}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>(0.17±0.04) x 10$^3$</td>
<td>(1.28±0.22) x 10$^{16}$</td>
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<tr>
<td></td>
<td>30</td>
<td>(0.07±0.05) x 10$^3$</td>
<td>(1.26±0.49) x 10$^{16}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O$_3$ Complex (formed at 100 nA beam current)</th>
<th>Temperature, K</th>
<th>$k_2$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$ ... O</td>
<td>11</td>
<td>(1.15±0.18) x 10$^3$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>(0.68±0.27) x 10$^3$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>(0.77±0.24) x 10$^3$</td>
</tr>
</tbody>
</table>

Migration distances of O($^1$D) atoms at 10, 15, 20 and 30 K are known to be 0.7, 0.8, 0.9 and 1.1 nm respectively in an Ar matrix (Ning et al, 2000). There is also evidence showing the O atom migration (~ 2 nm) in a Xe matrix is not dependent on temperature (Ning & Qin, 2001), at 10 – 30 K. Thermal O atoms are anticipated to be mobile ranging over distances from 0.7 to 2 nm dependent on temperature and the matrix. Thermal induced mobility is characterized by long
range migrations. Danilychev & Apkarian (1993) estimated a migration range greater than 10 nm by showing non-geminate recombination is first order at temperatures greater than 20K. Thus the barrier associated with \( \text{O}^3\text{D} \) mobility is expected to be negligible in an \( \text{O}_2 \) matrix. The above values are limited to the migration distances of \( \text{O}^3\text{D} \) (which gets slower and slower as time progresses, within a few picoseconds) and long range migrations cannot be expected with \( \text{O}^3\text{P} \) (Ning et al, 2000; Ning & Qin, 2001; Danilychev & Apkarin, 1994). Thermal excitation imparts mobility to atoms by allowing them to overcome the barrier to diffusion. Lattice defects, vacancies and lattice imperfections in the matrix can also increase \( \text{O}^3\text{P} \) migration range \( ^{41} \), which is possible in our sample as transition temperature for phase change in \( \text{O}_2 \) (Section 5.2.1) falls within the operating range of temperatures and this is also accompanied by a gradual change in density of solid \( \text{O}_2 \) matrix with temperature (Figure 5.3). Recombination should be dominated by the encounter of mobile atoms with stationary ones, because at any given time only a small fraction of the O atoms are expected to be activated. The migrating atomic oxygen is also expected to form ozone by non-geminate reaction with molecular oxygen during irradiation of the 20, 30K sample but to a lesser extent in comparison with the geminate \( \text{O}_2...\text{O} \) pair and also with reactions in equations 5.7 & 5.8. Hence after the irradiation phase the sample is a chemical mixture of ozone, molecular and atomic oxygen.

5.3.3 Isothermal phase

After irradiation the sample is kept under isothermal conditions. The temperature at which the sample is irradiated is maintained for an additional 3600 seconds after irradiation. In condensed molecular oxygen the production of atomic oxygen by electron irradiation is expected to produce \( \text{O}^3\text{D} \) which has lifetime to a maximum of 32 seconds and strongly varies with respect to the matrix with a minimum lifetime reported to be 780 ms (Mohammed 1990), before decaying to the \( ^3\text{P} \) ground state. So after 3600 seconds of isothermal condition without irradiation,
there should be no $O^{'(D)}$ present in the ice and all atomic oxygen atoms should be in their $^3P$ state.

It was discussed (section 5.2.3) that at temperatures of 20, 30K the irradiated sample produces molecular oxygen more than ozone production. In contrast during the isothermal phase there is no increase or decrease in ozone concentration, hence there is no dissociation or formation of new ozone molecules. It is important to note that all samples at 11, 20 and 30K produced ozone during irradiation, but once atomic oxygen is available, and the matrix is kept at isothermal temperatures of 11, 20 and 30K, further ozone production is not observed. This shows that the suprathermal atoms produced during irradiation are involved in producing ozone which is independent of temperature and so during the isothermal phase there is no increase in ozone which opens the thermal chemistry of the atoms after irradiation.

5.3.4 Annealing the irradiated ices

Warm-up of the irradiated sample was started after the isothermal phase at a rate of 0.5 K min$^{-1}$. Recall that upon the onset of the annealing phase all oxygen atoms stored in the matrix are expected to be in their electronic ground state ($^3P$). Also, at 11 K, atomic oxygen does not diffuse; recent experimental studies suggested lifetimes of $O(^3P)$ atoms to be in the order of days (Krueger & Weitz 1992). As the temperature is increased, the $[O_3...O]$ signal decreases. Simultaneously, the absorptions of the $O_3$ monomer (Figure 5.14) and of the $[O_3...O_3]$ complexes rises. As a matter of fact, the dissociation of $[O_3...O]$ and simultaneous formation of $[O_3...O_3]$ complexes is observed as soon as the warm-up phase starts. This suggests that at least some of the oxygen atoms in the $[O_3...O]$ complex react with a neighbouring oxygen molecule to form a $[O_3...O_3]$ complex. Also, it is worth noting that the column densities of the ozone monomer increase as the temperature rises (Table 5.4, Figure 5.14). This indicates that oxygen atoms trapped in the matrix can diffuse and react with molecular oxygen to form ozone.
Further warm-up of the irradiated sample revealed new bands above 47 K after the molecular oxygen has completely sublimed. \( v_1, v_2, v_1 + v_3 \) and \( 3v_3 \) combination bands of \( \text{O}_3 \) are observed at 1107 cm\(^{-1}\), 709 cm\(^{-1}\), 2108 cm\(^{-1}\) and 3033 cm\(^{-1}\) respectively (Figure 5.15). These assignments are in good agreement with a previous study carried out by depositing ozone directly onto a substrate and assigning the observed bands to the \( \beta-\text{O}_3 \) (crystalline) phase of ozone (Chaabouni, et al. 2000b). Absorptions of \( \beta-\text{O}_3 \) are also observed at \( 2v_3 \) (2049 cm\(^{-1}\)) and \( v_2 + v_3 \) (1725 cm\(^{-1}\)) (Table 5.5; Figure 5.16). So far the crystalline structure of solid ozone is not known. The 1049 cm\(^{-1}\) absorption feature, which appears only above 47 K, resides close to the ozone dimer and can be assigned to the formation of ozone clusters, \( (\text{O}_3)_n \) (Figure 5.17) (Chaabouni, Schriver-Mazzuoli, & Schriver 2000a; Chaabouni, et al. 2000b). Out of all the \( \beta\text{O}_3 \) bands observed, a phase transition from \( \alpha \) (amorphous) to \( \beta \) (crystalline) ozone is clearly observed by the \( v_2 \) (709 cm\(^{-1}\); O-O-O bend) band of \( \beta\text{O}_3 \), at 47K (Figure 5.18). The \( (\text{O}_3)_n, v_3-\beta\text{O}_3 \) band is not discrete even above 47K because it is overlapped by a broad feature in the \( v_3 \) band area. The \( v_1 + v_2 + v_3 \) band was observed only during warm-up of the sample in \( \alpha-\text{O}_3 \) phase and is not observed in the \( \beta-\text{O}_3 \) phase.

**Table 5.4: Column density of \( \text{O}_3 \) monomer during warm-up and end of irradiation.**

<table>
<thead>
<tr>
<th>Electron beam Current, nA</th>
<th>Temperature, K</th>
<th>( \text{O}_3 ) Column density, cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>At the peak of ( \text{O}_2 ) sublimation</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>((5.42\pm0.27) \times 10^{16})</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>((5.125\pm0.23) \times 10^{16})</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>((4.32\pm0.35) \times 10^{16})</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>((2.25\pm0.11) \times 10^{16})</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>((1.79\pm0.09) \times 10^{16})</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>((1.41\pm0.13) \times 10^{16})</td>
</tr>
</tbody>
</table>
Figure 5.14: The column density of $\nu_3$ band of ozone during warm-up of the sample at the rate of 0.5 K min$^{-1}$ for the samples irradiated at 11 K, 20 K, and 30 K at electron beam currents of (a) 100nA, (b) 10 nA. Error within $\pm$ 10%.
Table 5.5: Infrared bands of O$_3$ observed at 47 K.

<table>
<thead>
<tr>
<th>$\beta$O$_3$ Vibrational band assignment</th>
<th>Wavenumber, cm$^{-1}$</th>
<th>Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_1$</td>
<td>1107</td>
<td>O-O symmetric stretch</td>
</tr>
<tr>
<td>$N_2$</td>
<td>708</td>
<td>O-O-O bend</td>
</tr>
<tr>
<td>$v_3$</td>
<td>1036</td>
<td>O-O asymmetric stretch</td>
</tr>
<tr>
<td>$2v_3$ $^*$</td>
<td>2048.5</td>
<td>Overtone</td>
</tr>
<tr>
<td>$3v_3$</td>
<td>3033.5</td>
<td>Overtone</td>
</tr>
<tr>
<td>$v_1 + v_3$</td>
<td>2108.6</td>
<td>Combination band</td>
</tr>
<tr>
<td>$v_2 + v_3$ $^*$</td>
<td>1725</td>
<td>Combination band</td>
</tr>
<tr>
<td>$v_1 + v_2 + v_3$</td>
<td>Not observed</td>
<td>Combination band</td>
</tr>
</tbody>
</table>

*New bands observed in this work. # Does not match with the previous value obtained by (Chaabouni et al 2000) depositing pure O$_3$ or with a carrier gas due to lower resolution used in our experiments.
Figure 5.15: \( \beta \text{O}_3 \) bands observed at 47 K.

Figure 5.16: New bands of \( \beta \text{O}_3 \) observed in this work above 47 K.
Figure 5.17: Above 47 K, a band at 1049 cm\(^{-1}\) shows the presence of ozone clusters, \((O_3)_n\). This band is observed until complete O\(_3\) sublimation.

Figure 5.18: \(\nu_2\) fundamental band of O\(_3\) monomer is observed to have shifted by 6.7 cm\(^{-1}\) when the temperature reaches 47K, thereby indicating phase transition from \(\alpha\) to \(\beta O_3\).
Complete sublimation of ozone was observed at about 62 K. It should be noted that temperature at which O₃ sublimes depends strongly on the experimental conditions. For instance, β-O₃ can exist until 80 K either in the crystalline form, as a supercooled liquid, or as a metastable state of solid ozone (Hanson & Mauersberger 1986).

Figure 5.19: Ion current profile of subliming molecular oxygen (O₂) and ozone (O₃) monitored via a quadrupole mass spectrometer of the irradiated samples at 11 K (top; left), 20 K (top; right), and 30 K (bottom).
In order to support the infrared data, a complete data set on the sublimation of parent \((\text{O}_2)\) and product \((\text{O}_3)\) molecule was obtained using a mass spectrometer. Molecular oxygen—monitored via its mass-to-charge ratio \((m/z)\) of 32, was first seen to sublime at around 25 K close to the onset of the \(\alpha-\text{O}_2\) to \(\beta-\text{O}_2\) phase transition (Section 5.2.1). The molecular oxygen desorption plot was found to peak at around 37 ± 2 K. A second peak was monitored at about 55 K, which correlates nicely with the temporal evolution of ozone detected via its parent at \(m/z = 48\), and therefore the peak of \(m/z = 32\) at \(T = 55\) K is believed to originate from dissociative ionization of ozone in the electron impact ionizer of the mass spectrometer. Note that a small peak of \(m/z = 48\) was also observed at about 37 K (Figure 5.19). However, as this could also be seen in the blank sample (subliming oxygen ice without electron irradiation), the 37 K peak can be likely attributed to ion-molecule reactions in the ionizer of the mass spectrometer leading to an ion with \(m/z = 48\) (Figure 5.19). In these experiments, the sublimation peaks for molecular oxygen and ozone fall within 37 – 43 K and 62 – 66 K, respectively.

In summary, we can identify two temperature dependent reaction mechanisms to form ozone in the annealing phase of the ices, i.e. a reaction of oxygen atoms from the \([\text{O}_3\ldots\text{O}]\) complex and trapped oxygen atoms in the molecular oxygen matrix with oxygen molecules to form ozone.

### 5.4 Ice formed from mixture of oxygen isotopes \((^{16}\text{O}_2^{18}\text{O}_3)\)

In order to understand the product formation mechanisms involved in producing ozone a 1:1 gas mixture of oxygen -16 (99.99% pure) and oxygen -18 (98% pure) was prepared externally to the chamber and deposited on to a silver crystal for about 300 s at a chamber pressure of \(10^{-7}\) Torr and at a temperature of \(\sim 11\) K. Due to a small \(\text{CO}_2\) contamination in the ice matrix a dipole moment is induced and so bands of solid \(^{18}\text{O}_2\) and \(^{16}\text{O}_2\) are observed in the infrared spectra.
(Figure 5.20). The sample thickness cannot be determined using these bands because the intrinsic absorption coefficient is available only for a 10:1 mixture (Ehrenfreund et al 1995) of CO$_2$ : (^{16}O$_2$ + $^{18}$O$_2$), while in our sample CO$_2$ is present only in trace quantities.

![Figure 5.20: Fundamental vibrational bands of solid $^{18}$O$_2$ and $^{16}$O$_2$ sample kept at 20K.](image)

The ice film was then irradiated with 5KeV electrons for one hour. The electron beam, generated from a simple electron gun, was operated at 100nA current and scanned over 1.8 ± 0.3 cm$^2$ of the target exposing the target to approximately 1.8 x 10$^{16}$ electrons. Chemical changes in the ice film were monitored using a FTIR spectrometer operating in reflection-absorption-reflection mode with a reflection angle of 75$^\circ$ from the normal relative to the mirror surfaces. Spectra were collected over the range of 6000 -500 cm$^{-1}$ with an integration time of 2.5 minutes and at 2 cm$^{-1}$ resolution.
Figure 5.21: $v_3$ band of O$_3$ isotopomers observed during irradiation at 11 K. Dotted line shows the fits for deconvolution and curve fitting.

Ozone was seen to appear in the molecular oxygen ice immediately after electron irradiation commenced, the primary process for such ozone production is ascribed to the Chapman mechanisms discussed in chapter 1. Ozone was observed in the irradiated ice through the $v_3$ infrared band (arising from the O-O asymmetric stretch mode). Using earlier work (Andrews & Spiker 1972; Brewer & Wang 1972; SchriverMazzuoli et al. 1995; SchriverMazzuoli et al. 1996; Spoliti, Cesaro, & Mariti 1973), the broad spectral band lying between 960 cm$^{-1}$ to 1050 cm$^{-1}$ may be deconvoluted into six distinct peaks corresponding to the six possible ozone isotopomers. Bands at 977.5 cm$^{-1}$, 987.7 cm$^{-1}$, 1002.0 cm$^{-1}$, 1012.0 cm$^{-1}$, 1022.0 cm$^{-1}$ and 1035.0 cm$^{-1}$ are assigned to $^{18}$O$^{18}$O$^{18}$O, $^{18}$O$^{18}$O$^{16}$O, $^{16}$O$^{18}$O$^{16}$O, $^{18}$O$^{16}$O$^{18}$O, $^{16}$O$^{16}$O$^{18}$O and $^{16}$O$^{16}$O$^{16}$O (Figure 5.21, Table 5.6) respectively.
A very weak ν₂ band (O-O-O bend) is observed in the 11K ice after the end of irradiation but shows only ¹⁸O¹⁸O¹⁸O and ¹⁸O¹⁸O¹⁶O isotopomer bands at 662.4 cm⁻¹ and 677.3 cm⁻¹ respectively. However it should be noted that the ν₂ band positions for O₃ at 47K are in close agreement with those values calculated and observed for the O₃...O molecule (Schrivermazzuoli, et al. 1995). A study relating the temporal growth of associated ozone complexes has shown that O₃...O dissociates even at the time of irradiation and is not produced during the warm-up phase (Section 5.2.5). Another fundamental mode, ν₁ (arising from the O-O symmetric stretch) is observed at 1060.7 and 1090.1 cm⁻¹ corresponding to ¹⁸O¹⁸O¹⁶O and ¹⁶O¹⁶O¹⁸O unsymmetrical isotopomers. In any low temperature irradiated ice made of pure molecular oxygen (see section 5.2.2.1) the ozone dimer (O₃...O₃) may also be formed (Bahou et al. 1997; Schrivermazzuoli, et al. 1995). However the 2 cm⁻¹ resolution used in our experiment does not allow these to be distinguished from the ozone monomers.

5.4.1 Isotopomer formation mechanisms

In a mixed isotope oxygen matrix of ¹⁶O₂ & ¹⁸O₂, the production of ¹⁶O and ¹⁸O atoms, leads to the formation of ⁴⁸O₃, ⁵⁰O₃, ⁵²O₃, and ⁵⁴O₃, where ⁵⁰O₃, ⁵²O₃ have symmetric and asymmetric isotopomers. The temporal evolution of each of the possible six O₃ isotopomers (Figure 5.21) may be determined from an analysis of the ν₃ band during the irradiation phase. From this data the formation mechanism for each of these isotopomers can be derived.
Table 5.6: Infrared band centers of the new bands formed in the irradiated O₃ ice at 11K; * - calculated; Θ - in argon matrix; # - this work. **In the βO₃ all ν₂ bands are discrete. Before phase change to βO₃ only ¹⁸O¹⁸O¹⁸O, ¹⁸O¹⁸O¹⁶O and ¹⁸O¹⁶O¹⁶O bands are discretely strong, whereas the ¹⁸O¹⁶O¹⁸O and ¹⁶O¹⁶O¹⁶O isotopomers are too weak to be observed.

<table>
<thead>
<tr>
<th>Ozone isotopomer</th>
<th>End of irradiation*, (αO₃) at 11 K</th>
<th>Brewer &amp; Wang</th>
<th>Spoliti*</th>
<th>Andrew &amp; Spicer*</th>
<th>Schrizer -Mazzuoli</th>
<th>At transition temperature*, (βO₃) at 47 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν₃</td>
<td>ν₁</td>
<td>ν₃ ν₁</td>
<td>ν₃</td>
<td>ν₃ ν₁</td>
<td>ν₃</td>
</tr>
<tr>
<td>¹⁸O¹⁸O¹⁸O</td>
<td>977.5</td>
<td>-</td>
<td>1988.2</td>
<td>983*</td>
<td>1990</td>
<td>976</td>
</tr>
<tr>
<td>¹⁶O¹⁸O¹⁸O</td>
<td>987.7</td>
<td>1060.7</td>
<td>-</td>
<td>994*</td>
<td>-</td>
<td>986</td>
</tr>
<tr>
<td>¹⁶O¹⁸O¹⁶O</td>
<td>1002.0</td>
<td>-</td>
<td>-</td>
<td>1003</td>
<td>-</td>
<td>1000</td>
</tr>
<tr>
<td>¹⁸O¹⁶O¹⁸O</td>
<td>1012.0</td>
<td>-</td>
<td>-</td>
<td>1020*</td>
<td>-</td>
<td>1012</td>
</tr>
<tr>
<td>¹⁸O¹⁶O¹⁶O</td>
<td>1022.0</td>
<td>1090.1</td>
<td>-</td>
<td>1023</td>
<td>-</td>
<td>1020</td>
</tr>
<tr>
<td>¹⁶O¹⁶O¹⁶O</td>
<td>1035.0</td>
<td>-</td>
<td>-</td>
<td>1037</td>
<td>2110</td>
<td>1034</td>
</tr>
</tbody>
</table>
5.4.1.1 $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ isotopomer

Temporal evolution of $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ isotopomer up to the end of irradiation is obtained using the 1035 cm$^{-1}$ band (Figure 5.22). This isotopomer depends on the availability of $^{16}\text{O}$ atoms and $^{16}\text{O}_2$ molecule in the matrix. From our results it is clear that the formation of this molecule can be fitted easily using a pseudo first order reaction mechanism given in equation 5.2, because of the presence of excess $^{16}\text{O}_2$ and reaction controlling step is determined by the amount of $^{16}\text{O}$. The end on addition process to form this isotopomer is as follows:

$$^{16}\text{O}^{16}\text{O} + ^{16}\text{O} \rightarrow ^{16}\text{O}^{16}\text{O}^{16}\text{O} \quad (5.9)$$

The same formation mechanism (in equation 5.2) will also apply for the other oxygen species ($^{18}\text{O}$). This isotopic species produces $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ isotopomer via equation 5.10 and same pseudo first mechanism is used to fit the temporal growth obtained using 977.5 cm$^{-1}$ band (Figure 5.23). Values of rate constants are summarised in Table 5.7.

$$^{18}\text{O}^{18}\text{O} + ^{18}\text{O} \rightarrow ^{18}\text{O}^{18}\text{O}^{18}\text{O} \quad (5.10)$$

![Figure 5.22: Temporal evolution of $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ isotopomer formed via equation 5.9. Solid line indicates the fit using equation 5.2.](image-url)
Figure 5.23: Temporal evolution of $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ isotopomer formed via equation 5.10. Solid line indicates the fit using equation 5.2.

Table 5.7: Values of rate constants for fits using equation 5.2.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction pathway during irradiation</th>
<th>Product</th>
<th>Rate coefficient (k, s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{16}\text{O} + ^{18}\text{O}^{16}\text{O}$</td>
<td>End on addition</td>
<td>$^{16}\text{O}^{16}\text{O}^{18}\text{O}$</td>
<td>$4.2 \pm 0.5 \times 10^{2}$</td>
</tr>
<tr>
<td>$^{18}\text{O} + ^{16}\text{O}^{16}\text{O}$</td>
<td>End on addition</td>
<td>$^{18}\text{O}^{16}\text{O}^{18}\text{O}$</td>
<td>$2.3 \pm 0.1 \times 10^{2}$</td>
</tr>
</tbody>
</table>

5.4.1.2 $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ Isotopomer

The $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ isotopomers are identified using the 1022 cm$^{-1}$ and 987.7 cm$^{-1}$ bands, respectively, and these bands are used to obtain the temporal growth during irradiation. This molecule opens two reaction pathways [i] 'end-on addition' of oxygen atoms ($^{16}\text{O}, ^{18}\text{O}$) to oxygen molecules ($^{18}\text{O}_2, ^{16}\text{O}_2$), respectively, [ii] formation of scrambled oxygen ($^{16}\text{O}^{18}\text{O}$) in the first step and then end-on addition of $^{16}\text{O}$ to $^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}$ to $^{16}\text{O}^{16}\text{O}$ as the second step. Pathway [i] is a pseudo first order reaction mechanism and so equation 5.2 can be used to fit this, whereas pathway [ii] is a two step reaction mechanism that can be fitted using the following two step consecutive pseudo first order reaction

$$[\text{O}_3](t) = \frac{(a_2)}{(k_2 - k_1)} (k_2 (1-e^{-k_1t}) - k_1 (1-e^{-k_2t})) \quad (5.9)$$
The temporal growths of these two isotopomers are fitted with both equations 5.2 & 5.9 and values of rate constants are listed in Tables 5.8 & 5.9. Equation 5.9 gives a very good fit when compared with the pseudo first order fit but it should be noted that the data points during first 10 min of irradiation time had a very low signal to noise ratio in the infrared spectra. Nevertheless we propose the formation of $^{18}\text{O}^{18}\text{O}^{16}\text{O}$, $^{16}\text{O}^{14}\text{O}^{18}\text{O}$ isotopomers follows pathway (i) and not a two step consecutive reaction mechanism.

![Figure 5.24](image1.png)

**Figure 5.24:** Temporal evolution of $^{18}\text{O}^{18}\text{O}^{16}\text{O}$ isotopomer. Solid line indicates the fit using equation 5.2 and dotted line indicate the fit using equation 5.9.

![Figure 5.25](image2.png)

**Figure 5.25:** Temporal evolution of $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ isotopomer. Solid line indicates the fit using equation 2 and dotted line indicate the fit using equation 5.9.
Table 5.8: Values of rate constants for fits using equation 5.2.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction pathway during irradiation</th>
<th>Product</th>
<th>Rate coefficient (k, s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁶O + ¹⁸O *¹⁸O</td>
<td>End on addition</td>
<td>¹⁶O²⁰O²⁰</td>
<td>3.4 ± 0.2 x 10⁻²</td>
</tr>
<tr>
<td>¹⁸O + ¹⁶O *¹⁶O</td>
<td>End on addition</td>
<td>¹⁶O²⁰O¹⁶O</td>
<td>2.4 ± 0.2 x 10⁻²</td>
</tr>
</tbody>
</table>

Table 5.9: Values of rate constants for fits using equation 5.9.

<table>
<thead>
<tr>
<th>Product</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₁ (1st step)</td>
</tr>
<tr>
<td>¹⁸O¹⁶O²⁰O</td>
<td>3.9 ± 0.5 x 10⁻²  s⁻¹</td>
</tr>
<tr>
<td>¹⁶O¹⁶O²⁰O</td>
<td>3.9 ± 0.5 x 10⁻²  s⁻¹</td>
</tr>
</tbody>
</table>

5.4.1.3 ¹⁸O¹⁶O²⁰O and ¹⁶O¹⁸O¹⁶O isotopomer

The formation of the ¹⁶O¹⁸O¹⁶O and ¹⁸O¹⁶O¹⁸O isotopomers by end-on addition is unlikely due to the presence of an apex ¹⁸O and ¹⁶O atom, respectively. These isotopomers would therefore appear to be formed by a two step (consecutive) reaction mechanism in which ¹⁶O¹⁸O is formed initially and followed by end on addition of an ¹⁸O or ¹⁶O atom (Table 5.10). Trying to fit the growth curve of ¹⁶O¹⁸O¹⁶O isotopomer using equation (5.9) resulted in k values of 3.5 ± 0.8 x 10⁻² s⁻¹ (first step) and 4.7 ± 4.3 x 10⁻¹ s⁻¹ (second step) showing a fit (given in dotted lines in figure 5.26) similar to the one obtained by a pseudo first order fit using equation (5.2), where k = 2.7 ± 0.4 x 10⁻² s⁻¹. Therefore, two pathways are open for this molecule and hence the formation mechanism of the ¹⁶O¹⁸O¹⁶O isotopomer still remains an open question (Table 5.10). But this two step mechanism is followed by ¹⁶O¹⁶O¹⁸O formation,
note that formation of this molecule failed to satisfy equation (5.2), (given in dotted lines in figure 5.27), resulting in a \( k \) value of \( 1.76 \pm 2.39 \times 10^{-3} \) s\(^{-1}\).

For the \(^{16}\text{O}^{18}\text{O}^{16}\text{O}\) isotopomer, reaction in one step may be via the formation of an isomer in the cyclic (D\(_{3h}\)) form, which can be obtained by insertion of \(^{18}\text{O}\) followed by breaking of the bond between the two oxygen-16 atoms to obtain the open minimum, (C\(_{2v}\)) form (Table 5.10). There has been considerable debate as to the possibility in forming and stabilizing a ring structure of \( \text{O}_3 \). It is estimated that cyclic form lies \( \sim 1 \) eV above the dissociation limit. Flemmig et al (Flemmig, Wolczanski, & Hoffmann 2005) have further argued that the lifetime of cyclic form at low temperatures may be greater than 30 s. We therefore searched for evidence of this cyclic form which is predicted to have be at 1099.6 (\( v_1 \)), 782.9 (\( v_2, v_3 \)) cm\(^{-1}\) (Elliott et al. 2005) (these values are for \(^{48}\text{O}_3\)) but we found no evidence for this form of ozone suggesting either that it is not formed or its lifetime is much shorter than Fleming et al predict. Hence we propose that a two step formation mechanism is followed in the formation of this molecule.

![Figure 5.26: Temporal evolution of \(^{16}\text{O}^{18}\text{O}^{16}\text{O}\) isotopomer. Solid line indicates the fit using equation 5.2 and dotted line indicate the fit using equation 5.9.](image-url)
Figure 5.27: Temporal evolution of $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ isotopomer. Solid line indicates the fit using equation 5.9 and dotted line indicate the fit using equation 5.2.

Table 5.10: Values of rate constants for fits using equation 5.2 & 5.9.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction pathway during irradiation</th>
<th>Product</th>
<th>Rate coefficient $(k, \text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{18}\text{O} + ^{16}\text{O}$</td>
<td>$^{18}\text{O}^{16}\text{O} + ^{18}\text{O}$ (1st step)</td>
<td>$^{18}\text{O}^{16}\text{O}^{18}\text{O}$</td>
<td>$0.89 \pm 0.5 \times 10^{-2}$ (1st step, $k_1$)</td>
</tr>
<tr>
<td></td>
<td>End on addition (2nd step)</td>
<td></td>
<td>$2.7 \pm 1.5 \times 10^{-1}$ (2nd step, $k_2$)</td>
</tr>
<tr>
<td>$^{18}\text{O} + ^{16}\text{O}^{16}\text{O}$</td>
<td>Insertion ($D_{3h}$ symmetry) and ring opening</td>
<td>$^{16}\text{O}^{18}\text{O}^{16}\text{O}$</td>
<td>$2.7 \pm 0.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{18}\text{O} + ^{16}\text{O}$</td>
<td>$^{18}\text{O}^{16}\text{O} + ^{16}\text{O}$ (1st step)</td>
<td>$^{16}\text{O}^{18}\text{O}^{16}\text{O}$</td>
<td>$3.5 \pm 0.8 \times 10^{-2}$ (1st step, $k_1$)</td>
</tr>
<tr>
<td></td>
<td>End on addition (2nd step)</td>
<td></td>
<td>$4.7 \pm 4.3 \times 10^{-1}$ (2nd step, $k_2$)</td>
</tr>
</tbody>
</table>
5.4.2 Isothermal phase

After irradiation the sample was kept under isothermal conditions for an hour. Following irradiation oxygen atoms are stored in the ice matrix. Although O(D) are also produced in the matrix during irradiation after 3600s in an isothermal condition all these atoms are expected to relax into their ground state. The lifetime of these ground state atoms is known to be in order of days. The irradiated ice is therefore rich in atomic oxygen in its ground state (P) (See section 5.2.4). However it is important to note that during this period there is neither a decrease nor increase in the ozone isotopomers concentration thereby indicating no dissociation or formation at constant temperature even during the availability of atomic oxygen.

5.4.3 During warm-up

The irradiated ice was gently warmed at the rate of 0.5 K min⁻¹ and the subsequent chemical changes are observed both by FTIR and mass spectrometry. As the temperature is increased oxygen atoms start to diffuse within the ice. This diffusion process is not likely at 11K, but increases as the temperature is increased and two new reaction pathways are opened during warm-up. These are, (1) forming molecular oxygen due to recombination of oxygen atoms, and (2) forming ozone with the addition of an oxygen atom to molecular oxygen. Also at temperatures close to the oxygen phase transition sublimation of the oxygen ice was observed and very close to the peak sublimation temperature atomic oxygen has no barrier to diffuse, thereby reacting to produce ozone.

At temperatures close to the molecular oxygen sublimation a two fold increase for all of the ozone isotopomers formed by end on addition during irradiation is observed. In the case of O₁₈O₁₆O isotopomer only a slight increase was observed during warm-up (Figure 5.28). A barrier-less reaction of thermal oxygen atoms, stored in the matrix after irradiation, with O₂ is responsible for producing this additional O₃. The relative enhancement in the
\(^{18}\text{O}^{18}\text{O}, \ ^{16}\text{O}^{16}\text{O}^{18}\text{O}\ \text{and} \ ^{18}\text{O}^{16}\text{O}^{16}\text{O} \) formation is greater during warm-up, indicating more recombination of both thermal \(^{16}\text{O}\) and \(^{18}\text{O}\) atoms or greater concentration of \(^{16}\text{O}^{16}\text{O}\) \(^{34}\text{O}_2\) together with \(^{32}\text{O}_2\) or \(^{36}\text{O}_2\) in the irradiated ice.

After all of the oxygen molecules have desorbed from the surface at around 35 K, no further increase in \(\text{O}_3\) production is observed and only \(\text{O}_3\) is left on the surface. However at about 47 K, new bands appear in the IR spectra (Table 5.6) indicating the change of phase from \(\alpha\) (amorphous) to \(\beta\) (crystalline) ozone (Figure 5.29). Two bands, at 688.2 cm\(^{-1}\) and 673.2 cm\(^{-1}\) corresponding to the \(^{18}\text{O}^{18}\text{O}^{16}\text{O}\) and \(^{18}\text{O}^{16}\text{O}^{18}\text{O}\), only appear when the ice is warmed to 45 K and at 47 K all six bands appear in the region 660 – 710 cm\(^{-1}\) and are assigned to their respective isotopomers (Table 5.6). These band positions are observed to shift by 5 cm\(^{-1}\) at 47 K. A combination of \(v_1 + v_3\) fundamentals is observed at 1988.2 cm\(^{-1}\) and 1992.88 cm\(^{-1}\) for the \(^{18}\text{O}^{18}\text{O}^{18}\text{O}\) molecule (Table 5.6) when the ice matrix is at temperatures 10 and 47 K, respectively. There is no ozone isotopomers signature in the infrared spectra around 63 K.

In order to confirm FTIR spectral data at different temperatures desorbed species were monitored using a quadrupole mass spectrometer placed at 45\(^\circ\) to the target surface. As there is no significant increase in the measured ion current during irradiation at 11 K sputtering of any species from the surface of the ice film can be neglected. Sublimation of \(\text{O}_2\) and \(\text{O}_3\) containing both \(^{16}\text{O}\) and \(^{18}\text{O}\) were monitored by choosing the m/e ratios to be 32, 36, 48, 50, 52 and 54 corresponding to \(^{32}\text{O}_2\), \(^{36}\text{O}_2\), \(^{48}\text{O}_2\), \(^{50}\text{O}_2\), \(^{52}\text{O}_2\), and \(^{54}\text{O}_3\) respectively. Both \(^{32}\text{O}_2\) and \(^{36}\text{O}_2\) appear to desorb when the temperature is close to 28 K and peaks at approximately 35 K. All the ozone isotopomers are found to desorb from the ice surface at around 61K (Figure 5.30).
Figure 5.28: $v_3$ band area of ozone isotopomers during warm-up of the sample at the rate of 0.5 K min$^{-1}$ for the sample irradiated at $\sim$11 K. Error within $\pm$ 10%.
Figure 5.29: New bands of $v_2$ fundamental of O$_3$ isotopomers together with 5 cm$^{-1}$ shift in $^{18}$O$^{18}$O$^{18}$O band position at 47 K shows transition of $\alpha$ to $\beta$ O$_3$.

Two other desorption peaks are seen immediately after strong desorption at 35K one of which corresponds to $^{48}$O$_3$. However an identical signal was found from a non irradiated sample at this same temperature, which is interpreted as arising from an ion-molecule reaction leading to the O$_3^+$ in the electron impact ionizer, because no $^{48}$O$_3$ is identified in the solid matrix scanned by the FTIR.
Figure 5.30: Ion current profile of subliming molecular oxygen (O₂) and ozone (O₃) isotopomers monitored via a quadrupole mass spectrometer of the irradiated sample at ~11 K.

5.5 Proton irradiation of pure oxygen (¹⁶O₂) film

5.5.1 During irradiation

Proton irradiation experiments on pure molecular oxygen ices were carried out at Catania Astrophysical Observatory. O₂ was deposited at 16 K onto a Si substrate to calculate the number of molecules and thickness of the ice sample (see Chapter 3 and 4). The substrate was then changed to KBr and O₂ was deposited at 16 K in order to perform 200 keV proton irradiation. Irradiation was performed upto a dose of ~20 eV 16amu⁻¹. O₃ peaks together with O₃ associated complexes O₃...O and O₃...O₃ were observed in the ice and the band positions are in good agreement with those listed in Table 5.2. Figure 5.31, shows the O₃ growth at the
time of irradiation. From band area information the number of molecules produced at the end of irradiation was calculated to be $3.7 \times 10^{17}$ molecules cm$^{-2}$.

![Graph of Ozone band area versus Dose](image)

**Figure 5.31:** Growth of first three intense bands of O$_3$ during 200 keV proton irradiation of O$_2$ ice at 16 K. Error within $\pm 10\%$.

From the initial number of O$_2$ molecules present before irradiation (Table 5.2) and the number of O$_3$ molecules produced (Table 5.11), the conversion efficiency of the ice because of 200 keV proton irradiation implanting a dose of $\sim 20$ eV 16amu$^{-1}$ was then found to be about $\sim 12\%$. This value is higher than the amount observed by 5 keV electron irradiation implanting a dose of $\sim 0.9$ eV 16amu$^{-1}$. The irradiated ice was then immediately warmed up until all the ozone sublimes.

### 5.5.2 Annealing

Warm-up was carried out in the irradiated ice and spectra were recorded at 30, 40, 50, 65 and 70 K. It was very surprising to note that from our observation that more O$_3$ was
produced during warm-up of the electron irradiated ice was not observed in the proton irradiated ice (Figure 5.32). Instead very small changes in the band intensity of the 1040 cm⁻¹ band (Baragiola et al., 2007) due to temperature increase were observed. The other two bands at 704 and 2107 cm⁻¹ were largely unchanged by an increase in temperature. This implies that little O₃ was produced by warming the ice sample. However the phase change from α to β O₃ was observed and the band positions of β O₃ were in good agreement with those reported in Table 5.5 and complete sublimation was observed at around 70 K. One possible explanation could be that equilibrium was reached in the O₃ and O₂ ice mixture. From figure 5.31 it was clear that the amount of O₃ produced after 4 eV 16amu⁻¹ has reached a constant value and further irradiation upto 20 eV 16amu⁻¹ was maintaining the same amount, whereas during 5 keV electron irradiation only 0.9 eV 16amu⁻¹ was implanted onto the ice which still has to produce more O₃ in order to reach an O₂ − O₃ equilibrium and therefore more O₃ was being produced during warm-up of the electron irradiated ice.

Figure 5.32: Ozone band area during warm-up of the 200 keV proton irradiated O₂ ice. Error within ± 10%.
5.6 Conclusions

Ozone formation by electron irradiation of molecular oxygen ices was investigated in the temperature range of 11 K – 30 K. Various reaction mechanisms were derived from the experimental data. The amount of ozone formed via electron irradiation was shown to be strongly dependent on the sample temperature in the range of 11 K to 30 K. As the temperature increased, the ozone monomer column density actually decreased. During irradiation reactions of suprathermal oxygen atoms contributed to a temperature independent reaction pathway to form ozone. The loss of oxygen atoms by recombination to ‘recycle’ molecular oxygen was observed to be larger at higher temperatures hence forming less ozone at elevated temperatures. In the warm-up phase we identified two temperature-dependent reaction mechanisms to synthesize ozone, i.e. a reaction of oxygen atoms from the [O₃...O] complex with a neighbouring molecule - as was evident from the increase of signal of [O₃...O₂] complexes - and a reaction of trapped oxygen atoms in the molecular oxygen matrix with oxygen molecules to form the ozone monomer.

Ozone production in a binary mixture of solid oxygen ¹⁶O₂ and ¹⁸O₂ by 5 KeV electrons was studied experimentally. All six isotopomers were detected and their formation mechanisms determined. In the case of ¹⁴O¹⁶O¹⁶O, ¹⁶O¹⁸O¹⁸O, ¹⁸O¹⁸O¹⁸O and ¹⁸O¹⁶O¹⁶O formation arises from direct end on addition of an oxygen atom to the oxygen molecule in a single step process. Formation of the ¹⁸O¹⁶O¹⁸O isotopomer can be explained by recombination of two ¹⁸O atoms and one ¹⁶O atom. The ¹⁸O¹⁶O¹⁸O isotopomer together with ¹⁸O¹⁸O¹⁸O and ¹⁸O¹⁶O¹⁶O were observed to be produced with higher efficiency (relative to other isotopomers) during warm-up of the irradiated ice. In contrast the formation of ¹⁶O¹⁸O¹⁶O molecule that may only be described by a two step process and shows only a small increase in yield during warm up of the irradiated ice.
Proton irradiation was also performed upon pure molecular oxygen ices and compared with the electron irradiation experiments. More $O_3$ was produced by 200 keV proton irradiation and a saturation or equilibrium between $O_2$ and $O_3$ in the ice was reached at $\sim 4$ eV 16amu$^{-1}$ irradiation dose. This equilibrium had important effect during heating of the irradiated ice which maintained the $O_2 \rightarrow O_3$ equilibrium until $O_2$ sublimation. More experiments using proton irradiation at different temperatures and using isotopes will provide a detailed picture of the $O_2 \rightarrow O_3$ equilibrium.

These experiments can have profound implications to the oxygen chemistry in icy satellites. Although the laboratory simulation are focused on pure oxygen ices – which have not been observed in our Solar System to date – recent experiments suggested that localized concentrations of molecular oxygen may exist in water-rich Solar System ices (Zheng, Jewitt, & Kaiser 2006). Hence if sufficient molecular oxygen exists in water ice ozone can be certainly formed via irradiation with energetic electrons and protons. The production of ozone isotopomers by irradiation of an oxygen ice reveals that different isotopomers are formed at different rates such that oxygen fractionation may be induced by simple chemical synthesis at low temperatures.
CHAPTER 6: RADIATION CHEMISTRY IN CO₂ ICES

6.1 Introduction

Carbon dioxide (CO₂) ice is a major component of most of the solar system icy bodies (see Chapter 1). Liberation of oxygen atoms by dissociation of CO₂ may lead to the formation of ozone – indeed it may account for observation of ozone on Ganymede, Dione and Rhea (see chapter 1). However there is a lack of a detailed study on O₃ formation in CO₂ ices under different irradiation conditions. In this chapter the ozone yield from CO₂ under different irradiation environments and at different temperatures are compared and discussed. Irradiation environments include irradiation by high (0.8 MeV) and low energy (1.5 – 3 keV) ions and 10 keV electrons over temperature ranges from 10 – 80 K.

6.2 Electron irradiation

6.2.1 At 13K

CO₂ molecular gas was deposited onto a silver substrate kept at 13 K and the ice thickness was estimated to be ~ 2 µm (see Chapter 3). An infrared spectrum of the ice was recorded in the mid-infrared region 4000-400 cm⁻¹. Spectral features of CO₂ were observed at 2342 cm⁻¹ (ν₃), 1384 cm⁻¹ (ν₁), corresponding to the fundamental vibrations and two combination bands at 3600 cm⁻¹ and at 3708 cm⁻¹ (Figure 6.1). All the bands of CO₂ are listed in Table 6.1 (Bennett et al, 2004). Using the value of absorption coefficient (A_{CO₂} 4.5 x 10⁻¹⁹ cm molecule⁻¹ (Gerakines et al, 1995) at 14 K for the 3600 cm⁻¹ band the number of CO₂ molecules present before irradiation can be calculated. The A_{CO₂} (Absorption coefficient) for the 3600 cm⁻¹ band can be used to determine the number of molecules that were dissociated during the irradiation process since the more intense 2342 cm⁻¹ and 3708 cm⁻¹ bands of CO₂ were saturated in the thick ice sample.
Figure 6.1: Infrared spectrum of solid CO₂ at 13 K before irradiation.

Table 6.1: Infrared absorption band positions of solid CO₂ before irradiation at 13 K.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
<th>Characterisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>658/654</td>
<td>v₂</td>
<td>In / Out of plane bending</td>
</tr>
<tr>
<td>638</td>
<td>v₂</td>
<td>Isotope peak</td>
</tr>
<tr>
<td>1384</td>
<td>v₁</td>
<td>Symmetric stretch</td>
</tr>
<tr>
<td>2280</td>
<td>v₃</td>
<td>¹³CO₂</td>
</tr>
<tr>
<td>2342</td>
<td>v₃</td>
<td>Asymmetric stretch</td>
</tr>
<tr>
<td>3600</td>
<td>2ν₂ + ν₃</td>
<td>Combination</td>
</tr>
<tr>
<td>3708</td>
<td>ν₁ + ν₃</td>
<td>Combination</td>
</tr>
</tbody>
</table>
Electron irradiation at 10 keV was carried out for a total of 70 minutes with a beam current of 2 µA (see chapter 3, section 3.4). Spectra were recorded at 5, 10, 20 and 30 minute intervals. Upon irradiation the CO₂ ice matrix was observed to undergo chemical changes producing several new molecules, indicated by the observation of several new features in the absorption spectra at 2140 cm⁻¹, 1044 cm⁻¹ and at 2045 cm⁻¹ (Figure 6.2), these are ascribed to CO, O₃ and CO₃ (Bennett et al, 2004), respectively. At the end of the irradiation period several additional bands appeared in the spectrum and were identified either as overtones or combination bands of the above mentioned three primary irradiation products of CO₂. However, two bands that correspond to CO₄ and CO₅ molecules were observed at 1942.6 cm⁻¹ and 1914.5 cm⁻¹, respectively. New bands and their vibrational assignments are given in Table 6.2.

\[ \text{CO}_2 \rightarrow \text{CO} + \text{O} \left( ^1\text{D} \text{ or } ^3\text{P} \right) \]  \hspace{1cm} (6.1)

![Figure 6.2: Infrared spectra (in the 2200 - 600 cm⁻¹ region) recorded before and after irradiation.](image)
Table 6.2: New infrared bands observed in the CO\textsubscript{2} ice after electron irradiation.

<table>
<thead>
<tr>
<th>Wavenumber, cm(^{-1})</th>
<th>Molecule</th>
<th>Assignment</th>
<th>Characterisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>707</td>
<td>O\textsubscript{3}</td>
<td>(\nu_2)</td>
<td>O-O-O bend</td>
</tr>
<tr>
<td>975</td>
<td>CO\textsubscript{3}</td>
<td>(\nu_5)</td>
<td>C-O stretch</td>
</tr>
<tr>
<td>1044</td>
<td>O\textsubscript{3}</td>
<td>(\nu_3)</td>
<td>O-O asymmetric stretch</td>
</tr>
<tr>
<td>1068</td>
<td>CO\textsubscript{3}</td>
<td>(\nu_2)</td>
<td>O--O stretch</td>
</tr>
<tr>
<td>1879</td>
<td>CO\textsubscript{3}</td>
<td>--</td>
<td>Fermi resonance</td>
</tr>
<tr>
<td>1914.5</td>
<td>CO\textsubscript{3}</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1942.6</td>
<td>CO\textsubscript{4}</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2045</td>
<td>CO\textsubscript{3}</td>
<td>(\nu_1)</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>2093</td>
<td>(^{13}\text{CO})</td>
<td>(\nu_1)</td>
<td>(^{13}\text{CO}) stretching</td>
</tr>
<tr>
<td>2140</td>
<td>CO</td>
<td>(\nu_1)</td>
<td>CO stretching</td>
</tr>
</tbody>
</table>

Carbon monoxide (CO), a direct product from CO\textsubscript{2} dissociation was observed immediately upon commencing irradiation and the number of CO molecules produced can be regarded as a measure of the number of CO\textsubscript{2} molecules that dissociate during various stages of irradiation. However due to the spectral saturation in the 2140 cm\(^{-1}\) band area of CO direct observation was difficult. Therefore, CO\textsubscript{2} dissociation was monitored via the 3600 cm\(^{-1}\) band. Every CO\textsubscript{2} molecule that dissociates contributes a suprathermal oxygen atom (equation 6.1) to initiate further chemical reactions. O\textsubscript{3} was observed in the spectra immediately after irradiation began. O\textsubscript{3} will be produced once enough molecular oxygen becomes available in the matrix. SO O\textsubscript{3} was produced via a two step consecutive reaction pathway (Equation 6.2). On the other hand, oxygen atoms were also involved in the production of other molecules in reaction with CO\textsubscript{2}. CO\textsubscript{3} was also regarded as a primary product because this molecule was observed to form immediately after irradiation. The formation of this molecule was possible via addition of
atomic oxygen to CO$_2$. Higher molecular products (like CO$_4$ and CO$_5$) observed in the spectra, are produced by further reactions of atomic oxygen with CO$_3$ (Equation 6.3).

\[
O + O \rightarrow O_2 + O \rightarrow O_3
\]  
\[
CO_2 + O \rightarrow CO_3 + O \rightarrow CO_4 + O \rightarrow CO_5
\]  

6.2.2 Irradiation at higher temperatures

A fresh CO$_2$ sample was deposited at 10K before every irradiation and the ice thickness was maintained approximately equal to 2 µm. The ice was then warmed to the required temperatures (30, 50 and 70 K) for irradiation. Using the value of absorption coefficient ($A_{CO_2}$) 5.5 x 10$^{-19}$ cm molecule$^{-1}$ (Gerakines et al 1995) at 60K for the 3600 cm$^{-1}$ band the number of CO$_2$ molecules present before irradiation can be calculated for 50 and 70 K samples. Infrared spectra recorded at different temperatures revealed that there was no significant change in the spectral shape or band position of the CO$_2$ ice for temperatures ranging from 10 – 70 K.

Electrons with 10 keV energy and a beam current of 2 µA irradiated CO$_2$ ice samples at 30, 50 and 70K. The spectra were recorded at 5, 10, 20 and 30 minute intervals similar to the 13K sample. All the new bands observed were in good agreement with those listed in Table 6.2. Using the value of $A_{O_3} = 1.4 \times 10^{-17}$ cm molecule$^{-1}$ (Sivaraman et al., 2007) for the $\nu_3$ (1044 cm$^{-1}$) band for O$_3$ the number of molecules produced was calculated and compared with those molecules obtained from CO$_2$ ice irradiation at 13 K (Table 6.3). All the data obtained at 30, 50 and 70 K was normalised to those number of molecules present in the 13 K sample for direct comparison with the production and dissociation of molecules.
It was interesting to note that a 30 K irradiated CO$_2$ sample produced the same amount of O$_3$ (Figure 6.3) as the 13 K sample. The same trend was followed in the CO$_3$ production. These results indicate that there was no significant change in the dissociation and association reaction in the frozen CO$_2$ kept at 13—30 K irradiated by 10 keV electrons. However, at higher temperatures (50 and 70 K) the production of O$_3$ and CO$_3$ was notably reduced (Figure 6.3). Hence it was necessary to investigate other reaction channels that were open for oxygen atoms produced in the matrix by irradiation. The focus is on the oxygen atoms because their availability determines the new products. In detail, after the CO$_2$ dissociation to CO and O there were five reaction channels open for these oxygen atoms (i) reaction of two atomic oxygen to form molecular oxygen, (ii) reaction with molecular oxygen to produce O$_3$ (iii) adding to CO and recycling CO$_2$ (iv) reaction with CO$_2$ to produce CO$_3$ and (v) reaction with CO$_3$ to produce the heavier molecules CO$_4$ and CO$_5$.

From the infrared spectra of O$_3$ and CO$_3$ it was observed that all the molecules were produced in smaller amounts at 50 and 70 K (Figure 6.4 and 6.5) and so pathways (ii and iv) cannot be a dominant reaction channel for oxygen atoms at these temperatures. CO$_3$ production in turn dictates more production of CO$_4$, CO$_5$ (Figure 6.5) and so pathway (v) can be considered to be main reaction channel. Pathways (i) and (iii) were left for reactions involving atomic oxygen in the CO$_2$ ice, whereas pathway (i) gives a product (O$_2$) that is infrared inactive and hence the formation of this product cannot be quantified, but this reaction channel was considered significant because of the mobile oxygen atoms at higher temperatures (see chapter 5). Also pathway (iii) recycling CO$_2$ was another significant pathway for the loss of oxygen atoms during irradiation. The amount of CO$_2$ molecules present at the end of irradiation was compared after every sample irradiation and the difference between the number of CO$_2$ molecules present before irradiation to the number of molecules present after irradiation was found to have decreased by a factor of approximately two and four for 50 K
and 70 K samples, respectively (Table 6.3). Hence recycling CO$_2$ was found to be a major reaction channel for oxygen atoms at higher temperatures.

Table 6.3: Difference in the number of CO$_2$ molecules dissociated and the number of O$_3$ molecules produced at the end of electron irradiation at different temperatures.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Difference in CO$_2$ molecule (before – after) irradiation, cm$^{-2}$</th>
<th>O$_3$ Column density, cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>7.26E+17</td>
<td>2.11E+17</td>
</tr>
<tr>
<td>30</td>
<td>8.00E+17</td>
<td>2.10E+17</td>
</tr>
<tr>
<td>50</td>
<td>4.62E+17</td>
<td>1.07E+17</td>
</tr>
<tr>
<td>70</td>
<td>2.80E+17</td>
<td>2.29E+16</td>
</tr>
</tbody>
</table>

![Figure 6.3: Ozone production by electron irradiation of CO$_2$ ice at different temperatures. Error within ± 10%.](image)
Figure 6.4: Ozone band area at the end of electron irradiation period for CO$_2$ ice at temperatures at 13, 30, 50 and 70 K. Error within ± 10%.

Figure 6.5: CO$_n$ (n = 3,4,5) band area at the end of electron irradiation period for CO$_2$ ice at temperatures 13, 30, 50 and 70 K. Error within ± 10%.
6.3 High energy (0.8 MeV) proton (H\(^+\)) irradiation

In order to compare effects of proton and electron irradiation of CO\(_2\) ice we performed a set of experiments with an approximately 2 \(\mu\)m thick CO\(_2\) ice formed on a silver substrate at 10 K at Cosmic ice lab based in NASA Goddard Space Flight Centre. Infrared spectra recorded before irradiation shows the bands of CO\(_2\) were in good agreement with those values listed in Table 6.1. Protons at 0.8 MeV and 3 \(\times 10^{-7}\) A beam current irradiated the ice sample at temperatures 10, 30, 50 and 70 K.

![Figure 6.6: Ozone production using 0.8 MeV proton irradiation of CO\(_2\) ice at different temperatures. Error within \(\pm 10\%\).](image)

For irradiation at 30, 50 and 70 K a new ice was initially formed at 10 K and then warmed to 30, 50 and 70 K prior to irradiation. During irradiation new bands appeared in the infrared spectrum indicating the formation of new molecules. The band position of these new
bands were in good agreement with those values listed in Table 6.2 and hence qualitatively similar molecules were produced both in the electron and proton irradiation experiments on CO₂ ice.

Table 6.4: The number of CO₂ molecules dissociated and the number of O₃ molecules produced at the end of proton irradiation at different temperatures.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Difference in CO₂ molecule (before – after) irradiation, cm²</th>
<th>O₃ Column density, cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.59E+17</td>
<td>2.43E+17</td>
</tr>
<tr>
<td>30</td>
<td>14.91E+17</td>
<td>2.19E+17</td>
</tr>
<tr>
<td>50</td>
<td>3.74E+17</td>
<td>1.47E+17</td>
</tr>
<tr>
<td>70</td>
<td>8.79E+16</td>
<td>4.73E+16</td>
</tr>
</tbody>
</table>

Figure 6.7: Ozone band area at the end of proton irradiation period at temperatures 10, 30, 50 and 70 K. Error within ± 10%.
A quantitative analysis on the new products reveals the reactions that have taken place in the ice. From equation 6.1, CO₂ dissociation produces suprathermal oxygen atoms and equation 6.2, 6.3 explains the formation of O₃, CO₅ and other products from the reaction of oxygen atoms. Using the ν₃ (1044 cm⁻¹) band of O₅, ozone production was monitored until the end of irradiation at different temperatures (Figure 6.6). The lowest ice temperature (10 K) produced more O₃ (Figure 6.7, Table 6.4) during irradiation (similar to the pure oxygen ice; Chapter 5). Proton irradiation of a 30 K sample produced less O₃ than a 10 K sample, whereas no difference was observed between a 13 and 30 K sample irradiated by electrons (section 6.2.2). Here the O₃ loss at 30 K can be attributed to the O₃ dissociation during irradiation because more CO₂ molecules were dissociated during the 0.8 MeV proton irradiation (Table 6.4) in comparison with 10 keV electron irradiation (Table 6.3).
The lower formation of O$_3$ (Figure 6.7) (and the other molecules like CO$_3$, CO$_4$, CO$_4$ in figure 6.8) at higher temperatures can be attributed due to the recycling of CO$_2$ and production of O$_2$ as discussed earlier (see section 6.2.2).

### 6.4 Molecular formation during warm-up of the irradiated ice

Molecular CO$_2$ gas was deposited at 10 K and was warmed up to 70 K. The ice sample was then left at 70 K for about 120 minutes and no irradiation was performed. Infrared spectra were recorded once every 10 minutes. From figure 6.9 it was clear that there was no significant desorption of CO$_2$ molecules at 70 K.

![Figure 6.9: CO$_2$ ice kept at 70 K for 120 minutes without irradiation and the three vibrational band area of CO$_2$ were monitored. Error within ± 10%.

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Both the electron and proton irradiated CO$_2$ ice at different temperatures were slowly warmed up after irradiation and resulting chemical changes monitored in the infrared spectra. Warm-up was carried out at 20 K steps until 90 K and after that a 10 K step to record a spectrum at 100 K.

After irradiation oxygen atoms are stored in the CO$_2$ ice matrix and will contribute to thermal reactions during warm-up of the ice due to the increase in their mobility. No new products were found during the warm-up phase, indeed it should be noted from figure 6.10 that at 70 K O$_3$ was lost from the ice and this indicates that even during irradiation of the 70 K sample O$_3$ that was produced will also be desorbed from the ice. All the CO$_2$ ice desorbed from the substrate between 100 K and 110 K.

![Graph of O$_3$ Area vs Temperature](image)

Figure 6.10: Loss of O$_3$ in electron and proton irradiated CO$_2$ ice. Error within $\pm$ 10%.
6.5. Low energy ion irradiation

6.5.1. Using 1.5 keV Proton (H')

CO₂ ice was formed by depositing molecular CO₂ gas on a zinc selenide (ZnSe) substrate at 30K. The ice thickness was maintained ~ 2 µm. Infrared spectra of the ice were recorded in the mid infrared range 4000-600 cm⁻¹. The observed vibrational bands of CO₂ were in good agreement to those values given in Table 6.1. Low energy (1.5 keV) protons irradiated the ice sample at two beam currents of 300 nA for 60 minutes followed by 1 µA for another 60 minutes (see chapter 3, section 3.3). Irradiation resulted in CO₂ dissociation to give CO and O (Equation 6.1). Therefore new chemical species were produced once the atomic oxygen became available in the matrix. Also in these low energy proton irradiated ices we have to consider the H atoms because the low energy protons may be captured in the ice (see chapter 3) and become available in the ice matrix for reaction (Figure 6.11). At the end of the irradiation period new bands were observed in the recorded infrared spectra and except the ν₂ O₃ band all the other bands those given in Table 6.2 were observed. Formation of these products shows that similar reactions in equations 6.2 and 6.3 were taking place in the ice. In addition a weak and very broad 3500 – 3000 cm⁻¹ band observed can be attributed to the presence of H₂O formed via the following reaction in equation 6.4. Therefore O atoms that were produced in the ice (Figure 6.12) have several competing reactions that restricts the reaction to form O₂ even in an ice at lower temperature, but the loss due to addition of H atoms can be measured using a non reactive low energy ion to dissociate CO₂.

\[ \text{O} + \text{H} \rightarrow \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} \]  \hspace{1cm} (6.4)

During warm-up of the irradiated ice further O₃ production was not observed and so the oxygen atoms stored in the matrix selected other reaction pathways either recycling CO₂ or producing CO₃ and the other associated products like CO₉, CO₅ and reaction with H.
atoms. Almost all O; desorbed from the ice at temperature around 110 K and this slight increase in desorption temperature, compared with high energy proton and electron irradiation, was due to the formation of H₂O (Equation 6.4) on the substrate.

![Diagram of ion interaction at the ice surface and subsequent evolution.](image)

**Figure 6.11:** Ion interaction at the ice surface and subsequent evolution.

![Graph showing O; growth in 30 K CO₂ ice during irradiation by 1.5 keV H⁺ ions.](image)

**Figure 6.12:** O; growth in 30 K CO₂ ice during irradiation by 1.5 keV H⁺ ions.

Error within ± 10%.
6.5.2. D\textsuperscript{+} ion irradiation at 2.12 keV

2\textmu m thick CO\textsubscript{2} ice samples were prepared at 30 K and irradiated by 2.12 keV D\textsuperscript{+} at 4 \mu A current for about 60 minutes and subsequent chemical changes observed by monitoring mid-infrared region 4000 – 600 cm\textsuperscript{-1}. After irradiation all bands except the fundamental O–O stretch vibration of the O\textsubscript{3} molecule were observed in good agreement with those listed in Table 6.2. Dissociation of CO\textsubscript{2} and the formation of new molecules followed the reactions in equation 6.1 and 6.2 - 6.3, respectively. It should be noted that D\textsuperscript{+} ions at 2.12 keV will be captured upon implantation on the ice and become reactive. Comparison with H\textsuperscript{+} ions shows that D\textsuperscript{+} ions cause more CO\textsubscript{2} dissociation. Indeed using the absorption coefficient value of 1.1 x 10\textsuperscript{-17} cm molecule\textsuperscript{-1} for 2140 cm\textsuperscript{-1} band of CO\textsubscript{2}, the number of CO\textsubscript{2} molecules dissociated can be calculated and indicates that D\textsuperscript{+} ions dissociated twice as many CO\textsubscript{2} molecules as H\textsuperscript{+} ions (Table 6.5) resulting in higher O\textsubscript{3} production (Figure 6.13).

![Figure 6.13: O\textsubscript{3} growth in a 30 K CO\textsubscript{2} ice irradiated by 2.12 keV D\textsuperscript{+} ions.](image)

Error within ± 10%.
Table 6.5: The number of CO and O₃ molecules formed by irradiation of a 30 K CO₂ ice irradiated by 2.12 keV D⁺ and 1.5 keV H⁺ ions. Error within ± 10%.

<table>
<thead>
<tr>
<th>Ion</th>
<th>CO</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Column density, cm⁻²</td>
<td>Column density, cm⁻²</td>
</tr>
<tr>
<td>D⁺</td>
<td>6.81E+16</td>
<td>1.00E+16</td>
</tr>
<tr>
<td>H⁺</td>
<td>3.23E+16</td>
<td>5.03E+15</td>
</tr>
</tbody>
</table>

6.5.3. He⁺ irradiation

CO₂ ice was also irradiated with non reactive He⁺ ions (see chapter 3, section 3.3). A 2 µm thick ice sample were irradiated with 3 keV He⁺ ions at 400 nA for about 60 minutes followed by irradiation with 3 µA current for another 60 minutes. Dissociation and formation reactions in a CO₂ ice due to ion irradiation were discussed earlier (see section 6.5.1 and 6.5.2) and so the focus was upon the O₃ production due to non reactive low energy He⁺ ion irradiation.

Table 6.6: Number of CO and O₃ molecules present at the end of irradiation in a 30 K CO₂ ice irradiated by 1.5 H⁺ and 3 He⁺ ions. Error within ± 10%.

<table>
<thead>
<tr>
<th>Ion</th>
<th>CO</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Column density, cm⁻²</td>
<td>Column density, cm⁻²</td>
</tr>
<tr>
<td>H⁺</td>
<td>3.23E+16</td>
<td>5.03E+15</td>
</tr>
<tr>
<td>He⁺</td>
<td>3.35E+16</td>
<td>5.08E+15</td>
</tr>
</tbody>
</table>
He\(^+\) ions at 3 keV were known to produce molecular dissociation on CO\(_2\) ice closer to the damage induced by 1.5 keV H\(^+\) ions (see chapter 3). Following the two step consecutive reaction mechanism to form O\(_3\) (Equation 6.2) in CO\(_2\) ice matrix O\(_3\) was produced (Figure 6.14) is almost equal amounts as with the H\(^+\) ion irradiation. This indicates that O\(_3\) formation was not affected by the presence of any additional reactive species in low temperature ice at 30 K (Table 6.6).

![Figure 6.14: O\(_3\) formation in 30 K CO\(_2\) ice by irradiation with 3 keV He\(^+\) ions. Error within ± 10%.

6.5.4. Irradiation at higher temperature using D\(^+\) and He\(^+\) ions

CO\(_2\) ice samples prepared at 80 K were irradiated with both reactive (D\(^+\)) and non reactive (He\(^+\)) ions and compared with the low temperature ice irradiation results described in the previous sections. The formation of new products during and at the end of irradiation was recorded in the 4000- 600 cm\(^{-1}\) region of the infrared spectrum. The growth of
O$_3$ was monitored via the 1044 cm$^{-1}$ ($\nu_3$) band (Figure 6.15). Less O$_3$ was observed in the 80 K ice than the 30 K samples, similar to the experiments with electrons and high energy protons.

**Table 6.7:** The number of CO and O$_3$ molecules formed by 2.12 keV D$^+$ and 3 keV He$^+$ irradiation of a 80 K CO$_2$. Error within $\pm$ 10%.

<table>
<thead>
<tr>
<th>Ion</th>
<th>CO</th>
<th>O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Column density, cm$^{-2}$</td>
<td>Column density, cm$^{-2}$</td>
</tr>
<tr>
<td>D$^+$</td>
<td>1.93E+16</td>
<td>1.36E+15</td>
</tr>
<tr>
<td>He$^+$</td>
<td>6.56E+15</td>
<td>1.39E+15</td>
</tr>
</tbody>
</table>

**Figure 6.15:** O$_3$ formation in 80 K CO$_2$ ice by irradiation of 3 keV He$^+$ and 2.12 keV D$^+$ ions. Error within $\pm$ 10%.
From figure 6.15 it was clear that the $D^+$ ion irradiation produced almost the same amount of $O_3$ as non reactive $He^+$ ion. From this we can conclude that in the 80 K sample the oxygen atoms during $D^+$ irradiation were used in the reaction with deuterium ($D$) atoms and also with other molecules like CO, CO$_2$ and CO$_3$ even though twice as much as CO$_2$ were dissociated (Table 6.7) in comparison with the $He^+$ irradiation. Thus a reactive ion irradiating ice at a higher temperature affects the $O_3$ formation by consuming the oxygen atoms in reaction producing $D_2O$, $D_2O_2$ and $D_2CO$.

6.6. Conclusions

Ozone formation in a carbon dioxide ice was studied using various irradiation sources and at different temperatures. The dissociation of CO$_2$ to CO and O enables further reactions in the matrix producing $O_3$ in a two step consecutive reaction. 10 keV electron irradiation of 10 and 30 K CO$_2$ ices produced the same amount of $O_3$ whereas 0.8 MeV irradiated sample showed a small decrease in the $O_3$ molecules produced at 30 K. Oxygen atoms produced in the ice irradiated at higher temperatures, such as 50 and 70 K, had several additional reaction channels and thereby formed less $O_3$ than in lower temperature (10 and 30 K) ices. For a 70 K ice $O_3$ desorption from the ice was observed.

During low energy irradiation experiments the ions implanted on to the ice were trapped and with the oxygen atoms produced in the ice due to dissociation of CO$_2$. By targeting H$^+$ and D$^+$ ions on the CO$_2$ ice sample kept at 30 K we found that more $O_3$ was formed during D$^+$ ion irradiation. Irradiation with a non reactive ($He^+$) ion showed that the presence of an additional reactive species like H atoms did not affect the number of $O_3$ molecules produced in the low temperature ice at 30 K. When the temperature was raised to 80 K and the sample was irradiated by reactive ($D^+$) and non reactive ($He^+$) ion at this temperature, then the difference in the number of $O_3$ molecules produced was found to be
dependent on the irradiation source and this was because an equal amount of O$_3$ was observed in the 80 K ice even though a two fold increase in CO$_2$ dissociation was observed in the D$^+$ irradiated ice. Therefore the reactive ion implanted uses an increased fraction of the available oxygen atoms at higher temperature (80 K) thereby decreasing O$_3$ production.
CHAPTER 7: RADIATION CHEMISTRY IN N₂O ICES

7.1. Introduction

Although N₂O has not yet been detected in any of the outer solar system planets/satellites it is likely that it will be formed by irradiation of common ices like N₂, CO₂ and CO. Indeed irradiation of N₂ and carbon dioxide (CO₂) ice by energetic electrons at 5 keV (Jamieson et al. 2005) and protons at 0.8 MeV (Moore et al. 1983), has shown that N₂O is produced. Therefore it is important to study the irradiation of N₂O ices to determine subsequent chemical products. In an earlier experiment (Liang & Michl 1984) solid nitrogen oxides were bombarded using 4 keV atoms and ions of Ar producing O₂. Here we present the first results of electron and proton irradiation of solid N₂O.

7.2. Electron irradiation of a thick N₂O sample

Nitrous Oxide, 99.5% pure (from Argo International) was used to prepare the solid N₂O ice on a Zinc Selenide (ZnSe) substrate (see chapter 3, section 3.1). N₂O molecular gas, was deposited at the rate of 10⁻⁷ mbar for about 90 second at ~ 25 K. The aim was to prepare a thick ice sample so as to avoid any contamination from other oxygen bearing molecules since if any are present they will be diluted in the large bulk of N₂O molecules. Electrons at 1 keV and at a current of 10 μA irradiated the ice sample for about 90 minutes.

An infrared spectrum of a N₂O ice sample, kept at ~ 25K, before irradiation was measured over the 4000 – 600 cm⁻¹ region. The fundamental bands we observed ν₁ (1292.2 cm⁻¹), ν₃ (2237 cm⁻¹) were in close agreement with those values reported (Dows 1957; Lapinski et al. 2001; Smith et al. 1971), at 6K, 15K and 70K respectively. Eight other bands were observed at 1164.8 cm⁻¹, 2580.2 cm⁻¹ and 3861 cm⁻¹ (overtones bands 2ν₂, 2ν₁ and 3ν₁), and 1887.9 cm⁻¹, 2468.7 cm⁻¹, 2813.6 cm⁻¹, 3379.5 cm⁻¹ and 3508 cm⁻¹ (combination bands ν₁,
Table 7.1, shows a comparison of band positions in N₂O recorded by earlier authors at different temperatures. There may be phase changes taking place in the ice at higher temperatures forming a highly ordered crystalline ice matrix. The N₂O dimer has four distinctive absorption bands at 2213.1, 2214.3, 2220.7 and 2221.9 cm⁻¹. In our spectra a shoulder around 2219.6 cm⁻¹ can be attributed to (N₂O)_2 (Sodeau & Withnall 1985).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Wavenumber, cm⁻¹</th>
<th>This work (25K)</th>
<th>Lapinski et al (6K)</th>
<th>Dows (70K)</th>
<th>Smith et al (15K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₂</td>
<td>1164.8</td>
<td>1166.6</td>
<td>1165.6</td>
<td>1166.5</td>
<td></td>
</tr>
<tr>
<td>v₁</td>
<td>1292.2</td>
<td>1291.2</td>
<td>1293.4</td>
<td>1291.3</td>
<td></td>
</tr>
<tr>
<td>v₁ + v₂</td>
<td>1887.9</td>
<td>1885.3</td>
<td>1888.1</td>
<td>1885.9</td>
<td></td>
</tr>
<tr>
<td>v₃</td>
<td>2237.0</td>
<td>2235.6</td>
<td>2238.0</td>
<td>2235.9</td>
<td></td>
</tr>
<tr>
<td>v₁ + 2v₂</td>
<td>2468.7</td>
<td>2466.5</td>
<td>2468.5</td>
<td>2466.9</td>
<td></td>
</tr>
<tr>
<td>2v₁</td>
<td>2580.2</td>
<td>2575.3</td>
<td>2579.5</td>
<td>2576.0</td>
<td></td>
</tr>
<tr>
<td>v₂ + v₃</td>
<td>2813.6</td>
<td>2809.3</td>
<td>2813.7</td>
<td>2809.2</td>
<td></td>
</tr>
<tr>
<td>2v₂ + v₁</td>
<td>3379.5</td>
<td>3374.5</td>
<td>---</td>
<td>3373.8</td>
<td></td>
</tr>
<tr>
<td>v₁ + v₃</td>
<td>3508.0</td>
<td>3499.3</td>
<td>3508</td>
<td>3499.9</td>
<td></td>
</tr>
<tr>
<td>3v₁</td>
<td>3861.0</td>
<td>3853.7</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7.1: Infrared bands of solid nitrous oxide at ~25 K.
Table 7.2: Assignments of new IR bands that were observed during 1 keV electron irradiation of solid N$_2$O at a temperature of $\sim$ 25K.

<table>
<thead>
<tr>
<th>Wavenumber cm$^{-1}$</th>
<th>Molecule</th>
<th>Mode</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1039.6</td>
<td>O$_3$</td>
<td>$v_3$</td>
<td>A</td>
</tr>
<tr>
<td>1594.0</td>
<td>N$_2$O$_3$</td>
<td>?</td>
<td>B</td>
</tr>
<tr>
<td>1614.9</td>
<td>NO$_2$</td>
<td>$v_3$</td>
<td>A</td>
</tr>
<tr>
<td>1702.4</td>
<td>N$_2$O$_5$</td>
<td>$v_9$</td>
<td>A</td>
</tr>
<tr>
<td>1718.2</td>
<td>N$_2$O$_4$</td>
<td>?</td>
<td>B</td>
</tr>
<tr>
<td>1741.2</td>
<td><em>Trans</em>-N$_2$O$_2$</td>
<td>$v_5$</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>N$_2$O$_5$</td>
<td>$v_1$</td>
<td>A</td>
</tr>
<tr>
<td>1763.4</td>
<td><em>cis</em>-N$_2$O$_2$</td>
<td>$v_3$</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>sym-N$_2$O$_4$</td>
<td>$v_9$</td>
<td>A</td>
</tr>
<tr>
<td>1832.1</td>
<td><em>asym</em>-N$_2$O$_3$</td>
<td>$v_1$</td>
<td>A</td>
</tr>
<tr>
<td>1855.7</td>
<td><em>Trans</em>-N$_2$O$_2$</td>
<td>$v_1$</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td><em>cis</em>-N$_2$O$_2$</td>
<td>$v_1$</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td><em>asym</em>-N$_2$O$_4$</td>
<td>$v_1$</td>
<td>A</td>
</tr>
<tr>
<td>1867.0</td>
<td>N$_2$O$_3$</td>
<td>?</td>
<td>B</td>
</tr>
</tbody>
</table>

A – From Corey & Kaiser (2005) and references therein

B – From Fateley, Bent & Crawford (1959)

After irradiation several new infrared bands appeared in the spectrum indicating the presence of new molecules that have formed under the influence of electron irradiation. A band at 1039.6 cm$^{-1}$ was observed to appear in the IR spectrum (Figure 7.2(a)) immediately after irradiation began and is identified as the $v_3$ O-O asymmetric stretch of O$_3$. Several of these
new bands were found to be grouped within 1950 - 1550 cm\(^{-1}\) region (Figure 7.2(b)). They are at 1614.9 cm\(^{-1}\) (NO\(_2\)), 1594 cm\(^{-1}\) (N\(_2\)O\(_2\)), 1741.2 cm\(^{-1}\) (trans-N\(_2\)O\(_2\), N\(_2\)O\(_3\)), 1763.4 cm\(^{-1}\) (cis-N\(_2\)O\(_2\), sym N\(_2\)O\(_4\)), 1702.4 cm\(^{-1}\) (N\(_2\)O\(_3\)), 1718.2 cm\(^{-1}\) (O\(_2\)-N-NO), 1855.7 cm\(^{-1}\) (trans-N\(_2\)O\(_2\), cis-N\(_2\)O\(_2\), sym-N\(_2\)O\(_4\)) and 1832.1 cm\(^{-1}\) (asym-N\(_2\)O\(_3\)), Table 7.2. Other vibrational modes of newly formed products might be present in the saturated regions of the N\(_2\)O spectrum.

Electron impact dissociation of N\(_2\)O was expected to produce molecular nitrogen and atomic oxygen (Equation 7.1), since it requires 1.67 eV for dissociation of N-O bond in N\(_2\)O. Electron impact dissociation of N\(_2\)O in a microwave discharge was thought to produce O\((^1\text{D})\) in a spin allowed pathway (Ung 1975), but later (Piper & Rawlins 1986) showed that although a spin forbidden process, electron impact dissociation of N\(_2\)O is dominated by the production of oxygen in its ground state \(^3\text{P}\) rather than the excited O\((^1\text{D})\). There is a lack of electron impact dissociation data for solid N\(_2\)O at lower temperatures, therefore we may perhaps expect production of both O\((^3\text{P})\) and O\((^1\text{D})\). O\((^3\text{P})\) production by dissociation of N\(_2\)O by 1 keV electron impact was supported by the immediate formation of O\(_3\) molecule, observed at 1039 cm\(^{-1}\), that can form via a two step process, generating molecular oxygen in the first step and addition of another O\((^3\text{P})\) producing O\(_3\) in the second step (equation 7.2). Figure 7.3, shows the growth of ozone during irradiation, where O\(_3\) was formed in a two step mechanism, experiments using lower beam currents or less fluence will show growth trends during early stages of irradiation.

\[
\begin{align*}
\text{N}_2\text{O} + e^- & \rightarrow \text{N}_2 + \text{O}(^3\text{P} / ^1\text{D}) \quad (7.1) \\
\text{O} + \text{O} & \rightarrow \text{O}_2 + \text{O} \rightarrow \text{O}_3 
\end{align*}
\]
Figure 7.2: IR spectra of the new bands observed in solid N$_2$O during irradiation. [a] 1039.6 cm$^{-1}$ ($v_3$) band of O$_3$ and [b] spectral region between 1950 – 1550 cm$^{-1}$ showing oxides of nitrogen. Band assignments may correspond to more than one molecule and are listed in Table 7.2.
In an ice matrix kept at 25 K, O₃ production can be explained by the formation of the complex (N₂O...O₂) once molecular oxygen is generated in the matrix followed by dissociation of the form (N₂...O...O₂) and reaction within the matrix cage resulting in (N₂...O₃). It was well known that at 25K atomic oxygen can diffuse through the matrix and so the complex (N₂O...O₂) produced can follow the reaction in equation 7.3. The possibility of these reactions in N₂O molecular cages was likely due to the spectroscopic identification of complex (N₂O...O₂) (Bahou et al. 1998; Bahou et al. 1997).

\[ N_2O...O_2 + O \rightarrow N_2O + O_3 \]  

(7.3)

![Figure 7.3: O₃ growth during electron irradiation of a thick N₂O sample at 25 K. Error within ± 10%.](image)

Due to intersystem crossing, O(¹D) was a source for O(¹P) and at keV electron energies O(¹D) production was favourable (see Chapter 5). Detection of N₂O₂ during irradiation supports the availability of O(¹D) for reaction with N₂O. Reaction 7.4 is well
known to generate (NO)₂ (Liang & Michl 1984) known as dinitrogen dioxide (N₂O₂) and so
the presence of O('D) during irradiation in the ice matrix was evident.

\[ \text{N}_2\text{O} + \text{O ('D)} \rightarrow (\text{NO})_2 \]  \hspace{1cm} (7.4)
\[ \text{NO} + \text{O} \rightarrow \text{NO}_2 \]  \hspace{1cm} (7.5)

Additionally NO dimers were the source of NO monomers through the weak bond
(0.08 eV or 8 kJ mol⁻¹) between N-N in the (NO)₂. Thus atomic oxygen added to NO
monomer produce NO₂ (reaction 7.5), which was also observed in the spectrum at 1614.9
cm⁻¹. Therefore, the presence of NO was identified indirectly and so we can conclude that due
to a thick N₂O sample and a vibrational band at 1898 cm⁻¹, unambiguous detection of NO was
not possible. NO dimers, (NO)₂, were identified both in the cis and trans isomeric forms
(Figure 7.2 and Table 7.2).

Further reactions generate heavier molecular products N₂O₃, N₂O₄ and N₂O₅.
Dinitrogen trioxide (N₂O₃) can be formed in two ways: (i) reaction of NO₂ with NO and (ii)
addition of atomic oxygen to N₂O₂. During irradiation both these reactions might compete in
forming N₂O₃ molecules in the N₂O ice but reaction (i) was observed to be very efficient due
to the growth of 1594 cm⁻¹ N₂O₃ signature (reaction 7.6) and a corresponding decrease in the
NO₂ signature at 1614.9 cm⁻¹.

\[ \text{NO}_2 + \text{NO} \rightarrow \text{N}_2\text{O}_3 \]  \hspace{1cm} (7.6)
\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]  \hspace{1cm} (7.7)
\[ 2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \]  \hspace{1cm} (7.8)

NO₂ dimers dimerize to form N₂O₄ (reaction 7.8). A very weak band at 1702.4 cm⁻¹
was assigned to N₂O₅, the heaviest molecule that was produced in the N₂O ice. This molecule
may be formed by O₃ reacting with NO₂ molecules (reaction 7.9).
2NO₂ + O₃ → N₂O₅ + O₂ \hspace{1cm} (7.9)

7.3 Proton (0.8 MeV, H⁺) irradiation of a thin N₂O sample

This experiment was carried out in the apparatus based at the Cosmic ice lab, NASA Goddard Space Flight Centre. The substrate was cooled down to 10 K and N₂O molecular gas deposited to form a ~ 1 μm thick ice (see chapter 3, section 3.4). The infrared spectrum was recorded in the mid infrared region and the vibrational bands were in good agreement with those listed in Table 7.1. Protons at 0.8 MeV and at 3 x 10⁻⁷A beam current irradiated the ice sample. Irradiation at temperatures 10, 30 and 50 K were carried out and infrared spectra were recorded. For irradiation at 30 and 50 K, a new ice was initially formed at 10 K and then warmed to 30 and 50 K before the start of irradiation. After irradiation several new bands appeared in the spectra indicating the formation of new molecules (Figure 7.4, Table 7.2). Due to a thin sample there was no N₂O band overlap in the 1400 – 1200 cm⁻¹ region, because of the absence of less intense N₂O bands, and so new bands were observed at 1303.4 (N₂O₅), 1283.9, 1261 that corresponds to N₂O₄ and 1243.4 cm⁻¹ (N₂O₃) (Figure 7.4).

Identification of the same products in proton and electron irradiated ice suggests that similar reactions take place in reactions (7.1 – 7.9) in the N₂O matrix irradiated by protons. O₃ observed at 1039 cm⁻¹ was found to diminish during the later stages of irradiation at all temperatures (Figure 7.5). Less O₃ was produced in samples at 30 and 50 K in comparison to the sample irradiated at 10 K. This can be explained by the reaction of atomic oxygen being ‘used up’ by reactions 7.4 and 7.5; also association of two oxygen atoms producing molecular oxygen must be considered. There was no significant difference in the amount of O₃ produced in a 30 and 50 K irradiated sample and this suggests that there was no significant difference in the reactions that takes place for a proton irradiated solid N₂O at 30 and 50 K.
Figure 7.4: Infrared spectra after 0.8 MeV proton irradiation of solid N$_2$O at 10 K.

From figure 7.5 it was observed that O$_3$ was lost during the later stages of irradiation. The reduction in the amount of O$_3$ during irradiation can be attributed to two reactions (i) O$_3$ dissociation during irradiation and (ii) reaction of O$_3$ with NO$_2$ as given in equation 7.9. Pathway (ii) was known to produce N$_2$O$_5$ from O$_3$ and NO$_2$ during irradiation, upon close observation of the 1702.4 cm$^{-1}$ band N$_2$O$_5$ was found to grow during the later stages of irradiation at the expense of O$_3$, where the 1039 cm$^{-1}$ O$_3$ band starts to diminish.
7.4 Electron irradiation of a thin N₂O sample

Electron irradiation at 10 keV and at 2 μA beam current was carried out at The Open University on a N₂O ice sample prepared by depositing molecular N₂O gas on to a substrate kept at 10 K. Irradiation at temperatures 10, 30 and 50 K were carried out and infrared spectra were recorded 5, 10, 20 and 30 minute intervals. For irradiation at 30 and 50 K, a new ice was initially formed at 10 K and then warmed to 30 and 50 K before the start of irradiation. New bands were observed in the spectra of the irradiated ice and the band positions were in good agreement with those listed in Table 7.2. This suggests that similar reactions for dissociation of N₂O, equation 7.1, and formation of other products, equation 7.2 – 7.9, takes place in the 10 keV electron irradiated ice. The evolution of O₃ was monitored using the 1039 cm⁻¹ band.

Figure 7.5: O₃ formation during 0.8 MeV proton irradiation of solid N₂O at 10, 30 and 50 K. Error within ± 10%.
during various stages of irradiation at 10, 30 and 50 K (Figure 7.6). The 10 K sample was found to generate and contain more O₃ at the end of irradiation, whereas a 30 K sample produced more O₃ than a 10 K sample during the initial stages of irradiation (5 minutes), and at the end of irradiation contained much lesser O₃ when compared to a 10 K sample.

Figure 7.6: O₃ formation during 10 keV electron irradiation on thin solid N₂O at 10, 30 and 50 K. Error within ± 10%.

For an irradiated ice at 50 K O₃ production was slightly higher than in the 10 K sample during initial stages of irradiation (5 minutes) and at the end of irradiation a 50 K ice contained similar quantities of O₃ as observed for a 30 K sample. So O₃ was observed to be involved in a reaction with NO₂ during irradiation producing N₂O₅ (Equation 7.9) at all the temperatures for a thin N₂O sample, whereas more O₃ was lost in this reaction for ice irradiated at a higher temperature (30 and 50 K).
7.5. Warm-up of irradiated ices

$\text{O}^{{(P)}}$ atoms, generated during irradiation, are known to have a long lifetime (in days), in an ice matrix, and are known to be mobile at higher temperatures reacting with other atoms or molecules present. For a thicker $\text{N}_2\text{O}$ sample irradiated by 1 keV electrons at 25 K, during warm-up, no further increase in $\text{O}_3$ signature was observed but the sample was found to generate the $\text{O}_3$ dimer ($1041.5 \text{ cm}^3$) at temperatures close to 70 K. Such dimer formation was due to the close proximity of two $\text{O}_3$ molecules because no significant increase in $\text{O}_3$ was observed during warm-up. The reaction of $\text{O}_3$ with $\text{NO}_2$, producing $\text{N}_2\text{O}_5$, was expected to occur in the matrix during warm-up because the same reaction took place in the matrix during irradiation. However was impossible to observe any changes in the $\text{N}_2\text{O}_5$ concentration in the ice during warm-up due to the weak absorption band (Figure 7.2).

However during warm-up of the thin $\text{N}_2\text{O}$ sample irradiated both by 0.8 MeV protons and 10 keV electrons at temperatures 10, 30 and 50 K the $\text{O}_3$ band was observed to reduce and a simultaneous increase in the $\text{N}_2\text{O}_5$ band was clearly observed. This confirms that $\text{O}_3$ was involved in producing $\text{N}_2\text{O}_5$ during warm-up. Also desorption of $\text{O}_3$ at higher temperatures must be considered. Figure 7.8 shows $\text{O}_3$ loss during warm-up of ices irradiated at 10, 30 and 50 K. Using a mass spectrometer, the amount of $\text{O}_3$ molecule involved in a reaction and the amount that desorbs from the surface should be observable and this analysis will be carried out in the future experiments.
Figure 7.7: O₃ dimer formation at 70 K during warm-up of a 1 keV electron irradiated solid N₂O.

Figure 7.8: O₃ loss during warm-up of the proton and electron irradiated N₂O ice at 10, 30 and 50 K. Error within ± 10%.
A pressure increase in the ion gauge at 43 K indicates that some molecules were being desorbed from the N$_2$O ice. O$_2$ from combination of two oxygen atoms and N$_2$ from N$_2$O dissociation, were the most likely molecules to desorb at this temperature. Thus above 43 K O$_3$ production is likely to be hindered by the loss of oxygen molecules.

7.6. Conclusion

Ozone formation in a nitrous oxide ice sample was studied using electron and proton irradiation at different temperatures and at different ice thickness. The dissociation of N$_2$O to form N$_2$ and O enables further reactions in the matrix leading to O$_3$ formation in a two step consecutive reaction. Electron irradiation at 1 keV on a N$_2$O ice at 25 K produced O$_3$ and several oxides of nitrogen. Irradiation using 0.8 MeV protons and 10 keV electrons at 10, 30 and 50 K was observed to generate similar products and revealed the reaction of O$_3$ molecules with NO$_2$ to form N$_2$O$_5$ during irradiation. The lower temperature (10 K) ice was found to contain more O$_3$, whereas for the 30 and 50 K samples less O$_3$ was formed in the ice during irradiation. During warm-up of the ice atomic oxygen was found to be involved in reactions with oxides of nitrogen. O$_3$ left in the matrix after irradiation reacts with NO$_2$ producing N$_2$O$_5$ and hence the O$_3$ concentration was also found to decrease during the warm-up phase.
CHAPTER 8: PROTON IRRADIATION OF NO$_2$ ICE

8.1 Introduction

Nitrogen dioxide, NO$_2$, is well known as a catalytic destructor of ozone in the Earth's stratosphere. Although it has not yet been detected directly the presence of this molecule in the interstellar and circumstellar environments is indirectly confirmed by the presence of nitrous oxide, N$_2$O, that forms from a parent NO$_2$ and atomic nitrogen (N) (see Chapter 1 and 7). Several experiments (Moore et al, 2000; Strazzulla et al 2003; Jamieson et al 2005) that simulate the planetary and satellite ices involving nitrogen and oxygen bearing molecules has shown that an ice dominated by the mixture of these species produces oxides of nitrogen, which includes NO$_2$. Therefore, it is important to study the radiation chemistry of NO$_2$ ice. Here the first results of proton irradiation experiments carried out on solid NO$_2$ are reported.

8.2 Proton (H$^+$) irradiation on NO$_2$ ice at lower temperature

Nitrogen dioxide, 99.5% pure in liquid phase (from Sigma Aldrich) was used to prepare solid NO$_2$ ice on silicon (Si) and potassium bromide (KBr) substrates at Catania Astrophysical Observatory. NO$_2$ was deposited to form an ice of about one micron thick at either 16 or 60 K. The aim was to prepare a thin ice sample so that all the incident ions pass through the ice preventing any reaction of the H$^+$ in the ice. From TRIM calculations (see Chapter 3) an ice thickness of 1 µm is expected to allow all the ions to pass through the ice and strike the substrate.

An infrared spectrum of a NO$_2$ ice sample, kept at 16 K, before irradiation was obtained over the 4000 – 400 cm$^{-1}$ region with 1 cm$^{-1}$ resolution. Figure 8.1, shows the bands of NO$_2$ at 16 K at two different thicknesses before irradiation. 1 µm thick NO$_2$ ice was estimated to contain 1.62 x 10$^{18}$ molecules cm$^2$. Several bands were identified in the spectra recorded (Table 8.1) but it is quite difficult to assign all these bands to NO$_2$ because NO$_2$...
exists in equilibrium with N₂O₄ in the gas phase. Therefore there might be some contribution of N₂O₄ in the spectra recorded before irradiation. Table 8.2, gives the band positions of pure N₂O₄ ice at 20 K. N₂O₄ was not observed directly in our spectrum and this could be due to a shift in the N₂O₄ band positions in the presence of NO₂ ice or may be due to its small abundances. The spectral region 2400 – 600 cm⁻¹ was dominated by intense IR bands of NO₂ thus there were only a few regions in the spectrum where we could observe new bands. NO₂ bands positions are not assigned to any vibrational mode at the moment due to the lack of IR data for this molecule in the ice phase.

Table 8.1: Infrared band positions for solid NO₂ at 16 K.

<table>
<thead>
<tr>
<th>Wavenumber, cm⁻¹</th>
<th>Wavenumber, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>686.6</td>
<td>1720.4</td>
</tr>
<tr>
<td>742.3</td>
<td>1741</td>
</tr>
<tr>
<td>755.8</td>
<td>1765.5</td>
</tr>
<tr>
<td>784</td>
<td>1860</td>
</tr>
<tr>
<td>943.4</td>
<td>1950.9</td>
</tr>
<tr>
<td>1262.3</td>
<td>2235.1</td>
</tr>
<tr>
<td>1280.2</td>
<td>2346.5</td>
</tr>
<tr>
<td>1305.5</td>
<td>2905.8</td>
</tr>
<tr>
<td>1613.8</td>
<td>2973.4</td>
</tr>
</tbody>
</table>

Irradiation using 200 keV protons on solid NO₂ ice was performed until 16 eV 16amu⁻¹ energy deposition was reached in the ice. New infrared bands appeared in the spectrum (Figure 8.2) indicating the presence of new molecules that have formed under the influence of irradiation.
Table 8.2: Infrared band positions of N₂O₄ at 20 K. (From Andrews 1981).

<table>
<thead>
<tr>
<th>Wavenumber, cm⁻¹</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1780</td>
<td>v₁ + v₁₁</td>
</tr>
<tr>
<td>1759</td>
<td>v₁ + v₁₁</td>
</tr>
<tr>
<td>1750</td>
<td>v₁ + v₁₁</td>
</tr>
<tr>
<td>1737</td>
<td>v₉</td>
</tr>
<tr>
<td>1257</td>
<td>v₁₁</td>
</tr>
<tr>
<td>1240</td>
<td>v₁₁</td>
</tr>
<tr>
<td>761</td>
<td>v₆ + v₁₀</td>
</tr>
<tr>
<td>742</td>
<td>v₁₂</td>
</tr>
</tbody>
</table>

Figure 8.1: Infrared spectra of NO₂ at 16 K after 0.2 and 1 µm deposition.

A band at 1038.5 cm⁻¹ was observed to appear in the IR spectrum and was identified as the v₃ O-O asymmetric stretch of O₃. Other new bands were found at 784.5 cm⁻¹, 1243.9 cm⁻¹,
1304.2 cm$^{-1}$, 1339.4 cm$^{-1}$, 1597.4 cm$^{-1}$, 1833 cm$^{-1}$, 1868.2 cm$^{-1}$ and at 2234 cm$^{-1}$. These bands were identified to be vibrations from N$_2$O$_3$, N$_2$O$_4$, N$_2$O$_5$ and N$_2$O (Table 8.3).

Table 8.3: Assignments of new IR bands that were observed during 200 keV H$^+$ irradiation upon solid NO$_2$ at temperature 16 K. (Sivaraman et al, 2008 & references therein).

<table>
<thead>
<tr>
<th>Wavenumber cm$^{-1}$</th>
<th>Molecule</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>784.5</td>
<td>N$_2$O$_3$</td>
<td>?</td>
</tr>
<tr>
<td>1038.5</td>
<td>O$_3$</td>
<td>v$_3$</td>
</tr>
<tr>
<td>1243.9</td>
<td>N$_2$O$_5$</td>
<td>v$_{10}$</td>
</tr>
<tr>
<td>1304.2</td>
<td>asym-N$_2$O$_3$</td>
<td>v$_1$</td>
</tr>
<tr>
<td></td>
<td>asym-N$_2$O$_4$</td>
<td>v$_3$</td>
</tr>
<tr>
<td></td>
<td>N$_2$O$_5$</td>
<td>v$_2$</td>
</tr>
<tr>
<td>1339.4</td>
<td>N$_2$O$_5$</td>
<td>?</td>
</tr>
<tr>
<td>1597.4</td>
<td>N$_2$O$_3$</td>
<td>?</td>
</tr>
<tr>
<td>1833</td>
<td>asym-N$_2$O$_3$</td>
<td>v$_1$</td>
</tr>
<tr>
<td>1868.2</td>
<td>N$_2$O$_3$</td>
<td>?</td>
</tr>
<tr>
<td>2234</td>
<td>N$_2$O</td>
<td>v$_1$</td>
</tr>
</tbody>
</table>
Figure 8.2: IR spectra at [a] 1500 - 600 cm⁻¹ and [b] 2500 - 1500 cm⁻¹ region showing new bands observed in 16 K solid NO₂ (in equilibrium with N₂O₄) ice at the end of irradiation. Bands that are not marked correspond to NO₂.
To form these new molecules NO$_2$ has to dissociate providing new atoms for chemical reactions. Dissociation of solid NO$_2$ was expected to produce nitric oxide (NO) and atomic oxygen given in reaction (8.1) due to fracture of the weaker N-O bond. The production of NO from NO$_2$ dissociation was not unambiguously identified but this may be due to band overlap, as discussed above. The irradiated ice was found (Figure 8.2) to be dominated by the presence of N$_2$O$_3$, which can be produced by reaction between NO$_2$ and NO molecules. Another possibility of producing N$_2$O$_3$ was from the dissociation of N$_2$O$_4$ as given in reaction (8.3).

$$\text{NO}_2 \rightarrow \text{NO} + \text{O} \tag{8.1}$$

$$\text{NO}_2 + \text{NO} \rightarrow \text{N}_2\text{O}_3 \tag{8.2}$$

$$\text{N}_2\text{O}_4 \rightarrow \text{N}_2\text{O}_3 + \text{O} \tag{8.3}$$

$$\text{O} + \text{O} \rightarrow \text{O}_2 + \text{O} \rightarrow \text{O}_3 \tag{8.4}$$

Atomic oxygen released in the dissociation process was used in a reaction to produce ozone which was produced in a two step reaction as given in reaction (8.4). The production of this molecule was low during the initial stages of irradiation but was produced throughout the irradiation process (Figure 8.3), unlike N$_2$O ice where a decrease in O$_3$ was observed at longer periods of irradiation (Chapter 7).
Figure 8.3: Ratio of column densities of O₃ to NO₂ (in equilibrium with N₂O₄) until the end of H⁺ irradiation in a NO₂ ice sample at 16 K. Error within ± 10%.

Therefore ozone production was favoured in NO₂ ice under a continuous irradiation environment. Using a value of $A_{O_3} = 1.4 \times 10^{17}$ cm molecule$^{-1}$ the number of ozone molecules produced were obtained using equation 4.5, (see Chapter 4). At the end of irradiation, the ratio of the column density of ozone produced to the column density of NO₂ molecules initially present before irradiation shows nearly 1-2 % of ozone in the ice (Figure 8.3).

Radiation induced reactions also produced N₂O₄, N₂O₃ and N₂O. Though N₂O₄ is already present in the ice, irradiation induced N₂O₄ formation will take place according to reaction 8.5. Similar products were observed in N₂O ice with N₂O₃ being the heaviest molecule produced. The availability of O₃ is thought to be essential to produce this molecule (see Chapter 7) under the reaction 8.6. The identification of the band at 2234 cm$^{-1}$ can only be assigned to the strong vibration from N₂O where this molecule was expected to form from either or both of the reactions 8.7 and 8.8. Nitrogen is a requirement to produce this molecule.
either as atomic nitrogen (N) as in equation (8.7) or as molecular nitrogen (N₂) in equation (8.8). After NO₂ dissociation, equation 8.1, further dissociation of NO will led to the availability of atomic nitrogen and oxygen (equation 8.8). After atomic nitrogen becomes available it has to combine with another nitrogen and oxygen atom in order to facilitate N₂O production via reaction (8.8). Hence the identification of N₂O in solid NO₂ provides evidence for complex chemistry involving oxygen atoms released by NO₂ dissociation.

\[
2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \quad (8.5)
\]

\[
2\text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 \quad (8.6)
\]

\[
\text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O} \quad (8.7)
\]

\[
\text{N} + \text{N} \rightarrow \text{N}_2 + \text{O} \rightarrow \text{N}_2\text{O} \quad (8.8)
\]

8.3 Proton (H⁺) irradiation on NO₂ ice at higher temperature

In order to understand the effect of temperature on the chemical reactions in an NO₂ ice deposition and irradiation was carried out at 60 K. After deposition the ice is estimated to contain 1.349 x 10¹⁹ molecules cm⁻² before irradiation. At the higher temperature, 60 K, the proportion of N₂O₄ in equilibrium with NO₂ might be higher due to the increased mobility of NO₂ molecules at 60 K.
Figure 8.4: IR spectra at [a] 1500 – 600 cm\(^{-1}\) and [b] 2500 – 1500 cm\(^{-1}\) region showing new bands observed in 60 K solid NO\(_2\) (in equilibrium with N\(_2\)O\(_4\)) ice at the end of irradiation. Bands that are not marked correspond to NO\(_2\).
Irradiation using 200 keV protons was performed until a dose of 26 eV 16amu\(^1\) was deposited into the ice. This value was slightly higher compared to the dose used for a lower (16 K) temperature sample where irradiation ceased after 16 eV 16amu\(^1\) energy deposition. At higher temperatures the mobility of the atoms plays an important role in controlling the column densities of molecules produced, relative to those amounts produced for a 16 K sample, so an increase in dose implies greater availability of atoms for various reactions occurring in an ice under irradiation.

The irradiated ice was found to contain a variety of molecules (Figure 8.4) including \(\text{O}_3\), \(\text{N}_2\text{O}\) and \(\text{N}_2\text{O}_y\) (\(x = 2, y = 3-5\)). This was similar to those molecules observed in the 16 K sample after irradiation (Table 8.3). The percentage of ozone produced at higher (60 K) temperature was found to reach the same value (1-2 %, for 16 eV 16amu\(^1\)) only at the end of 26 eV 16amu\(^1\) energy deposition (Figure 8.5). Therefore, the production of ozone was less for an ice irradiated at a higher temperature when compared with lower temperature for a given irradiation dose. This result was similar to those observed for other ices like \(\text{O}_2\), \(\text{CO}_2\) and \(\text{N}_2\text{O}\).

8.4 Warm-up of the irradiated NO\(_2\) ice

NO\(_2\) ices irradiated both at 16 and 60 K will contain atoms of oxygen and nitrogen together with NO\(_2\), NO and other new molecules (section 8.2, 8.3) produced. These atoms and molecules will be available for reactions induced by thermal energy input which was achieved by increasing the temperature of the sample. The ice sample was then probed by IR spectra and the stability of product ozone was monitored using the very intense \(\nu_3\) band (Figure 8.6).
Figure 8.5: Ratio of column densities of O₃ and NO₂ (in equilibrium with N₂O₄) until the end of H⁺ irradiation in NO₂ ice sample at 60 K. Error within ± 10%.

Figure 8.6: Ozone ν₃ band area at various temperatures (16 – 200 K) during warm-up of the irradiated ice at both 16 and 60 K. Error within ± 10%.
A sample irradiated at 16 K was warmed to 30 K and found to lose only a small amount of O₃ (Figure 8.6). This could be due to ozone reaction with NO₂ as given in reaction 8.6. Above 30 K ozone concentrations were constant to ~120 K after which it began to sublime with last traces of ozone lost at ~200 K. A similar pattern was seen in warming irradiated 60 K irradiated samples. It was hard to quantify any changes in N₂O₅ molecular concentrations because of the band overlap but only small changes seemed to occur suggesting N₂O₅ is stable up to 200 K (Figure 8.7).

Figure 8.7: 1500 – 600 cm⁻¹ region of the infrared spectra recorded after warming up the irradiated NO₂ ice at 16 K to different higher temperatures.
Ozone formation in the nitrogen dioxide ice sample (with a small proportion of nitrogen tetraoxide) ice sample was studied using proton irradiation at two different temperatures 16 and 60 K. The dissociation of NO$_2$ to NO and O enables further reactions in the matrix and O$_3$ was observed to form via a two step reaction, producing molecular oxygen in the first step then addition of another atomic oxygen in the second step. O$_3$ production was observed until the end of irradiation unlike our experiments in N$_2$O ice where O$_3$ was observed to diminish after reaching a maximum during irradiation. Once again lower O$_3$ column densities were observed in the ices irradiated at 60 K. N$_2$O$_3$, N$_2$O$_4$ and N$_2$O$_5$ were also produced. The presence of N$_2$O$_5$ in the irradiated ice indicates reaction involving O$_3$ at the time of irradiation. Therefore part of the O$_3$ produced was immediately lost within the ice. NO that formed from NO$_2$ dissociation was indirectly observed to further dissociate into N and O. The availability of atomic nitrogen enables the formation N$_2$O molecule. Therefore a wealth of chemistry together with O$_3$ production was observed to take place in the NO$_2$ ice under these proton irradiation conditions.
CHAPTER 9: CONCLUSION

9.1 Summary of research reported in this thesis

9.1.1 Ice parameters

In any irradiation experiment on astrochemical ice analogues it is necessary to characterize the physical and chemical properties of the ice target. In this thesis pure ice parameters such as the refractive index, density and thickness were determined from deposition experiments performed under carefully controlled conditions to obtain column density and integrated absorption coefficient values. The derived absorption coefficients could then be used to calculate directly the column density of chemical species in irradiated ices.

9.1.2 Oxygen ices

Ozone formation by electron irradiation of molecular oxygen ices was investigated in the temperature range of 11 K to 30 K. Several reaction mechanisms were derived from the experimental data. The temperature during irradiation was found to affect the number of ozone molecules being produced. In contrast to previous expectations larger concentrations of ozone were produced during irradiation of ice maintained at the lowest temperature (11 K). VUV spectra of the condensed oxygen ice films revealed the presence of oxygen dimers within the ice. Hence, again in contrast to prior expectations we have shown that much of the ozone is formed within the dimer, a hypothesis supported by our direct observation of the ozone related complexes, [O₃...O] and [O₃...O₃] in the oxygen irradiated ices. After irradiation ozone production was found to double when the ice temperature was increased up to 70 K, an observation that could be explained by the entrapment of O atoms in the ice during irradiation that are subsequently liberated to diffuse through the ice at higher temperatures. A phase change in the crystalline ozone was also observed to take place when the ice temperature reaches 47 K.
Proton irradiation of the same oxygen ice showed that ozone formation was a major process but, in contrast to electron irradiation, the formation of ozone reached an equilibrium after a certain dose was deposited.

The formation pathways for the production of ozone were explored by the use of isotopic mixtures of oxygen ($^{16}\text{O}_2$ and $^{18}\text{O}_2$). All the possible combinations of ozone isotopomers were observed to be produced during electron irradiation. As there are two possible formation pathways available to produce ozone, the results showed that end on addition of oxygen atoms to be the dominant pathway. Those isotopomers that were formed in a two step process showed smaller yields during warm-up of the irradiated ice.

### 9.1.3 CO$_2$ ices

Solid CO$_2$ ice was irradiated in several experiments using protons, ions and electrons at different energies, simulating different irradiation environments on lunar surfaces. Energetic particle irradiation modified the ice and several products were observed in varying quantities depending on the irradiation dose. The major products were found to be ozone and carbon monoxide. Ices maintained at 10 and 30 K showed no difference in the amount of ozone produced by 10 keV electron irradiation whereas 0.8 MeV proton irradiation showed a slight decrease in the amount of ozone formed in samples irradiated at 30 K. Ion implantation experiments using low energy reactive and non-reactive ions implied that the presence of an reactive species in the ice had no major effect in the amount of ozone molecules produced. Warm-up of the irradiated sample showed no increase in the ozone formation therefore indicating that all the product oxygen atoms had been used to form other molecules.

### 9.1.4 N$_2$O ices

Irradiation of solid nitrous oxide (N$_2$O) revealed significant ozone production though the molecule has only one constituent oxygen atom. Dissociation of this molecule into
molecular nitrogen and atomic oxygen enables ozone production due to increased life time of
the atomic oxygen in the ice phase. When the sample was irradiated with proton and electron
irradiation sources at different temperatures it was found that product ozone concentrations
were higher at lower temperatures.

Irradiation of N₂O ice was found to synthesize higher molecular weight molecules
such as N₂O₄ and N₂O₅, the latter being formed by reactions of ozone as demonstrated by
correlation between loss of ozone and rise of N₂O₅ at longer irradiation times. Further
increase in temperature of the irradiated samples show no increase in ozone production.

9.1.5 NO₂ ices

Irradiation of nitrogen dioxide ice was also investigated. Within such ices dimer
formation is prevalent. The availability of twice as many oxygen atoms in comparison with
nitrous oxide results in a steady production of ozone although ozone was also lost in the
production of N₂O₅. Once again the rate of ozone formation was reduced in higher
temperatures ices. Nitrous oxide was also identified in the irradiated ice indicating a complex
chemistry induced by irradiation.

9.2 Future work

9.2.1 Modification to the experimental apparatus

The existing astrochemistry apparatus based at The Open University can perform
experiments using liquid helium cooled cryostat to achieve low temperatures down to 15 K.
Therefore the availability of liquid helium limits the number and frequency of the experiments
performed. Another limitation of the experimental chamber is that irradiation can only be
performed after molecular ice formation by gas deposition, whereas depositing additional
molecular gas during irradiation, so called co-deposition, is expected to influence the
chemistry in the production of new molecules. Therefore a slight modification by extending
the needle valve in the experimental chamber (Figure 9.1) has been made to enable co-deposition to be explored and to study the differences in the chemical changes that can occur. In this co-deposition condition a measure of gas flow rate during irradiation is necessary and therefore a calibrated leak valve must be fitted onto the gas line to let in known amounts of gas to the vacuum chamber.

![Figure 9.1: Schematic of the co-deposition method for gas deposition during irradiation.](image)

The molecular substrate used in the experimental chamber based at The Open University is ZnSe. This substrate window is transparent to infrared and therefore the FTIR spectrometer is operated at transmission mode to collect data. Allowing molecular gas into the vacuum chamber and directing the needle valve towards one side of the substrate will stick most of the molecules onto the front side but as the substrate but some molecules will stick onto the reverse (non irradiated) side of the substrate. This will bring some error into the identification of number of molecules present in the ice phase because of transmission mode used for infrared detection. Therefore using a gas shield with a small extended opening for the infrared beam to pass through, as shown in figure 9.2, will prevent the molecules sticking onto the reverse side. This will be implemented in our future experiments using ZnSe window.
Figure 9.2: Gas deposition shield to prevent molecules sticking on the unirradiated face of the substrate.

The limitation imposed by the liquid helium availability can be overcome by the use of a closed cycle helium refrigeration system. A commercial product has been purchased and the apparatus is currently being modified for its inclusion. This will replace the existing liquid helium cooled cryostat by August 2008 and will be ready for experiments to be performed in the autumn.

9.2.2: Future experiments

It would be interesting to explore the formation of ozone in other ‘oxygen rich’ ices for example SO$_2$ and H$_2$O. Ozone formation in the latter remains controversial since ozone destruction by OH radicals may prevent its formation. Research should then be expanded to explore mixtures of ices as found in the ISM and on planetary surfaces and compare these results with astronomical observations.

9.3 Final conclusions

This thesis has described a series of experiments that have been performed to understand ozone formation from various molecular species commonly found in the interstellar medium and on planetary surfaces under a range of different irradiation environments. The production yield for ozone differs with the target molecule, irradiation
dose and the temperature, however ozone formation is generic to most oxygen containing ices. Further warm-up of the irradiated sample was observed to produce more ozone for the oxygen ice but little or no increase in the case for other molecular ices like carbon dioxide, nitrous oxide and nitrogen dioxide. These experiments are expected to have implication for the detection of ozone on other planetary systems and hence its potential as a biomarker in exoplanetary studies.

The rich chemistry observed in the irradiation of even the simplest pure nitrogen oxides ices suggest that astrochemistry is a rich area for further exploration requiring studies of ice mixtures that may provide details on the probability of forming more complex molecules that are important in understanding where the 'building blocks' of life are formed and whether life is possible across the universe.
APPENDIX A

PROCEDURE TO CALCULATE THE STOPPING POWER

1] Open SRIM
2] TRIM calculation
3] DAMAGE: Detailed calculation with full damage cascades.
4] BASIC PLOT: Ion distribution with recoils projected on Y-plane
5] Choose, Ion, energy, angle, thickness, and composition of the ice and then change the density.
6] Change number of iterations: normally 9999 used.
7] Save in a folder: ionization and energy to recoil
8] Delete all the text in the two files saved (in the above step)
9] Use the first two columns of these files to plot.
10] Change the two files to .DAT extension
11] Open these two files with ORIGIN and plot the first two columns
12] Select and delete those values those are reading 0 (zero) in the second column
13] Choose: ANALYSIS – CALCULUS – INTEGRATE
14] Plot two graphs separately ionisation and e2recoil.opj and then calculate the area under the curve.
15] Divide the area obtained with the film thickness, in the case of implantation use the range.
16] The stopping power is obtained in terms of eV/Angstrom
17] Multiply by $10^8$ to changes units to eV/cm
18] Now to derive stopping power in eV cm$^2$ / molecule, use the following steps:
   (i) Derive the number of molecules/ cm$^3$ from density of the molecular ice: which is obtained by dividing density (d) by the a.m.u and proton mass ($1.66 \times 10^{-24}$ g) and the result obtained will be in units of mol/cm$^3$.
   (ii) Now divide this value from the stopping power obtained in eV/cm, and the resulting units will be in eV cm$^2$/molecule. Note this term is unique for the molecule used.
LIST OF PUBLICATIONS

[1] From Chapter 5

[2] From Chapter 7

[3] From Chapter 7
Proton and electron irradiation of nitrous oxide and implications for solar system ices. B Sivaraman, M Moore, N J Mason, Accepted for publication Advances in Space Research from COSPAR '08.

[4] From Chapter 6
Formation and destruction of ozone in astrochemical ices, M. Moore, B. Sivaraman, R.L. Hudson, N.J. Mason, Accepted for publication Advances in Space Research from COSPAR '08.

[5] From Chapter 5 and 6
Electron, proton and ion induced molecular synthesis and VUV spectroscopy of interstellar molecules in the ice phase, B.Sivaraman et al, Accepted for publication in the IAU' 251 symposium publication through Cambridge University Press.

[6] From Chapter 5

[7] From Chapter 4

[8] From Chapter 6

[9] From Chapter 8


[12] UV spectroscopy and photo-processing of astrochemical ices: an experimental Study, Nigel J. Mason, Anita Dawes, Philip D. Holtom, Robin J. Mukerji, Michael P. Davis,
ORAL PRESENTATIONS


POSTER


GRANT


[2] BRITISH COUNCIL - RESEARCHER EXCHANGE PROGRAM – 2007, for exchange visit to Catania Astrophysical Observatory, Italy. Value 2880 GBP.

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D Gerlich and M Smith `Laboratory astrochemistry: studying molecules under inter- and circumstellar conditions, Phys. Scr. 73, 2006, C25.


