Mass independent isotopic enrichment in ozone and its transfer to other molecules through exchange

A thesis submitted to

Gujarat University

for the degree of Doctor of Philosophy in Physics

By

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March, 2007

CERTIFICATE

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any University or Institution.

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To My Parents

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Acknowledgements

I would like to express my sincere gratitude and appreciation to my supervisor Professor S. K. Bhattacharya for his advice, criticism and providing me all possible facilities required for this work. His constant encouragement and untiring queries regarding the progress of the work greatly helped me to finish the thesis in the stipulated time. I thank him for his patience and encouragement that carried me on through difficult times. I also thank him for critically going through the manuscript and for making important suggestions towards its improvements.

I am greatly indebted to Prof. R. Ramesh for his encouragement and advice that helped to shape my research skills. His understanding of the subject, encouraging attitude and personal guidance has been the source of inspiration for me.

Special thanks to Prof. J. N. Goswami and Prof. S. Krishnaswami for the stimulating discussions I had with them on many occasions.

I gratefully acknowledge many fruitful discussions with Prof. S. V. S. Murty, Prof. M. M. Sarin, Prof. A. K. Singhvi, Dr. J. R. Trivedy , Dr. P. Panigrahi, Dr. Bhas Bapat, Dr. Dilip Angom, Dr. P. Subramanian and Dr. D. Banerjee. I sincerely thank them. I greatly acknowledge the help provided at some stage or the other by Dr. Sunil Singh, Dr. J. S. Ray, Dr. Navin Juyal, Dr. M. G. Yadav, Mr. R. D. Deshpande, Mr. Som Sharma, Mr. Ravi Bhusan and Mr. Anil Shukla.

I thank Prof. S. D. Rindani, Dr. P. Sharma and other members of the Academic Committee for critically reviewing the progress of my work and giving valuable suggestions at various stages of my research in this laboratory.

Special thanks are due to Mr. R. A. Jani and Mr. D. K. Rao for their help and support

in maintaining mass spectrometer and various instruments in the laboratory. I thank Mr. Pranav R. Adhyaru, Mr. G. D. Panchal and Mr. V. G. Shah for helping me in maintaining the electronics units. I truly acknowledge Mr. Sivasankaran, Mr. Kurup and Mr. Bankim for excellent and skillful glass blowing work.

I accord my thanks to all other members of the Planetary and Geosciences Division for providing a pleasant working atmosphere in the division during the entire course of my research.

I am also thankful to the staff members of PRL Library, Maintenance, Workshop, Liquid Nitrogen Plant and Computer Center for assisting me during the various phases of this journey.

I would like to thank Department of Space (DOS) for setting up the scholarship and providing support for the research.

I wish to express my sincere gratitude to my seniors, Dr. S. Chakraborty and Dr. P. Sanyal who taught me the experimental skills in my early days of research. I am thankful to my juniors, Sasadhar and Alok and other PRL friends who helped me in various ways. My special thanks to all the members of the 'STAIL- group' as scientific discussions with all of them have always been rewarding for me.

I take this opportunity to thank Vandana and Dilip. I am pleasantly obliged to Vandana for her careful and patient reading of the text and making useful suggestions. Special thanks to Dilip for helping me in LaTeX. I would also like to thank them for many relaxing evenings in the IIM canteen.

Last but not the least, I thank my parents for always being there when I needed them most and for supporting me through all these years. Without their support and sacrifice, I would not have reached this point.

Antra

Abstract

A large and unusual isotope effect in ozone is known for about more than two decades but its origin on a molecular level has been investigated only recently. At first, processes related to ozone molecular symmetry were thought to play a major role in its anomalous enrichment. But the recent measurements of various isotope specific formation rate coefficients of ozone showed that molecular symmetry alone cannot be the driving force for causing this anomaly. As of now, the underlying microscopic process causing such a large anomalous effect is not clearly understood. The recombination reaction of O and CO provides a unique opportunity to study the role of symmetry of the intermediate complex in causing anomalous isotope enrichment. The case of CO_2 is slightly simpler than ozone since, unlike ozone, no heavy symmetric CO_2 molecule is possible. Study of $O+CO\rightarrow CO_2$ reaction also gives an opportunity to quantify the mass dependent fractionation that occurs through analysis of carbon isotopes since carbon being the central atom in CO₂ is not affected by the symmetry related part of the enrichment process. One of the goals of the present work was to investigate the unusual oxygen isotope effect in CO₂ produced from O+CO reaction. A chemical reaction model KINTECUS was used to calculate the expected CO₂ composition based on available reaction rates and their modifications for isotopic variants of the participating molecules. A comparison of the two (experimental data and model predictions) shows that the product CO₂ is anomalously enriched in heavy oxygen isotopes. The enrichment is similar to that observed in case of O_3 produced by $O+O_2$ reaction and varies from 65 to 107‰ for ¹⁸O and 41 to 82‰ for ¹⁷O. The enrichment observed in CO₂ does not depend on the isotopic composition of the O atom or the sources from which it is produced. A plot of $\Delta(\delta^{17}O)$ versus $\Delta(\delta^{18}O)$ (two enrichments) shows

linear correlation with the best fit line having a slope of ~0.97±0.05. The value of $\Delta(\delta^{13}\text{C})$ (change in carbon isotopic composition of the product CO₂ from the initial CO) varies from -14.6 to 3.8‰ and the increase in δ -values correlates with decrease in CO pressure. This is because surface induced stabilization of intermediate complex CO₂* dominates at low pressure. No anomalous enrichment is observed in ¹³C of CO₂ as in case of oxygen.

Another important issue is related to the internal distribution of heavy oxygen isotopes in an ozone molecule. The distribution of heavy oxygen isotopes in ozone molecule does not obey the simple statistical rule. Several attempts have been made to measure the internal distribution of ¹⁸O in ozone molecule using remote sensing, TDLAS, FTAS techniques but with large uncertainty in measurement owing to small abundance of ¹⁸O. There is no study for the internal distribution of ¹⁷O whose abundance is still lower. Their studies show that for ¹⁸O, the abundance is more at base position than at apex position and the enrichment of ¹⁸O at both the base and apex position increases with increase in total enrichment in ozone. But there is no data available for ¹⁷O. Additionally, the distributions of both ¹⁸O and ¹⁷O are not known in cases when ozone is not enriched. We have determined ¹⁷O distribution using the available information in case of ¹⁸O by a novel method in which ozone was made to react with freshly cleaned silver foil. The analysis shows that internal distribution of heavy oxygen isotopes (¹⁸O and ¹⁷O) is not same which is contrary to what has been assumed in the past. The difference between terminal and central position enrichments is seen to be more in case of ⁴⁹O₃ than ⁵⁰O₃. For both ⁵⁰O₃ and ⁴⁹O₃, the difference between the two enrichments is not constant but decreases with increase in total ozone enrichment. The variation of the r⁵⁰ (the ratio of ¹⁸O abundance in terminal to that in apex position) is from 1.93 to 2.13 whereas the corresponding variation in r^{49} (for 17 O) is from 2.04 to 2.15. The value of r^{49} is higher than that of r^{50} by an amount ~ 0.06 due to effect of zero point energy(ZPE) difference.

In case of zero-enriched ozone, the symmetric species is more enriched in ¹⁸O and ¹⁷O as compared to asymmetric species which is opposite to what is observed in case of enriched ozone samples. This is because symmetric ozone has the heavy isotope located in more tightly bound position and is preferred as compared to the purely statistical distribution. For zero enriched ozone, the value of r^{50} and r^{49} is always less than two. The r^{50} value lies within 1.76 to 1.88 whereas the r^{49} value lies within 1.88 to 1.99. The exact value cannot be derived due to limitation in knowledge of fractionation correction.

The results of this study can be used in understanding the observed anomaly in different oxygen containing species in earth's atmosphere. In stratosphere, the anomalous isotopic signature of ozone gets transferred by interaction of ozone with other trace gases, like CO₂, CO. For example, stratospheric CO₂ is found to be anomalously enriched in heavy oxygen isotopes and the slope relating the two enrichments is found to be about ~ 1.7 which is radically different from that of ozone presumed to be the origin of the enrichment. We applied the information of intramolecular isotopic distribution in ozone to explain the transfer mechanism of heavy oxygen isotopes from ozone to CO₂ (with particular reference to the case of stratospheric CO₂) by a chemical kinetic reaction model. The exchange rate is faster for ¹⁷O than that of ¹⁸O yielding a slope relating the two enrichments greater than one. It is clear from the model that neither the enrichment of ¹⁷O in CO₂ nor the slope can be explained by simple mixing of ozone with CO₂.

It is known that the $O(^{1}D)$ - CO_{2} exchange is a spin forbidden reaction but takes place due to spin-conserving interactions (like spin-orbit interaction). To explain the data we propose that the nuclear spin (5/2) of ¹⁷O adds an extra component in the total spin-orbit coupling term which enhances the exchange rate of ¹⁷O(¹D) relative to ¹⁸O(¹D). A nuclear spin of nearly 12% in exchange of ¹⁷O relative to ¹⁸O is required to get good agreement with observed results.

CHAPTER **1**

Introduction

The term *isotopes*, coined by Frederick Soddy (1914), literally means *same place* in the Periodic Table of elements. Isotopes of a particular element are atoms which contain different number of neutrons in their nuclei. For example, oxygen has three stable isotopes: ¹⁶O, ¹⁷O and ¹⁸O. Their respective abundances in atmosphere are 99.763%, 0.0375% and 0.1995%. The various isotopes of an element have slightly different chemical and physical properties partly because of their mass differences and thus offer an excellent way of observing the influence of atomic mass on chemical reactions.

The stable isotopes have a wide range of applications. Stable isotope ratios are used as *tracers* for understanding physical, chemical, and biological processes in nature. The variation in isotope ratios provides information about the relative strengths of different sources and sinks of trace gases and about the transport processes which influence its distribution. For example, variations in the ratio of stable isotopes of hydrogen and oxygen give information about the processes that govern the hydrosphere and lower atmosphere. This also helps in understanding the origin, phase transitions and transport of water in the hydrological cycle. Oxygen and hydrogen isotope ratios provide remarkable information on the origin of rocks and on the processes that subsequently affect them. Another famous application relates to life cycle of oceanic foraminifera where oxygen isotopic composition of their shells is indicative of the temperature at which the calcium carbonate in the shell exchanged its oxygen isotopes with the surrounding water. This study is useful in paleoceanography and can be used to reconstruct the Earth's past climate. The stable isotope

ratios are also used as tracers in various reactions.

1.1 Basic definitions

This section deals with definitions and terminologies used in the study of isotopes. The isotopic composition of a specific element in a sample is usually expressed as the ratio of abundance of the minor isotope to the abundance of the major isotope. For example,

$${}^{18}\mathrm{R} = \frac{[{}^{18}\mathrm{O}]}{[{}^{16}\mathrm{O}]} = 0.0019997$$

where '[]' denotes concentration of a given isotope in a sample. Isotopes of an element behave slightly differently in many physical, chemical and biological processes in nature such as evaporation, condensation of water, mixing of two or more sources of fluid or the metabolic activity of organisms which results in fractionation. Isotope fractionation is a physical phenomenon which causes changes in the relative abundance of isotopes due to their differences in mass or other properties.

The process of isotope fractionation in a physical or chemical change of phase A \rightarrow phase B is mathematically described by comparing the isotope ratios of the two phases. The isotope fractionation factor (α) is then defined as the atomic ratio of heavy to light isotope of the same element present in two phases A and B,

$$\alpha = \frac{R_A}{R_B} \tag{1.1}$$

For example, the fractionation factors (α_{l-v}) for the water liquid-vapor phase transition in equilibrium are 1.0098 and 1.084 at 20°C for ¹⁸O and ²H, respectively which means that the first phase (or liquid water) has more abundance of heavy isotopes of oxygen and hydrogen compared to the second or vapor phase.

In general, isotope effects are small. Fractionation process imparts a small variation in isotope concentration (change occurs at fifth or sixth decimal places). Therefore, the deviation of α from 1 is widely used rather than the fractionation factor itself and is expressed in delta (δ) notation which is a measure of relative deviation of a sample from the respective reference (or standard) material. Because δ is a small number, it is generally given in % (per mil, equivalent to parts per thousand).

For example, in case of carbon, the natural abundance of $\binom{^{13}\text{C}}{^{12}\text{C}}$ ratio $^{^{13}}\text{R}$ is commonly compared to Vienna Peedee Belemnite (V-PDB), a virtual scale identical to an internationally accepted standard CaCO₃ deposit from the Peedee formation of South Carolina with $^{^{13}}\text{R}$ =0.0112372. A positive $\delta^{^{13}}\text{C}$ value indicates that the sample has more $^{^{13}}\text{C}$ than the standard or is *enriched*. Negative values indicate *depletion* of $^{^{13}}\text{C}$ in the sample. The commonly accepted standard for hydrogen and oxygen is Vienna Standard Mean Ocean Water (V-SMOW) and the standard for nitrogen is atmospheric N₂.

1.2 Causes for isotopic fractionation

A chemical reaction occurs due to collision of the molecules involved and making and breaking of bonds within them. Both are molecular property which depends on its mass.

The heavier isotopic molecules have a lower mobility. The kinetic energy of a molecule is determined by temperature:

$$\frac{3}{2}kT = \frac{1}{2}mv^2 \tag{1.2}$$

where, k = Boltzmann constant, T = absolute temperature, m= molecular mass, v = average molecular velocity. Therefore at same temperature, all isotopes have same kinetic energy but different translational velocity depending upon their masses. The heavier molecules have a lower velocity. Since collision frequency depends on translational velocity, heavier molecules have lower reaction rate. The lighter molecules react faster and get accumulated in the product whereas the heavier molecules do so in the reactant.

The second reason for isotopic fractionation is due to difference in bond energy of different isotopic molecules. Bonds involving lighter isotopes are broken more easily than equivalent bonds of heavier isotopes because molecules containing heavy isotopes have a higher dissociation energy and are more stable. Hence, chemical reaction rates where such a bond is broken will show an isotope effect. However, in a given chemical reaction, the isotope effect alters the reaction rate only slightly because the energy differences associated with isotope effects are about 1000 times smaller than the total Gibbs free energy change (ΔG) associated with the reaction.

1.3 Mass dependent fractionation

Based on published theoretical and experimental researches in Isotope Geochemistry, H. Craig proposed a simple rule relating fractionation of the isotopes of an element and their mass. For example, in case of oxygen:

$$\left(\frac{{}^{17}R_1}{{}^{17}R_2}\right) = \left(\frac{{}^{18}R_1}{{}^{18}R_2}\right)^{0.52} \tag{1.3}$$

where ${}^{17}R_1$, ${}^{18}R_1$ and ${}^{17}R_2$, ${}^{18}R_2$ represents ${}^{17}O_{16O}$ and ${}^{18}O_{16O}$ ratio in phase 1 and 2 respectively. This rule expressed in δ - notation for cases of small fractionation in oxygen isotopes is given by,

$$\delta^{17} \mathcal{O} = 0.52 \times \delta^{18} \mathcal{O} \tag{1.4}$$

The slope ~ 0.5 is a feature of mass dependent fractionation in oxygen which means that the magnitude of fractionation is proportional to the relative mass difference of the isotopes involved. The exact value of the slope may vary from 0.50 to 0.52 depending on the processes involved. Measurements of oxygen isotopic composition in many natural samples e.g. terrestrial and lunar rocks, minerals, water (both oceanic and meteoric) and air O₂ show $\delta^{17}O/\delta^{18}O \sim 0.5$. Figure 1.1 shows this graphically for many types of oxygen containing samples with a best-fit mass dependent fractionation line having slope 0.5. $\frac{17O}{16O}$ and $\frac{18O}{16O}$ ratios of nearly all oxygen -bearing terrestrial materials follow this relationship, with small systematic differences depending on the actual fractionation processes involved.

There are two categories of isotope effects: kinetic and equilibrium.

1.3.1 Kinetic isotope effect

Kinetic fractionation is associated with dynamic processes that are fast, incomplete or unidirectional like evaporation, diffusion, dissociation reactions and biological effects which results from motions that are described by simple classical mechanics. The magnitude of a kinetic isotope fractionation depends on the reaction pathway, reaction rate, and relative bond energies of the bonds being formed or broken by the reaction.



Figure 1.1: Oxygen isotopic compositions of various oxygen bearing species.

1.3.2 Equilibrium isotope effect

Equilibrium isotopic fractionation involves transfer or redistribution of isotopes in equilibrated system consisting of two or more phases which have a common element. The equilibrium isotope effects usually reflect the relative differences in bond strengths of isotopes present in various components of system. The heavy isotope concentrates in the component in which the element is bound more strongly. *H. C. Urey* [1947] explained how the mass dependence of vibrational and rotational frequencies alters the quantum mechanical partition functions of isotopomers and produces a measurable difference in chemical equilibria or chemical reaction rates, which causes isotopic fractionation.

1.4 Anomalous or mass independent fractionation

There are several other processes in nature which show significant deviation from the mass dependent rule and are usually referred to as anomalous or mass independent. In case of oxygen, the deviation from the mass dependent fractionation is expressed as

$$\Delta^{17} O = \delta^{17} O - 0.5 \times \delta^{18} O \tag{1.5}$$

This gives a quick measure of mass independent fractionation, i.e., the excess or deficiency in ¹⁷O relative to that expected from simple mass dependence.

1.4.1 Examples of Anomalous isotope effect

A large deviation from mass dependent relation of oxygen was observed by *Clayton et al.* [1973] in high temperature Ca, Al rich inclusions in the Allende meteorite with an isotope composition $\frac{\delta^{17}O}{\delta^{18}O} \sim 1$ rather than 0.5 (shown in Figure 1.1). Martian meteorites also possess mass independent oxygen isotopic composition. The oxygen isotopic compositions in water extracted from hydrated minerals and CO₂ extracted from carbonates from SNC (Shergottites, Nakhlites, Chassignites) [*Karlsson et al.*, 1992; *Farquhar et al.*, 1998, 2000] group of Martian meteorites show anomalous behavior which are known to be produced by gas phase chemical processes and are subsequently transferred to regolithic materials. There are many other solid reservoirs (both from extra-terrestrial and terrestrial) where mass-independent isotopic effects have been observed [*Thiemens et al.*, 2001].

In earth's atmosphere, stratospheric ozone [*Mauersberger et al.*, 1981, 1987, 2001; *Rinsland et al.*, 1985; *Abbas et al.*, 1987; *Schueler et al.*, 1990; *Meier and Notholt*, 1996; *Irion et al.*, 1996; *Johnson et al.*, 2000; *Lammerzahl et al.*, 2002; *Haverd et al.*, 2005; *Liang et al.*, 2006] show enrichment in heavy isotopes ¹⁷O and ¹⁸O relative to the parent molecular oxygen reservoir from which it is formed. Both ¹⁷O and ¹⁸O are enriched by ~ 100‰ and δ ¹⁷O is not half of δ ¹⁸O as expected in case of normal mass dependent fractionation process.

Besides ozone, this type of anomalous effect has also been observed in a wide range of atmospheric molecules like CO₂ [*Gamo et al.*, 1989, 1995; *Trolier et al.*, 1996; *Thiemens et al.*, 1991, 1995a, 1995b; *Brenninkmeijer et al.*, 1995; *Alexander et al.*, 2001; *Lammerzahl et al.*, 2002; *Boering et al.*, 2004; *Bhattacharya et al.*, 2006a], N₂O [Yoshida and Matsuo, 1983; Johnston et al., 1995; *Rahn and Wahlen*, 1997; *Cliff et al.*, 1997, 1999; Yoshida and Toyoda, 2000; *Rockmann et al.*, 2001a, 2001b; *Kaiser et al.*, 2002; *McLinden et al.*, 2003; *Morgan et al.*, 2004; *Yung et al.*, 2004] and CO [*Brenninkmeijer et al.*, 1995; *Huff and Thiemens*, 1998; *Rockmann et al.*, 1998b] demonstrating that the non mass dependent enrichment processes are not restricted to ozone formation [*Katakis and Taube*, 1962; *Thiemens*, 1999; *Lyons*, 2001; *Brenninkmeijer et al.*, 2003c]. Mass independent enrichment has also been observed in the reactions O + CO \rightarrow CO₂ [*Bhattacharya and Thiemens*, 1989a, 1989b; *Pandey and Bhattacharya*, 2006], SF₅ + SF₅ \rightarrow S₂F₁₀ [*Bains-Sahota and Thiemens*, 1989],

isotopic exchange in case of $O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$ [Yung et al., 1991, 1997; Wen and Thiemens, 1993; Johnston et al., 2000; Chakraborty and Bhattacharya, 2003d; Boering et al., 2004; Shaheen et al., 2006; Liang et al., 2006], NO+O₃ \rightarrow NO₂+O₂ [van den et al., 1982, 1984] and reaction OH + CO \rightarrow CO₂ + H [Rockmann et al., 1998a, 1999; Feilberg et al., 2002; Chen and Marcus, 2005, 2006]. Oxygen and sulfur isotopic compositions of atmospheric aerosol (particulate) nitrate [Michalski et al., 2002, 2003] and sulfate [Lee et al., 2001, 2002; Savarino et al., 2000, 2003; Thiemens et al., 2001; Alexander et al., 2002; Romero and Thiemens, 2003; Baroni et al., 2007] show mass-independent behavior and also demonstrate that mass independent characters are well preserved in solids.

1.5 Anomalous isotope effect in Ozone

Chapman reactions describe the ozone formation mechanism in atmosphere (ignoring isotope-specific processes) as:

$$O_2 + h\nu \to O + O \tag{1.6}$$

$$O + O + M \rightarrow O_2 + M$$
 (1.7)

$$O_2 + O + M \rightarrow O_3 + M \tag{1.8}$$

$$O_3 + h\nu \to O + O_2 \tag{1.9}$$

$$O_3 + O \to 2O_2 \tag{1.10}$$

In the middle and upper stratosphere, atomic oxygen is produced by dissociation of molecular oxygen by solar photons of energy \sim 5.2 eV which recombines with oxygen molecule to produce ozone in presence of a third body.

The ozone molecule forms an open triangle and has a binding energy of 1.1eV. This low energy makes ozone a very reactive molecule. Since ozone molecule can be formed from three stable oxygen isotopes ¹⁶O, ¹⁷O and ¹⁸O, a large number of isotopic combinations are possible. Because of its triangular geometry the singly -substituted heavy oxygen atom can be found in the apex or at either end (terminal position) of the triangle. In the first case, ozone molecule is symmetric; when the heavy oxygen atom is located at either end, the molecule is asymmetric.

Whenever oxygen atoms are available to react with molecular oxygen and form ozone, fast isotope exchange reactions rapidly recycle the atoms through many molecules before

ozone is produced by collisional stabilization of an atom-diatom pair. The exchange reaction is about 1000 times faster than ozone formation. The equations describing isotope exchange equilibria are:

$${}^{18}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \rightleftharpoons {}^{18}\text{O}{}^{16}\text{O} + {}^{16}\text{O} \tag{1.11}$$

$$^{17}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \Rightarrow {}^{17}\text{O}{}^{16}\text{O} + {}^{16}\text{O}$$
 (1.12)

Since the exchange reactions are much faster than the ozone formation process, O-atom is always in equilibrium with the oxygen gas mixtures. Because of the different zero-point energies of the O₂ molecules that participate in the above exchange reactions, the rate coefficients are higher for exothermic processes, from left to right in equation 1.11 and 1.12 and lower for endothermic (right to left). Thus the distribution of the three oxygen isotopes is governed by fast exchange which would lower ¹⁸O and ¹⁷O in atomic oxygen reservoir compared to what would be expected from statistically distributed O-isotopes in molecular oxygen and thus the two heavy isotopomers ⁴⁹O₃ and ⁵⁰O₃ are supposed to be lower than expected. However, measurements showed enrichments in ⁴⁹O₃ and ⁵⁰O₃ demonstrated that a new and anomalous isotope fractionation has been found. This surprising effect cannot be explained by standard mass dependent processes.

1.5.1 Atmospheric ozone and laboratory produced ozone

The first measurement of isotopic composition of stratospheric ozone done by *Mauersberger* [1981] showed that stratospheric ozone possesses enormously large enrichment in ¹⁸O (as high as 400‰). But there was a large uncertainty in those measurements. It was later showed that there is nearly equal ¹⁷O and ¹⁸O enhancements but they are of variable magnitude. A set of more precise ozone isotope measurements [*Schueler et al.*, 1990] confirmed that the isotopic composition of stratospheric ozone is mass independently fractionated with $\frac{\delta^{17}O}{\delta^{18}O} \sim 1$.

Several researchers have carried out isotope measurements of stratospheric ozone using a variety of techniques from mass spectrometry to infrared spectroscopy [*Abbas et al.*, 1987; *Goldman et al.*, 1989; *Irion et al.*, 1996; *Meier and Notholt*, 1996; *Johnson et al.*, 2000; *Wolf et al.*, 2000; *Krankowsky et al.*, 2000; *Mauersberger et al.*, 2005]. Measurements

of the stratospheric ozone isotopic composition by ground-based FTIR (Fourier Transform Infrared) instrumentation, satellite measurements using ATMOS (Atmospheric Trace Molecule Species Experiment) have also confirmed these measurements and have provided further details of the isotopomeric distribution of ozone in the stratosphere [*Irion et al.*, 1996; *Haverd et al.*, 2005].

The first chemically produced mass independent isotopic fractionation was discovered in ozone produced in the laboratory by O_2 discharge [*Thiemens et al.*, 1983, 1987, 1988]. It was observed that ozone was produced with equal ¹⁷O and ¹⁸O enrichment with respect to the starting molecular oxygen.

The effect of temperature [*Morton et al.*, 1990], pressure [*Thiemens et al.*, 1988, 1990; *Guenther et al.*, 1999; *Bhattacharya et al.*, 2002] and presence of molecular third-body [*Anderson et al.*, 1997; *Sehested et al.*, 1998; *Guenther et al.*, 2000] on ozone isotope anomaly have also been investigated in laboratory experiments. At 100 mbar pressure or below and at nearly room temperature, the enrichments measured are about 110 and 130‰ in $^{49}O_3$ and $^{50}O_3$ respectively [*Mauersberger et al.*, 1993].

The enrichment decreases towards high pressure. In a pressure range 200-600 torr (at room temp), 4.9-160 torr (liquid nitrogen trapping) the enrichment are: $\delta^{18}O \cong \delta^{17}O \cong$ 85-100 ‰. In the pressure region 8 to 45 atmospheres, the enrichment in ¹⁸O and ¹⁷O decreases by nearly 84‰. For pressures between 45 to 66 atmosphere, the enhancement decreases by 6‰ and is absent at 56 atmospheres. For pressures 56 to 87 atmosphere, the product ozone is depleted in ¹⁸O in a nearly mass dependent fashion [*Thiemens and Jackson*, 1990].

The temperature dependence of the isotope fractionation strongly influences the magnitude of the enrichments in ⁴⁹O₃ and ⁵⁰O₃. *Morton et al.*[1990] measured the change between 170 K and 370 K by analyzing ozone generated in pure natural oxygen in a photolysis-recycling process and showed that the enrichment increases with increase in temperature. Photolysis of air produces O₃ isotopically similar to that from pure O₂, indicating that the effect of a different (non-O₂) third body is negligible on ozone anomaly. It was also concluded from the experiment that the ozone isotope effect is an intrinsic molecular effect and does not depend on the isotopic composition of the starting O₂ gas. The enrichment or depletion in the product isotopomers is determined by the pressure and temperature of the oxygen gas in which ozone is produced.

1.5.2 Rate coefficients of isotope specific ozone formation channels

An important advancement in the development of a theory for the fractionation processes occurred after the investigation of the relative rates of ozone formation as a function of isotopic substitution [*Yang and Epstein*, 1987; *Mauersberger et al.*, 1993, 1999; *Anderson et al.*, 1997; *Janssen et al.*, 1999, 2001, 2002; *Wolf et al.*, 2000; *Tuzson and Janssen*, 2005; *Tuzson* 2005]. Oxygen heavily enriched in ¹⁷O was used to produce various ozone isotopomers like ¹⁶O¹⁷O¹⁷O of mass 50 or ¹⁷O¹⁷O¹⁷O of mass 51 (Figure 1.2). *Anderson et al.* [1997] measured the rate coefficients of four selected ozone formation channels. Later on *Janssen et al.* [2001] developed a tunable diode laser (TDL) experiment in combination with mass spectrometer analysis to measure the relative rates for the ¹⁶O-¹⁸O system which are summarized in Table 1.1. This analysis was another important contribution to the discovery of the origin of the ozone isotope effect.



Figure 1.2: Oxygen isotopic fractionation for all possible ozone isotopologues. Ozone was produced (at 70 torr and room temperature) in two isotopically enriched oxygen mixtures of well-known composition. The statistical abundance of each isotopomer was calculated. The isotopic fractionation was derived from the measured values and the calculated values. Measured enrichment or depletion of all possible ozone isotopomers (normalized to ⁴⁸O₃) are shown. The notation 6,7 and 8 denotes ¹⁶O,¹⁷O and ¹⁸O respectively.

Reaction	Ozone mass	Relative rate coefficient
$^{16}O + ^{16}O^{16}O \rightarrow ^{16}O^{16}O^{16}O$	48	1.0
$^{18}O + ^{16}O^{16}O \rightarrow ^{18}O^{16}O^{16}O$	50	0.92
$^{16}O + ^{18}O^{18}O \rightarrow ^{16}O^{18}O^{18}O$	52	1.50
$^{18}O + ^{18}O^{18}O \rightarrow ^{18}O^{18}O^{18}O$	54	1.03
$^{17}O + ^{16}O^{16}O \rightarrow ^{17}O^{16}O^{16}O$	49	1.03
$^{17}O + ^{18}O^{18}O \rightarrow ^{17}O^{18}O^{18}O$	53	1.31
$^{18}O + ^{17}O^{17}O \rightarrow ^{18}O^{17}O^{17}O$	52	1.03
$^{16}O + {}^{17}O^{17}O \rightarrow {}^{16}O^{17}O^{17}O$	50	1.23
$^{17}O + ^{17}O^{17}O \rightarrow ^{17}O^{17}O^{17}O$	51	1.02
$^{16}O + ^{16}O^{18}O \rightarrow ^{16}O^{16}O^{18}O$	50	1.45
$^{16}O + ^{18}O^{16}O \rightarrow ^{16}O^{16}O^{18}O$	50	1.08
$^{18}O + ^{16}O^{16}O \rightarrow ^{16}O^{18}O^{16}O$	50	0.01
$^{18}O + ^{16}O^{18}O \rightarrow ^{16}O^{18}O^{18}O$	52	1.04
$^{18}O + ^{18}O^{16}O \rightarrow ^{18}O^{16}O^{18}O$	52	0.92
$^{16}O + ^{18}O^{18}O \rightarrow ^{18}O^{16}O^{18}O$	52	0.03

Table 1.1: *Measured rate coefficients relative to the standard reaction of* ${}^{16}O + {}^{16}O{}^{16}O + M$ *are shown.*

It was observed that the enrichment factor (normalized to ¹⁶O¹⁶O¹⁶O) varies significantly depending on the type of ozone isotopologue. ¹⁶O¹⁷O¹⁸O species has a maximum enrichment of about 180 ‰ with respect to the purely symmetric species whereas a minimum enrichments of about 80 ‰ was noted for mass 53 amu (¹⁷O¹⁸O, ¹⁸O, ¹⁸O¹⁷O¹⁸O). The fastest rates are observed for reactions that lead to production of ¹⁶O¹⁶O¹⁸O and ¹⁶O¹⁸O¹⁸O ozone. The reactions producing symmetric ¹⁸O¹⁶O¹⁸O, ¹⁶O¹⁸O¹⁶O ozone are significantly slower. This shows that there is a remarkable difference in rate for a structural isotopic difference (Figure 1.2).

To get an insight in the variation of rate constant, *Janssen et al.* [2001] pointed out that for asymmetric ozone molecules, a given channel of formation is always associated with an exchange reaction. For example,

$${}^{16}\text{O} + {}^{16}\text{O}{}^{18}\text{O} \rightleftharpoons {}^{18}\text{O} + {}^{16}\text{O}{}^{16}\text{O} : \text{Exchange}$$
 (1.13)

and

$${}^{16}\text{O} + {}^{16}\text{O}{}^{18}\text{O} + \text{M} \to {}^{16}\text{O}{}^{16}\text{O}{}^{18}\text{O} + \text{M} : \text{Ozone formation}$$
 (1.14)

In such cases, the ozone formation rate (in equation 1.14) is found to correlate with change in ZPE of the oxygen molecule in the corresponding exchange reaction (i.e., reaction 1.13) - the rate is high if the change is positive and large. In the above example,

$\Delta ZPE = ZPE(^{16}O^{16}O) - ZPE(^{16}O^{18}O)$

which is +23 cm⁻¹ and the corresponding rate is 1.45 (normalized) close to the largest observed. This becomes clearly evident when all the data are plotted (Figure 1.3). The graph suggests that endothermic exchange reactions (in eqn 1.13) carry high rate coefficients. This is because in an endothermic process, the exit channel has an energy barrier due to the higher zero point energy of the product diatom which results in a longer lifetime of the collision complex and thus to an increased probability of becoming stabilized to an ozone molecule. In contrast, exothermic reactions have smaller rate coefficients as a result of shorter complex lifetimes.



Figure 1.3: A plot of relative rate coefficients of isotope-specific ozone reactions vs. zero point energy differences in oxygen molecules of the corresponding isotope exchange reactions. Exothermic or endothermic reactions are characterized by $\Delta(ZPE) < 0$ and $\Delta(ZPE) > 0$ respectively; full and open circle denotes reactions which are collisions with homonuclear diatoms and heteronuclear molecules. The data points clearly show a linear correlation with the ZPE change. The line is a best fit to the collisions with homonuclear oxygen molecules. The full and open squares denote reactions involving neutral exchange and are well below the line. [Janssen et al., 2001]

1.6 Theoretical developments

After the discovery of mass independent isotope effect in ozone, several theoretical models were developed by various groups to explain this unique isotope effect [*Valentini*, 1987; *Robert et al.*, 1988; *Bates*, 1990; *Gellene*, 1992, 1993, 1996; *Griffith and Gellene*, 1992; *Hathorn and Marcus*, 1999, 2000, 2001; *Gao et al.* 2001a, 2001b, 2002; *Marcus*, 2004; *Robert and Camy-Peret*, 2001; *Charlo and Clary*, 2002; *Miklavc and Peyerimhoff*, 2002; *Pack and Walker*, 2004; *Robert*, 2004].

In 1986, *Heidenreich and Thiemens* first suggested that molecular symmetry plays an important role in the isotopic fractionation process associated with ozone formation. They proposed that the lifetime of the excited state O_3^* molecule, formed during an oxygen atom-molecule collision, is enhanced for the asymmetric species with respect to the symmetric species. This enhanced lifetime arises owing to the doubling of the asymmetric states with respect to the symmetric states, which provide a more effective energy distribution.

Recently, *Gao and Marcus* [2001a] developed a semi-empirical model based on modification of Rice, Ramsperger, Kassel, Marcus (RRKM) theory of unimolecular reaction rate to explain the strange and unconventional ozone isotope effect. According to this theory, ozone formation process as given below involves various steps:

$${}^{x}O + {}^{y}O{}^{z}O \to ({}^{x}O{}^{y}O{}^{z}O)^{*}$$
(1.15)

where x, y, z may be the same isotope or any combination of different isotopes ¹⁶O, ¹⁷O and ¹⁸O. Equation 1.15 describes the formation of a vibrationally excited ozone complex $(^{x}O^{y}O^{z}O)^{*}$. The vibrational-rotational energy of $(^{x}O^{y}O^{z}O)^{*}$ is assumed to be statistically distributed among its vibrational-rotational modes, consistent with the given total energy E and total angular momentum J. The collisional complex $(^{x}O^{y}O^{z}O)^{*}$ can redissociate,

$${}^{x}O + {}^{y}O{}^{z}O \Leftrightarrow ({}^{x}O{}^{y}O{}^{z}O)^{*} \Leftrightarrow {}^{x}O{}^{y}O + {}^{z}O$$
(1.16)

or lose its excess energy by collisions with bath gas molecules and eventually form a stabilized ${}^xO^yO^zO$ molecule. The unimolecular dissociation rate constant k_{EJ} for a vibrationally excited molecule of vibrational-rotational energy E and total angular momentum J is

$$k_{\rm EJ} = N_{\rm EJ} / h \rho_{\rm EJ} \tag{1.17}$$

where N_{EJ} is number of channels (states) perpendicular to the reaction coordinate which are accessible to the transition state for a particular energy E and rotational state J. ρ_{EJ} is the density (number per unit energy) of quantum states of the vibrationally excited molecule. Since this theory is a quantum mechanical theory, zero point energy of the two product channels is also included. After the formation of the vibrationally excited molecule, the subsequent redistribution of the energy among its vibrational-rotational modes at the given E and J proceeds at some finite rate and may be incomplete during the typical life time of the molecule. In order to form stable molecule (O₃), it has to redistribute its excess energy among its various modes of vibration within its typical life time. If k_{EJ} is large, dissociation of the complex is fast and, therefore, ozone formation for that isotope combination is less.

To produce the anomalous isotope effect in ozone the original statistical RRKM theory was slightly modified. In addition to the usual conventional symmetry number of 2, two other factors were introduced: η factor and a partitioning factor Y. η is a empirical non-statistical factor which describes the difference in density of dynamically active O₃* states in symmetric and asymmetric ozone molecule. It is argued that the value of ρ_{EJ} (for both symmetric and asymmetric species) is less than the statistical value. The decrease in the ρ_{EJ} value is more for symmetric species ($^{x}O^{y}O^{x}O$) than for asymmetric species ($^{x}O^{x}O^{y}O$). This is because symmetry restricts the number of intramolecular resonances and energy coupling terms like anharmonic vibration-vibration and Coriolis vibration-rotation. So for the symmetric molecule the density of the reactive (or coupled) quantum states is less as compared to asymmetric molecule.

Therefore, the non-statistical effect of $\rho_{\rm EJ}$ is expected to be greater for ${}^{x}O^{y}O^{x}O$ than for ${}^{x}O^{x}O^{y}O$. In addition to the number of states, asymmetric molecule has additional stabilization pathways (more coupled states) which helps faster energy transfer. The asymmetric species can redistribute its excess energy better within its typical life time as compared to symmetric species and is more likely to couple to the exit channel i.e. unimolecular dissociation rate $k_{\rm EJ}$ is relatively less for asymmetric species i.e., it has more propensity to form a stable molecule.

In this model, there is no mass dependency but rather a subtle symmetry factor that produces the anomalous ozone. η effect is dominant in determining the mass-independent isotope enrichments in scrambled conditions and it was shown that the Y-effect vanishes

in such a case. The value of η is chosen to be 1.18 to fit the experimental data. In actual calculation, the density of states of the symmetric molecules are lowered by this factor to reduce its relative formation rates. Two parameters were adjusted to fit the measured relative formation rates for the two extreme cases: 0.92 for the reaction ${}^{18}\text{O}{+}^{32}\text{O}_2$ and 1.53 for the reaction ${}^{16}\text{O}{+}^{32}\text{O}_2$. The chosen value of η is seen to match the experimental observation that the formation rates for the symmetric molecules are about 20% below the linear fit curve [Figure 1.3].

The second factor (Y) is invoked to explain the mass-dependence observed in the recombination rates. This factor depends on the differences in zero-point energies of the two transition states that connect with isotopically different O_2 molecules.

The two key isotope effects of this theory, determined by η and Y, are symmetry driven. The Y values are responsible for the large differences in individual rate constants and their ratios. The origin of η is also a consequence of symmetry. It is predicted from the theory that in a gas phase reaction whenever the intermediate has a symmetry, the η factor comes into the picture.

By adjusting several parameters, the experimental data are well reproduced with this model. *Gao and Marcus* calculated the exchange reaction rate coefficients, relative formation rate coefficients for the 15 known rates and predicted others. This model not only accounts for the ozone isotopic measurements, but also extends fundamental understanding of gas phase reaction and collisional processes. It helps in developing a theoretical structure to show that the observed oxygen isotope effect is general and not a specific reaction feature confined to ozone. Recently, the work has been extended to explain the mechanism for the production of mass-independent oxygen isotopic components on the surface of solids under nebular conditions [*Marcus*, 2004].

An independent quantum mechanical approach was developed by *Babikov et al.* [2003a, 2003b] to calculate the energy transfer in processes by which metastable ro-vibrational states of ozone are formed and then stabilized by collisions with a third body. He calculated the life-time of the collision resonant states and could show qualitative difference among them. The starting point was the reaction:

$${}^{x}O + {}^{y}O{}^{z}O \Leftrightarrow ({}^{x}O{}^{y}O{}^{z}O)^{*} \Leftrightarrow {}^{x}O{}^{y}O + {}^{z}O$$
(1.18)

As mentioned before, the metastable states $(^{x}O^{y}O^{z}O)^{*}$ can be formed from and decay

to either the right-or left- hand side of this reaction. The ZPE of the O_2 molecules on the right and left hand sides will be different for different oxygen isotopes involved and thus the above reaction can be slightly exothermic or endothermic and exhibit slightly different rates. For example, ¹⁶O¹⁸O¹⁸O molecule can be formed in the following two recombination reactions:

$${}^{16}\text{O} + {}^{18}\text{O}{}^{18}\text{O} + \text{M} \Rightarrow {}^{16}\text{O}{}^{18}\text{O}{}^{18} + \text{M}$$
 (1.19)

$${}^{16}O^{18}O + {}^{18}O + M \Rightarrow {}^{16}O^{18}O^{18}O + M$$
 (1.20)

Thus, there are two entrance channels for ${}^{16}O^{18}O^{18}O$: ${}^{16}O + {}^{18}O^{18}O$ and ${}^{16}O^{18}O + {}^{18}O$ [Figure 1.4].



Figure 1.4: Schematic for the formation of ${}^{16}O^{18}O^{18}O^{18}O$ isotopologue. The metastable states, $({}^{16}O^{18}O^{18}O)^*$ above the Δ ZPE energy can be formed from both entrance channels: ${}^{16}O^{+18}O^{18}O$ on right and ${}^{16}O^{18}O^{+18}O$ on the left. The metastable states in the Δ ZPE part of the spectrum are formed only from the ${}^{16}O^{+18}O^{18}O$ entrance channel. The metastable states formed in the energy range between zero and Δ ZPE are responsible for the anomalous difference in rates for the two reaction channels. The experimentally measured relative rate of formation of the two channels are 1.53 and 0.98 for the right and left channels. [Babikov et al., 2003a, 2003b]

Experimentally, reactions (1.19 and 1.20) exhibit very different rates: 1.53 and 0.98 respectively [*Janssen et al.*, 2001] relative to the reactions with all atoms being ¹⁶O. The energy difference between the two entrance channels is the Δ ZPE. The metastable states at energies above the Δ ZPE can be formed from both entrance channels. However, the metastable

states at energies below the Δ ZPE can be formed only from the lower entrance channel, ¹⁶O + ¹⁸O¹⁸O [Figure 1.4]. Thus, the metastable states formed in the energy range between zero and Δ ZPE are responsible for the anomalous difference in rates for reactions (1.19 and 1.20). The above considerations were confirmed by *Babikov et al.*[2003a, 2003b] who calculated the life time of the collision complex and showed that the spectra of metastable states exhibit very non-statistical features: the lower part of the spectra (below Δ ZPE, E<29 K for ¹⁶O¹⁸O¹⁸O) contain many metastable states with lifetimes in the picoseconds but the higher energy region of the spectra is very sparse and contains only a few such resonances resulting in less efficient stabilization. Thus, the change in zero point energy is the dominant factor in controlling the lifetimes of the O₃* and producing the large differences in the relative rates.

1.7 Motivation for Thesis

A large and unusual isotope effect in ozone is known for about more than two decades but the origin of anomalously large enrichment of heavy oxygen isotopes in ozone on a molecular level has been investigated only recently. The processes related to ozone molecular symmetry were thought to play a major role but the exact mechanism was not clear. Subsequent measurements of various isotope specific formation rate coefficients of ozone showed that molecular symmetry plays a subtle role in causing this anomaly [*Gao and Marcus*, 2000, 2001, 2002]. As discussed above, the recently proposed modified RRKM theory calculates isotopic fractionation in ozone produced by $O+O_2$ recombination reaction under restrictions of symmetry and argues that the isotopic enrichment crucially depends on the symmetry of the intermediate complex produced during the collision.

As of now, the underlying microscopic process causing such a large anomalous effect is not clearly understood though influence from symmetry of the molecule is recognized to be the principal cause. The role of symmetry in causing isotopic anomaly can be further constrained if reactions other than $O+O_2$ reaction can be investigated. One such reaction is $O+CO\rightarrow CO_2$, which is also expected to show a mass independent oxygen isotopic fractionation in product CO_2 because the relevant isotopic symmetry of O+CO is same as that of $O+O_2$. The study of $O+CO\rightarrow CO_2$ reaction offers a nice possibility to test the validity of the non-RRKM model of Marcus and his coworkers. In the present thesis, a study of

O+CO reaction in laboratory was undertaken to see if there is any anomalous enrichment of heavy oxygen isotopes in the product CO_2 as observed in case of ozone.

Another important issue is the internal distribution of heavy oxygen isotopes in ozone molecule. A heavy isotopologue of ozone (having a triangular shape) like ⁵⁰O₃ can have heavy isotope ¹⁸O located either at the central (apex) position (¹⁶O¹⁸O¹⁶O, symmetric type) or at the terminal (base) position (¹⁶O¹⁶O¹⁸O, asymmetric type). Statistically, asymmetric type ozone is expected to be exactly twice more abundant compared to symmetric type ozone and thus their ratio, $r^{50} = [{}^{16}O^{16}O^{18}O] / [{}^{16}O^{18}O^{16}O]$ should be equal to two. However, this rule is found to be violated in case of naturally enriched ozone. Determination of this ratio is quite important. In stratosphere, the anomalous isotopic signature gets transferred by interaction of ozone with other trace gases, like CO₂, CO. For example, stratospheric, CO₂ is found to be anomalously enriched in heavy oxygen isotopes and the slope relating the two enrichments is found to be about ~ 1.7 which is radically different from that of ozone which is known to be the origin of the enrichment. The transfer of anomaly from ozone to other species can occur in two ways: via isotopic exchange with O(¹D) produced from ozone by UV photolysis or by direct reaction with ozone. This subject is of great importance as anomalous isotopic enrichment in trace gases provides tracers for studying stratospheric transport processes and/or tropospheric oxidation reaction pathways. In order to explain the mass independent isotopic anomaly in these gases, the isotopic composition of O(¹D) has to be known. But this cannot be measured directly due to its short life time. However, it can be calculated theoretically if we know: (i) the intramolecular distribution of heavy oxygen isotopes in ozone and (ii) the relative probability of terminal and central atom emission during ozone dissociation.

In this context, some laboratory experiments have been done to calculate the isomeric distribution of ¹⁸O in heavy ozone [*Anderson et al.*, 1989; *Larsen et al.*, 1994, 2000] using TD-LAS and FTAS. But these data are associated with large errors and uncertainty in certain spectroscopic parameters. Notwithstanding the errors, both TDLAS and FTAS data show that for ⁵⁰O₃ species, ¹⁸O enrichment in asymmetric species is more than that of symmetric species. In the present thesis, we have used a novel method to determine r^{49} using the available information of r^{50} . Since above work could establish the internal distribution of both ¹⁷O and ¹⁸O in ozone one could use the information to model the CO₂-O₃ exchange process which was studied in our laboratory by earlier workers [*Chakraborty and*]

Bhattacharya, 2003d]. We use the KINTECUS Reaction Simulation model to explain the experimental data on exchange.

The main goals of the thesis can be summarized as:

- To investigate the role of molecular symmetry in causing anomalous oxygen isotope fractionation by studying a reaction similar to the ozone formation, namely, O+CO→CO₂ reaction.
- 2. To determine the internal distribution of heavy oxygen isotopes in ozone using mass spectrometric technique.
- 3. To apply the information of intramolecular isotopic distribution in ozone to explain the transfer of heavy oxygen isotopes from ozone to CO_2 (with particular reference to the case of stratospheric CO_2) by a chemical kinetic reaction model.

CHAPTER 2

Experimental Technique

The purpose of this chapter is to describe in detail the experimental techniques used in the present study.

2.1 Isotope Ratio Mass Spectrometry (IRMS)

The precise measurement of the small abundances of the isotopes and their small variations are done using a mass spectrometer. Two mass spectrometers were used in the present study. Both are dual inlet, triple collector, gas source stable isotope ratio mass spectrometers (VG-903 and GEO 20-20).

2.1.1 Principle

Mass spectrometry is a technique for separating ions by their mass to charge (m/q) ratios. It is normally achieved by ionizing molecules of the sample gas and separating ions of differing masses and recording their relative abundances by measuring intensities of ion flux. A typical mass spectrometer comprises of three parts (as shown in Figure 2.1):

- 1. Ion source: generate, accelerate, and collimate the ions.
- 2. Analyzer: separate the ion beams depending upon their masses.
- 3. Collector: ion beams of different masses are electronically counted and compared.



Figure 2.1: Schematic of a mass spectrometer.

In a dual inlet system, the gas sample is introduced into the source chamber through a long (~ 1 m) capillary that have a small diameter (typically 10^{-4} m) so that the gas flows inside with a relatively high pressure gradient creating a steady mass flow. It also prevents the back diffusion of gas sample which helps in maintaining a non fractionating condition. A changeover valve allows for the quick interruption of flow of the sample gas and its replacement with a standard gas and permits rapid and repeated comparison of the sample with reference.

The source consists of an electron gun composed of a tungsten filament (thoria coated) which is kept at about 2000°C to emit electrons by thermo-ionic processes. The electrons are given sufficient kinetic energy \sim 90 eV so that it can ionize the gas molecules on collision.

The extracting potential (0-5kV) is applied to accelerate the ions. The collimating plates and electronic lenses are used to focus the ions into a narrow beam (<1mm).

In the analyzer, a strong magnetic field (\sim 1 Tesla) either generated by permanent magnet (in VG-903) or electromagnet (in GEO 20-20) is maintained so as to force the ions to move along a circular path that depends on their momenta.

The collector consists of faraday cups which quantifies the ion beams by detecting and measuring the tiny currents generated by their neutralization.

2.1.2 Mathematical representation of isotope separation

The kinetic energy (k) of a positively charged 'q' molecule of mass 'm' when it is accelerated by an electric field 'V' to gain a final velocity 'v' is:

$$k = qV = \frac{mv^2}{2}$$
(2.1)

The ions moving through a magnetic field 'B' encounter a Lorentz force of magnitude $q(v \times B)$ which imparts a centripetal force $(\frac{mv^2}{r})$ of equal magnitude.

$$q(\mathbf{v} \times \mathbf{B}) = \frac{\mathbf{m}\mathbf{v}^2}{\mathbf{r}}$$
(2.2)

For an orthogonal oriented B field the ions follow a circular path of radius 'r' which is expressed as,

$$r = \sqrt{\frac{2Vm}{B^2q}}$$
(2.3)

So the ions with same $\frac{m}{q}$ follow the same radial path. If q is same, ions of different masses follow different radial paths and get separated in the magnetic field. The Faraday cups are so located that each collects ions of a particular mass when focussing conditions are satisfied.

2.2 Ozone preparation

2.2.1 Ozone made by Tesla discharge and UV photolysis

By Tesla discharge: Oxygen gas was taken inside a cylindrical reaction chamber (made of Pyrex glass with diameter = 2.9 cm and volume \sim 70 cc) at desired pressure. Few strands of thin copper wire were wrapped around the middle of the reaction chamber and connected to the tip of a Tesla coil electrode. The bottom part of the chamber upto the wire was cooled by liquid nitrogen to condense the ozone as soon as it forms. Tesla discharge was done for a period of 2 to 55 min. The left over oxygen was pumped away while keeping the ring of ozone inside the LN₂ level. Ozone with different enrichments was produced by varying the O_2 pressure, time of discharge, position of LN_2 trap and temperature of the discharge zone.

By UV photolysis: In these cases, ozone was produced in a 5 liter spherical chamber (made of Pyrex glass) fitted with a MgF₂ side window (2 mm thick and 24 mm diameter) by irradiating oxygen taken from the tank at different pressures with UV light generated by a Hg resonance lamp (184.9 nm and 253.6 nm) driven by a micro-wave generator (OPTHOS, Inc.; Model: MPG-4M at 2450 MHz) for time periods ranging from 60 to 180 mins. After photolysis, product ozone was frozen by LN_2 in a cold finger attached to the chamber and the remaining oxygen pumped away till 2 mtorr pressure (vapor pressure of ozone at LN_2). Ozone samples with different compositions were made by changing the O_2 pressure.

2.3 Analysis of oxygen isotopes in ozone

In the present work, we are interested in ${}^{17}\text{O}/{}^{16}\text{O}$ and ${}^{18}\text{O}/{}^{16}\text{O}$ ratio of various oxygen containing gases (O₂, O₃, CO or CO₂). However, mass spectrometer analysis is done on molecular species. So one has to derive isotopic ratio in atomic species from the measured quantities. The most abundant isotopomers of molecular oxygen are:

$${}^{32}O_2 = {}^{16}O^{16}O (99.52\%)$$
$${}^{33}O_2 = {}^{16}O^{17}O (0.08\%)$$
$${}^{34}O_2 = {}^{16}O^{18}O (0.4\%)$$

For oxygen molecules, mass spectrometer gives two measured ratios, 33 R and 34 R which are expressed in δ -notation as,

$$\delta^{33} O_2 = \left[\left(\frac{{}^{33}R}{{}^{33}R_s} \right) - 1 \right] \times 10^3$$
(2.4)

$$\delta^{34}O_2 = \left[\left(\frac{^{34}R}{^{34}R_s} \right) - 1 \right] \times 10^3$$
 (2.5)

where,

$${}^{33}R = \frac{{}^{33}O_2}{{}^{32}O_2} = \frac{[{}^{16}O^{17}O]}{[{}^{16}O^{16}O]} = \frac{2[{}^{17}O]}{[{}^{16}O]} = 2^{17}R$$
(2.6)

$${}^{34}R = \frac{{}^{34}O_2}{{}^{32}O_2} = \frac{[{}^{16}O^{18}O]}{[{}^{16}O^{16}O]} = \frac{2[{}^{18}O]}{[{}^{16}O]} = 2^{18}R$$
(2.7)

Since the factor of 2 cancels out in definition of δ we get $\delta^{17}O = \delta^{33}O_2$ and $\delta^{18}O = \delta^{34}O_2$

The isotopic compositions of oxygen gas samples were measured with respect to a laboratory standard BOC-O₂ and then expressed with respect to international standard VSMOW. BOC-O₂ was calibrated against V-SMOW as described below. The isotopic composition of BOC-O₂ is δ^{17} O=12.5 ‰ and δ^{18} O=24.6‰ relative to V-SMOW.

It is difficult to determine ozone isotope ratios by analysing the gas as ozone due to its unstable nature. Therefore, its isotopic composition is normally measured by converting it fully to oxygen. For isotopic measurements, ozone was cryogenically transferred to a trap containing molecular sieve (pellet 13X) and converted to oxygen by heating and freezing in succession for two or three times.

The oxygen isotopic measurements were done using a VG 903 mass spectrometer. To check the accuracy of the data obtained from VG machine, an inter laboratory comparison was done. In this comparison, two ozone and two oxygen (tank BOC-O₂) samples were first measured in VG-903 at PRL. Subsequently, the samples were taken back completely from the mass spectrometer in small sample bottles and were sealed. These samples were sent to the laboratory of Prof. Mark Thiemens at UCSD (University of California, San Diego, USA) for its oxygen isotopic measurements. The data obtained from the two laboratories are compared in Table 2.1.

To check the machine precision, aliquot of tank BOC-O₂ was taken and measured against the laboratory working standard (BOC-O₂) several times. The data are shown in Table 2.2. The uncertainties (1 σ) in δ^{18} O and δ^{17} O measurement are 0.05‰ and 0.2‰ respectively.

Amount of ozone (expressed as equivalent μ mol of molecular oxygen gas) was measured by a capacitance manometer (Baratron 626 A type, full scale range ~ 1 torr). The error associated with the amount measurement is ~0.5%.

Table 2.1: The oxygen isotopic composition of the same samples (two ozone and two BOC- O_2) were first measured in VG-903 at PRL and later at MAT 251 at UCSD. The isotopic compositions are expressed with respect to VSMOW. The results from the two laboratories agree reasonably well.

Sample	PRL data		UCSD data		Difference (PRL-UCSD)	
	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}\mathrm{O}$	$\Delta \delta^{18} O$	$\Delta \delta^{17} O$
	‰	‰	‰	‰	‰	%
A-O ₃	121.4	101.5	119.7	101.1	+1.7	+0.4
$B-O_3$	125.5	105.5	126.9	107.4	-1.4	-1.9
A-BOC- O_2	24.2	12.7	24.3	12.2	-0.1	+0.5
$B-BOC-O_2$	24.1	12.6	24.1	12.1	0.0	+0.5
				Mean	0.05	-0.1

Table 2.2: The isotopic composition of gas samples taken from tank BOC-O₂ was measured several times against the laboratory working standard (a 5l chamber filled with BOC-O₂) ($\delta^{18}O=24.6\%$, $\delta^{17}O=12.5\%$) relative to VSMOW. These data show that the VG-903 mass spectrometer can measure $\delta^{18}O$ and $\delta^{17}O$ with a precision of 0.05‰ and 0.2‰ respectively.

Sample	$\delta^{18}O$	$\delta^{17}O$
	‰	‰
1	0.04	0.3
2	0.05	0.2
3	0.04	0.3
4	0.01	-0.1
5	0.02	0.1
6	-0.02	-0.3
7	0.1	0.1
8	-0.06	0.2
9	0.1	-0.3
10	-0.01	-0.1
Std (1σ)	0.05	0.2
Experimental Technique

2.4 Analysis of oxygen and carbon isotopes in CO₂

The most abundant CO₂ isotopomers are:

$${}^{44}\text{CO}_2 = {}^{16}\text{O}{}^{12}\text{C}{}^{16}\text{O}$$

$${}^{45}\text{CO}_2 = {}^{16}\text{O}{}^{12}\text{C}{}^{17}\text{O}, {}^{16}\text{O}{}^{13}\text{C}{}^{16}\text{O}$$

$${}^{46}\text{CO}_2 = {}^{16}\text{O}{}^{12}\text{C}{}^{18}\text{O}, {}^{16}\text{O}{}^{13}\text{C}{}^{17}\text{O}, {}^{17}\text{O}{}^{12}\text{C}{}^{17}\text{O}$$

Mass spectrometric measurement of CO₂ gives two ratios $\frac{^{45}CO_2}{^{44}CO_2}$ and $\frac{^{46}CO_2}{^{44}CO_2}$ which can be expressed in terms of the individual oxygen and carbon isotope ratios as follows:

$$\frac{{}^{45}\text{CO}_2}{{}^{44}\text{CO}_2} = \frac{\left[{}^{16}\text{O}{}^{12}\text{C}{}^{17}\text{O}\right] + \left[{}^{16}\text{O}{}^{13}\text{C}{}^{16}\text{O}\right]}{\left[{}^{16}\text{O}{}^{12}\text{C}{}^{16}\text{O}\right]} = \frac{2\left[{}^{17}\text{O}\right]}{\left[{}^{16}\text{O}\right]} + \frac{\left[{}^{13}\text{C}\right]}{\left[{}^{12}\text{C}\right]}$$

$$\frac{{}^{46}\text{CO}_2}{{}^{44}\text{CO}_2} = \frac{\left[{}^{16}\text{O}{}^{12}\text{C}{}^{18}\text{O}\right] + \left[{}^{16}\text{O}{}^{13}\text{C}{}^{17}\text{O}\right] + \left[{}^{17}\text{O}{}^{12}\text{C}{}^{17}\text{O}\right]}{\left[{}^{16}\text{O}{}^{12}\text{C}{}^{16}\text{O}\right]}$$

$$(2.8)$$

$$\approx \frac{2[^{18}\text{O}]}{[^{16}\text{O}]} = 2^{18}\text{R}$$
(2.9)

Mass 46 is mainly due to ¹⁸O bearing isotopomers. But mass 45 represents mainly ¹³C-bearing isotopomer and the contribution from ¹⁷O bearing isotopomer is only \sim 6.5%. In terms of delta notation,

$$\delta^{46} \text{CO}_2 = \left[\left(\frac{{}^{46}\text{R}}{{}^{46}\text{R}_{\text{s}}} \right) - 1 \right] \times 10^3 = \left[\left(\frac{{}^{18}\text{R}}{{}^{18}\text{R}_{\text{s}}} \right) - 1 \right] \times 10^3 = \delta^{18}\text{O}$$
(2.10)

$$\delta^{45} \text{CO}_2 = \left[\left(\frac{^{45}\text{R}}{^{45}\text{R}_{\text{s}}} \right) - 1 \right] \times 10^3 = \left[\left(\frac{(2^{17}\text{R} + ^{13}\text{R})}{(2^{17}\text{R} + ^{13}\text{R})_{\text{s}}} \right) - 1 \right] \times 10^3$$

$$= \left[\frac{^{13}\text{R}}{^{13}\text{R}_{\text{s}}} + 2\frac{^{17}\text{R}}{^{13}\text{R}_{\text{s}}} - 1 - 2\frac{^{17}\text{R}_{\text{s}}}{^{13}\text{R}_{\text{s}}}}{1 + 2\frac{^{17}\text{R}_{\text{s}}}{^{13}\text{R}_{\text{s}}}} \right] \times 10^3$$

$$= \left[\frac{\left(\frac{^{13}\text{R}}{^{13}\text{R}_{\text{s}}} - 1 \right) + 2\left(\frac{^{17}\text{R}}{^{13}\text{R}_{\text{s}}} - \frac{^{17}\text{R}_{\text{s}}}{^{13}\text{R}_{\text{s}}} \right)}{1 + 2\frac{^{17}\text{R}_{\text{s}}}{^{13}\text{R}_{\text{s}}}} \right] \times 10^3$$

$$= \left[\frac{\delta^{13}\text{C} + 2\frac{^{17}\text{R}_{\text{s}}}{^{13}\text{R}_{\text{s}}} \left(\frac{^{17}\text{R}}{^{17}\text{R}_{\text{s}}} - 1 \right) \times 10^3}{1 + 2\frac{^{17}\text{R}_{\text{s}}}{^{13}\text{R}_{\text{s}}}} \right]$$

Experimental Technique

$$= \frac{\delta^{13}C + 2 z \delta^{17}O}{1 + 2 z}, \text{where}\left(z = \frac{{}^{17}R_{s}}{{}^{13}R_{s}}\right)$$
(2.12)

$$\delta^{17} \mathcal{O} = \left(\frac{1+2z}{2z}\right) \delta^{45} \mathcal{CO}_2 - \left(\frac{1}{2z}\right) \delta^{13} \mathcal{C}$$
(2.13)

It is not possible to calculate the values of two unknown parameters δ^{13} C and δ^{17} O from a single δ^{45} CO₂ equation. To determine δ^{17} O of product CO₂ one has to obtain another constraining equation relating these quantities.

The common methods used are:

- 1. To convert CO₂ to O₂ with BrF₅ at ~ 800°C for 48 hrs [*Bhattacharya and Thiemens*, 1989] and measure the oxygen isotopic composition of O₂.
- To convert CO₂ to methane and water followed by decomposition of water to H₂ and O₂ with flourine [*Brenninkmeijer and Rockmann*, 1998]. For complete conversion, the oxygen isotopic composition of O₂ represents that of CO₂.
- 3. To equilibrate CO₂ with water. CO₂ is put in a large amount of water for nearly 8 hrs. After the exchange, CO₂ is purified and its isotopic composition is remeasured in mass spectrometry. This provides two more equations relating ¹⁷O (modified), ¹⁸O (modified) and ¹³C (old) as δ^{45} CO₂ (ex) and δ^{46} CO₂ (ex). Assuming δ^{13} C does not change in exchange with water and CO₂ is recovered almost quantitatively, the values of δ^{17} O and δ^{13} C are calculated by solving four equations δ^{45} CO₂, δ^{45} CO₂(ex), δ^{46} CO₂, and δ^{46} CO₂(ex).
- 4. To equilibrate CO₂ with a hot metal oxide (CeO₂) [Assonov and Brenninkmeijer, 2001].

The first two procedures are time consuming and the yield of CO_2 is poor. Additionally, in case of small CO_2 amount occasionally unknown fractionation occurs. CO_2 -water equilibration is also not very accurate because: (1) CO_2 is highly soluble in water so it is difficult to recover the CO_2 quantitatively free from water. This invalidates the constant $\delta^{13}C$ assumption. (2) Water- CO_2 exchange is considerably slow.

In the present study, the method of equilibrium exchange of CO_2 with CeO_2 was employed [Assonov and Brenninkmeijer, 2001]. CeO_2 is an ideal oxygen exchange medium which is water free, exchanges oxygen with CO_2 in a reasonably short time, produces minimal contamination and have a high recovery yield of CO_2 . The exchange study by *Assonov et al.* [2003] on several oxides demonstrates that oxygen exchange rate for CeO_2 is highest. It is estimated that around 25% of the CeO_2 lattice oxygen participates in the CeO_2 -O₂ gas exchange at temperature up to 600°C.

2.4.1 Experimental set up for CO₂-CeO₂ exchange

A reaction tube (made of Quartz, 20 cm in length and 1 cm in diameter and positioned horizontally) with a small cold finger was connected to the main vacuum line by a stop-cock. Approximately 10 g of CeO₂ (preheated at $\sim 1000^{\circ}$ C in air and crushed to make grains of size 0.25-0.5 mm) was kept in the reaction tube with silica glass wool as filter plug to prevent fine grains escaping to the vacuum line. Before each CO₂ exchange, CeO₂ was preconditioned by flushing it with tank oxygen at 650°C under high vacuum and then evacuating for more than 1 hour to remove excess oxygen. In order to heat CeO₂ a cylindrical jacket heater was put over the reaction chamber. The sample CO₂ gas was first analyzed in the mass spectrometer and then taken back into the sample bottle. Subsequently, it was transferred to the cold finger attached to the CeO₂ reaction chamber. After ensuring complete transfer, reaction of CO₂ with CeO₂ was allowed to proceed. At 650°C the exchange reaction reaches equilibrium in 30 min. After this, the CO₂ was collected back in the cold finger, transferred to the sample tube and re-analyzed.

Mass spectrometric measurements of CO₂ after exchange yield two equations,

$$\delta^{46} \mathrm{CO}_2(\mathrm{ex}) = \delta^{18} \mathrm{O}(\mathrm{ex}) \tag{2.14}$$

and

$$\delta^{45} \text{CO}_2(\text{ex}) = \left(\frac{1}{1+2z}\right) \delta^{13} \text{C}(\text{ex}) + \left(\frac{2z}{1+2z}\right) \delta^{17} \text{O}(\text{ex})$$
(2.15)

As the exchange is known to be a mass dependent, so

$$\delta^{17} O(ex) = 0.512 \times \delta^{18} O(ex)$$
 (2.16)

The value of δ^{17} O is calculated from the above equation and was used in equ 2.15 to calculate δ^{13} C(ex).

Since, there is no appreciable loss in CO_2 amount, it is assumed that,

$$\delta^{13}\mathcal{C} = \delta^{13}\mathcal{C}(\mathrm{ex}) \tag{2.17}$$

Putting the value of δ^{13} C in equation 2.13, δ^{17} O value is calculated. The values of δ^{18} O, δ^{17} O and δ^{13} C of sample CO₂ were determined by solving these sets of equations.

In a few test runs, CO_2 of known isotopic composition was put into the CeO_2 chamber for equilibration, collected back and re-measured. The average recovery was ~ 99 % and the change in $\delta^{13}C$ was small ~0.06‰ [Table 2.3].

Measurements of carbon and oxygen isotopic compositions of CO₂ were done using a Europa GEO 20-20 mass spectrometer. The value of the laboratory reference gas (Vadilal-CO₂) is δ^{18} O=17.4‰, δ^{17} O=9.1‰ with respect to VSMOW and δ^{13} C=-36.5‰ relative to VPDB-CO₂. To check the machine precision, one aliquot of the tank Vadilal-CO₂ was taken and measured against the laboratory working standard several times [Table 2.4]. Typical error in isotopic measurement of CO₂ was 0.02‰ for both δ^{45} CO₂ and δ^{46} CO₂.

2.5 Separation of ozone and CO₂ mixture

To separate the mixture of ozone and CO₂, the hot nickel method [*Johnston et al.*, 2000; *Chakraborty and Bhattacharya*, 2003d] was used. The CO₂-O₃ mixture was transferred to a chamber containing cleaned, preheated nickel foil. Subsequently, the nickel chamber was heated to 120°C to decompose the adsorbed ozone to oxygen which does not freeze on the surface at LN₂ temperature. Again LN₂ trap was put to freeze CO₂ and the non-condensable O₂ was collected on a molecular sieve for isotope measurement. Subsequently, the nickel chamber was heated slightly for a few minutes and the pure CO₂ was collected for isotopic analysis. Few control experiments were done to check if hot nickel modifies the oxygen isotopic composition of CO₂. Pure CO₂ of known isotopic composition was put in the nickel chamber and was heated to 120°C for 30 minutes. The CO₂ was then collected back and its isotopic composition was measured. The data shown in Table 2.5 show that the shift produced by hot nickel surface on δ^{46} CO₂ is 0.09‰ and negligible (0.01‰) for δ^{45} CO₂.

	Initial	CO_2 com	nposition	Recovered	$\Delta(\delta^{13}C)$
Sample	amount	$\delta^{45}\mathrm{CO}_2$	$\delta^{46}\mathrm{CO}_2$	amount	
	(μmol)	‰	‰	(μ mol)	‰
1	110.2	0.28	3.13	109.8	0.02
2	25.8	0.31	2.34	25.5	0.08
3	82.9	0.35	3.27	82.5	0.09
4	-	0.30	2.54	-	0.06

Table 2.3: Change in carbon isotope ratio of CO_2 during CO_2 -CeO₂ exchange. The starting isotopic composition of CO_2 (before exchange) is $\delta^{45}CO_2=0.16\%$ and $\delta^{46}CO_2=0.56\%$.

Table 2.4: Isotopic measurement of several samples of tank Vadilal-CO₂ against the laboratory working standard (Vadilal-CO₂) whose isotopic compositions are: ($\delta^{18}O=17.4\%$, $\delta^{17}O=9.1\%$ and $\delta^{13}C=-36.5\%$ relative to VPDB-CO₂.

Sample	$\delta^{46} \text{CO}_2$	$\delta^{45}\mathrm{CO}_2$
	‰	‰
1	0.03	0.02
2	0.01	0.02
3	-0.02	0.03
5	0.03	-0.01
4	-0.01	0.02
Std (1σ)	0.02	0.02

Table 2.5: Effect of hot nickel on oxygen isotopic composition of CO_2 during separation of ozone- CO_2 mixture.

Sample	$CO_2 com$ (bef	nposition ore)	$CO_2 com$	nposition ter)	Diffe	rence
No.	$\delta^{46}\mathrm{CO}_2$	δ^{45} CO ₂	$\delta^{46}\mathrm{CO}_2^{\dagger}$	$\delta^{45}\mathrm{CO}_2^\dagger$	$\Delta(\delta^{46}\mathrm{CO}_2)$	$\Delta(\delta^{45}\mathrm{CO}_2)$
	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
1	2.70	11.57	2.79	11.59	0.09	0.02
2	2.40	8.85	2.52	8.84	0.12	-0.01
3	2.15	11.70	2.21	11.71	0.06	0.01

CHAPTER 3

Photochemical simulation model (KINTECUS)

A commercially available software program, KINTECUS (Windows Version 3.8, 2005) developed by *James C. Ianni*, Vast Technologies Development, USA (www.kintecus.com) was utilized to simulate the experimental conditions of resultant products for interpreting the laboratory data. The important features of this model and its applicability to the field of isotopes are discussed briefly in this chapter.

3.1 Brief description of the model

KINTECUS is a program written in C^{++} language which can be used to model chemical reactions in a large chamber (negligible surface effect). It can handle large number of reactions (~12,000) in a relatively short time. The simulation time can be varied from femtoseconds to years. In addition to this, one can fit/optimize any numerical value (rate constant, initial concentration, third body enhancement, activation energy, starting temperature etc.) against an experimental data set [*Benson*, 1976; *Chang et al.*, 1994; *Dunker*, 1985; *Field and Noyes*, 1974; *Gear*, 1971a, 1971b; *Kee*, 1989; *Showalter et al.*, 1978; *Yu et al.*, 1995]. KINTECUS uses three input spreadsheet files namely:

- Model description or reaction spreadsheet
- Species description spreadsheet
- Parameter description spreadsheet

3.1.1 Model description or reaction spreadsheet

The reactions and the corresponding rate constants are entered in the Reaction spreadsheet. The reaction field holds either a reversible (represented by a single "=") or an irreversible (represented by "== \rangle ") reactions. The reactions can be defined either in k (rate constants) or (A, m, E_a) (thermodynamic parameters) format. An appropriate comment to any reaction can be entered after putting "#", or double quotes. At the end of the Reaction description sheet, "END" is typed. The reactions entered below END or placed after # is ignored by KINTECUS. There is also a provision to define enhanced body, fall-off reactions and special reactions represented by +M [...] and they are not considered as reactants. KINTECUS looks for this MODEL.dat as the default reaction filename.

3.1.2 Species spreadsheet

KINTECUS automatically generates the Species spreadsheet file using the Reaction spreadsheet. This spreadsheet has several options like, Species, Residence time in Continuous Stirred Tank Reactors (CSTR), Initial Concentration, Display Output fields, External concentration, Steady State Approximation (SSA) and Constant file. The species field holds the name of those species that are described in the Reaction spreadsheet. The Initial Concentration field holds the starting concentration of each species in the reaction and is expressed in molecules per cc. Phase information can be accomplished by appending the species name with the phase name surrounded by braces, for example, CH₃COO-{aq} represents aqueous phase. No symbol at the end of the species name signifies gaseous phase. KINTECUS uses the gas phase information mainly for third body reactions involving [M], pressure fall-off reactions and enhanced third body reactions used in [M]. The Residence Time in CSTR and the External Concentration fields are used together for the process that contains well mixed, isothermal reactions with external flux in and flux out. At the end

of the species description spreadsheet, it is necessary to type "END". The Species description spreadsheet has a special feature "Constant File Field" where one can enter a filename containing a temperature program. KINTECUS treats temperature programs exactly like perturbations to species concentrations.

The Display Output field can hold either a Yes or No. Entering "Y" in the display output fields allows to view the concentration of the species at selected time intervals as the simulation runs and also stores the concentration of the respective species in the default output file "CONC.TXT".

3.1.3 Parameter Spreadsheet

In the Parameter spreadsheet, various parameters like, time of simulation, temperature, concentration etc. are entered. Simulation length has five fields: DAYS, HOURS, MINUTES, SECOND, and PICOSECONDS. This easily allows one to set the total time of the simulation during a run from yearly events to femtosecond laser experiments. The E_a Units field allows to specify the units associated with the energy of activation used in the exponent of the expanded Arrhenius equation $exp(-E_a/RT)$. These fields control the length of the simulation. Temperature is always entered in Kelvin and this is used only when the model is using the Arrhenius expression.

The Percent (%) field is used to limit the size of the output concentration file without causing distortion. KINTECUS will only output the concentration of all the species when one or more displayed species has changed more than Percent previous output value. A value of 0% will output all the values. The Starting Integration Time, Maximum Integration Time and Accuracy fields determine how fast KINTECUS can integrate the model and the error in the final concentration. Accuracy determines how far out in the decimal place to keep the concentration accurately computed. A value of 1.0×10^{-9} keeps the first nine digits of the integrated concentration accurately computed. The Starting Integration Time (in seconds) determines the starting time step to integrate the model. After the first integration, it changes according to the set value of accuracy. KINTECUS looks for the Parameter description spreadsheet under PARM.DAT as the default filename.

After defining the Reaction description file (MODEL.DAT) and the Parameter description file (PARM.DAT), KINTECUS is directed to create a Species spreadsheet by clicking on the option "Make Species spreadsheet" present on the Control sheet. This automatically generates the Species spreadsheet file, (ADDSPEC.TXT). After entering the various parameters in this spreadsheet (as discussed above), KINTECUS is run by clicking on 'RUN' option available on the Control sheet.

It uses all the three description spreadsheets to calculate the concentration of the selected species at a given simulation time. It shows the concentration of the species that are displayed as an output file only if its concentration has changed significantly from its past values.

An output file (CONC.TXT) containing the concentration profile of all the species that are being displayed are saved in this file. The concentration profile of all the displayed species can be viewed by loading this file in a plotting software (Microsoft Excel).

3.2 Performance test of the model

KINTECUS model is normally not used for calculating the abundances of various isotopomers in a reaction set involving isotope exchange. So it is important to investigate whether this model can be used for predicting isotopomer abundances correctly in the type of work undertaken in the present study.

The validity of the model was confirmed by comparing the model predictions with observations in a simple case. The process of ozone dissociation has been studied earlier by many workers [*Bhattacharya and Thiemens*, 1988; *Wen and Thiemens*, 1991; *Liang et al.*, 2006; *Cole and Boering*, 2006] including our own group [*Chakraborty and Bhattacharya*, 2003a, 2003b] and this reaction scheme was used as a test case.

3.2.1 Experimental detail

In order to test the model, a simple experiment was carried out where ozone of known amount and composition was dissociated by visible light. Ozone was made (see Chapter 2 for detail) by Tesla discharge in a small chamber (\sim 70 cc). Ozone was cryogenically separated from the left over oxygen and was brought into gaseous phase. A halogen-filled tungsten projection lamp (see Figure 3.1) was used for ozone dissociation.

After photolysis, the product oxygen was separated from the left over ozone and its isotopic composition and amount were measured. The left over ozone was also collected on a molecular sieve and its amount and isotopic composition were measured [see Chapter



Figure 3.1: Characteristics of the lamp used for dissociation of ozone (Philips projection lamp, halogen-filled, tungsten filament, model 13163, 24V input and 250 watt output power). Lamp emission lies in the range: 350 to 900 nm with peak at 640 nm.

2]. The isotopic composition and amount of the initial ozone was determined from the mass balance.

3.2.2 Input parameters for the model

A. Details of the reactions considered in the Model

All the basic combination/recombination reactions as well as isotopic exchange reactions involving isotopes and isotopomers of O, O_2 and O_3 (a total of twenty-seven reactions) were incorporated in the KINTECUS model. These reactions (grouped into four reaction sets: R1 to R4) are summarized in Table 3.1.

The rate constants were obtained mostly from *Anderson et al.* [1985], *DeMore et al.* [1997] and *Janssen et al.* [2001]. The rate of reaction involving a given isotopically substituted species, was calculated by correcting it for the mass dependent collision factor. The reaction constants have units of cm³ molecule⁻¹ sec⁻¹ for two-body and cm³ molecule⁻² sec⁻¹ for three body reactions.

Table 3.1: List of various gas phase reactions along with the rate constants used in the kinetic model (KIN-TECUS) for simulation of photolysis of ozone by visible light. The ozone dissociation rate (k_1) was estimated to be 2.5×10^{-3} , by comparing the yield of O_2 in the experiment with the value predicted by the model. The dissociation rate of O-Q and O-P bond was reduced by a factor of 0.972 and 0.988 (relative to O-O bond) respectively [Wen and Thiemens, 1991].

	Reactions	Rate coefficient
	R1 (Ozone photolysis)	
R(1a)	$OOO+h\nu \rightarrow O+OO$	$k_1 = 2.5 \times 10^{-3}$
R(1b)	$OOQ+h\nu \rightarrow O+OQ$	k_2 =0.5× k_1
R(1c)	$OOQ+h\nu \rightarrow Q+OO$	$k_3 = 0.5 \times 0.972 \times k_1$
R(1d)	$OQO+h\nu \rightarrow O+OQ$	$k_4 = 0.972 \times k_1$
R(1e)	$OOP+h\nu \rightarrow O+OP$	$k_5 = 0.5 \times k_1$
R(1f)	$OOP+h\nu \rightarrow P+OO$	$k_6 = 0.5 \times 0.988 \times k_1$
R(1g)	$OPO+h\nu \rightarrow O+OP$	$k_7 = 0.988 \times k_1$
	R2 (Isotopic exchange of O atom with oxygen)	
R(2a)	$Q+OO \rightarrow O+OQ$	$k_8 = 2.9 \times 10^{-12}$
R(2b)	O+OQ→Q+OO	$k_9 = 1.34 \times 10^{-12}$
R(2c)	$P+OO \rightarrow O+OP$	k_{10} =2.9×10 ⁻¹²
R(2d)	$O+OP \rightarrow P+OO$	k_{11} =1.39×10 ⁻¹²
	R3 (Ozone formation)	
R(3a)	$O+OO+M \rightarrow OOO+M$	k_{12} =6.0×10 ⁻³⁴
R(3b)	$O+OQ+M \rightarrow OOQ+M$	k_{13} =0.5×1.45× k_{12}
R(3c)	$O+OQ+M \rightarrow OQO+M$	k_{14} =0.5×1.08× k_{12}
R(3d)	$Q+OO+M \rightarrow OOQ+M$	k_{15} =0.92× k_{12}
R(3e)	$Q+OO+M \rightarrow OQO+M$	k_{16} =0.006× k_{12}
R(3f)	O+OP+M→OOP+M	k_{17} =0.5×1.36× k_{12}
R(3g)	O+OP+M→OPO+M	k_{18} =0.5×1.06× k_{12}
R(3h)	$P+OO+M \rightarrow OOP+M$	k_{19} =0.98× k_{12}
R(3i)	$P+OO+M \rightarrow OPO+M$	k_{20} =0.006× k_{12}
	R4 (Ozone decomposition)	
R(4a)	OOO+O→OO+OO	k_{21} =8.0×10 ⁻¹⁵
R(4b)	OOO+Q→OO+OQ	k_{22} =0.957× k_{21}
R(4c)	OOQ+O→OO+OQ	k_{23} =0.995× k_{21}
R(4d)	OQO+O→OQ+OO	k_{24} =0.995× k_{21}
R(4e)	OOO+P→OO+OP	k_{25} =0.978× k_{21}
R(4f)	OOP+O→OO+OP	k_{26} =0.997× k_{21}
R(4g)	OPO+O→OP+OO	$k_{27}=0.997 \times k_{21}$

In the ozone molecule, each of the two base atoms is bonded to the apex atom by a weak bond (bond energy ~1.1 ev) but there is no bonding between the base atoms themselves. Therefore, in ozone dissociation, emission of one of the base atoms is expected to be easier and more frequent than the apex atom emission. This was supported by trajectory calculation of *Sheppard and Walker* [1983] using a ground state potential energy surface, which predicts low (9%) emission probability of the apex atom. We assume that during ozone photolysis ($O_3 \Rightarrow O_2 + O$) the O atom is derived only from the base position.

The value of ozone dissociation rate constant (k_1) that should be used in our experimental configuration is not known. The rate of dissociation of ozone depends on the integration of the product of flux of photons at a given λ and corresponding cross-section of absorption over the wavelength range given by the tungsten lamp. Even though the relative flux of photons at various λ (from 350 to 900 nm) was known (Figure 3.1) the absolute flux inside the reaction chamber was not. The ozone dissociation rate constant (k_1) in this experimental configuration is determined by using the model itself to match the total O₂ production.

During ozone photolysis, the rates of formation of O, Q and P atoms are not the same. The bond energies of O-Q and O-P are slightly more than the O-O bond and therefore it is relatively more difficult to break the O-Q and O-P bonds. In this context, we note the estimation of Chakraborty and Bhattacharya [2003b] who studied visible light (630 nm) dissociation of ozone and predicted fractionation factors (α_{CB}) of 0.985 and 0.992 for O-Q and O-P bond dissociation (relative to O-O bond dissociation) respectively. Wen and Thiemens [1991] also studied the visible light dissociation of ozone and reported fractionation factors $(\alpha_{\rm WT})$ of 0.972 and 0.988 for O-Q and O-P bond dissociation, which are different from the values quoted above. They dissociated ozone in a smaller reaction vessel (76 cc) where surface effect may have operated leading to a larger fractionation (i.e. lower α). In ozone dissociation case both the values were used to calculate the isotopic composition of the product O₂ and the left over O₃. The data obtained are compared in Table 3.2 and discussed in the next section. In the reaction Set R1, the rate constants (k_3, k_4) and (k_6, k_7) were multiplied by factors 0.972 and 0.988 respectively whereas k₂ and k₅ were taken to be same as k₁ as they involve breakage of O-O bond. Note the factor 0.5 for rate constants in reactions involving two product channels.

For the isotopic exchange reaction (reaction set R2) between Q and OO, the forward

exchange rate $k_8 = 2.9 \times 10^{-12}$ cm³ molecule⁻¹ sec⁻¹ (at T=298 K) was taken from *An*derson et al. [1985]. The backward exchange rate was obtained by considering the equilibrium constant for the corresponding two-way exchange reaction (Q+OO \Leftrightarrow O+OQ) since isotope exchange reaction is so much faster than ozone formation. *Kaye and Strobel* [1983] calculated K_{eq} for this reaction using a rigid rotor harmonic oscillator approximation and obtained K_{eq} = 1.94 × exp(32/T) [see appendix A.1]. The backward exchange rate was obtained from the relation:

$$k_9 = \frac{k_8}{K_{eq}} = 1.34 \times 10^{-12} \text{ cm}^3 \text{molecule}^{-1} \text{sec}^{-1} (K_{eq} = 2.16 \text{ at } T = 298 \text{K})$$

For the exchange reaction of P and OO, the forward rate k_{10} was taken to be same as k_8 . This is justified since the exchange is fast and changes the P/O and Q/O ratio very quickly compared to the speed of ozone formation. Following *Kaye-Strobel* method we obtained $K_{eq} = 1.97 \times exp(16.6/T)$ for the reaction involving ¹⁷O [see appendix A.1]. Similarly, the backward rate k_{11} is obtained as 1.39×10^{-12} cm³ molecule⁻¹ sec⁻¹ (K_{eq} = 2.08 at T=298 K)[appendix A.1].

For ozone formation reaction (Reaction set R3), most of the rate constants were taken from the recent experimental data of Janssen et al. [2001]. In reactions R(3b) and R(3c), an O atom collides with heteronuclear oxygen molecule OQ and leads to the formation of OOQ. The relative reaction probability for these reactions given by Janssen et al. [2001] are $k_{13} = 1.45 \times k_{12}$ and $k_{14} = 1.08 \times k_{12}$. The corresponding relative rate coefficients were obtained by dividing these numbers by two (two product channels). For reactions R(3f) and R(3g), we used the argument of Janssen et al. [2001] relating change in zero point energy of the corresponding exchange reaction ($O+OP \Leftrightarrow P+OO$) with the relative reaction probability and used the same linear relation (k= [$0.013 \times \Delta ZPE + 1.2$] k₁₂. In R(3f), the zero point energy change is 11.7 $\rm cm^{-1}$ which corresponds to k_{17} = $1.35 \times k_{12}$ which is close to the value 1.36 given by Gao and Marcus [2002] and adopted here. The value of rate coefficient (k_{18}) of symmetric ozone formation channel was not measured. Gao and Marcus [2002] calculated this rate to be 1.02 at 300 K. If we consider the symmetric channel for ¹⁸O, the value of k_{14} calculated by Gao and Marcus [2002] is 1.04 in contrast to 1.08 measured by Janssen et al. [2001]. There is a discrepancy of 0.04 between the calculated and experimentally measured value. Applying the same discrepancy as in k_{14} (0.04) the value of k_{18} is taken to be 1.06. The average relative rate coefficient for both the asymmetric channels (k_{17} and k_{19}) for the formation of OOP was derived to be 1.17 by *Mauersberger et al.* [1999]. Since the relative rate coefficient (k_{17}) is taken to be 1.36, the value of relative rate coefficient (k_{19})for other asymmetric channel has to be 0.98 ($\frac{1.36+0.98}{2}$ = 1.17). Additional factor of 0.5 is applied to obtain the rate coefficient in order to account for two product channels.

The reaction set R4 describes a secondary channel of ozone dissociation by its collision with O atom. O and O₃ collision rate (k_{21}) is taken from *DeMore* [1997]. Other rates were calculated by correcting for frequency factors obtained from relative reduced masses of the colliding pairs as explained before. In the reactions R(4b) and R(4e), a simple twobody collision is considered, where Q and P atoms collide with O₃ at rates of 0.957 and 0.978 times that of O and O₃. Similarly OOQ and OOP collide with O atom at rates of 0.995 and 0.997 times that of O and O₃ collision.

B. Calculation of concentration of various isotopomers and isotopologues of ozone

The total amount of ozone measured contains mainly [${}^{16}O^{16}O^{16}O$] species and a small contribution from other isotopically substituted species. The most abundant ozone species are ${}^{48}O_3$ (99.28%), ${}^{49}O_3$ (0.12%) and ${}^{50}O_3$ (0.59%).

As input to the model, the abundances of the individual ozone species are calculated as described below. For convenience, the following notations were used: $O= {}^{16}O$, $Q= {}^{18}O$ and $P= {}^{17}O$. To simplify the calculations, multiply substituted species (OQP, QQQ, QQP) having very small abundances were not included. The effect of neglecting these species on the final isotopic composition of the products are within 2-3 ‰.

Total ozone amount measured (t_1) is expressed as,

$$[OOO] + [OOQ] + [OQO] + [OOP] + [OPO] = t_1$$
 (3.1)

As the enrichment in ozone was small, a statistical ratio was assumed,

$$\frac{[\text{OOQ}]}{[\text{OQO}]} = 2 = \frac{[\text{OOP}]}{[\text{OPO}]}$$
(3.2)

Delta for a given heavy isotope in a molecular species is defined relative to VSMOW by calculating the ratio of the total concentration of that isotopomer (singly substituted species only) to the total light isotope concentration considering all the isotopomers of that molecule.

$${}^{18}R_{O_2} = x_1 = \frac{[OOQ] + [OQO]}{3 \times [OOO] + 2 \times [OOQ] + 2 \times [OQO] + 2 \times [OOP] + 2 \times [OPO]}$$
(3.3)

$$^{17}R_{O_2} = y_1 = \frac{[OOP] + [OPO]}{3 \times [OOO] + 2 \times [OOQ] + 2 \times [OQO] + 2 \times [OOP] + 2 \times [OPO]}$$
 (3.4)

Solving these equations,

$$[OQO] = \frac{x_1 t_1}{1 + x_1 + y_1} \tag{3.5}$$

$$[OOQ] = 2 \times [OQO] \tag{3.6}$$

$$[OPO] = \frac{y_1 t_1}{1 + x_1 + y_1} \tag{3.7}$$

$$[OOP] = 2 \times [OPO] \tag{3.8}$$

$$[OOO] = t_1 - [[OOQ] + [OQO] + [OOP] + [OPO]]$$
(3.9)

As an example, in case C of Table 3.2, the amount of ozone measured was 55 μ mol. The concentration (molecules/cc) of various ozone species are calculated as:

 $[OQO] = 6.575972 \times 10^{14}$ $[OOQ] = 1.315194 \times 10^{15}$ $[OPO] = 1.211635 \times 10^{14}$ $[OOP] = 2.423270 \times 10^{14}$ $[OOO] = 3.187035 \times 10^{17}$

3.2.3 Simulation result and determination of dissociation rate constant (k_1)

As mentioned earlier, the ozone dissociation rate constant (k_1) in our experimental configuration is not known a priori and is determined by using the model itself to match the total O₂ production. Plugging in the initial ozone concentration and the photolysis time (Table 3.2) as input parameters the dissociation rate in the model was adjusted to get the observed amounts of product oxygen and left over ozone (for cases A and B in Table 3.2). The details of model and experimental data are shown in Table 3.2. The effect of k_1 on amount and isotopic composition of left over ozone and product O₂ is shown in Table 3.3. We obtain a value of $2.5 \times 10^{-3} \text{ sec}^{-1}$ as the best estimate for k_1 [Table 3.3].

To investigate the isotope ratios, the KINTECUS model was run to simulate the ozone dissociation process after plugging in the initial ozone concentration and the isotopic composition of data in case C of Table 3.2 with $k_1 = 2.5 \times 10^{-3}$. The time development of the number densities of [OOO], [OO], [OOQ], [OQO], [OOP] and [OPO] are shown in Figure 3.2 and 3.3. The changes in isotopic composition of the left over ozone and the product ozone with time are shown in Figure 3.4.



Figure 3.2: Model run for the case C of Table 3.2. In this experiment ozone with known isotopic composition was dissociated in visible light. The plot shows the time evolution of OOO and OO species. At time t=0, the concentration of ozone was 3.18×10^{17} molecules\cc. With increase in exposure time, O₃ concentration decreases and O₂ concentration starts building up.

Table 3 sociation C). Moa Thiemen =24.6‰ data wit	2: Comparison of n <i>i</i> rate coefficient k_1 <i>i</i> let results using frat <i>is</i> , 1991]) for O-Q a and δ^{17} O =12.5‰ and δ^{17} O =12.5‰	nodel predic was adjuste stionation fa rud O-P bon relative to on.	ted values d (2.5×10 d (2.5×10 ictors ($\alpha_{\rm CH}$ ictors ($\alpha_{\rm CH}$ d respectite V -SMOW V -SMOW	with the ex) ⁻³) to obta B: 0.985 an bely are sho vely are sho vely are sho vely ozo	perimental r in the correct d 0.992, [Ch wn. Isotopic me dissociati	esults in case o t amount (in ca akraborty and i compositions a on rate coefficie	<i>f</i> ozone di ses A, B Bhattacha <i>Bhattacha</i> <i>re express</i> <i>nt</i> $k_1 = 2$.	issociated and C) a rrya, 200. sed relatii 5×10 ⁻³	by visible lamp nd isotopic comp 3d]) and $(\alpha_{WT}$: ve to the laboratc gives the best ag	[Figure 3.1]. oosition of pro 0.972 and 0.9 ory working st reement of the	The photodis- lucts (in case 88, [Wen and andard: $\delta^{18}O$ experimental
Case	observation	Ozone amount (μmol)	$\frac{O_3 \text{ com}}{\delta^{18} O}$	position δ ¹⁷ Ο ‰	Exposure time (sec)	Product-O ₂ amount (µmol)	$\frac{\text{Produ}}{\delta^{18}\text{O}}$	$\frac{\operatorname{ct}\operatorname{O}_2}{\delta^{17}\mathrm{O}}$	Left-over O ₃ amount (µmol)	Left-over O. δ^{18} O %	$\frac{1}{\delta^{17}O}$
A	Experimental Model(α_{CB}) Model(α_{WT})	62.1	,		124	28.1 28.4 28.4	- -7.4 -10.6		34.0 33.8 33.8	- 5.2 7.9	- 5.7 6.5
В	Experimental Model($\alpha_{\rm CB}$) Model($\alpha_{\rm WT}$)	82.8	I	ı	60	23.8 21.2 21.2	- -8.3 -12.1	- -2.6 -3.7	59.0 61.5 61.5	- 2.1 3.4	- 3.7 4.1
U	Experimental Model(α_{CB}) Model(α_{WT})	55.0	-0.6	2.1	120	23.0 24.5 24.5	-12.4 -7.4 -10.6	-4.3 -2.1 -3.0	32.0 30.5 30.5	7.9 4.9 7.5	6.7 5.5 6.3

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Rate	Product	Produ	lct O,	Left-over	Left-ov	ver O ₃	I	Difference		Д	ifference		
constant	O_2	compc	sition	O ₃	compc	sition	in	Product C	$)_2$	in l	eft-over C	D_3	
\mathbf{k}_1	amount	$\delta^{18} O$	$\delta^{17}O$	amount	$\delta^{18} O$	$\delta^{17}O$	amount	$\Delta\delta^{18}$ O	$\Delta \delta^{17} O$	amount	$\Delta\delta^{18} O$	$\Delta \delta^{17} O$	χ^2
(sec^{-1})	μ mol	%00	%00	μ mol	%00	%00	μ mol	%0	<u>%</u> 00	μ mol	%00	<u>%00</u>	
1.0×10^{-2}	48.9	-5.6	-0.9	6.1	39.3	26.6	-25.9	-6.8	-3.4	25.9	-31.4	-19.9	1438.8
$1.0{ imes}10^{-3}$	11.6	-12.2	-3.7	43.3	2.6	3.7	11.4	-0.2	-0.6	-11.3	5.3	3.0	38.0
1.5×10^{-3}	16.6	-11.7	-3.5	38.5	4.2	4.5	6.4	-0.7	-0.8	-6.5	3.7	2.2	19.8
$2.0{ imes}10^{-3}$	20.8	-11.1	-3.3	34.3	5.8	5.4	2.2	-1.3	-1.0	-2.3	2.1	1.3	8.6
$2.1{ imes}10^{-3}$	21.6	-11.0	-3.2	33.4	6.2	5.6	1.4	-1.4	-1.1	-1.4	1.7	1.1	7.3
2.2×10^{-3}	22.4	-10.9	-3.2	32.6	6.5	5.7	0.6	-1.5	-1.1	-0.6	1.4	1.0	6.3
2.3×10^{-3}	23.2	-10.8	-3.1	31.9	6.8	5.9	-0.2	-1.6	-1.2	0.1	1.1	0.8	5.5
2.4×10^{-3}	23.9	-10.7	-3.1	31.2	7.2	6.1	-0.9	-1.7	-1.2	0.8	0.7	0.6	5.1
2.5×10^{-3}	24.6	-10.6	-3.0	30.5	7.5	6.3	-1.6	-1.8	-1.3	1.5	0.4	0.4	5.0
2.6×10^{-3}	25.2	-10.5	-3.0	29.6	7.9	6.5	-2.2	-1.9	-1.3	2.4	0.0	0.2	5.2
$2.7{ imes}10^{-3}$	25.9	-10.4	-3.0	29.0	8.2	6.7	-2.9	-2.0	-1.3	3.0	-0.3	0.0	5.8
2.8×10^{-3}	26.6	-10.3	-2.9	28.4	8.6	6.9	-3.6	-2.1	-1.4	3.6	-0.7	-0.2	6.6
$2.9{ imes}10^{-3}$	27.3	-10.2	-2.9	27.8	8.9	7.0	-4.3	-2.2	-1.4	4.2	-1.0	-0.3	7.8
$3.0{ imes}10^{-3}$	27.9	-10.1	-2.8	27.1	9.3	7.2	-4.9	-2.3	-1.5	4.9	-1.4	-0.5	9.3
$4.0{ imes}10^{-3}$	33.5	-9.2	-2.5	21.6	12.9	9.3	-10.5	-3.2	-1.8	10.4	-5.0	-2.6	44.7
$1.0 { imes} 10^{-4}$	1.3	-13.3	-4.2	53.6	-0.3	2.3	21.7	0.9	-0.1	-21.6	8.2	4.4	87.4



Figure 3.3: *Time development of the number densities of* [OOQ], [OQO], [OOP] *and* [OPO] *species for case-C* [*Table 3.2*].

For case C sample, the experimental values of δ^{18} O and δ^{17} O of the product O₂ and the left over ozone were (-12.4, -4.3) and (7.9, 6.7) respectively [Table 3.2]. The corresponding model predictions for α_{CB} were (-7.4, -2.1) and (4.9, 5.5) which differs significantly (by ~ 3 ‰) from the experimental value. In contrast, the model predictions were (-10.6, -3.0) and (7.5, 6.3) for α_{WT} that are closer to the expected values. Therefore, in modelling the visible light dissociation experiments, we have used α_{WT} .

This comparison shows that by assuming a value of $k_1 = 2.5 \times 10^{-3}$ the model prediction agrees well with the observed amount and isotopic composition of the product oxygen as well as the left over ozone. This agreement provides a well-constrained value of k_1 and also indicates that the model is suitable for estimating the isotopic fractionations properly. The model predicts amount and oxygen isotopic composition with an accuracy of 2 µmol and ~ ±2‰ respectively.



Figure 3.4: Model run for case C (Table 3.2). δ -values are expressed relative to V-SMOW. The ozone ($\delta^{18}O = -0.6 \%$ and $\delta^{17}O = 2.1 \%$) was dissociated in visible light for 120 secs. As expected from the earlier studies, the left over ozone ($\delta^{18}O = 7.9\%$ and $\delta^{17}O = 6.7 \%$) was enriched whereas the product O_2 ($\delta^{18}O = -12.4 \%$ and $\delta^{17}O = -4.3 \%$) was depleted relative to the starting ozone composition. The model predicted δ -values of the left over ozone ($\delta^{18}O = 7.5\%$ and $\delta^{17}O = 6.3 \%$) and the product O_2 ($\delta^{18}O = -10.6\%$ and $\delta^{17}O = -3.0 \%$) are close to the experimental values.

CHAPTER 4

Anomalous enrichment of heavy oxygen isotopes in CO₂ produced from O+CO reaction

4.1 Motivation

The occurrence of anomalous heavy isotope enrichment in ozone has been established by a series of measurements in stratosphere and laboratory. As discussed in Chapter 1, *Mauersberger* [2001] observed that the ozone in stratosphere is enriched in ¹⁸O by as much as $\sim 100\%$ relative to air oxygen. Later, evidence of mass independent enhancement of two heavy isotopologues of ozone (⁴⁹O₃ and ⁵⁰O₃) was reported for stratosphere [Mauersberger, 1987, 2001] as well as in ozone produced in the laboratory [Thiemens and Heidenreich, 1983, 1987; Thiemens and Jackson, 1987, 1988, 1990; Morton et al., 1990; Bhattacharya et al., 2002]. Besides ozone, this type of anomalous effect has also been observed in a wide range of atmospheric molecules like CO₂ [Gamo et al., 1989; Thiemens et al., 1991, 1995a, 1995b; Gamo et al., 1995; Brenninkmeijer et al., 1995; Lammerzahl et al., 2002; Liang et al., 2006; Bhattacharya et al., 2006], N₂O [Yoshida and Matsuo, 1983; Johnston et al., 1995; Rahn and Wahlen, 1997; Cliff et al., 1997, 1999; Yoshida and Toyoda, 2000; Rockmann et al., 2001a, 2001b; Kaiser et al., 2002; McLinden et al., 2003; Morgan et al., 2004; Yung et al., 2004], CO [Brenninkmeijer et al., 1995; Huff and Thiemens, 1998; Rockmann et al., 1998a, 1998b, 1999] and aerosol sulfate [Alexander et al., 2002; Lee and Thiemens, 2001; Romero and Thiemens, 2003; Savarino et al., 2003], CH₄ [Brenninkmeijer et al., 1995; Irion et al., 1996], sulfur [Baroni et al., 2007] demonstrating that the non mass dependent enrichment processes are not

restricted to ozone formation. Mass independent enrichment has also been observed in the reactions $O + CO \rightarrow CO_2$ [Bhattacharya and Thiemens, 1989a, 1989b; Pandey and Bhattacharya, 2005], $SF_5 + SF_5 \rightarrow S_2F_{10}$ [Bains-Sahota and Thiemens, 1989], isotopic exchange in case of $O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$ [Yung, 1991, 1997; Wen and Thiemens, 1993; Johnston et al., 2000; Chakraborty and Bhattacharya, 2003d; Perri et al., 2003, 2004; Boering et al., 2004; Shaheen et al., 2006; Liang et al., 2006] and reaction $OH + CO \rightarrow CO_2 + H$ [Miyoshi et al., 1994; Rockmann et al., 1998a, 1999; Feilberg et al., 2002; Chen and Marcus, 2005, 2006]. Interestingly, all these observations involve symmetric molecular products.

Therefore, early attempts to explain these anomalous isotope effects lead to the conclusion that symmetry controls the relevant fractionation process. During the last 25 years, several theoretical models have been proposed to explain this anomalous enrichment [*Kaye and Strobel*, 1983; *Valentini*, 1987; *Bates*, 1990a, 1990b; *Griffith and Gellene*, 1992; *Hathorn and Marcus*, 1999, 2000, 2001; *Gao and Marcus*, 2001, 2002; *Marcus*, 2004; *Babikov et al.*, 2003a, 2003b; *Ivanov et al.*, 2004; *Robert et al.*, 1988, 2001; *Robert*, 2004]. In recent years, measurement of specific rate coefficients [*Anderson et al.*, 1997; *Mauersberger et al.*, 1999; *Janssen et al.*, 1999, 2001; *Janssen and Tuzson*, 2006] of several possible ozone forming channels has brought out the complexities of the isotopic enrichment process. There are surprisingly large differences in the rates of formation of various ozone isotopomers and isotopologues, which suggests that molecular symmetry operates along with many associated quantum restrictions for generating this anomaly. As of now, the underlying microscopic process causing such a large anomalous effect is not clearly resolved though influence from molecular symmetry is suspected to be the principal cause.

A phenomenological theory [*Hathorn and Marcus*, 1999, 2000, 2001; *Gao and Marcus*, 2001, 2002; *Marcus*, 2004] has been proposed recently based on a modification of the standard RRKM model of unimolecular dissociation, which calculates isotopic fractionation in ozone produced by $O+O_2$ recombination reaction under restrictions of symmetry. As discussed in Chapter 1, they introduced a symmetry driven parameter η in the conventional reaction rate model of RRKM to explain the anomalous isotopic fractionation in ozone formation when the isotopes are allowed to exchange (scrambled case). η is primarily a phenomenological parameter and its microscopic origin is not clear but it could be a collisional effect during stabilization of ozone. Its purpose is to introduce a small relative deviation in the statistical density of states for symmetric isotopomers compared with the asymmetric isotopomers, which reduces the recombination rate for the symmetric ozone molecules. In the model, magnitude of η essentially reflects the characteristics of the intermediate complex like the density of states (ρ) near the dissociation threshold. This means that η could be different for different molecules [*Marcus*, 2004], which makes it amenable to further experimental investigations. For example, ozone has relatively low dissociation energy of about 1.1 eV, so its ρ is comparatively small. But for molecules having large dissociation energies like SiO₂, AlO₂, CO₂ etc, ρ is likely to be larger and is expected to show more statistical behavior.

It is evident that the role of symmetry in causing isotopic anomaly can be further constrained if reactions other than $O+O_2$ reaction can be investigated. One such reaction is $O+CO\rightarrow CO_2$, which should produce a mass independent oxygen isotopic fractionation in the product CO_2 because the relevant isotopic symmetry of O+CO is same as that of $O+O_2$.

CO₂ molecule has a linear form possessing Σ electronic states and two O-atoms are present in two equivalent positions around the central carbon atom. So the wave function possesses a definite symmetry with respect to exchange of the oxygen atoms when they are isotopically identical. This makes CO₂ a candidate to show mass independent oxygen isotopic fractionation similar to that of ozone. Additionally, the case of CO₂ is slightly simpler since no heavy symmetric molecule is possible (for normal abundances of isotopes) and the central carbon atom does not play a direct role in the fractionation of oxygen isotopes. Therefore, the study of O+CO→CO₂ reaction offers a nice possibility to test the validity of non-RRKM theory of Marcus and his coworkers for non-ozone systems. For example, it could be of interest to find if there is any enrichment of heavy oxygen isotopes as observed in case of ozone and if yes, what would be the value of η in this case.

The O+CO reaction was first studied by *Bhattacharya and Thiemens* [1989a, 1989b] (referred as BT) who demonstrated a large mass independent oxygen isotopic enrichment in the product CO_2 . However, for several reasons there is a need for further investigation.

In the BT experiments, O_2 (180 to 630 μ mol) and CO (20 to 40 torr) were taken in a 5.2 liter chamber and the mixture was photolysed by UV photons from either a Hg lamp (180 to 260 nm) or a Kr lamp (continuum 120 to 160 nm) for a period of 10 to 15 hours. The UV photons dissociate O_2 into atoms, which subsequently react with CO to produce CO_2 . They observed a large variation in $\delta^{18}O$ (10 to 60%) of the product CO_2 .

The oxygen atoms in CO₂ come from two sources having different isotopic composi-

tion, a well-characterized CO reservoir and an isotopically unknown O atom reservoir. In order to interpret the oxygen isotopic enrichment in CO₂, the isotopic composition of the O-reservoir must be known. In case of $O + O_2 \rightarrow O_3$, interpretation of isotopic enrichment in ozone is relatively easier because the O atom and the O₂ molecule are both from the same source which constitutes a unique reference reservoir for comparison.

In BT experiments, presence of UV light allows many parallel reactions to occur with attendant complications. For example, O_2 dissociation produces both $O(^1D)$ and $O(^3P)$. The O(¹D) can undergo an isotopic exchange with CO while quenching and produce isotopically depleted O(³P) which modifies the original O pool composition. Moreover, UV dissociation of O₂ also produces enriched ozone whose subsequent dissociation generates enriched O-atoms. These two sources of O(³P) introduce complication in determining its composition and the enrichment observed in product CO₂ is therefore difficult to interpret. One of the motivations behind the present experiment was to achieve a better constraint on the O atom composition. In our experiment, ozone with known isotopic composition was photodissociated using visible lamp to produce only O(³P). Additionally, in BT experiments, as a parallel process, the product CO₂ dissociates at 184.5 nm and 130 nm, producing lighter oxygen molecules [Bhattacharya et al., 2000]. Thus, the left over CO₂ gets enriched in heavy oxygen isotopes by an uncertain amount. Moreover, to avoid isobaric influence of ¹³C the product CO₂ was converted to O₂ by reacting it with bromine pentafluoride (BrF₅), which requires somewhat large amount of CO₂; this can introduce uncertainty in the case of small CO₂.

In case of ozone, a short lived excited complex forms during the recombination reaction which transfers its extra energy by collision to the bath gas molecules in order to become a stable molecule. This deactivation by collisional stabilization process has a mass dependent fractionation. In case of ozone molecules it is not possible to separate the mass dependent part of total fractionation experimentally. Study of $O+CO\rightarrow CO_2$ reaction gives an opportunity to quantify the mass dependent fractionation that occurs through analysis of carbon isotopes since carbon being the central atom in CO_2 is not affected by the symmetry related part of the fractionation process. The $\delta^{13}C$ of the product CO_2 was measured in the present case which was not done in BT experiments.

4.2 Experimental details

To investigate the O+CO \rightarrow CO₂ recombination reaction, four different sets of experiments were carried out. In Set 1, 2 and 3 ozone was dissociated by visible light to produce O atoms whereas in Set 4, O atom was produced by dissociating pure O₂ with UV light (as in BT). CO was taken directly from a cylinder of high purity. The isotopic composition of tank-CO is δ^{13} C = -26.6‰ (relative to VPDB-CO₂), δ^{18} O= 28.7‰ , δ^{17} O= 14.9‰ and of tank-O₂ is δ^{17} O = 24.6‰ , δ^{17} O = 12.5‰. The oxygen isotopic compositions are expressed relative to VSMOW.

4.2.1 Preparation of ozone by Tesla (Set 1: constant O₃ composition and Set 2: variable O₃ composition) and by UV (Set 3)

In Set 1 and 2 experiments, ozone was made by Tesla discharge of oxygen [see Chapter 2]. For all samples of Set 1, the discharge conditions (pressure of oxygen, time of discharge, position of LN₂ trap, pumping time and fraction of oxygen converted to ozone) were kept the same to obtain ozone of nearly same composition and amount. The average isotopic composition of O₃ was $\delta^{18}O= 27.6\pm3.2\%$ and $\delta^{17}O= 14.7\pm2.3\%$ and average amount of ozone was 89 ± 11 (in μ mol O₂) (based on 15 determinations, see Table 4.1). However, in case of Set 2, the conditions were purposely varied and an aliquot was collected in each case for determining the amount and isotopic composition of ozone. In a few cases, samples having (${}^{18}O/{}^{16}O$) and (${}^{17}O/{}^{16}O$) abundance ratios close to that of the O₂ was made (by converting nearly 100% of O₂ by Tesla discharge). In Set 3 samples, ozone was produced by UV discharge of O₂ taken at 300 torr [Chapter 2]. The amount and isotopic compositions of the product ozone for this case are also given in Table 4.1.

	Amount	Ozone con	mposition
Sample	$(O_2 equivalent)$	$\delta^{18}O$	$\delta^{17}O$
_	(µmol)	(‰)	(‰)
	Set 1		
1	87	26.9	13.7
2	91	27.5	14.4
3	80	28.6	15.7
4	107	23.2	10.9
5	104	23.0	11.3
6	88	23.8	11.2
7	72	32.0	19.5
8	76	27.9	15.4
9	78	30.4	15.7
10	95	21.6	13.3
11	101	30.3	16.3
12	103	30.1	15.4
13	96	29.1	15.7
14	85	30.1	16.8
15	78.5	28.8	15.6
Mean	89.4±11.2	27.6±3.2	14.7±2.3
	Set 3		
1	78	129.7	101.9
2	87	129.1	103.2
3	74	129.8	101.8
4	78	128.3	101.8
5	90	126.5	100.4
Mean	$81.4{\pm}6.8$	128.7±1.3	101.8±1.0

Table 4.1: Average oxygen isotopic composition of ozone. O_2 was taken at ~ 50 torr in a ~70 cc chamber and Tesla was switched on for ~2 mins (Set 1) whereas in Set 3, O_2 taken at 300 torr pressure in a 5 liter flask was photolysed by UV.

4.2.2 Photolysis of (O_3+CO) mixture by visible light (Set 1-3)

The product ozone was frozen by LN_2 and the remaining oxygen pumped away till 2 mtorr pressure (vapor pressure of ozone at LN_2). Keeping the ozone in condensed form in LN_2 temperature, CO was admitted to the reaction chamber (between 7 to 447 torr pressure). Subsequently, the liquid nitrogen trap was removed and the O₃-CO mixture (in room temperature) was photolysed by visible lamp [Figure 3.1] for 30 to 360 min. The number of experiments in three sets are- Set 1: sixteen experiments (A1-A16, Table 4.2), Set 2: sixteen experiments (AC1-AC17, Table 4.3) and Set 3: five experiments (AS1-AS5, Table 4.4).

4.2.3 Photolysis of (O_2+CO) mixture by UV light (Set 4)

In Set 4, approximately 100 to 400 μ mol of O₂ was taken in the 5 liter chamber and isolated from the main vacuum line. The residual oxygen was pumped out from the vacuum manifold. Subsequently, CO at a higher pressure (100 to 300 torr) was taken in the vacuum manifold and the isolating stopcock of the reaction chamber was slowly open to introduce the CO. The back flow of O₂ to the vacuum line should be small under this condition. CO pressure decreased to 10 to 26 torr after equilibration. The O₂-CO mixture was photolysed with UV photons from a Hg lamp for 350 to 1330 min. Four experiments (AB1-AB4, Table 4.4) were done in this set.

| $\Delta\delta^{17}$ O |)
Î | 58.9 | 51.4 | 54.4

 | 61.5 | 61.6 | 71.9 | 50.1 | 50.2 | 57.8 | 68.8

 | 71.3

 | 50.2 | 55.0 | 54.4 | 65.7
 | 59.3 |
|---------------------------------------|---|---|---
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--|--|--|---|--|---|--
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--|---
---|---|---|---|
| $\Delta \delta^{18} O$ |)

 | 84.7 | 74.6 | 77.9

 | 85.3 | 86.5 | 92.0 | 74.4 | 73.7 | 80.9 | 94.4

 | 99.1

 | 75.2 | 80.3 | 82.1 | 92.6
 | 85.0 |
| δ ¹⁷ Ο |) | -17.1 | -12.9 | -21.0

 | -22.6 | -20.5 | -20.1 | -17.5 | -16.7 | -20.5 | -18.5

 | -19.0

 | -17.7 | -20.5 | -21.8 | -19.4
 | -19.6 |
| δ^{18} O |) | -31.2 | -24.7 | -37.1

 | -39.3 | -36.2 | -35.8 | -31.9 | -30.6 | -36.4 | -34.9

 | -35.7

 | -33.7 | -36.4 | -38.3 | -36.3
 | -36.4 |
| δ ¹⁷ Ο |) | 41.8 | 38.6 | 33.5

 | 38.9 | 41.1 | 51.8 | 32.5 | 33.5 | 37.3 | 50.2

 | 52.2

 | 32.5 | 34.5 | 32.6 | 46.3
 | 39.7 |
| δ ¹⁸ Ο |) | 53.6 | 49.9 | 40.8

 | 46.0 | 50.3 | 56.3 | 42.4 | 43.0 | 44.5 | 59.5

 | 63.4

 | 41.5 | 43.8 | 43.8 | 56.3
 | 48.7 |
| Amount of
CO ₃ produced | (μmol) | 46 | 59 | 16

 | 26 | 34 | 35 | 43 | 45 | 31 | 15

 | 12

 | 13 | 30 | 26 | ß
 | 7 |
| Exposure
time | (min) | 50 | 50 | 150

 | 240 | 210 | 30 | 40 | 100 | 330 | 300

 | 180

 | 180 | 180 | 180 | 180
 | 180 |
| Amount
of CO | (μmol) | 1587 | 1633 | 1633

 | 1587 | 1582 | 1313 | 1177 | 1189 | 1022 | 67

 | 67

 | 25 | 1008 | 1035 | 46
 | 109 |
| Sample
No. | | A1 | A2 | A3

 | A4 | A5 | $\mathbf{A6}$ | A7 | A8 | A9 | A10

 | A11

 | A12 | A13 | A14 | A15
 | A16 |
| | Sample Amount Exposure Amount of Λ^{18} O δ^{17} O δ^{18} O δ^{17} O δ^{18} O δ^{17} O | Sample Amount Exposure Amount of $\ No. \ of CO \ time \ CO_2 \ produced \ \delta^{18}O \ \delta^{17}O \ \delta^{18}O \ \delta^{17}O \ \Delta\delta^{18}O \ \Delta\delta^{17}O \ (\mu mol) \ (min) \ (\mu mol)$ | Sample Amount Exposure Amount of
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(μmol) (min) (μmol)
A1 1587 50 46 53.6 41.8 -31.2 -17.1 84.7 58.9 | Sample Amount Exposure Amount of N_0 . $of CO$ time CO_2 produced $\delta^{18}O$ $\delta^{17}O$ $\delta^{17}O$ $\delta^{17}O$ $\Delta\delta^{18}O$ $\Delta\delta^{17}O$ No. of CO time CO_2 produced $\delta^{18}O$ $\delta^{17}O$ $\delta^{17}O$ $\Delta\delta^{18}O$ $\Delta\delta^{17}O$ $\Delta\delta^{18}O$ $\Delta\delta^{17}O$ $\Delta\delta^{11}O$ <t< td=""><td>SampleAmountExposureAmount of
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lent			$\Delta \delta^{17} O$		3.1	9.9	0.0	\$2.4	5.4	8.1	70.6	52.2	55.8	5.6	4.8	3.2	8.7	1.1	1.7	70.1
Enrichn			$\Delta \delta^{18}$ O 2		65.1 4	68.3 3	76.2 E	60.8 3	86.0 5	90.6	98.1 7	77.6 5	80.8 5	92.6 é	95.5 é	88.2 é	95.7 é	65.6 4	72.3 4	104.1 7
lel	ction		$\delta^{17}O$		-5.9	-4.4	-2.8	-17.8	-0.7	-3.4	17.9	-13.3	-13.6	-8.7	6.9	-8.3	1.0	-20.0	-23.1	20.7
Moc	predic		$\delta^{18} { m O}$		-25.0	-22.4	-19.8	-34.1	-19.0	-23.0	-0.6	-31.2	-29.9	-25.0	-7.5	-24.3	-12.4	-35.9	-40.5	9.4
O_2	osition		$\delta^{17} O$		37.2	32.2	47.2	14.6	54.7	54.6	88.5	38.9	42.2	56.8	71.6	54.9	69.7	21.1	18.6	90.8
Ŭ	compo		$\delta^{18} { m O}$		40.1	46.0	56.4	26.8	67.0	67.5	97.5	46.4	50.9	67.5	88.0	64.0	83.3	29.7	31.8	113.5
		Amount of	CO ₂ produced	(μmol)	10	18	104	37	13	9	11	ı	30	28	14	36	24	30	11	6
		Exposure	time	(min)	120	150	65	120	60	70	115	135	140	150	120	65	180	115	125	180
		Amount	of CO	(μmol)	129	654	329	309	46	46	46	46	1269	1269	170	1353	1212	386	386	88
one	osition		$\delta^{17} { m O}$		43.8	46.2	46.2	12.7	50.7	46.8	89.1	25.7	28.1	48.8	70.3	46.7	69.0	11.7	11.1	101.8
Ozo	compe		$\delta^{18} { m O}$		52.7	56.2	56.5	22.1	61.3	55.7	101.9	36.3	38.3	62.6	89.6	60.4	88.9	24.3	23.1	128.1
		Amount	of O_3	(μmol)	58	62	335	36	68	65	71	76	68	74	48	89	47	97	91	68
		Sample	No.		AC1	AC2	AC3	AC4	AC6	AC7	AC8	AC9	AC10	AC11	AC12	AC13	AC14	AC15	AC16	AC17

Table 4.3: Oxygen isotopic compositions of CO_2 samples from Set 2. Model predicted values are also shown. The difference between observed δ -values of CO_2 and model prediction is defined as enrichment. All values are relative to VSMOW in %.

Oxygen isotopic composition of CO_2 produced from $CO+O$ reaction for Set 3 and Set 4. In Set 3 ozone was made by UV discharge of O_2 .	otopic composition and amount of ozone are δ^{18} O=128.7±1.3% and δ^{17} O=101.8±1% and 80±7µmol respectively. In Set 4 O ₂ and CO	is photolysed. The isotopic composition of O ₂ and CO are: (24.6, 12.5) and (28.7,14.9) relative to VSMOW. Model predicted values are also	g with the enrichment in each case defined as Observed value-Model value.
Table 4.4: Oxygen isot	Average isotopic compo	nixture was photolysed	shown along with the ev

					:			- - -	
				$CO_2 CO_2$	mposition	Model]	orediction	Enricr	ument
Sample	Amount	Exposure	Amount of						
No.	of CO	time	CO ₂ produced	$\delta^{18} { m O}$	$\delta^{17} { m O}$	$\delta^{18} { m O}$	$\delta^{17} { m O}$	$\Delta\delta^{18}$ O	$\Delta\delta^{17} O$
	(μmol)	(min)	(μmol)						
					Set 3				
AS1	3889	180	13	84.7	70.2	-22.6	-6.4	107.2	76.6
AS2	5834	06	10	74.9	64.9	-29.6	-12.4	104.5	77.3
AS3	5834	360	12	71.9	63.4	-28.6	-11.6	100.5	75.0
AS4	5834	06	6	70.2	54.6	-29.6	-12.4	99.8	67.0
AS5	7778	06	26	71.8	67.5	-27.3	-10.7	99.1	78.2
					Set 4				
AB1	4521	355	7	53.6	48.2	-41.0	-23.3	94.6	71.5
AB2	4589	610	10	51.3	48.4	-43.4	-24.7	94.7	73.0
AB3	7013	1330	21	59.5	57.0	-43.7	-24.8	103.2	81.8
AB4	7013	550	18	57.1	53.8	-43.0	-24.4	100.2	78.2

4.2.4 Measurement of δ^{18} O, δ^{17} O and δ^{13} C of the product CO₂

After photolysis, the product CO_2 and left over ozone, if any, were frozen and non condensable gases (CO and O_2) were pumped out. To separate CO_2 from the left over ozone, the condensed gases were transferred to a chamber containing cleaned nickel foil and heated to 120°C to decompose any ozone [details are given in Chapter 2]. In most of the experiments, the quantity of O_2 resulting from ozone dissociation on hot nickel surface was not measurable and pumped out. Subsequently, pure CO_2 was collected for isotopic analysis.(see section 2.5 for details and blank).

In order to determine ${}^{17}\text{O}/{}^{16}\text{O}$ ratio in product CO₂, we need to resolve the isobaric effect of ${}^{13}\text{C}/{}^{12}\text{C}$ in mass 45. For this, the equilibrium exchange method of CO₂ with hot CeO₂ was employed. Hot CeO₂ reacts with CO₂ and changes its oxygen isotopic composition to one where mass dependence rule is obeyed. The ${}^{13}\text{C}/{}^{12}\text{C}$ ratio remains unchanged. Experimentally, the average recovery of CO₂ was ~ 99% and the change in $\delta^{13}\text{C}$ was ~0.06‰ [see Chapter 2]. Measurements of carbon and oxygen isotopic compositions of product CO₂ were done using a Europa GEO 20-20 mass spectrometer and oxygen isotopic topic measurement of ozone was done using a VG 903 mass spectrometer.

4.3 Results and Discussion

4.3.1 Oxygen isotope fractionation

The results of photolysis experiments pertaining to Set 1 are given in Table 4.2 and shown in Figure 4.1. The cross-plot of δ values for CO₂ defines a line with a slope 0.96±0.07. The maximum δ^{18} O value observed is 63.4‰ and the corresponding δ^{17} O value is 52.2‰. In most of the cases, δ^{17} O value of a given CO₂ sample is close to the δ^{18} O. The results for Set 2 experiments are given in Table 4.3 and the δ - values of CO₂ are plotted in Figure 4.2. The data points fall on a line with a slope of 0.90± 0.04. The highest δ^{18} O value (113.5‰) is obtained in experiment AC17 where the δ^{18} O value of the source ozone was also the highest. Additionally, the CO₂ amount was low in this case. We note that if CO amount does not change significantly (for example, in sample numbers AC6, AC7, AC8 and AC9 where the CO amount is ~ 50 µmol the δ -value of CO₂ increases with that of the ozone. A change of 106‰ in δ^{18} O value of ozone results in a change of 87‰ in δ^{18} O value of CO₂.

It is to be noted that in samples AC4, AC15 and AC16, the δ^{18} O values of CO₂ were low and close to that of CO. In these cases, the ozone had no enrichment as the δ -values were close to that of the tank O₂



Figure 4.1: Oxygen isotopic composition (in ‰ relative to VSMOW) of product CO_2 (Set 1 samples) defining a line with slope of 0.96 ± 0.07 . The average $\delta^{18}O$ and $\delta^{17}O$ values of CO_2 samples calculated from the KINTECUS model are -34.7‰ and -19.1‰. Note that CO_2 is enriched in heavy oxygen isotopes in an anomalous fashion.

The δ -values of CO₂ produced in Set 3 and Set 4 are summarized in Table 4.4 and the δ -values are plotted against each other in Figure 4.3 displaying again a mass independent signature. The average δ^{18} O and δ^{17} O values of Set 3 CO₂ samples are 74.7 and 64.1% respectively and for samples of Set 4 they are 55.4 and 51.9%. As mentioned before, in Sets 3 and 4 two different sources of O atom were used. In Set 3, O₃ + CO mixture was photolysed in presence of visible light whereas in Set 4 a mixture of O₂ and CO was photolysed using UV light from Hg lamp for various time periods.



Figure 4.2: Oxygen isotopic compositions of CO₂ samples from set 2. The best-fit line relating $\delta^{17}O$ with $\delta^{18}O$ gives a slope of 0.90 ± 0.04 suggesting anomalous enrichments in heavy oxygen isotopes. Ozone compositions used in these experiments are also shown in the plot. The average isotopic composition of CO₂ samples as predicted by the KINTECUS model is: $\delta^{18}O = -21.3\%$ and $\delta^{17}O = -4.7\%$. The maximum enrichment seen in this set is 104.1 and 70.1‰ in $\delta^{18}O$ and $\delta^{17}O$ respectively corresponding to ozone composition of 128.1‰ and 101.8‰ in $\delta^{18}O$ and $\delta^{17}O$ respectively.



Figure 4.3: A three-isotope plot of the experimental data observed in Set 3 and Set 4 along with results of model simulation. In Set 3, O_3 -CO mixture was photolysed using visible lamp whereas in Set 4, O_2 -CO mixture was photolysed in UV light. The average $\delta^{17}O$ and $\delta^{17}O$ enrichments (difference between observed data and model prediction) are: (102.2, 74.8) in Set 3 and (98.2, 76.1) in Set 4.

4.3.2 Carbon isotope fractionation

It is interesting to note the nature of variation of δ^{13} C of CO₂ (relative to the starting CO composition) with pressure. The change in δ^{13} C can be defined as

$$\Delta(\delta^{13}C) = \delta^{13}C(CO_2) - \delta^{13}C(CO)$$

 $\Delta(\delta^{13}C)$ and CO pressure for all the four Sets are listed in Table 4.5 and plotted against each other in Figure 4.4. $\Delta(\delta^{13}C)$ values vary from +3.8‰ to -14.6‰. At high CO pressure (between 270 to 445 torr), the average value is -12.1‰. With CO pressure below 270 torr $\Delta(\delta^{13}C)$ tends to increase with decrease in pressure becoming positive at very low pressures. The most positive value of $\Delta(\delta^{13}C)$ = 3.8‰ is obtained at 18 torr (sample A10).



Figure 4.4: Difference between $\delta^{13}C$ value of the product CO_2 and the $\delta^{13}C$ value of initial $CO(\Delta\delta^{13}C = \delta^{13}C(CO_2) - \delta^{13}C(CO))$ plotted against CO pressure. In Set 1 and 2, between 270 to 445 torr the average $\Delta\delta^{13}C$ value is -12.1‰, which is close to the expected value (see text). At lower pressures, $\Delta\delta^{13}C$ value increases. The pattern suggests a surface effect at lower pressures where the discrimination between ^{13}C and ^{12}C diminishes. In Set 3 and Set 4, experiments were carried out in a 5 liter chamber where the pressure is low but the surface effect is smaller due to lower surface/volume ratio.

Sample	CO	Observed	Mode	result	Sample	CO	Observed	Mode	l result
No.	pressure	$\Delta(\delta^{13}\mathrm{C})$	$\Delta(\delta^{13} C)$ †	$\Delta(\delta^{13}{ m C})\ddagger$	No.	pressure	$\Delta(\delta^{13}C)$	$\Delta(\delta^{13}C)\dagger$	$\Delta(\delta^{13}{ m C})\ddagger$
	torr)		(A)	(A-4.3%)		torr)		(Y)	(A-4.3%)
		(%)	(%)	(%)			(%)	(%)	(%)
		Set 1				Set 2			
A1	432	-11.1	-6.0	-10.3	AC1	35	3.0	-5.9	-10.2
A2	444	-11.3	-6.0	-10.3	AC2	57	0.9	-5.9	-10.2
A3	444	-12.5	-6.1	-10.4	AC3	89	-3.6	-5.0	-9.3
A4	432	-12.2	-6.1	-10.4	AC4	84	0.9	-6.0	-10.3
A5	430	-14.2	-6.1	-10.4	AC6	12	0.3	-5.3	-9.6
A6	357	-14.6	-6.0	-10.3	AC7	12	-0.3	-5.7	-10.0
A7	320	-11.2	-6.0	-10.3	AC8	12	2.0	-5.3	-9.6
A8	324	-10.9	-6.0	-10.3	AC9	12	0.8	-5.4	-9.7
A9	278	-12.4	-6.0	-10.3	AC10	345	-11.6	-6.0	-10.3
A10	18	3.8	-5.4	-9.7	AC11	345	-11.5	-6.1	-10.4
A11	18	-0.1	-5.5	-9.8	AC12	46	-3.7	-5.9	-10.2
A12	7	3.3	-4.3	-8.6	AC13	368	-11.0	-6.0	-10.3
A13	274	-12.0	-6.0	-10.3	AC14	330	-12.5	-6.1	-10.4
A14	282	-11.4	-6.0	-10.3	AC15	105	-4.1	-5.9	-10.2
A15	12	2.0	-5.6	-9.9	AC16	105	-3.5	-6.0	-10.3
A16	30	-0.3	-5.8	-10.1	AC17	24	3.8	-5.8	-10.1
		Set 3				Set 4			
AS1	14	-10.7	-6.1	-10.4	AB1	16	-4.9	-6.1	-10.4
AS2	21	-8.9	-6.1	-10.4	AB2	17	-7.6	-6.1	-10.4
AS3	21	-9.3	-6.1	-10.4	AB3	25	-10.6	-6.1	-10.4
AS4	21	-8.6	-6.1	-10.4	AB4	25	-10.0	-6.1	-10.4
A.55	28	-9.4	-6.1	-10.4					

Anomalous enrichment of heavy oxygen isotopes in CO_2 produced from O+CO reaction
4.3.3 Preliminary analysis by considering exchange and collision

While interpreting the oxygen isotopic composition of the product CO_2 we note that one of the oxygen atoms is primarily derived from ozone dissociation. However, exchange of the O-atom with CO and O_2 plays an important role and therefore, an essential prerequisite to determine the $\delta^{18}O$ value of CO_2 is to know the O atom composition just before it interacts with CO.

In the present experiment, the possible sources and sinks of oxygen atoms are determined by the following reactions:

$$O_3 + h\nu \to O_2 + O$$
 $k_a = 2.5 \times 10^{-3}$ (4.1)

$$O + O_3 \to 2O_2$$
 $k_b = 8 \times 10^{-15}$ (4.2)

$${}^{18}O(^{3}P) + {}^{12}C^{16}O \Leftrightarrow {}^{16}O(^{3}P) + {}^{12}C^{18}O \qquad \qquad k_{c} = 8.3 \times 10^{-16}$$
(4.3)

$$O(^{3}P) + CO + M \rightarrow OCO + M$$
 $k_{e} = 4.3 \times 10^{-36}$ (4.5)

(the reaction constants have units of cm^3 molecule⁻¹ sec⁻¹ for two-body and cm^3 molecule⁻² sec⁻¹ for three body reactions, [*Anderson et al.*, 1985; *DeMore et al.*, 1997])

The immediate fate of O-atoms after formation is to undergo isotopic exchange with O_2 and CO via collisions. As an example, we discuss experiment AC1 (of Set 2) to estimate the effect of exchange and collision on the isotopic compositions of O and CO and determine that of CO₂ assuming a simple mixing. The ratio of exchange rate of O with O₂ to that of O with CO is:

$$R = \frac{k_{d}[O][O_{2}]}{k_{c}[O][CO]} \approx 3.5 \times 10^{3} \frac{[O_{2}]}{[CO]}$$
(4.6)

For sample AC1, $[O_2]/[CO] \sim 0.4$. Thus the value of R is ~ 1500 i.e., O-O₂ exchange is 1500 times faster than the O-CO exchange. It is also to be noted that the rate of the isotopic exchange of O with CO is ~ 175 times faster than O+CO+M recombination rate. As a consequence of fast collision rate (~10⁹ per sec) and rapid isotopic exchange, the O-atoms attain a composition determined effectively by the exchange equilibrium of O-atom with O₂/CO reservoir before they react with CO. Therefore, the O-atom composition does not depend significantly on the ozone composition but is mainly determined by the isotopic composition of O₂. Following *Urey* [1947], and *Bigeleisen and Mayer*, [1947] the equilibrium constant for exchange reaction between the compound considered (CO or O₂) and the separated atoms (O) is given by the reduced partition function ratio of the compound which also expresses ¹⁸O/¹⁶O ratio (¹⁸R) of the molecular species relative to the ratio of the O-atoms i.e., ¹⁸R(O₂ or CO)/¹⁸R(O). The reduced partition function ratio [*Richet et al.*, 1977] for CO + O system is 1.1064 and for O₂ + O system is 1.077, which indicates that at equilibrium, exchange between O-atom and CO results in relative enrichment of ¹⁸O isotope in CO and O₂ by 106.4‰ and 77‰ respectively. In our case, the CO and O₂ reservoirs are very large compared to the number of O-atoms and therefore, no appreciable change occurs in their composition. But for the atomic oxygen reservoir, this exchange results in ~70‰ depletion in δ^{18} O of O-atoms relative to the O₂ composition. For sample AC1, simple calculation shows that the O-atom composition (initially at δ^{18} O ~ 52.7, δ^{17} O ~ 43.8‰) effectively decreases to -22.6, 5.8‰ respectively due to exchange (under assumption of full equilibrium condition). In actual case, the progress of the reactions and development of the products are calculated by the KINTECUS model.

We surmise that the atoms from this modified pool (where composition changes with time) collide with CO molecules (comprising all possible isotopologues) with collision rate proportional to the relative velocity of the colliding partners. In a simple collision model, the relative velocity effect is taken into account by assuming the rate coefficient for the chemical reaction to be inversely proportional to $\sqrt{\mu}$, where μ is the reduced mass of the colliding pair. In this scenario, the mass dependent collision rate and consequent isotopic fractionation for a given reaction can be calculated from

$$\frac{k_{\rm Q}}{k_{\rm O}} = \sqrt{\frac{\mu_{\rm O}}{\mu_{\rm Q}}} \tag{4.7}$$

For simplicity, we consider this fractionation to comprise of two parts. First, one partner is ¹⁶O and other partners are various CO isotopologues (${}^{12}C{}^{16}O$, ${}^{12}C{}^{17}O$, ${}^{12}C{}^{18}O$) which would modify only the CO isotopic composition. Second, one partner is ${}^{12}C{}^{16}O$ molecule and other partners are ¹⁶O, ¹⁷O and ¹⁸O which would result in a change of Oatom composition. In the first case, the rates at which ${}^{12}C{}^{17}O$ and ${}^{12}C{}^{18}O$ collide with ¹⁶O are 0.994 and 0.988 relative to the rate at which ${}^{12}C{}^{16}O$ collides with ¹⁶O. This results in a mass dependent collisional fractionation where the effective CO composition is lighter by 12.2‰ and 6.3‰ in $\delta^{18}O$ and $\delta^{17}O$ respectively. In our case, the effective CO composition (having initial $\delta^{18}O = 28.7$ and $\delta^{17}O = 14.9 \%$) would therefore be $\delta^{18}O = 16.5\%$ and $\delta^{17}O = 8.6\%$. Similarly, the rates at which ${}^{12}C{}^{16}O$ molecule collides with ${}^{17}O$ and ${}^{18}O$ are 0.981 and 0.964 of the rate at which it collides with ${}^{16}O$ respectively. This effectively lowers the $\delta^{18}O$ and $\delta^{17}O$ value of O-atoms by 36.0 and 18.9‰ respectively. The effective O-atom composition would, therefore, be $\delta^{18}O = -58.6$ and $\delta^{17}O = -13.1 \%$ (for the simple case in AC1).

There is another source of collisional fractionation that should be considered. Combination of O-atom with CO forms a short-lived excited complex CO_2^* which is in a rovibrational metastable state; this gets stabilized by a series of collisional deactivation processes leading to a stable CO_2 molecule. The energy transfer mechanism can be written as: $QCO^* + M \rightarrow QCO + M$.

 CO_2^* transfers its extra energy to molecules of the bath gas CO or O_2 in discrete steps of ΔE per collision. Finally, CO_2^* molecules with energy less than ΔE leads to a deactivated or stable CO_2 molecule. The deactivating collision frequency is again inversely proportional to the reduced mass of the colliding pair involved, i. e.

$$\frac{\omega'}{\omega} = \sqrt{\frac{\mu_{CO_2,M}}{\mu_{CO'_2,M}}} \tag{4.8}$$

where μ indicates reduced mass of different CO₂ isotopomers. ¹⁶O¹²C¹⁸O and ¹⁶O¹²C¹⁷O collide with ¹²C¹⁶O at rates lower by 0.992 and 0.996 factors relative to collisional rate of ¹⁶O¹²C¹⁶O with ¹²C¹⁶O. This results in 8.5‰ and 4.3‰ depletion in ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios of the stable CO₂ molecule respectively. Considering all these fractionations the expected values of δ^{18} O and ¹⁷O of the product CO₂ are calculated to be -29.5 and -6.6 respectively. These are clearly different from the values observed experimentally for AC1 sample i.e., δ^{18} O = 40.1 and δ^{17} O = 37.2‰. This shows that O+CO reaction leads to large and anomalous enrichment ($\Delta\delta^{17}$ O ~44 and $\Delta\delta^{18}$ O ~70) of heavy oxygen isotopes in the product CO₂.

The above procedure of estimation of enrichment, though correct to some degree, assumes instantaneous establishment of equilibrium (as soon as O-atoms form) and does not take into account all possible reactions and details of various rate constants. To quantify the enrichment more accurately, it is necessary to estimate the expected CO_2 composition after considering all the processes that are involved rather than only exchange and collision. Some of these processes are:

- 1. preferential dissociation of ¹⁶O-¹⁶O bond during ozone photolysis which is relatively weaker than ¹⁸O-¹⁶O or ¹⁷O- ¹⁶O bond,
- secondary process of ozone dissociation on collision with O-atom which depletes the O-atom pool,
- 3. secondary ozone formation.

To quantify the effect of all the processes and calculate the expected CO_2 composition as the reaction chain evolves we need to use a detailed reaction kinetic model like KINTECUS.

4.4 Model Simulation

The chemical reaction model (KINTECUS) was used to calculate the expected isotopic composition of the product CO_2 from O+CO reaction. The description of the model, the performance test and the accuracy of the model predictions are described in Chapter 3 in detail.

4.4.1 Input parameters for visible light dissociation of ozone in (O₃+CO) mixture (Sets 1-3)

The reactions (Reaction Sets R1 to R6) incorporated in the model are summarized in Table 4.6. The details of the reaction rates of reaction Sets 1-4 are given in Chapter 3.

As discussed before, we assume that during ozone photolysis the O atom is derived only from the base position. The total enrichment in ozone can be expressed in terms of enrichment in asymmetric and symmetric species as,

$$E_{total}^{50} = \frac{2}{3} E^{50}(asymmetric) + \frac{1}{3} E^{50}(symmetric)$$
 (4.9)

$$E_{\text{total}}^{49} = \frac{2}{3} E^{49}(\text{asymmetric}) + \frac{1}{3} E^{49}(\text{symmetric})$$
(4.10)

Based on various studies using spectroscopic methods [*Anderson et al.*, 1989; *Larsen et al.*, 1994, 2000] it has been shown that $E^{50}_{asym} \neq E^{50}_{sym}$. It is therefore, important to obtain the isotopic composition of the base atoms which is not known a-priori. Recently *Janssen* [2005] and *Bhattacharya et al.* [2006] have given formulae relating the enrichment in δ^{18} O

and δ^{17} O (expressed in ‰) in asymmetric species with corresponding total enrichment in ozone as

$$E^{50}(asymmetric) = -17.04 + 1.33 \times E^{50}_{total} - 3.93 \times 10^{-4} (E^{50}_{total})^2$$
(4.11)

$$E^{49}(asymmetric) = 3.12 + 1.22 \times E^{49}_{total} - 3.19 \times 10^{-4} (E^{49}_{total})^2$$
(4.12)

It is noted that for asymmetric species, enrichment in ¹⁷O is more than that of ¹⁸O for a given value of total enrichment. Using these two equations (4.11 and 4.12), the enrichment of heavy oxygen isotopes at base position (asymmetric species) corresponding to a given total enrichment was calculated in case of Set 2 and Set 3 experiments where ozone enrichment was large. In Set 1, the enrichment in asymmetric ozone species was taken to be same as that of total ozone since the ozone enrichment was small ($\sim 3\%$) [*Janssen*, 2005].

The value of ozone dissociation rate constant (k_1) was determined experimentally and taken to be 2.5×10^{-3} sec⁻¹ (see Chapter 3 for details). The dissociation rates for O-Q and O-P bond are lower by 0.972 and 0.988 compared to O-O bond [*Wen and Thiemens*, 1991]. Note the factor 0.5 for rate constants in reactions involving two product channels.

For isotopic exchange reaction (reaction set R5) between oxygen atom with CO and DO (D denotes ¹³C) the backward reaction rate k_{29} , k_{31} , k_{33} and k_{35} were obtained from the forward reaction rate k_{28} [*Jaffe and Klein*, 1966] and the equilibrium constant by considering a rigid rotor harmonic oscillator approximation [see appendix A.1].

Slanger and Black [1972] showed that the O+CO recombination rate (reaction set R6) is dependent on the characteristics of the third body (M) and found the rate constants to be $2.3\pm0.4\times10^{-36}$, $3.9\pm0.7\times10^{-36}$, $6.2\pm0.9\times10^{-36}$ cm³ molecule⁻² sec⁻¹ for M= N₂, CO and CO₂ whereas Yung and DeMore [1999] reported 4.3×10^{-36} and 1.1×10^{-35} cm³ molecule⁻² sec⁻¹ for M= CO and CO₂ respectively. In our case, the rate constant k₃₆ was taken to be 4.3×10^{-36} cm³ molecule⁻² sec⁻¹. However, this yields much lower amount of product CO₂ compared to what we obtained experimentally. We are not sure of the exact reason but suspect that the assumed reaction rate may not be valid where M represents mixed gases like CO, O₂ and O₃. Additionally, surface induced stabilization might have played a role.

Table 4.6: List of various gas phase reactions along with the rate constants used in the kinetic model (KIN-TECUS) for simulation of products from O_3 +CO photolysis by visible light. The reaction constants have units of cm³ molecule⁻¹ sec⁻¹ for two-body and cm³ molecule⁻² sec⁻¹ for three body reactions. O, Q, P, C and D denotes ¹⁶O, ¹⁸O, ¹⁷O, ¹²C, ¹³C.

	Reactions	Rate coefficient
	R1 (Ozone photolysis)	
R(1a)	$OOO+h\nu \rightarrow O+OO$	$k_1 = 2.5 \times 10^{-3}$
R(1b)	$OOQ+h\nu \rightarrow O+OQ$	$k_2 = 0.5 \times k_1$
R(1c)	$OOQ+h\nu \rightarrow Q+OO$	$k_3 = 0.5 \times 0.972 \times k_1$
R(1d)	$OQO+h\nu \rightarrow O+OQ$	$k_4 = 0.972 \times k_1$
R(1e)	$OOP+h\nu \rightarrow O+OP$	$k_5 = 0.5 \times k_1$
R(1f)	$OOP+h\nu \rightarrow P+OO$	$k_6 = 0.5 \times 0.988 \times k_1$
R(1g)	$OPO+h\nu \rightarrow O+OP$	$k_7 = 0.988 \times k_1$
	R2 (Isotopic exchange of O atom with oxygen)	
R(2a)	Q+OO→O+OQ	$k_8 = 2.9 \times 10^{-12}$
R(2b)	O+OQ→Q+OO	k_9 =1.34×10 ⁻¹²
R(2c)	$P+OO \rightarrow O+OP$	k_{10} =2.9×10 ⁻¹²
R(2d)	O+OP→P+OO	$k_{11}\text{=}1.39{\times}10^{-12}$
	R3 (Ozone formation)	
R(3a)	O+OO+M→OOO+M	k_{12} =6.0×10 ⁻³⁴
R(3b)	$O+OQ+M \rightarrow OOQ+M$	k_{13} =0.5×1.45× k_{12}
R(3c)	$O+OQ+M \rightarrow OQO+M$	k_{14} =0.5×1.08× k_{12}
R(3d)	$Q+OO+M \rightarrow OOQ+M$	k_{15} =0.92× k_{12}
R(3e)	$Q+OO+M \rightarrow OQO+M$	k_{16} =0.006× k_{12}
R(3f)	$O+OP+M \rightarrow OOP+M$	k_{17} =0.5×1.36× k_{12}
R(3g)	O+OP+M→OPO+M	k_{18} =0.5×1.06× k_{12}
R(3h)	$P+OO+M \rightarrow OOP+M$	k_{19} =0.98× k_{12}
R(3i)	$P+OO+M \rightarrow OPO+M$	$k_{20} {=} 0.006 {\times} k_{12}$
	R4 (Ozone decomposition)	
R(4a)	OOO+O→OO+OO	k_{21} =8.0×10 ⁻¹⁵
R(4b)	$OOO+Q \rightarrow OO+OQ$	k_{22} =0.957× k_{21}
R(4c)	$OOQ+Q \rightarrow OO+OQ$	k_{23} =0.995× k_{21}
R(4d)	$OQO+Q \rightarrow OQ+OO$	k_{24} =0.995× k_{21}
R(4e)	OOO+P→OO+OP	k_{25} =0.978× k_{21}
R(4f)	OOP+O→OO+OP	k_{26} =0.997× k_{21}
R(4g)	OPO+O→OP+OO	k_{27} =0.997× k_{21}
	R5 (Isotopic exchange of O-atom with CO)	
R(5a)	$Q+CO \rightarrow O+CQ$	k_{28} =8.3×10 ⁻¹⁶
R(5b)	O+CQ→Q+CO	k_{29} =7.5×10 ⁻¹⁶
R(5c)	$Q+DO \rightarrow O+DQ$	k_{30} =8.3×10 ⁻¹⁶
R(5d)	$O+DQ \rightarrow Q+DO$	k_{31} =6.9×10 ⁻¹⁶
R(5e)	$P+CO \rightarrow O+CP$	k_{32} =8.3×10 ⁻¹⁶
R(5f)	O+CP→P+CO	k_{33} =7.9×10 ⁻¹⁶
R(5g)	$P+DO \rightarrow O+DP$	k_{34} =8.3×10 ⁻¹⁶
R(5h)	$O+DP \rightarrow P+DO$	k_{35} =7.3×10 ⁻¹⁶

	Reactions	Rate coefficient
	R6 (CO ₂ formation)	
R(6a)	$O+CO+M \rightarrow COO+M$	k_{36} =4.3×10 ⁻³⁶
R(6b)	$O{+}DO{+}M{\rightarrow}DOO{+}M$	k_{37} =0.994× k_{36}
R(6c)	$O{+}CQ{+}M{\rightarrow}COQ{+}M$	k_{38} =0.988× k_{36}
R(6d)	$O{+}DQ{+}M{\rightarrow}DOQ{+}M$	k_{39} =0.982× k_{36}
R(6e)	$Q{+}CO{+}M{\rightarrow}COQ{+}M$	k_{40} =0.964× k_{36}
R(6f)	$Q{+}DO{+}M{\rightarrow}DOQ{+}M$	k_{41} =0.956× k_{36}
R(6g)	$O+CP+M \rightarrow COP+M$	k_{42} =0.994× k_{36}
R(6h)	$O{+}DP{+}M{\rightarrow}DOP{+}M$	k_{43} =0.988× k_{36}
R(6i)	$P{+}CO{+}M{\rightarrow}COP{+}M$	k_{44} =0.981× k_{36}
R(6j)	$P{+}DO{+}M{\rightarrow}DOP{+}M$	$k_{45} {=} 0.975 {\times} k_{36}$

4.4.2 Determination of enhancement factor 'f' for [M] to obtain correct CO₂ amount and its significance

As discussed above, the model could not reproduce the experimental CO_2 amount in Set 1 and 2 whereas in case of Set 3 and 4 the predictions were close to the observed value.

This discrepancy could arise from collision with surface of the reaction vessel during the stabilization of the intermediate complex CO_2^* , which causes an enhancement in production rate. The stabilization rate depends on many experimental parameters like, pressure, temperature, nature of the third body, etc. For example, increase in pressure and temperature leads to higher number of collisions per unit time in per unit of reaction volume which helps the intermediate complex to transfer its excess energy to the bath gas molecules efficiently. This increases the stabilization rate and the production of stable molecule (CO_2).

In addition to this, nature (or molecular property) of the third body also influences the stabilization rate to a great extent. Polyatomic molecules as a third body can take away the excess energy from the excited complex more efficiently as compared to diatomic or monatomic molecules because it has higher degree of freedom and can accommodate more energy within its various modes. Surface or wall of the reaction vessel can also serve as an excellent third body because the molecules present at the lattice sites have an infinite capacity to take away the energy from the excited complex. Later on this energy gets dissipated from the lattice as a phonon or lattice heat. It is possible for an intermediate complex to transfer all of its excess energy to the wall in a single collision and become

stable.

KINTECUS model considers an infinite volume reaction cell and does not include the effect of surface on the reaction rates. In Set 1 and 2, experiments were done in 70 cc reaction vessel with relatively higher surface to volume ratio as compared to Set 3 and 4 where experiments were done in 5 liter chamber. This means that the effect of surface on the stabilization rate of CO_2 could be variable among these cases.

To get the model CO_2 amount close to that obtained in the experiments, the total concentration of all the molecules [M] in the chamber was enhanced by a suitable factor 'f' determined separately in each case. A plot of 'f' against CO pressure [Figure 4.5] shows that 'f' increases with decrease in pressure.



Figure 4.5: Variation of factor 'f' (which enhances CO_2 production by increasing [M]) with pressure. f increases with decrease in CO pressure suggesting increased importance of surface induced stabilization of CO_2^* . For high CO pressure or experiments done in 5 liter chamber, 'f' ranges from 1 to 55 whereas for low CO amount, value of 'f' range up to ~ 600 (except in one very high value of 1270.

This is quite expected because surface mediated stabilization reactions should dominate at lower pressures. The value of 'f' was 1 to 55 for experiments involving high CO amount or done in the 5 liter chamber whereas for experiments involving low CO amount, value of 'f' was 60 to 590. Only in one case (sample A12) 'f' was as high as 1270. The change in carbon isotopic composition of the product CO₂ relative to the initial CO ($\Delta \delta^{13}$ C) also shows a similar correlation with the initial CO pressure [Figure 4.4] and supports the hypothesis of wall-effect at lower pressures in Set 1 and 2 experiments. However, the factor 'f' is found to have no correlation with $\Delta \delta^{13}$ C probably because the two effects operate at different scales.

Enhancing [M] by this way increases the amount of CO₂ produced but it also has effect on δ^{18} O and δ^{17} O values (higher 'f' results in higher δ -values; Table 4.7) though not on δ^{13} C. The average change in δ^{18} O is ~ 5‰ except in two cases where the values are high (~ 18.8 (sample A2) and 14.5‰ (Sample AC14). For further interpretation we take 'f' values to be as determined in each case.

4.4.3 Input parameters for UV dissociation of (O_2+CO) mixture (Set 4)

In case of Set 4, six more reaction Sets (RR1 to RR6 of Table 4.8) in addition to those in R1 to R6 of Table 4.6, describing the production of singlet and triplet atoms and their quenching to ground state were considered. The O₂ and O₃ photolysis rate constants were calculated from the available photochemical cross-section data [*DeMore*, 1997] and known photon flux ~1×10¹⁵ photons cm⁻² s⁻¹ of the Hg lamp. Earlier studies [*DeMore*, 1997; *Atkinson*, 1996] showed that during ozone photolysis in UV light, production of singlet species (O(¹D), O₂(¹ Δ)) takes place in 90% cases whereas only in 10% cases triplet products form. Therefore, rate constants of reaction set 2 and 3 are multiplied by factor of 0.9 and 0.1 respectively.

Sample	CO_2]	Model A		Ν	lodel B	Difference
no.	amount		Amount	$\delta^{18} O$		Amount	$\delta^{18}O$	A-B
	(observed)	f	(μ mol)	‰	f	(μ mol)	‰	‰
	(μmol)							
Set 1								
A1	46.0	1	11.5	-43.3	16.8	45.9	-31.2	-12.2
A2	59.3		12.0	-43.3	55.0	54.1	-24.7	-18.7
A3	15.9		9.8	-41.3	3.5	16.3	-37.2	-4.2
A4	25.5		13.9	-41.8	3.3	26.9	-39.4	-2.5
A5	33.7		13.8	-41.8	6.8	35.9	-36.3	-5.6
A6	34.8		7.5	-44.2	10.2	34.3	-35.8	-8.5
A7	42.9		7.0	-43.6	22.0	42.4	-32.0	-11.7
A8	44.6		8.8	-42.3	27.0	45.1	-30.7	-11.6
A9	30.7		7.9	-41.4	10.8	30.9	-36.5	-5.0
A10	14.5		0.1	-37.0	375.0	15.0	-34.9	-2.1
A11	12.2		0.1	-37.3	250.0	11.8	-35.7	-1.6
A12	13.0		0.03	-36.6	1270.0	11.9	-33.7	-2.9
A13	30.3		7.5	-41.6	10.9	30.7	-36.5	-5.2
A14	26.1		7.8	-41.7	6.6	25.1	-38.4	-3.4
A15	4.9		0.07	-36.9	202.0	6.9	-36.3	-0.6
A16	7.3		0.2	-37.8	111.0	11.6	-36.4	-1.4
Set 2								
AC1	9.6	1	0.3	-27.4	96.5	10.2	-25.0	-2.4
AC2	17.7		0.6	-27.4	95.0	17.1	-22.4	-5.0
AC3	104.1		1.4	-28.0	228.0	106.0	-19.8	-8.1
AC4	37.0		9.7	-42.2	80.0	15.2	-34.1	-8.2
AC6	12.8		0.05	-21.4	590.0	11.4	-19.0	-2.4
AC7	6.3		0.05	-23.9	230.0	6.0	-23.0	-0.9
AC8	11.3		0.06	-1.2	500.0	10.7	-0.6	-0.7
AC9	_		0.06	-32.8	440.0	10.3	-31.2	-1.7
AC10	30.0		9.3	-38.9	12.0	30.9	-29.9	-9.0
AC11	27.9		9.6	-31.9	6.6	26.9	-25.0	-6.9
AC12	14.3		0.4	-13.8	130.0	14.1	-7.5	-6.3
AC13	35.6		9.8	-32.9	8.5	34.7	-24.3	-8.7
AC14	23.7		7.8	-26.8	10.9	22.6	-12.4	-14.5
AC15	30.4		1.6	-41.7	60.0	30.5	-35.9	-5.8
AC16	11.3		1.6	-42.1	12.0	12.1	-40.5	-1.6
AC17	9.0		0.15	9.1	154	9.8	9.4	-0.3
Set 3								
AS1	13.6	1	2.4	-28.52	9.4	12.8	-22.6	-5.6
AS2	10.0		4.4	-31.8	2.8	9.6	-29.6	-2.3
AS3	12.0		4.5	-31.9	3.9	12.1	-28.6	-3.3
AS4	8.9		4.4	-31.8	2.8	9.6	-29.6	-2.3
AS5	25.9		6.8	-33.9	7.5	26.1	-27.3	-6.6

Table 4.7: Effect of factor 'f' on the predicted oxygen isotopic composition of the product CO_2 . Model A is for f=1. In model B, [M] was enhanced by 'f' to reproduce the observed amount of CO_2 . The average difference between the two predictions is ~ 5‰.

	Reactions	Rate coefficient
	RR1(Oxygen photolysis)	
R(1A)	$OO+h\nu \rightarrow O+O$	$k_1 = 8.7 \times 10^{-7}$
R(1B)	$OQ+h\nu \rightarrow O+Q$	$k_2 = 0.983 \times k_1$
R(1C)	$OP+h\nu \rightarrow O+P$	$k_3 = 0.989 \times k_1$
	RR2(Ozone photolysis:singlet product	s)
R(2A)	$OOO+h\nu \rightarrow O(^{1}D)+OO(^{1}\Delta)$	k_4 =0.9×(1×10 ⁻²)
R(2B)	$OOQ+h\nu \rightarrow O(^{1}D)+OQ(^{1}\Delta)$	$k_5=0.5 imes k_4$
R(2C)	$OOQ+h\nu \rightarrow Q(^{1}D)+OO(^{1}\Delta)$	$k_6 = 0.5 \times 0.983 \times k_4$
R(2D)	$OQO+h\nu \rightarrow O(^{1}D)+OQ(^{1}\Delta)$	$k_7 = 0.983 \times k_4$
R(2E)	$OOP+h\nu \rightarrow O(^{1}D)+OP(^{1}\Delta)$	$k_8=0.5 \times k_4$
R(2F)	$OOP+h\nu \rightarrow P(^{1}D)+OO(^{1}\Delta)$	$k_9 = 0.5 \times 0.989 \times k_4$
R(2G)	$OPO+h\nu \rightarrow O(^{1}D)+OP(^{1}\Delta)$	k_{10} =0.989× k_4
	RR3(Ozone photolysis:triplet products	5)
R(3A)	OOO+h <i>v</i> →O+OO	k_{11} =0.1×(1×10 ⁻²)
R(3B)	$OOQ+h\nu \rightarrow O+OQ$	k_{12} =0.5× k_{11}
R(3C)	$OOQ+h\nu \rightarrow Q+OO$	k_{13} =0.5×0.983× k_{11}
R(3D)	$OQO+h\nu \rightarrow O+OQ$	k_{14} =0.983× k_{11}
R(3E)	$OOP+h\nu \rightarrow O+OP$	k_{15} =0.5× k_{11}
R(3F)	$OOP+h\nu \rightarrow P+OO$	k_{16} =0.5×0.989× k_{11}
R(3G)	$OPO+h\nu \rightarrow O+OP$	k_{17} =0.989× k_{11}
	RR4 (Ozone decomposition)	
R(4A)	OOO+O→OO+OO	k_{18} =8.0×10 ⁻¹⁵
R(4B)	$OOO+Q \rightarrow OO+OQ$	k_{19} =0.957× k_{18}
R(4C)	OOQ+O→OO+OQ	k_{20} =0.995× k_{18}
R(4D)	OQO+O→OQ+OO	k_{21} =0.995× k_{18}
R(4E)	OOO+P→OO+OP	k_{22} =0.978× k_{18}
R(4F)	OOP+O→OO+OP	k_{23} =0.997 $ imes k_{18}$
R(4G)	OPO+O→OP+OO	k_{24} =0.997 $ imes k_{18}$
R(4H)	$OOO+O(^{1}D)\rightarrow OO+O+O$	k_{25} =0.5×1.2×10 ⁻¹⁰
R(4I)	$OOO+O(^{1}D) \rightarrow OO+OO$	k_{26} = k_{25}
R(4J)	$OOO+Q(^{1}D)\rightarrow OO+O+Q$	k_{27} =0.957× k_{25}
R(4K)	$OOO+Q(^{1}D)\rightarrow OO+OQ$	k_{28} = k_{27}
R(4L)	$OOQ+O(^{1}D)\rightarrow OO+Q+O$	k_{29} =0.5×0.995× k_{28}
R(4M)	$OOQ+O(^{1}D)\rightarrow OQ+O+O$	k_{30} = k_{29}
R(4N)	$OOQ+O(^{1}D)\rightarrow OO+OQ$	k_{31} =0.995× k_{25}
R(4O)	$OQO+O(^{1}D)\rightarrow OQ+O+O$	k_{32} =0.995× k_{25}
R(4P)	OQO+O(¹ D)→OQ+OO	$k_{33}=k_{32}$

Table 4.8: List of various gas phase reactions along with the rate constants used in the kinetic model (KIN-TECUS) for simulation of products from O_2 +CO photolysis by UV light. In addition to these reactions, reaction set R1 to R6 of Table 4.6 was also included in the model.

	Reactions	Rate coefficient
	RR4 (Ozone decomposition) continued	
R(4Q)	$OOO+P(^{1}D) \rightarrow OO+O+P$	k_{34} =0.978× k_{25}
R(4R)	$OOO+P(^{1}D)\rightarrow OO+OP$	$k_{35} = k_{34}$
R(4S)	$OOP+O(^{1}D)\rightarrow OO+P+O$	k_{36} =0.5×0.997× k_{25}
R(4T)	$OOP+O(^{1}D) \rightarrow OP+O+O$	$k_{37} = k_{25}$
R(4U)	$OOP+O(^{1}D)\rightarrow OO+OP$	k_{38} =0.997× k_{25}
R(4V)	$OPO+O(^{1}D) \rightarrow OP+O+O$	k_{39} =0.997× k_{25}
R(4W)	$OPO+O(^{1}D) \rightarrow OP+OO$	$k_{40}=k_{39}$
R(X)	$OOO+OO(^{1}\Delta) \rightarrow OO+OO+O$	k_{41} =3.8×10 ⁻¹⁵
R(4Y)	$OOO+OQ(^{1}\Delta) \rightarrow OO+OO+Q$	k_{42} =0.5×0.982× k_{41}
R(4Z)	$OOO+OQ(^{1}\Delta) \rightarrow OO+OQ+O$	k_{43} = k_{42}
R(4AA)	$OOQ+OO(^{1}\Delta) \rightarrow OO+OQ+O$	k_{44} =0.992× k_{41}
R(4AB)	$OQO+OO(^{1}\Delta) \rightarrow OQ+OO+O$	k_{45} =0.992× k_{41}
R(4AC)	$OOO+OP(^{1}\Delta) \rightarrow OO+OO+P$	k_{46} =0.5×0.991× k_{41}
R(4AD)	$OOO+OP(^{1}\Delta) \rightarrow OO+OP+O$	$k_{47} = k_{46}$
R(4AE)	$OOP+OO(^{1}\Delta) \rightarrow OO+OP+O$	k_{48} =0.996× k_{41}
R(4AF)	$OPO+OO(^{1}\Delta) \rightarrow OP+OO+O$	k_{49} =0.996× k_{41}
	RR5 (O(¹ D) quenching)	
R5(A)	$O(^{1}D)+OO \rightarrow O+OO$	k_{50} =4.0×10 ⁻¹¹
R5(B)	$Q(^{1}D)+OO \rightarrow Q+OO$	k_{51} =0.962× k_{50}
R5(C)	$P(^{1}D)+OO \rightarrow P+OO$	k_{52} =0.980× k_{50}
	RR6(OO($^{1}\Delta$) quenching)	
R6(A)	$OO(^{1}\Delta)+M \rightarrow OO+M$	k_{53} =1.7×10 ⁻¹⁸
R6(B)	$OQ(^{1}\Delta)+M \rightarrow OQ+M$	k_{54} =0.986× k_{53}
R6(C)	$OP(^{1}\Delta)+M \rightarrow OP+M$	k_{55} =0.993× k_{53}

4.4.4 Initial concentration of the reactant species

As described in Chapter 3, the concentration of various species of O_2 , O_3 and CO were calculated as follows:

A. Concentration of ozone species

In cases of high ozone enrichment (Set 2 and 3), the corresponding enrichments in base (asymmetric species) and apex (symmetric species) positions were calculated using equations 4.9 to 4.12. Using these values, the ratio of the abundance of asymmetric to symmetric species were calculated as,

$$[OOQ]/[OQO] = a \tag{4.13}$$

$$[OOP]/[OPO] = b \tag{4.14}$$

In case of Set 1 samples, where total ozone enrichment was small, the value of 'a' and 'b' were taken to be 2 as predicted by statistics. The concentration of all the species were calculated (see section 3.2.2) as,

$$[OQO] = \frac{3x_1t_1}{(1+a)(1+x_1+y_1)}$$
(4.15)

$$[OPO] = \frac{3y_1t_1}{(1+b)(1+x_1+y_1)}$$
(4.16)

$$[OOQ] = a[OQO] \tag{4.17}$$

$$[OOP] = b[OPO] \tag{4.18}$$

$$[OOO] = t_1 - [[OOQ] + [OQO] + [OOP] + [OPO]]$$
(4.19)

where, x_1 and y_1 are the absolute abundance of ${}^{18}\text{O}$ and ${}^{17}\text{O}$ in ozone and t_1 is the total amount of ozone.

B. Concentration of O₂ species

$$[OQ] = \frac{2x_2t_2}{1 + x_2 + y_2} \tag{4.20}$$

$$[OP] = \frac{2y_2 t_2}{1 + x_2 + y_2} \tag{4.21}$$

$$[OO] = t_2 - [OQ] - [OP]$$
 (4.22)

where, x_2 , and y_2 are the absolute abundance of ¹⁸O and ¹⁷O in O₂ and t_2 is the total amount of O₂.

C. Concentration of CO species

$$[CQ] = \frac{x_3 t_3}{(1 + z_1)(1 + x_3 + y_3)}$$
(4.23)

$$[DQ] = z_1[CQ] \tag{4.24}$$

$$[CP] = \frac{y_3 t_3}{(1+z_1)(1+x_3+y_3)}$$
(4.25)

$$[DP] = z_1[CP] \tag{4.26}$$

$$[CO] = \frac{t_3}{(1+z_1)(1+x_3+y_3)}$$
(4.27)

$$[DO] = t_3 - [CO] - [CQ] - [DQ] - [CP] - [DP]$$
(4.28)

where, x_3 , y_3 and z_1 are the absolute abundance of ¹⁸O, ¹⁷O and ¹³C in CO respectively and t_3 is the total amount.

Plugging in the initial concentrations of all the reactant species and the photolysis time as input parameters, the model was run. The isotopic composition of the product CO_2 was defined as,

$$\delta^{18} \mathcal{O}(\mathcal{CO}_2) = \left[\frac{\frac{[\mathcal{COQ}] + [\mathcal{DOQ}]}{2 \times [\mathcal{COO}] + 2 \times [\mathcal{DOO}] + [\mathcal{COQ}] + [\mathcal{COP}] + [\mathcal{DOQ}] + [\mathcal{DOP}]}{\binom{18}{16}_{O}}_{VSMOW} - 1\right] \times 10^3$$
(4.29)

$$\delta^{17} O(CO_2) = \left[\frac{\frac{[COP] + [DOP]}{2 \times [COO] + 2 \times [DOO] + [COQ] + [COP] + [DOQ] + [DOP]}}{\binom{170}{160}_{VSMOW}} - 1 \right] \times 10^3$$
(4.30)

$$\delta^{13} C(CO_2) = \left[\frac{\frac{[DOO] + [DOQ] + [DOP]}{[COO] + [COQ] + [COP]}}{\left(\frac{^{13}C}{^{12}C}\right)_{VPDB-CO_2}} - 1 \right] \times 10^3$$
(4.31)

The value of ${}^{18}\text{O}/{}^{16}\text{O}$ = 0.00200520, ${}^{17}\text{O}/{}^{16}\text{O}$ = 0.00037287 for VSMOW and ${}^{13}\text{C}/{}^{12}\text{C}$ = 0.01117960 for VPDB-CO₂.

4.5 Simulation Results and Discussion

4.5.1 Oxygen isotope enrichment

The oxygen isotopic compositions (in ‰ relative to VSMOW) of CO₂ predicted by the simulation model corresponding to various sets are summarized in Tables 4.2 and 4.3 and plotted against each other in Figure 4.1, 4.2 and 4.3. The δ^{18} O values vary from -39.3 to -24.7 (Set 1), -40.5 to 9.4 (Set 2), -29.6 to -22.6 (Set 3) and -43.7 to -41.0 (Set 4); corresponding variations in δ^{17} O values are -22.6 to -12.9, -23.1 to 20.7, -12.4 to -6.4 and -24.8 to -23.3 respectively. For further discussion, we define the enrichment as: $\Delta(\delta^{18}\text{O}) = \delta^{18}\text{O}$ (observed) - δ^{18} O (model) and same for $\Delta(\delta^{17}\text{O})$. The average enrichment values (in ${}^{18}\text{O}/{}^{16}\text{O}$) corresponding to the four Sets are: 83.7, 82.3, 102.2 and 98.2 ; the respective enrichments in ${}^{17}\text{O}/{}^{16}\text{O}$ are 58.9, 54.3, 74.8 and 76.1. The maximum CO₂ enrichment occurs in Set 3 and Set 4. It is interesting to note that enrichments of Set 3 and Set 4 samples are similar even though the O atom sources were different. Apparently, it does not matter whether the O-atom is produced by visible light dissociation of O₃ or UV light dissociation of O₂. This must be due to the fast isotopic exchange between O-O₂ and O-CO, which changes the isotopic composition of O-atom significantly before it recombines with CO to produce CO₂. Due to fast exchange, the O-atom loses memory of its source and initial composition.

Enrichment in CO_2 shows a weak correlation with the amount of product CO_2 . In cases where the product CO_2 amount was relatively less enrichments in ¹⁸O and ¹⁷O were higher.

4.5.2 Carbon isotope fractionation

The average value of ($\Delta \delta^{13}$ C) (defined as change in δ^{13} C of the product CO₂ relative to the initial CO) predicted by the model is -5.9% (see Table 4.5) and is constant for all samples, whereas the observed ($\Delta \delta^{13}$ C) value varies from -14.6‰ to +3.8‰. There is a simple explanation for this discrepancy. We note that carbon isotope fractionation in the gas phase recombination reaction $O+CO \rightarrow CO_2$ is a combination of two mass dependent fractionation processes arising due to collision. During O+CO recombination forming CO₂*, lighter CO isotopologues collide with O at slightly higher rates due to lower reduced mass of the colliding pair. ¹³C¹⁶O collides with ¹⁶O atoms at a rate of 0.994 of the collision rate of $^{12}C^{16}O$. Consequently CO_2^* is depleted in heavy carbon isotope by 6.3‰. After its formation, CO₂* undergoes various activation and deactivation collisions and transfers its extra energy to the bath gas molecules in discrete steps of ΔE per collision. The ratio of the collision rates for the colliding pairs, ${}^{16}O^{13}C^{16}O^{-12}C^{16}O$ and ${}^{16}O^{12}C^{16}O^{-12}C^{16}O$ is 0.996 resulting in 4.3‰ depletion in ¹³C of CO₂. Therefore, the formation and stabilization of CO_2^* in gas phase is expected to be associated with 10.6% depletion of ¹³C in the product CO₂. The observed average value of $\Delta \delta^{13}$ C in the pressure range of 270 to 445 torr is -12.1 % , which is close to this calculated value. Since the CO₂^{*} collisional stabilization process is not included in the model, it predicts a lower magnitude of $(\Delta \delta^{13}C)(\sim -5.9\%)$.

To explain the positive $\Delta \delta^{13}$ C values (in Set 1 and 2) at low pressures we invoke the concept of surface mediated stabilization mechanism that is expected to occur at lower pressures. Surface-induced stabilization helps the activated complex to loose its extra kinetic energy quite efficiently and become a stable molecule. We postulate that the activated complex CO₂* has a long-range weak interaction with a reactive atom of the surface forming a transient bond. The amount of energy released from the activated complex is absorbed as vibrations of the lattice and dissipated as heat from the surface. The complex remains on the surface for a short time determined by its sticking coefficient and vibrates in a shallow potential well. The process can be written as: $CO_2^* + W \rightarrow (CO_2^*...W) \rightarrow CO_2$ +W. In a surface induced stabilization process, transfer of excess energy depends mainly on the sticking coefficient of the molecule. A recent study [*Halas et al.*, 2004] has shown that sticking coefficient is higher for heavier isotopomers due to their lower zero point energy. Therefore, ¹³CO₂* is expected to have a larger sticking coefficient and therefore, more chance to form stable molecule. It is not clear as to how much enrichment occurs

due to this process but a value of ~ 10‰ would account for the maximum observed value of ~ 3.8‰ after cancelling the offset of -6.3‰ (due to O and CO collisions in gas phase as explained above). In a range of 50 to 110 torr, $\Delta \delta^{13}$ C have positive as well as negative values and show large variation from -4.1‰ to +0.9‰. This could be due to competitive influence of surface induced stabilization and deactivating collisional stabilization the former having temperature dependence. The role of surface is supported by comparison of Set 3 and Set 4 data with Set 1 and 2 data, e.g., for samples AS1 (Set 3) and A15 (Set 1), AC6, AC7, AC8 and AC9 (Set 2). All these experiments were done at the same pressure (12 to 14 torr), but they show large difference in $\Delta \delta^{13}$ C value (-10.7‰ to 2.0‰ respectively). AS1 experiment was done in the 5 liter chamber, which minimized the role of surface during the recombination process resulting in negative $\Delta \delta^{13}$ C value. It is noted that there is no anomalous enrichment in carbon isotope since carbon being the central atom in CO₂ molecule is not affected by the symmetry related part of the total fractionation process.

4.6 Simulation of earlier O+CO experimental data

We also re-examined the experimental data of *Bhattacharya and Thiemens* [1989] in the light of KINTECUS model. Model result shows that expected δ^{18} O value of the CO₂ varies from -51.2 to -48.0 whereas the respective variation in δ^{17} O is from -28.6 to -26.7‰ (Table 4.9). The enrichment in ¹⁸O of CO₂ varies from 61.7 to 109.5. Data from both sets of experiments are plotted in Figure 4.6. A small difference in enrichment could be due to low CO/O₂ ratio (6 to 53) in Set 4 as compared to that of BT experiments where this ratio was much higher (178 to 423).

	O_2	CO_2	Exposure	Amount	Ŭ	O_2	Mo	del	Enrich	nment
	initial	ratio	time	of CO_2	compc	sition	predi	ction	in (CO_2
	amount		(min)	produced	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$	$\Delta(\delta^{18}O)$	$\Delta(\delta^{17}O)$
	(hmol)			(μmol)	%00	%	%00	%00	%00	%
1	185	423	1020	16	12.2	25.5	-49.5	-27.6	61.7	53.1
	353	246	2325	58	38.2	39.2	-50.5	-28.2	88.7	67.4
	282	298	960	50	33.1	33.0	-48.7	-27.1	81.8	60.1
	265	422	1060	58	37.4	36.3	-48.2	-26.8	85.6	63.1
	260	345	1330	63	29.5	29.4	-49.2	-27.4	78.7	56.8
	254	353	1020	20	13.2	18.6	-48.7	-27.1	61.9	45.7
	245	229	1320	23	10.1	14.3	-50.8	-28.4	60.9	42.7
	630	178	1110	35	16.3	24.0	-48.0	-26.7	64.3	50.7
	253	343	1065	41	60.6	59.3	-48.9	-27.2	109.5	86.5
	250	314	2660	49	51.6	55.1	-51.2	-28.6	102.8	83.7

Table 4.9: *Result of model simulation of Bhattacharya and Thiemens data* [O₂ *and CO mixture was photolysed with UV lamp (case 1 to 8 Hg lamp and 9,10 Kr lamp)] (5 values are in ‰ relative to VSMOW). Enrichments defined as the difference of observed value from the model prediction are also shown.*



Figure 4.6: A three isotope plot showing the oxygen isotopic composition of the product CO_2 in case of Set 4 and BT experiments. The average enrichment observed in BT experiments is: $\delta^{18}O = 79.6$ and $\delta^{17}O = 61.0$ whereas in Set 4 (present experiment) the values are $\delta^{18}O = 98.2$ and $\delta^{17}O = 76.1$.

The enrichments in ${}^{17}\text{O}/{}^{16}\text{O}$ and ${}^{18}\text{O}/{}^{16}\text{O}$ of CO₂ show good correlations (Figure 4.7). The best-fit line has slope of 0.97±0.05. We obtained the same slope in Figure 4.1 and 4.2 where the measured isotopic compositions of the product CO₂ (which do not involve any model calculations) are plotted. This clearly shows that CO₂ produced from O+CO reaction has heavy oxygen isotopes enriched in a mass independent fashion.

Ozone produced from the recombination reaction of O and O₂ follows a slope ~ 1 whereas the dissociation of ozone to O and O₂ is a mass dependent process and follows slope half [*Wen and Thiemens*, 1999; *Chakraborty and Bhattacharya*, 2003c; *Cole and Boering*, 2006]. It is believed that both the processes play an important role in stratosphere or in the experiments where both formation and dissociation are important and determine the resultant slope which should be between 1 and 0.52. This is why ozone produced in the laboratory show a slope 0.8 to 1 whereas stratospheric ozone (at ~ 25 km) exhibits a slope of about 0.62. In case of stratosphere, ozone formation dominates at lower altitudes whereas at higher altitudes photolysis of ozone becomes increasingly important and therefore, their

combined effect makes the slope ~ 0.62 at 20-30 km.



Figure 4.7: Three isotope plot showing correlation between enrichments in ¹⁸O and ¹⁷O of the CO₂ produced from O+CO reaction with a slope of 0.97 ± 0.05 for the best-fit line.

4.7 Implications

The present set of experiments confirms the earlier results of BT and establishes the level of anomalous oxygen isotope enrichments in product CO₂ arising from O+CO reaction. As discussed in Chapter 1, Marcus and his collaborators [*Hathron and Marcus*, 1999, 2000, 2001; *Gao and Marcus*, 2001, 2002; *Marcus*, 2001, 2004] proposed and developed a phenomenological theory, which has been fairly successful to explain many features of the unusual isotope effect associated with ozone formation processes. This theory is based on restrictions of symmetry on the process of energy sharing among the rotational/vibrational states of the ozone isotopomers and their influence on the rate of stabilization of a given ozone isotopomer. They introduced a symmetry driven parameter η , which denotes a small relative deviation from the statistical density of states for symmetric isotopomers (density of states

is reduced by a factor of η) compared with asymmetric isotopomers. As mentioned by *Marcus*, [2004] the η effect could arise from both intramolecular and intermolecular energy transfer properties of a molecule.

We apply the same arguments to explain the enrichment in CO₂ case. Collision of Q and CO or O and CQ involves formation of a rovibrationally excited OCQ* complex which must redistribute its excess energy among the available vibrational - rotational modes to become stable OCQ. The process of energy randomization depends on the strength of vibration-rotation and vibration-vibration coupling as well as the number of pathways. Asymmetric OCQ* has a comparatively stronger coupling due to the presence of anharmonic vibration-vibration and Coriolis vibration-rotation coupling terms compared to the symmetric species OCO*. So it is relatively easier for OCQ* to redistribute the excess energy among its modes as compared to OCO*. The faster randomization yields a longer lifetime of that particular complex. This results in a higher formation rate for OCQ type. The intramolecular effect thus depends on the symmetry type of isotopologues.

Gas phase chemical reaction rates are strongly dependent on the intermolecular collisional energy transfer. In the intermolecular collisional energy transfer, energy is transferred between the excited CO_2^* and a bath gas molecule in discrete steps of ΔE per collision. The energetic molecule with energy less than ΔE above the threshold leads to a deactivated molecule. Energy transfer from rotation to translation ($R \rightarrow T$) and vibration to rotation (V \rightarrow R) is more efficient than vibration to vibration (V \rightarrow V) and vibration to translation (V \rightarrow T). Energy transfer rate depends on the number of rotational and vibrational states present in CO₂* near the dissociation limit and on the coupling between them. The density of states in OCQ* is twice more than the symmetric OCO. Therefore, the transfer of excess energy is more efficient which leads to a higher rate of formation of OCQ. The formation rate also depends on amount of energy transferred per collision (ΔE). If ΔE is small a weak collision is sufficient for energy transfer. Since ΔE is smaller for OCQ*(compared to OCO) randomization is faster and the rate of formation of OCQ is higher. Therefore, both the intramolecular energy randomization and intermolecular energy transfer lead to higher rate of formation of asymmetric molecules (i.e. heavy isotopomers). Since the symmetry is independent of mass, the enrichment in CO₂ shows a non-mass dependent effect.

4.7.1 Comparison of enrichments in CO_2 and O_3

Ozone has two isotopologues corresponding to mass 50: ${}^{16}O^{18}O(asymmetric)$ and ${}^{16}O^{18}O^{16}O(symmetric)$. It has been seen that the enrichment in ozone has contribution from both asymmetric and symmetric species but the contributions are different. For example if the total enrichment in ozone ($\delta^{50}O_3$) is 131%, the enrichments in asymmetric and symmetric species are 151 and 92% respectively. In contrast to this, enrichment in CO₂ is only due to asymmetric species (${}^{16}O^{12}C^{18}O$). It has no heavy symmetric species (for normal abundance levels). So for comparing enrichments in O₃ and CO₂, we should consider only asymmetric species of ozone (${}^{16}O^{16}O^{18}O$).

At a pressure of about ~30 torr a total enrichment of about 130‰ in ozone (combination of both species) is observed corresponding to an enrichment of ~150‰ in asymmetric ozone. Our experiments show that enrichment in CO₂ varies from ~ 78 to 107.4‰ in the CO pressure range of about 14 to 28 torr. For comparison, only Set 3 and 4 data are to be considered because other data show a relatively lower enrichment due to the surface effect (discussed above). Therefore, the average enrichment in CO₂ (~83‰) is less than that of ozone (~150‰) by about 67%.

We may speculate about the reason for ~67 % lower enrichment in CO₂. This could be due to the presence of relatively larger density of states (ρ) in CO₂ near the threshold of dissociation. The magnitude of ρ at threshold depends on the dissociation energy of the molecule. CO₂ has relatively higher dissociation energy of about 5.5 eV compared to O₃ (~ 1.1 eV); so the value of ρ is comparatively higher for CO₂ than O₃. The enrichment is expected to be a function of $\Delta \rho / \rho$ where $\Delta \rho$ is the difference between the density of states of asymmetric and symmetric species. A smaller value of this ratio means less discrimination and the molecule is "less apt to show non-statistical behavior" [*Marcus*, 2004]. Since the ratio $\Delta \rho / \rho$ is less in CO₂, it has lower enrichment.

There is another way to look at the effect following Bates [1990a, 1990b]. It is known that in a coupled oscillator the transfer of energy between the two oscillators occurs with a frequency, which is the difference in the two normal frequencies or so-called "beat frequency". Higher the beat frequency faster is the energy transfer and consequent randomization. In molecules, energy gets transferred from one mode to the other in a similar way. The asymmetric and symmetric stretch mode frequencies in O₃ are 1104 cm⁻¹ and 1039 cm⁻¹ and in CO₂ they are: 2349 cm⁻¹ and 1388 cm⁻¹. The beat frequency ($\nu_1 - \nu_2$) in CO₂

is 961 cm⁻¹ which is higher than that of O₃ (65 cm⁻¹). Therefore, the flow of energy within the modes is comparatively faster in case of CO₂, which results in less discrimination.

4.8 Investigation of effect of nuclear spin on O+CO reaction

It is interesting to investigate the effect of nuclear spin on the reaction $O(^{3}P) + CO(^{1}\Sigma^{+})$ \leftrightarrow CO₂*(³B₂) \rightarrow CO₂(¹ Σ_q^+). The overall reaction is spin forbidden. The perturbation produced by the spin-orbit coupling in the molecule can, however, make it go. It is possible that nuclear spin can play a role in the triplet-singlet transition part of the reaction as a result of which the rate of formation of CO₂ containing ¹⁷O and ¹³C may be enhanced since ¹⁷O has spin of $\frac{5}{2}$ and ¹³C has spin of $\frac{1}{2}$. However, our experiments do not show any unusual enhancement which can be ascribed to the spin effect. The reason for this becomes clear as we outline various steps of the reaction as follows. The collision of a triplet Oatom with a singlet CO molecule results in the formation of an electronically-vibrationally excited CO_2^* in a triplet state (³B₂). To become stable, it has to give away its excess energy through a series of collisions with the surrounding molecules. While doing so, it steps down the ladder of vibrational levels ultimately reaching the lowest vibrational level of the same electronic state (³B₂). Transition from this triplet state to the singlet ground state by photon (radiation) emission is forbidden. However, this transition can occur in the presence of a spin-orbit coupling in the following way. According to Clyne and Thrush [1962], CO_2^* undergoes a radiative transition from the triplet state (${}^{3}B_2$) to a low-lying triplet state followed by radiationless transition to the singlet ground state $({}^{1}\Sigma_{q}^{+})$. The reversal of spin occurs in the latter step due to spin-orbit coupling. Since all molecules in this state are destined to make the transition (aided by either electron spin or nuclear spin) there is no isotope selection in this step.

4.9 Conclusion

A set of experiments were carried out to study oxygen isotope fractionation in CO_2 formed by O+CO reaction. The expected isotopic composition of the product CO_2 was computed using a commercially available model of chemical reaction simulation (KINTE-CUS) incorporating standard mass dependent reaction rate constants. The isotopic composition of the product CO_2 is found to be anomalously enriched in heavy oxygen isotopes relative to that expected based on the simulation. The enrichment in heavy oxygen isotopes of CO_2 varies from 65 to 107‰ (in ¹⁸O) and 41 to 82‰ (in ¹⁷O). The enrichment is not dependent on the isotopic composition of O atom used for the reaction since it is nearly the same irrespective of the source from which it is produced. The level of enrichment seen in the CO_2 produced by O+CO reaction is in general similar to that observed earlier in case of O₃ produced by O+CO reaction. Since both these reactions involve symmetric and asymmetric product molecules ($^{16}O^{12}C^{16}O$ and $^{16}O^{12}C^{18}O$ in case of CO_2 and $^{16}O^{16}O^{16}O$ and $^{16}O^{16}O^{18}O$ in case of O₃) the mechanism proposed for explaining the isotopic enrichment in ozone by Marcus and his collaborators may be applicable for CO_2 . Small difference in enrichment between the two cases (lower enrichment in case of CO_2) can be explained by a higher state density in case of CO_2 resulting in less deviation from statistical abundances.

It is interesting to note a change in carbon isotopic composition of the product CO₂ from the initial CO defined as $\Delta(\delta^{13}C)$. The value of $\Delta(\delta^{13}C)$ varies from -14.6 to 3.8‰ and the increase in δ -values correlates with decrease in CO pressure. Negative values of $\Delta(\delta^{13}C)$ obtained at high pressure of CO or done in bigger chamber suggests that if O+CO reaction occurs mainly in gas phase there is preference for lighter carbon isotope. At lower pressures, surface mediated stabilization assumes importance which makes $\Delta(\delta^{13}C)$ value positive indicating preference for heavy isotope. No anomalous enrichment is observed in ¹³C of CO₂ as carbon being a central atom does not participate in the symmetry related part of the fractionation process.

CHAPTER 5

Determination of intramolecular isotope distribution of ozone

5.1 Motivation

As discussed earlier, stratospheric ozone [Mauersberger et al., 1981, 1987, 2001; Rinsland et al., 1985; Abbas et al., 1987; Schueler et al., 1990; Meier and Notholt, 1996; Irion et al., 1996; Lammerzahl et al., 2002] and laboratory-made ozone [Thiemens and Heidenreich, 1983; Thiemens and Jackson, 1987, 1988; Morton et al., 1990; Bhattacharya et al., 2002] have unusual propensity of heavy isotopes ¹⁷O and ¹⁸O relative to the parent molecular oxygen reservoir from which they are formed. Both 17 O and 18 O are enriched by $\sim 100\%$ and surprisingly, δ^{17} O is not half of δ^{18} O as expected in case of normal mass dependent fractionation process. Another important anomaly relates to the position dependence of distribution of heavy isotopes inside an ozone molecule. A heavy isotopologue of ozone (having a triangular shape) like ${}^{50}O_3$ can have the heavy isotope ${}^{18}O$ located either at the central (apex) position (${}^{16}O{}^{18}O{}^{16}O$ with C_{2v} symmetry) or at the terminal (base) position (${}^{16}O{}^{16}O{}^{18}O$ with C_s symmetry). Statistically, C_s or asymmetric type ozone is expected to be exactly twice more abundant compared to C_{2v} or symmetric type ozone and thus their ratio, r^{50} = $[{}^{16}O{}^{16}O{}^{18}O{}^{16}O{}^{16}O]$ should be equal to two. However, this rule is found to be violated in case of ozone [Anderson et al., 1989; Larsen et al., 1994, 2000; Janssen, 2005]. For highly enriched ozone ($\delta^{18}O$ >60‰) the distribution of ¹⁸O among the two types (C_{2v} and C_s) is such that the abundance of asymmetric species is higher compared to that expected from statistics. The departure of r from the statistical value of two is ultimately related to

variation in the rate of formation of various ozone isotopomers arising out of combination of isotopes involved in O+O₂ collision [*Anderson et al.*, 1997; *Janssen et al.*, 1999, 2001]. For example, ¹⁶O¹⁶O¹⁸O can result from collision of ¹⁶O with ¹⁶O¹⁸ or collision of ¹⁸O with ¹⁶O¹⁶O but the rates are very different (1.45 and 0.92 respectively when expressed relative to the rate of ¹⁶O + ¹⁶O¹⁶O \rightarrow ¹⁶O¹⁶O¹⁶O) [*Janssen et al.*, 2001]. Similarly, ¹⁶O¹⁶O¹⁸O and ¹⁶O¹⁸O have different rates of formation though both can be produced from collision of ¹⁶O with ¹⁶O¹⁸O. We should note that collision of an O-atom with an O₂ molecule can also result in isotope exchange rather than ozone formation. *Janssen et al.* [2001] showed that in case of homonuclear oxygen molecules the relative rate coefficient of a given ozone formation reaction shows a linear correlation with the enthalpy (or change in zero point energy) of the associated exchange reaction. It seems that when exchange of an oxygen isotope with an oxygen molecule has an energy barrier there is increased probability of ozone formation in the corresponding channel. The reason for this was clarified by *Janssen et al.* [2001] who proposed that endothermic exchange corresponds to longer lifetime of the collision complex resulting in a higher recombination rate with the same isotopic partners.

To explain the above results, a phenomenological theory was proposed by Marcus and co-workers to explain the rate coefficient variation among isotopic partners in ozone formation process. The proposal is based on a modification of RRKM theory of unimolecular dissociation which takes into account reduction in density of states (a non-RRKM effect) due to limitation in mode coupling or non-randomness [Hathorn and Marcus, 1999, 2000; Gao and Marcus, 2001, 2002]. They showed that asymmetric reaction intermediate formed in O+O₂ collision has a relatively larger density of states permitting enhanced randomness and longer life time than that of symmetric reaction intermediate which results in its more efficient quenching to ground state ozone. Since the non-RRKM effect differs between asymmetric and symmetric types of ozone the expected enrichment in the two types will differ. Expressed in another way, the terminal and central position in the ozone molecule should have different isotopic enrichment i.e., one would expect an intramolecular isotopic variation resulting in ratio $r^{50} > 2$. Since terminal position and central position enrichments are connected with the abundance of asymmetric molecules and symmetric molecules (relative to their statistical abundances) respectively, the ratio r^{50} can simply be expressed in terms of enrichment in asymmetric ($\delta_a^{50} = \delta_a^{18}$ O) and symmetric species ($\delta_s^{50} = \delta_s^{18}O$) which are defined here in terms of ratio of the abundance of these species

relative to the abundance based on statistical distribution. It follows that:

$$r^{50} = 2(1 + 10^{-3} \times \delta_{a}^{18} O) / (1 + 10^{-3} \times \delta_{s}^{18} O)$$
(5.1)

The statistical ratio $r^{50} = 2$ is possible only if enrichments $\delta_a{}^{50}O$ and $\delta_s{}^{50}O$ are equal or in particular, both are zero. An important question to be asked is whether $r^{50} > 2$ implies enrichment in asymmetric species only or there is enrichment in both the species with more preference for asymmetric type. Another related question is whether the partitioning of ${}^{18}O$ and ${}^{17}O$ among asymmetric and symmetric species are same and if not, how it varies with total ozone enrichment.

In this context, some pioneering laboratory experiments were done to investigate the partitioning of heavy isotopes in ozone and to determine r⁵⁰ [Anderson et al., 1989; Larsen et al., 1994, 2000]. The isomeric distribution of ¹⁸O in heavy ozone was first studied by Anderson et al. [1989] using infrared tunable diode laser absorption spectroscopy (TDLAS) but with a large error in the measurement. Later, Larsen et al. [1994, 2000] applied Fourier transform absorption spectroscopy (FTAS) technique to determine r⁵⁰. Large uncertainties are normally associated with the spectroscopic techniques due to experimental limitations and uncertain line strength information. Nonetheless, both TDLAS and FTAS showed that for ${}^{50}O_3$ species, ${}^{18}O$ enrichment in asymmetric species is more than that of symmetric species. In a recent review, Janssen [2005] has summarized all the earlier experimental results obtained by TDLAS and FTAS and concluded that for ¹⁸O containing ozone isotopomers, both asymmetric and symmetric type species are enriched but the enrichment in asymmetric type is larger for bulk enrichment greater than about 50‰. This means that for bulk enrichment >50 ‰, r^{50} >2. He also showed that both δ_a and δ_s are positive which indicates that the bulk enrichment is not exclusively due to the asymmetric species but is also contributed by symmetric species. An apparent contradiction was noted in the FTAS study of *Larsen et al.* [2000] who reported a ratio $r^{50} = 1.99$. However, this discrepancy was resolved by Janssen [2005] by invoking temperature dependence of isotopic enrichment. Janssen concluded that the ratio [16O16O18O/16O18O16O] i.e., r⁵⁰ is often quite different from 2.00 and ranges from 1.99 to 2.14 when the total ozone enrichment itself varies from 47% to 156%. As of now, there is no study for ¹⁷O distribution in ozone isotopologue ⁴⁹O₃ due to difficulties in spectroscopic measurement owing to its small abundance. One of the motivations for the present study was to determine the value of r^{49} .

The intramolecular distribution of isotopes in ozone is of interest due to several reasons. In stratosphere, the anomalous isotopic signature gets transferred from ozone to other oxygen containing trace gases, like NO, CO₂, HNO₃, H₂SO4, N₂O [van den Ende et al., 1982, van den Ende and Stolte, 1984; Gamo et al., 1989; Yung et al., 1991, 1997; Thiemens, 1999, 2001; Lyons, 2001; Lammerzahl et al., 2002; McLinden, 2003; Savarino et al., 2000; Michalski et al., 2002, 2003; Lee et al., 2001, 2002; Johnston et al., 1995; Kaiser et al., 2002; Morgan et al., 2004; Yung et al., 2004; Rockmann et al., 2001]. The transfer can occur in two ways: via isotopic exchange with O(¹D) produced from ozone by UV photolysis or by direct reaction with ozone. This subject is of great importance as anomalous isotopic enrichment in trace gases provides tracers for studying stratospheric transport processes and/or tropospheric oxidation reaction pathways. In order to explain the mass independent isotopic anomaly in molecules arising out of reaction or exchange with ozone, the isotopic composition of $O(^{1}D)$ and intramolecular isotope distribution in O_{3} should be known. But direct isotopic measurement of $O(^{1}D)$ is not yet possible due to its small lifetime. It is, of course, clear that the isotopic composition of $O(^{1}D)$ should depend on: (i) the intramolecular distribution of heavy oxygen isotope in ozone and (ii) the relative probability of terminal and central atom emission during ozone dissociation. Regarding the latter point, an earlier theoretical study [Sheppard and Walker, 1983] indicated that in ozone dissociation by photons, it is quite probable that only one of the two terminal atoms is emitted since the probability of central atom emission is calculated to be less than 9%. The reason for this preference lies in the structure of the ozone molecule. Ozone has a triangular structure with an apex angle of 116.8°. The terminal atoms are close to the central atom (1.27 a.u), but are far away from each other. Additionally, the central atom is attached to each of the terminal atoms by a weak bond (bond energy \sim 1.1 eV) but there is no bonding between the two terminal atoms. As a consequence, ozone can dissociate easily by losing one base atom [Babikov et al., 2003; Janssen, 2005]. Therefore, the isotopic composition of O(¹D) emitted by ozone dissociation can be estimated accurately if the values of asymmetric/symmetric ratio, r⁵⁰ and r^{49} are known. More generally, O_3 is a strong oxidant molecule that reacts directly with many trace species in stratosphere, including nitrogen oxides, sulfur oxides, halogens and organic matters. During such oxidation reactions, oxygen atoms from the ozone are incorporated into the products, thereby transferring its anomalous isotope composition to the end-product of oxidation. It is possible that even though photodissociation favors the

ejection of a terminal atom, direct contact of ozone with molecules may result in partial abstraction of the central oxygen atom [*van den Ende et al.*, 1982; *van den Ende and Stolte*, 1984]. In either case, to establish an isotopic anomaly transfer budget, knowledge of the internal oxygen isotope distribution of O_3 is absolutely necessary. If the high oxidative reactivity of ozone is due to the ease with which the terminal atoms can be dislodged and made to react with other atoms we have a nice possibility of detecting the intramolecular isotope distribution in ozone by chemical reaction method. To our knowledge, no direct chemical reaction of isotopically enriched ozone with another molecule has been carried out in laboratory to probe its internal make up.

It is known that ozone reacts with silver foil at an extremely fast rate and forms silver oxide as a thin layer [*Waterhouse et al.*, 2001]. In the present work, we have used this reaction as a chemical probe by characterizing the isotope transfer. The advantage of studying this reaction is that it does not involve the formation of O atom and thus there is no possibility of oxygen isotope exchange with the reactant and molecular oxygen as happens in case of O_3 -CO reaction [*Bhattacharya and Thiemens*, 1989; *Pandey and Bhattacharya*, 2006] or O_3 -CO₂ exchange [*Wen and Thiemens*, 1993; *Chakraborty and Bhattacharya*, 2003d; *Johnston et al.*, 2000; *Shaheen et al.*, 2006] reaction via involvement of O(¹D). The isotopic composition of the reacting ozone and the oxygen extracted from silver oxide then provide information about the intramolecular distribution of two (¹⁷O and ¹⁸O) heavy oxygen isotopes.

5.2 Experimental details

The experiments were carried out in two places: the Laboratoire de Glaciologie et Gophysique de l'Environnement (LGGE), Grenoble, France and the Physical Research Laboratory, Ahmedabad, India. At PRL, ozone was produced by Tesla discharge of oxygen kept in a chamber (volume ~ 200 cc) at various pressures. In a few cases, ozone was produced by UV discharge of pure O₂. At LGGE, ozone was produced only by Tesla discharge of oxygen. In ozone production by Tesla discharge, both temperature of the chamber (-196°C to 80°C) and O₂ pressure were varied to get variable enrichments in the product ozone whereas in case of ozone made by UV dissociation only the O₂ pressure was varied (at room temperature). The amount of ozone produced was always kept small relative to the oxygen reservoir (within about 10%). The product ozone was cryogenically separated from the left over oxygen and was transferred to a small cold finger isolated from the main line but connected via a stopcock to a chamber containing freshly cleaned and degassed silver foil. After complete transfer, the cold finger was isolated from the main line and ozone was brought in gaseous phase. The stopcock to the silver chamber was then opened. Ozone instantaneously reacts with silver making a layer of grayish-blackish silver oxide. However, there is a parallel reaction whereby a major part of the ozone gets decomposed almost simultaneously at the silver oxide surface by catalysis [Waterhouse et al., 2001, 2002]. The isotopic effect of catalytic decomposition of ozone on silver oxide was evaluated by control experiments and is described in Appendix A.2. After a few minutes, the introduced ozone is completely decomposed by combined action of reaction and catalysis. The oxygen left over in the chamber (from reaction and catalysis) was collected in sample bottles containing molecular sieve (pellet 13 X) for amount and isotope measurements. Subsequently, silver oxide (Ag₂O) was heated to \sim 500°C which releases the silver bound oxygen totally; this was collected for isotope analysis. The amount of initial ozone is obtained by adding these two components and the isotopic composition of starting ozone is determined by isotope mass balance from these two components. In some cases, the mass balance estimate was crosschecked by taking an aliquot of the initial ozone. However, we preferred to use the mass balance estimate for further calculation since taking isotopically as well as quantitatively representative aliquot of ozone was rather difficult. Beside the case of isotopically enriched ozone it is also of interest to determine the internal distribution of heavy oxygen isotopes in an ozone sample when it is not enriched at all (designated as zero-enriched ozone). For this purpose, ozone was made by converting nearly 100 % of the starting O_2 by Tesla discharge. In these cases, the starting O_2 pressure was made to vary from 3 to 15 torr.

Molecular oxygen isotopic measurements were done with a Finnigan MAT 253 at LGGE with typical errors of 0.05‰ on both δ^{18} O and δ^{17} O and with a VG 903 at PRL with typical errors of 0.05‰ and 2‰ in δ^{18} O and δ^{17} O respectively. Amount of oxygen was measured using MKS Baratron in both places.

5.3 Results and Discussion

The oxygen isotopic composition of ozone and silver-bound oxygen (Ag₂O) (expressed in ∞ , relative to the initial oxygen reservoir) for PRL and LGGE experiments are given in Table 5.1, 5.2 and 5.3. δ^{17} O values plotted against δ^{18} O values for silver-bound oxygen and for ozone (Figure 5.1) define two parallel lines showing that even though the δ -values are different the characteristics of the ozone isotopic distribution are preserved in its reaction with silver.



Figure 5.1: The cross-plot of $\delta^{18}O$ and $\delta^{17}O$ of silver bound oxygen and starting ozone for both LGGE and PRL data. The $\delta^{18}O$ and $\delta^{17}O$ values of Ag_2O and O_3 fall on a line with slope 0.86 ± 0.01 and 0.89 ± 0.01 respectively. The composition of silver-oxide (^{18}O , ^{17}O) (expressed in ‰ relative to the initial oxygen reservoir) vary from (-1.4, 22.4) to (120.8, 126.9) which correspond to a variation of (13.7, 16.6) to (115.6, 106.3) in δ - values of ozone.

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Sample	0	orone		Ag_2O	oxyge	ر ا	Fractionation		For 18 () in ozone		For ¹⁷ C) in ozor	Je
No.	Amoun	t δ^{18} O	$\delta^{17} O$	Amount	$\delta^{18}O$	$\delta^{17}O$	$lpha(^{18}{ m O})$	$\delta_{ m asy}$	$\delta_{ m sym}$	r ⁵⁰ error	$\delta_{ m asy}$	$\delta_{ m sym}$	r^{49}	error
	(μmol)			(μmol)				2	•	$\operatorname{in} \mathrm{r}^{50}$	2	•		$\ln r^{49}$
					PRL	, data (Tesla ozone)							
P-1	52	13.7	16.6	10	-1.4	22.4	0.9975	1.1	38.9	1.927 0.08	23.7	2.3	2.043	0.06
P-2	136	18.3	21.7	10	4.6	26.4	0.9974	7.2	40.5	1.936 0.08	27.7	9.6	2.036	0.06
P-3	122	22.0	23.9	13	13.9	35.8	1.0018	12.1	41.9	1.943 0.07	34.9	2.0	2.066	0.05
P-4	48	33.6	30.4	8	28.4	43.3	1.001	27.4	46.2	1.964 0.07	42.8	5.7	2.074	0.05
P-5	25	34.5	35.1	6	13.6	34.5	0.9855	28.5	46.6	1.965 0.07	42.1	21.1	2.041	0.05
P-6	91	40.8	37.8	12	31.8	49.3	0.9953	36.7	49.1	1.976 0.07	51.8	9.7	2.083	0.05
P-7	9	43.1	40.5	С	39.3	50.3	0.9997	39.6	50.0	1.980 0.07	50.5	20.5	2.059	0.05
P-8	57	44.4	41.0	10	38.5	54.7	0.9972	41.4	50.3	1.983 0.07	56.2	10.6	2.090	0.05
P-9	60	46.9	44.1	10	43.2	59.3	0.9987	44.6	51.7	1.986 0.06	60.0	12.2	2.094	0.05
P-10	71	47.2	41.8	6	45.5	59.1	1.0006	44.9	51.7	$1.987 \ 0.06$	58.8	7.9	2.101	0.05
P-11	47	49.3	45.1	10	31.2	49.9	0.9842	47.8	52.5	1.991 0.06	58.3	18.6	2.078	0.05
P-12	17	51.1	43.3	З	25.3	40.9	0.9765	50.0	53.4	1.994 0.06	53.4	23.1	2.059	0.05
P-13	76	51.3	43.4	6	31.6	43.5	0.9823	50.2	53.5	1.994 0.06	52.9	24.5	2.055	0.05
P-14	30	51.9	47.6	4	43.9	56.9	0.9931	51.2	53.5	1.995 0.06	60.6	21.5	2.076	0.05
P-16	72	56.1	48.6	5	35.2	51.7	0.9799	56.4	55.3	2.002 0.06	62.4	20.8	2.082	0.05
P-17	36	59.0	53.0	IJ	46.0	58.1	0.9867	60.1	56.7	2.006 0.06	65.2	28.7	2.071	0.05
P-18	40	62.6	50.8	7	46.1	54.9	0.9825	64.7	58.2	2.012 0.06	64.3	23.9	2.079	0.05
P-19	76	67.4	63.7	11	71.2	83.1	1.0003	70.9	60.3	2.020 0.06	82.9	25.2	2.113	0.05
P-20	51	68.7	64.5	6	68.3	81.7	0.9960	72.6	61.0	2.022 0.05	83.9	25.7	2.113	0.05
P-21	96	69.1	63.9	12	71.5	83.3	0.9985	73.1	61.2	2.022 0.05	84.1	23.4	2.119	0.05
P-22	87	71.3	66.4	11	77.1	87.3	1.0012	75.8	62.1	2.026 0.05	86.6	26.0	2.118	0.05
P-24	46	77.3	70.3	8	76.3	87.4	0.9933	83.6	64.8	2.035 0.05	91.1	28.8	2.121	0.05
P-25	47	78.0	70.5	8	76.3	86.4	0.9924	84.5	65.0	2.037 0.05	90.6	303	2.117	0.05

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: In these experiments ozone was made by UV dissociation. The enrichment in ozone (¹⁸ O, ¹⁷ O) varies from (54.7 to 115.6) and (51.3 to 106.3)	ly. The corresponding variation in r^{49} is from 2.051 to 2.145.	
Table 5.2: In these expe	respectively. The corresp	

_ '	0	zone		Ag_2O	oxygei	ب لیک ا	ractionation		For ¹⁸ C) in ozone		For ¹⁷ C	D in ozoi	e
'	Amount	$\delta^{18}{ m O}$	$\delta^{17}{ m O}$	Amount	$\delta^{18}{ m O}$	$\delta^{17} O$	$\alpha(^{18}\text{O})$	δ_{asy}	$\delta_{ m sym}$	r ⁵⁰ error	δ_{asy}	$\delta_{ m sym}$	r^{49}	error
	(μmol)			(μmol)						$\mathrm{in}~\mathrm{r}^{50}$				${ m n}~{ m r}^{49}$
					PRI	<u>data (l</u>	JV ozone)							
1	38	54.7	51.3	7	44.8	55.2	0.9907	54.6	54.9	1.999 0.06	60.1	33.7	2.051	0.05
	136	72.5	71.0	13	71.8	81.4	0.9947	77.5	62.5	2.028 0.05	84.3	44.5	2.076	0.05
	343	81.4	76.9	16	87.3	93.9	0.9987	88.7	66.7	2.041 0.05	94.6	41.5	2.102	0.05
	107	89.9	83.5	12	99.5	103.3	1.0001	99.4	70.7	2.054 0.04	103.2	44.0	2.113	0.04
	49	91.8	88.1	6	91.8	101.9	0.9908	101.9	71.5	2.057 0.04	107.0	50.4	2.108	0.04
	28	97.1	92.6	9	89.8	9.66	0.9830	108.6	74.1	2.064 0.04	109.1	59.6	2.093	0.04
	45	101.8	87.2	6	90.2	94.6	0.9782	114.5	76.5	2.071 0.04	106.7	48.2	2.112	0.04
	139	102.0	95.6	13	118.6	121.6	1.0035	114.7	76.6	2.071 0.04	119.9	47.0	2.139	0.04
	35	102.4	96.3	7.7	94.6	104.4	0.9815	115.2	76.8	2.071 0.04	114.8	59.3	2.105	0.04
	76	104.3	95.9	10	100.5	106.6	0.9847	117.6	77.7	2.074 0.04	115.2	57.4	2.109	0.04
	70	104.7	98.2	10	100.7	108.8	0.9844	118.1	78.0	2.075 0.04	117.6	59.5	2.110	0.04
	99	111.6	104.3	6	120.8	126.9	0.9948	126.7	81.3	2.084 0.03	129.8	53.3	2.145	0.04
	72	112.8	102.0	15	108.8	115.4	0.9828	128.2	82.1	2.085 0.03	125.1	55.7	2.132	0.04
	26	115.6	106.3	Ŋ	113.9	122.7	0.9843	131.7	83.5	2.089 0.03	131.6	55.7	2.144	0.04

Sample	0	zone		Ag	₂ ^O oxyg∈	ue	Fractionation	H	^r or ¹⁸ O	in ozone		For ^{1′}	⁷ O in (ozone	
No.	Amour	ιθ ¹⁸ Ο	$\delta^{17} O$	Amount	$\delta^{18} \mathrm{O}$	$\delta^{17} O$	$\alpha(^{18}\text{O})$	δ_{asy}	$\delta_{ m sym}$	r^{50} erro	$r \delta_{as}$	$_{ m y}$ $\delta_{ m sy}$	m r^4	⁹ erroi	
	(hmol)			(hmol)						IU				IN r ¹	
					L(GGE data	(Tesla ozone,								
L-1	84	10.7	11.7	11	-1.4	17.4	1.0014	-2.8	37.7	1.922 0.08	16.	7 1.6	5	030 0.06	
L-2	58	20.7	21.7	8	5.0	25.8	0.9948	10.3	41.5	1.940 0.07	28.	5 8.1	5	041 0.05	
L-3	125	28.1	29.0	വ	19.4	36.6	0.9995	20.0	44.3	1.953 0.07	36.	9 13.	.3	046 0.05	
L-4	66	39.4	40.4	10	26.0	45.5	0.9915	34.8	48.6	1.974 0.07	50.	0 21.	2.2	056 0.05	
L-5	39	45.9	45.4	4	35.4	52.1	0.9926	43.2	51.3	1.985 0.07	56.	0 24.	2 2.	062 0.05	,
L-6	84	52.3	51.6	10	42.1	58.2	0.9911	51.5	53.9	1.995 0.06	62.	9 29.	0.2	066 0.05	
L-7	27	53.1	51.3	ъ С	38.7	56.1	0.9868	52.9	54.3	1.997 0.06	63.	.1 27.	5.2	069 0.05	
L-8	119	60.7	57.1	ю	58.2	66.3	0.9961	62.4	57.3	2.010 0.06	68.	4 34.	4 2.	066 0.05	
L-9	98	64.4	60.4	6	56.7	70.4	0.9902	67.1	58.9	2.016 0.06	75.	7 29.	.6 2.	090 0.05	2
L-10	126	76.4	70.4	6	72.6	82.2	0.9909	82.4	64.3	2.034 0.05	87.	2 37.	.0	097 0.05	
L-11	110	83.9	75.4	12	76.5	85.9	0.9859	91.9	67.9	2.045 0.05	93.	6 39.	.1 2.	105 0.05	
L-12	84	84.1	76.6	9	81.0	88.5	0.9900	92.0	68.3	2.044 0.05	93.	9 41.	8.2.	100 0.05	
L-13	47	86.4	76.8	Э	88.0	88.2	0.9936	95.0	69.0	2.049 0.05	91.	7 47.	.0	085 0.05	
L-14	62	98.2	84.5	12	88.1	93.4	0.9840	109.9	74.8	2.065 0.04	10^{4}	45. 45.	.1 2.	113 0.04	
L-15	52	106.2	91.8	8	100.8	104.6	0.9829	120.0	78.6	2.077 0.03	11,	4.1 47.	2 2.	128 0.04	
					Zero	-enrichec	ł data (PRL di	ata)							
1	63	-9.5	-5.5	10	-55.7	-26.8	0.9916	-47.2	65.9	1.788	-22	.4 28.	.3 1.	901	
7	38	-8.9	-4.4	6	-57.6	-28.8		-49.1	71.6	1.755	-24	l.4 35.	.6 1.	884	
ю	150	-8.8	-4.9	16	-47.5	-19.3		-38.9	51.3	1.828	-14	l.9 15.	.3 1.	941	
4	135	-8.2	-4.2	12	-46.7	-19.4		-38.1	51.6	1.829	-10	5.0 17.	4 1.	936	
Ŋ	91	-7.5	-3.7	13	-48.9	-22.2		-40.4	58.2	1.814	-17	7.8 24.	.5 1.	917	
9	124	-6.3	-3.5	33	-40.0	-13.2		-31.4	43.7	1.856	8	8 6.9	, <u>1</u> .	696	
7	75	-5.4	-3.3	16	-40.8	-14.4		-32.2	48.3	1.846	-10	0.0 10.	2 1.	960	
8	201	-4.6	-2.1	14	-36.0	-11.2		-27.3	40.7	1.869	-9-	8 7.2		972	
6	134	-3.7	-2.1	16	-33.7	-9.0		-25.0	39.0	1.877	-4.,	5 2.9	1.	985	

Determination of intramolecular isotope distribution of ozone

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The results (excluding zero-enriched ozone data) are also displayed in Figure 5.2 where $\delta(Ag_2O)$ values are plotted against $\delta(O_3)$ values for each of the two heavy isotopes. It is seen that both $\delta^{18}O$ and $\delta^{17}O$ values of silver-bound oxygen increase linearly with increase in ozone δ -values. The cross-plots define two best fit lines with slopes 1.16 (¹⁸O) and 1.12 (¹⁷O). It is intriguing to note that the $\delta^{18}O$ values of Ag₂O are mostly less than those of ozone, i.e., $\delta^{18}O(Ag_2O) < \delta^{18}O(O_3)$ whereas in case of $\delta^{17}O$ it is mostly the other way around, i.e., $\delta^{17}O(Ag_2O) > \delta^{17}O(O_3)$. In PRL experiments, the values of $\delta^{18}O$ and $\delta^{17}O$ of silver-bound oxygen vary from -1.4 to 120.8 and from 22.4 to 126.9 respectively corresponding to a variation of 13.7 to 115.6 and 16.6 to 106.3 in δ - values of ozone. Similarly, in case of LGGE experiments, variation of $\delta^{18}O$ and $\delta^{17}O$ values of Ag₂O from -1.4 to 100.8 and from 17.4 to 104.6 correspond to a variation of 10.7 to 106.2 and 11.7 to 91.8 respectively in the δ - values of ozone.



Figure 5.2: The correlation plot of $\delta(Ag_2O)$ and $\delta(O_3)$ (for enriched ozone cases only) which shows that $\delta^{17}O$ and $\delta^{18}O$ values of silver-bound oxygen increase with increase in ozone δ -values in a linear fashion. The $\delta^{18}O$ value of Ag_2O is mostly less than that of initial O_3 due to chemical fractionation. In contrast, the values of $\delta^{17}O$ of Ag_2O are more than that of O_3 . This indicates that the difference between enrichment in terminal position and central position is more in case of ${}^{17}O$ than in case of ${}^{18}O$ (see text).

The oxygen isotopic compositions of ozone obtained by converting $\sim 100\%$ of starting

oxygen (case of zero-enriched ozone) are also given in Table 5.3 and shown in Figure 5.1. As before, the ozone isotopic composition was determined by mass balance. It is noted that the collected ozone is slightly depleted in heavy oxygen isotopes relative to the cylinder oxygen gas in a mass dependent fashion. The value of δ^{18} O and δ^{17} O of ozone varies from -9.5 to -3.7 and -5.5 to -2.1 corresponding to pressure variation in initial oxygen from 3 to 15 torr. Ideally, these δ -values should be zero if one can convert whole of oxygen to ozone. However, the progress of ozone formation reduces very much when the residual pressure reaches about 0.2 torr in the Tesla chamber and one has to stop the discharge to go ahead with the rest of the experiment. This means that there is about 5% unconverted oxygen left in the chamber. It is known from an early experiment by Bains-Sahota and Thiemens [1987] using microwave discharge at a flow system that at very low pressures (less than 25 torr) the isotope selectivity in ozone reverses and there is depletion of heavy oxygen isotopes which follows a δ^{17} O- δ^{18} O slope of ~ 0.7. Therefore, it seems that in going from a pressure of 3 to 15 torr up to ~0.2 torr the total accumulated ozone may have slightly negative δ value instead of zero. In these cases, silver-bound oxygen is much more depleted in both the heavy isotopes compared to the enriched ozone cases. The values of δ^{18} O and δ^{17} O of Ag₂O vary from -55.7 to -33.7 and -26.8 to -9.0 corresponding to the variation in ozone mentioned above. As we shall see, this contrast is indicative of a totally different internal distribution of heavy isotopes in zero-enriched ozone.

As mentioned before, during the reaction of ozone with silver, oxygen atoms in the ozone reservoir get distributed in two phases: a solid phase where oxygen atoms (about 10 to 15% of total) are chemically bound as silver oxide layer and a gaseous phase comprising oxygen generated in two processes:

- 1. oxygen molecules produced by reaction of ozone with silver $(O_3 + 2Ag \rightarrow Ag_2O + O_2)$
- 2. oxygen molecules produced by secondary catalytic reaction of ozone with freshly formed silver oxide $(2O_3+Ag_2O\rightarrow Ag_2O+ 3O_2)$.

It is clear from Figure 5.2 that though the δ -value of silver oxide faithfully represents the ozone isotopic composition it is associated with a mass dependent fractionation. The total fractionation (ε_{tot} of silver oxide relative to ozone) comprises of two parts:

1. a fractionation due to kinetic effect (ε_k) associated with the chemical reaction initiated by the ozone gas which diffuses into the silver chamber and reacts with the silver foil
rapidly

2. a fractionation due to catalytic decomposition (ε_{cat}) of ozone by freshly formed silver oxide.

Part of the kinetic fractionation arises due to different bond strengths of various ozone isotopologues. The formation of silver oxide involves breakage of one O-O bond in ozone followed by formation of one Ag-O-Ag bond. It is well known that ¹⁶O-¹⁶O bond breaks relatively easily compared to ¹⁶O-¹⁸O bond due to its higher zero point energy. For example, if only the terminal atom extraction is involved the difference in values of asymmetric stretch frequency of ozone molecules ${}^{16}O{}^{16}O{}^{18}O$ (1090 cm⁻¹) and ${}^{16}O{}^{16}O{}^{16}O$ (1103 cm⁻¹) lead one to expect a faster dissociation rate of the second molecule by at least 12‰ [(1103-1090/1103 = 11.8%]. However, this value is not directly applicable since the production of silver oxide probably proceeds through two steps: formation of a transient complex involving ozone and silver atoms and the break-up of this complex where formation of $Ag_2^{18}O$ would be preferred over $Ag_2^{16}O$ due to zero point energy effect. The net result of these three effects (diffusion, complex formation and complex break down) determines whether the silver-bound oxygen is depleted or enriched in heavy isotopes. Based on theoretical reaction rate studies of isotopic molecules [Bigeleisen, 1949; Bigeleisen and Wolfsberg, 1958] one normally expects lighter species to have a faster reaction rate leading to negative fractionation in silver oxide. This inference is also supported by a study of Dole et al. [1954] who showed that lighter oxygen isotopes are chemisorbed preferentially on metal surfaces. The catalytic fractionation arises due to catalytic dissociation of ozone by newly formed silver oxide. It is likely that in this process heavy oxygen isotopes of ozone exchanges partly with the lighter oxygen of the pre-formed silver oxide phase. Consequently, the catalytic fractionation probably acts in a positive direction. As in kinetic fractionation, the magnitude of catalytic fractionation is not constant and depends on various parameters governing the catalysis, like ozone amount and its isotopic composition. A set of control experiments carried out to determine this effect showed that unless the difference between initially reacting ozone and the modifier ozone undergoing catalysis is large the change is expected to be small (see appendix A.2). When both catalysis and reaction are induced by the same ozone (as happens in the experiments described above) there is no extra fractionation by catalysis. In other words, the fractionation involved in catalysis is same as that of the fractionation associated with the ozone-silver reaction.

Thus, though the net fractionation is expected to be determined by the balance between these fractionations and can vary depending on the relative contribution of each of them, on the whole, we expect it to be negative.

In addition to fractionation, we also have to consider whether the oxygen atom is extracted from the central position or the terminal position of ozone in forming the silver oxide. As mentioned before, it is highly probable that the reaction occurs mostly with the terminal atoms [*Babikov et al.*, 2003a, 2003b]. The hypothesis of terminal atom reaction also helps to explain the intriguing difference between δ^{17} O and δ^{18} O of Ag₂O i.e., why δ^{17} O of Ag₂O is mostly higher than that of ozone whereas δ^{18} O is not. A lower δ^{18} O (Ag₂O) is easily explained by net negative fractionation. However, in case of ¹⁷O it is apparent that even though the δ^{17} O value of ozone is nearly equal to the δ^{18} O value, the fractionation in ¹⁷O (being mass dependent) is only half that of ¹⁸O (Ag₂O) < δ^{17} O value of terminal position is higher than that of whole ozone by an amount more than the ¹⁷O fractionation we may get δ^{17} O (Ag₂O) > δ^{17} O(O₃) even when δ^{18} O (Ag₂O) < δ^{18} O(O₃). The contrasting pattern between ¹⁷O and ¹⁸O, therefore, seems consistent with our assumption that terminal atoms of ozone are the ones to react with silver (albeit with a negative fractionation) (Figure 5.3).

5.3.1 Calculation of $\delta_{\rm a}$, $\delta_{\rm s}$ and r^{49}

It is clear from the above discussion that to determine the r-values related to the internal distribution of heavy isotopes in ozone from these data one has to correct the silver oxide isotope ratios for kinetic and chemical fractionation. Since we do not have a priori knowledge about this we cannot derive both r^{50} and r^{49} . However, we can estimate r^{49} using published r^{50} values. This is done by following the steps described below. Since the isotope ratio is always expressed relative to the starting oxygen reservoir we do not distinguish between enrichment and δ -values. Our method depends critically on *Janssen*'s analysis [2005]. As mentioned before, *Janssen* [2005] has carefully evaluated all the earlier FTAS and TDLAS data and tabulated the values of r^{50} for a set of ozone enrichment values ranging from 6‰ to 156‰. Based on this evaluation he proposed an equation, which relates the ¹⁸O-enrichment in asymmetric species (E_a^{50}) with total ozone enrichment (E^{50}) as:



Figure 5.3: A schematic three-isotope figure showing the relationship among the enrichments corresponding to the bulk, symmetric, and asymmetric ozone. It is clear that for small fractionation values $\delta^{17}O(Ag_2O) > \delta^{17}O(O_3)$ but $\delta^{18}O(Ag_2O) < \delta^{18}O(O_3)$. It also shows clearly that only the terminal atoms (asymmetric ozone) are involved otherwise it would be impossible to produce $\delta^{17}O(Ag_2O) > \delta^{17}O(O_3)$.

$$E_{a}^{50} = -3.8 \times 10^{-3} (E^{50})^{2} + 1.33 \times E_{50} - 1.7$$
(5.2)

where enrichment is expressed in %. We assume that the above relation is valid in ozone samples prepared for the present experiment and apply it to calculate the expected enrichment in asymmetric species ($\delta_a^{18}O_{exp}$) corresponding to each ozone enrichment value $\delta_t^{18}O_{O_3}$ (see Table 5.1, 5.2 and 5.3; note that in calculating enrichments, ⁵⁰O₃ corresponds to ¹⁸O and ⁴⁹O₃ to ¹⁷O).

The initial ozone isotopic composition $\delta_t^{18}O(O_3)$ indicating "total enrichment" can be expressed in terms of asymmetric $\delta_a^{18}O(O_3)$ and symmetric $\delta_s^{18}O(O_3)$ enrichment as:

$$\delta_{t}^{18}O(O_{3}) = (1/3)\delta_{s}^{18}O(O_{3}) + (2/3)\delta_{a}^{18}O(O_{3})$$
(5.3)

 $\delta_s^{18}O(O_3)$ and $\delta_a^{18}O(O_3)$ are multiplied by 1/3 and 2/3 because the statistical weight is two times higher for the asymmetric type compared to the symmetric type. Assum-

ing reaction by the base atoms only, the observed isotopic composition of silver oxide $\delta^{18}O(Ag_2O)$ should be determined only by $\delta_a{}^{18}O(O_3)$ except for a correction due to chemical fractionation. In terms of isotope ratio ${}^{18}O/{}^{16}O=R^{18}$, one can write (subscript 'exp' and 'obs' indicate expected and observed) this as,

$$R_{a}^{18}(O_{3}) = R_{exp}^{18}(Ag_{2}O) = R_{obs}^{18}(Ag_{2}O)/\alpha^{18}$$
(5.4)

The fractionation factor α^{18} was calculated in each case using the observed $\delta_{obs}^{18}O(Ag_2O)$ and $\delta_a^{18}O(O_3)$ which equals $\delta^{18}O_{exp}(Ag_2O)$ calculated from equation (5.2) and converting them to R-values. The combined LGGE and PRL data show that the fractionation α^{18} is not constant and varies from 1.0035 to 0.9815 (Table 5.1, 5.2 and 5.3); i.e., fractionation can be negative as well as positive. A near normal distribution is seen in the frequency plot of $\varepsilon_{tot} = (\alpha^{18}-1) \times 1000$ with mean of -8.4 and standard deviation of 10.0 (Figure 5.4). This attests to the randomness in the relative contribution of the fractionating processes. Samples with ε_{tot} values within 1.5 σ (σ =standard deviation) of the mean were only considered for further analysis the outliers (total number = 4) being rejected as suspect.

The minimum value of ${}^{18}\varepsilon_{tot}$ (~ -20‰) probably denotes the maximum extent of kinetic fractionation (ε_k) and the spread in the values could be due to the variability discussed above. Given the fractionation for 18 O, the fractionation factor for 17 O (α^{17}) can be derived by assuming the fractionation to be mass dependent, i.e., $\alpha^{17} = (\alpha^{18})^{0.5}$. Then, using the measured δ -value of silver oxide δ^{17} O_{obs}(Ag₂O) and α^{17} , enrichment in asymmetric species $\delta_a{}^{17}$ O(O₃) can be calculated in each case. Using this value and calculating $\delta_s{}^{17}$ O(O₃) from equation 5.3, values of r for 17 O can then be obtained (shown in Table 5.1, 5.2 and 5.3) using the formula

$$r=2\times [1+\frac{\delta_a}{1000}]/[1+\frac{\delta_s}{1000}]$$

Such calculation shows that in case of ¹⁷O also, both terminal and central positions are enriched in heavy oxygen isotopes with extra preference for terminal position at all enrichment levels. An increase in total enrichment in ⁵⁰O₃ from 13.7 to 115.6 corresponds to an increase in enrichment from 1.1 to 131.7 in asymmetric species and 38.9 to 83.5 in symmetric species. For ¹⁷O, the total enrichment range of (16.6 to 106.3) corresponds to enrichment range of (23.7 to 131.6) and (2.3 to 55.7) in asymmetric and symmetric species



Figure 5.4: The frequency distribution of $\varepsilon_{\text{total}}$ for ¹⁸O. The spread in distribution is due to variable magnitude of fractionation associated with the ozone catalysis by silver oxide which depends on the amount and isotopic composition of ozone. (Data within 1.5 sigma standard deviation was considered).

respectively. A δ^{17} O- δ^{18} O correlation plot (Figure 5.5) for whole ozone, asymmetric ozone and symmetric ozone shows different slopes and range of values for the three types.

It is interesting to note that the intramolecular distributions for ¹⁸O and ¹⁷O are not the same. The difference between terminal and central position enrichments is more in case of ⁴⁹O₃ than in case of ⁵⁰O₃. This finding is consistent with an independent calculation of r^{50} and r^{49} using the values of relative rate coefficient of formation of asymmetric and symmetric species obtained from literature (for a specific ozone enrichment) which shows higher value of r^{49} relative to r^{50} (see next section). A second point to note is, the difference between the two enrichments (⁵⁰O₃ and ⁴⁹O₃) at a given position is not constant but decreases with increase in the total ozone enrichment (compare the trends in Figure 5.6 a and 5.6 b).



Figure 5.5: $\delta^{17}O$ - $\delta^{18}O$ correlation plot for total ozone, symmetric ozone and asymmetric ozone showing the *difference in the three species.*



Figure 5.6: (*a*) Enrichment in asymmetric species is plotted against its corresponding total ozone enrichment for both PRL and LGGE data which shows that the internal distribution of two heavy oxygen isotopes is not same. At higher ozone enrichment (above ~50 ‰) the terminal position is enriched in both ¹⁸O and ¹⁷O than that of the total ozone enrichment. The difference between the enrichment in ¹⁸O and ¹⁷O in asymmetric species decreases with the increase in total enrichment. The total ozone enrichment of (13.7, 16.6) and (115.6, 106.3) in ¹⁸O and ¹⁷O corresponds to (1.1, 23.7) and (131.7, 131.6) enrichment in asymmetric species respectively. (b) Plot showing the abundance of ¹⁸O and ¹⁷O at the central position of the ozone molecule. A total enrichment of 115.6 and 106.3 ‰ in ¹⁸O and ¹⁷O in ozone corresponds to an enrichment of 83.5 and 55.7‰ respectively in symmetric species. Note decrease in difference between δ_s^{50} and δ_s^{49} with increase in δ_t .

We derive the following equation for ¹⁷O for the best fit line relating enrichment of asymmetric species with that of bulk ozone:

$$\delta_{a}^{17}O = 3.12 + 1.22(\delta_{t}^{17}O) - 3.19 \times 10^{-4}(\delta_{t}^{17}O)^{2}$$
(5.5)

PRL data show a variation of r^{49} from 2.04 to 2.15 (Table 5.1, 5.2 and 5.3). In contrast to r^{50} , r^{49} value never goes below 2.00 for enriched ozone. The ratio r^{50} (using equation of *Janssen* [2005]) and r^{49} are plotted against the bulk enrichment values in ¹⁸O and ¹⁷O respectively in Figure 5.7. It is noted that ozone made form Tesla and UV discharge has same r^{49} value. The total error estimated in r^{49} varies from 0.06 to 0.04 (see appendix A.4).



Figure 5.7: The ratio of asymmetric to symmetric species for ${}^{50}O_3$ and ${}^{49}O_3$ is plotted against the total enrichment for PRL+LGGE data. The value of r^{49} is more than that of r^{50} indicating different internal distribution of heavy isotope in ${}^{50}O_3$ and ${}^{49}O_3$ isotopologues. The value of r^{49} varies from 2.04 to 2.15. The variation in total ozone enrichment is from 16.6 to 106.3‰ in ${}^{17}O$. The value of r^{49} is same for ozone whether made by Tesla or UV discharge.

There is a systematic increase in the ratio with total enrichment suggesting a more rapid increase in enrichment of asymmetric species over that of symmetric one. It is remarkable to note that the extrapolated value of r^{49} for a total enrichment of 116‰ agrees with the calculated value using estimates of relative rate coefficient of symmetric and asymmetric

ozone formation channels that are available in literature for this particular enrichment (discussed below). As an academic exercise, the data were also analyzed by taking the base atom reaction probability, x=0.9. It is observed that the estimated values of r^{49} become higher for x=0.9 than that for x=1 case and the values range from 2.08 to 2.19.

In case of zero-enriched ozone, the value of fractionation cannot be calculated by the procedure mentioned above because *Janssen*-equation (eqn 5.2) is valid only in cases where ozone is enriched (made by converting a small fraction of oxygen reservoir so that the isotopic composition of the reservoir remains essentially unchanged). To calculate r^{49} and r^{50} in zero-enriched cases, an average fractionation value of 0.9916 for ¹⁸O (i.e., the mean fractionation value determined in enriched cases) is assumed. Under this assumption, the value of r^{50} and r^{49} is always less than two. The variation in r^{50} is from 1.76 to 1.88 whereas the variation in r^{49} is from 1.88 to 1.99. It is apparent that the assumption of a constant fractionation value disregards possible variation and results in an artificial large spread of r-values even though all points refer to zero-enriched ozone samples (Figure 5.7).

It is interesting to note that for zero-enriched ozone the symmetric species is more enriched in ¹⁸O and ¹⁷O compared to asymmetric species which is opposite to what is observed in case of enriched ozone samples. We should mention that r-values less than two for zero-enriched ozone made by complete conversion of oxygen are quite expected. In a closed system, as the oxygen is quantitatively converted to ozone, several changes take place. The oxygen bath itself changes its isotopic composition and the pressure reduces to levels where O₃ starts to form with negative and mass dependent fractionation [Bains-Sahota and Thiemens, 1987; Heidenreich and Thiemens, 1985]. Finally, when nearly 100% of oxygen is converted to ozone the net fractionation is, of course, negligible but the distribution of a heavy isotope (¹⁷O or ¹⁸O) inside the molecule is expected to be determined solely by ZPE consideration. Since symmetric ozone has the heavy isotope located in more tightly bound position it will be preferentially abundant compared to the purely statistical distribution (i.e., r =2.00). A simple consideration of ZPE of ${
m ^{16}O^{18}O^{16}O}$ (2776 cm⁻¹) and $^{16}O^{16}O^{18}O$ (2840 cm⁻¹) yields a vibrational partition function ratio of 1.070 (Q^{sym}/Q^{asym}) suggesting at least 70‰ relative enrichment in the symmetric species which is close to the lower end of the values observed.

5.3.2 Calculation based on published rate constant values

Janssen et al. [2001] summarized the relative rate coefficients of reaction channels of several possible oxygen isotope combinations leading to ozone molecules at ambient pressure of 267 hPa corresponding to total ozone enrichment (in ¹⁸O) of ~ 130‰. The relevant equations (along with relative rate coefficients) which lead to formation of asymmetric and symmetric ozone species are:

$${}^{16}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \to {}^{16}\text{O}{}^{16}\text{O} \qquad \mathbf{k}_1 = 1.00$$
 (5.6)

For ¹⁸O-containing species:

$${}^{16}\text{O} + {}^{16}\text{O}^{18}\text{O} \to {}^{16}\text{O}^{16}\text{O}^{18}\text{O} \qquad \mathbf{k}_2 = 1.45$$
 (5.7)

$${}^{16}\text{O} + {}^{16}\text{O}{}^{18}\text{O} \to {}^{16}\text{O}{}^{18}\text{O}{}^{16}\text{O} \qquad k_3 = 1.08$$
 (5.8)

$${}^{18}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \to {}^{16}\text{O}{}^{16}\text{O}{}^{18}\text{O} \qquad \text{k}_4 = 0.92$$
 (5.9)

$${}^{18}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \to {}^{16}\text{O}{}^{18}\text{O}{}^{16}\text{O} \qquad k_5 = 0.006$$
(5.10)

For ¹⁷O-containing species, all rates are not available from *Janssen et al.* [2001]; however, we estimate them as below:

$${}^{16}\text{O} + {}^{16}\text{O}{}^{17}\text{O} \to {}^{16}\text{O}{}^{16}\text{O}{}^{17}\text{O} \qquad \mathbf{k}_6 = 1.36$$
 (5.11)

$${}^{16}\text{O} + {}^{16}\text{O}{}^{17}\text{O} \to {}^{16}\text{O}{}^{17}\text{O}{}^{16}\text{O} \qquad \mathbf{k}_7 = 1.06$$
 (5.12)

$${}^{17}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \to {}^{16}\text{O}{}^{17}\text{O} \qquad k_8 = 0.98$$
 (5.13)

$${}^{17}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \to {}^{16}\text{O}{}^{17}\text{O}{}^{16}\text{O} \qquad k_9 = 0.006$$
 (5.14)

The formation rate of ${}^{16}O^{16}O^{16}O$ has a value of $k_1=6.0\times10^{-34}$ cm⁶ s⁻¹ (see Chapter 3 for details). Using the above values of relative rate coefficients, the total enrichment as well as that in asymmetric and symmetric species for both ${}^{18}O$ and ${}^{17}O$ at 300 K were calculated (see Appendix A.3) which shows that r⁴⁹ (2.16) is indeed more than r⁵⁰ (2.12).

The reason for the difference in the internal distributions of ¹⁷O and ¹⁸O can be inferred based on the argument of *Janssen et al.* [2001] linking Δ ZPE with the lifetime of the collision complex and the attainment of stability of a particular ozone isotopic configuration. If the pathway leading to asymmetric ozone is linked with an exchange which has positive Δ ZPE the complex has a larger lifetime which leads to a higher rate of stable ozone formation. The value of r^{49} is more than that of r^{50} because the mass dependent exchange favors ¹⁷O relative to ¹⁸O in the atomic oxygen pool as apparent from detailed calculation shown in Appendix A.3. The values of Δ^{17} O (defined as δ^{17} O-0.52 × δ^{18} O) are calculated for total, terminal and apex positions (Table 5.4 and 5.5) and shown in Figure 5.8.



Figure 5.8: The value of $\Delta^{17}O$ (defined as $\delta^{17}O$ -0.52× $\delta^{18}O$) is plotted for asymmetric, symmetric and total (bulk) ozone which shows that asymmetric ozone species has higher $\Delta^{17}O$ than that of symmetric.

It is observed that Δ^{17} O for the terminal position is higher than that of the apex position. Very recently, *Janssen and Tuzson* (2006) have published an interesting paper dealing with TDLAS measurement of internal distribution of both ¹⁷O and ¹⁸O in ozone. However, due to "large (~ 10%) systematic uncertainties in the line strengths of individual ozone isotopomers" they did not analyze ozone enrichment relative to bath oxygen gas but measured the enrichment relative to another ozone sample made under low pressure conditions in an electric discharge. It was assumed that the "low-pressure ozone" does not have the usual enrichment and can provide a reference for comparison. However, as noted by *Bains-Sahota and Thiemens* [1987] at low-pressure the formed ozone is fractionated negatively in a mass dependent fashion. Consequently, unless the "low-pressure ozone"

Sample	Ozone	composition	Δ	17 O in ozor	ne
No.	$\delta^{18} \mathrm{O}$	¹⁷ O	Total	Terminal	Apex
	‰	‰	‰	‰	‰
]	PRL data (Tes	la ozone	e)	
P-1	13.7	16.6	9.4	23.1	-17.9
P-2	18.3	21.7	12.2	24.0	-11.5
P-3	22.0	23.9	12.5	28.6	-19.8
P-4	33.6	30.4	12.9	28.5	-18.4
P-5	34.5	35.1	17.1	27.3	-3.2
P-6	40.8	37.8	16.5	32.7	-15.8
P-7	43.1	40.5	18.1	29.9	-5.5
P-8	44.4	41.0	17.9	34.6	-15.5
P-9	46.9	44.1	19.6	36.8	-14.7
P-10	47.2	41.8	17.3	35.4	-19.0
P-11	49.3	45.1	19.4	33.5	-8.6
P-12	51.1	43.3	16.7	27.4	-4.7
P-13	51.3	43.4	16.7	26.8	-3.3
P-14	51.9	47.6	20.5	34.0	-6.3
P-16	56.1	48.6	19.4	33.1	-8.0
P-17	59.0	53.0	22.4	34.0	-0.8
P-18	62.6	50.8	18.3	30.6	-6.4
P-19	67.4	63.7	28.7	46.1	-6.1
P-20	68.7	64.5	28.8	46.1	-5.9
P -2 1	69.1	63.9	27.9	46.1	-8.4
P-22	71.3	66.4	29.4	47.2	-6.3
P-24	77.3	70.3	30.1	47.6	-4.9
P-25	78.0	70.5	29.9	46.6	-3.5
		PRL data (UV	/ ozone)	
P-15	54.7	51.3	22.9	31.7	5.2
P-23	72.5	71.0	33.3	44.0	12.0
P-26	81.4	76.9	34.6	48.5	6.8
P-27	89.9	83.5	36.8	51.6	7.3
P-28	91.8	88.1	40.4	54.0	13.2
P-29	97.1	92.6	42.1	52.6	21.0
P-30	101.8	87.2	34.3	47.2	8.4
P-31	102.0	95.6	42.6	60.3	7.1
P-32	102.4	96.3	43.0	54.8	19.3
P-33	104.3	95.9	41.7	54.0	17.0
P-34	104.7	98.2	43.7	56.1	19.0
P-35	111.6	104.3	46.3	64.0	11.0
P-36	112.8	102.0	43.3	58.5	13.0
P-37	115.6	106.3	46.2	63.2	12.3

Table 5.4: $\Delta^{17}O$ defined as: $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$ was calculated for total, terminal and apex positions. The data shows that the value of $\Delta^{17}O$ is higher at the terminal position than that of apex position.

Sample	Ozone	composition	Δ	17 O in ozoi	ne
No.	$\delta^{18} \mathrm{O}$	¹⁷ O	Total	Terminal	Apex
	‰	‰	‰	‰	‰
	L	GGE data (Te	sla ozor	ne)	
L-1	10.7	11.7	6.1	18.2	-18.0
L-2	20.7	21.7	10.6	23.2	-13.5
L-3	28.1	29.0	14.4	26.5	-9.7
L-4	39.4	40.4	19.9	31.9	-4.0
L-5	45.9	45.4	21.6	33.5	-2.4
L-6	52.3	51.6	24.4	36.2	0.9
L-7	53.1	51.3	23.6	35.8	-0.7
L-8	60.7	57.1	25.5	36.0	4.6
L-9	64.4	60.4	26.9	40.8	-1.0
L-10	76.4	70.4	30.7	44.3	3.5
L-11	83.9	75.4	31.8	45.8	3.8
L-12	84.1	76.6	32.9	46.1	6.3
L-13	86.4	76.8	31.9	42.2	11.1
L-14	98.2	84.5	33.5	47.1	6.2
L-15	106.2	91.8	36.6	51.7	6.3
	Zerc	-enriched dat	ta (PRL	data)	
1	-9.5	-5.5	-0.6	2.1	-6.0
2	-8.9	-4.4	0.2	1.1	-1.6
3	-8.8	-4.9	-0.3	5.3	-11.4
4	-8.2	-4.2	0.1	4.8	-9.5
5	-7.5	-3.7	0.2	3.2	-5.7
6	-6.3	-3.5	-0.2	7.5	-15.8
7	-5.4	-3.3	-0.5	6.8	-14.9
8	-4.6	-2.1	0.3	7.4	-14.0
9	-3.7	-2.1	-0.1	8.5	-17.4

Table 5.5: $\Delta^{17}O$ calculated for total, terminal and apex positions for LGGE data and Zero-enriched PRL data.

is quantified in terms of enrichment (or depletion) as defined here (i.e., relative to source oxygen) we cannot compare our results with these data. There is another point of concern. Their present result on symmetric ¹⁸O-species does not agree with their earlier TDLAS study [*Janssen et al.*, 1999] and they state that "the origin of the higher enrichment found for ¹⁶O¹⁸O¹⁶O in the earlier experiment remains yet unexplained" [*Janssen and Tuzson*, 2006]. Since the r-values derived here are very sensitively dependent on the two enrichments (symmetric and asymmetric) we believe that further TDLAS studies are required before one can compare them with the high precision mass spectrometric data as reported here.

5.4 Application to atmospheric studies

The values of r⁴⁹ as a function of total ¹⁷O enrichment in ozone find immediate application in stratospheric ozone chemistry. Such a study has been carried out recently by *Liang et al.* [2006] who could reproduce the observed ozone isotope profiles (both ¹⁷O and ¹⁸O) by considering two dominant processes: Formation and Photolysis. The profiles of enrichments of symmetric and asymmetric species using formation process alone [as given in Figure 7 of *Liang et al.*, 2007] can be easily converted to r^{50} and r^{49} as defined here and compared to our results. Such a comparison is given in Figure 5.9 showing variation of r^{50} and r⁴⁹ as a function of enrichment in ¹⁸O and ¹⁷O respectively. The r⁵⁰ values of *Janssen* (as adopted here) agree well with the values of Liang et al. [2007]. However, there is some disagreement in case of r⁴⁹ between *Liang et al.* curve and our results (shown in Table 5.6 and Figure 5.9). In *Liang et al.* curves at enrichment level of ~ 100 ‰ the values of ¹⁷O in asymmetric species are slightly higher ($\sim 8\%$) and the value of ¹⁷O in symmetric species are slightly lower ($\sim 20\%$). This makes their r⁴⁹ slightly higher than that of this work by 0.01 to 0.05 but the difference is within the error of our r^{49} values (~ 0.06). The values of r⁵⁰ and r⁴⁹ obtained by *Liang et al.*[2006] refer to their model calculation applicable to stratosphere (involving large number of reactions) while our experiments deal with only ozone made in laboratory by Tesla discharge. In view of this the small differences in r⁴⁹ (from 0.02 to 0.06) are probably not significant.

Table 5.6: A comparison of r^{50} and r^{49} values obtained from Liang et al.[2006], Janssen [2005] and this work. The r^{49} values calculated from Liang et al. are slightly higher than that of this work (by 0.01 to 0.05) whereas r^{50} values agree with Janssen or this work.

Total ozone	r^{50}	r^{49}	r^{50}	r^{49}	Difference
enrichment	Liang et al.	Liang et al.	Janssen	This work	
(‰)		(A)		(B)	(A-B)
75	2.015	2.118	2.029	2.106	0.012
80	2.028	2.129	2.036	2.111	0.019
85	2.039	2.145	2.044	2.116	0.029
91	2.056	2.158	2.054	2.122	0.036
97	2.078	2.174	2.063	2.128	0.046



Figure 5.9: The values of r^{50} and r^{49} obtained from Liang et al. [2006], Janssen [2005] and present study are compared. The r^{49} values from Liang et al. are higher than that of our study.

5.5 Conclusion

We have investigated the internal distribution of ¹⁷O isotope in ozone isotopomers using a simple oxidation reaction of ozone with silver. Assuming that the transfer of an O-atom to silver occurs mainly from the terminal position of the ozone molecule it is possible to deduce the distribution of the heavy ¹⁷O isotope inside the ozone molecule. Using the results published by Janssen [2005] on ¹⁸O distribution we derived the value of kinetic fractionation associated with silver oxidation and calculated the ratio of asymmetric to symmetric type of ozone isotopologues for ¹⁷O species given by r⁴⁹. r⁴⁹ values are consistently larger than the r⁵⁰ values for similar level of enrichment. This difference is consistent with calculation based on available rate constant values for ¹⁷O and ¹⁸O species (for one particular case of ozone enrichment). These results will be useful in calculating transfer of heavy isotopes from ozone to other atmospheric molecules during their interaction with ozone in stratosphere. The information on r^{50} and r^{49} values in ozone has also interesting application in deciphering reaction processes involving ozone. For example, in reactions involving direct contact of ozone, the position of the participating O-atom is not always clear. If both positions are involved we need to know the proportion in which they react. Knowing the internal isotopic distribution of ozone and measuring the bulk isotopic transfer between O₃ and a given species one can get idea about these two factors which would elucidate many features of molecular reaction dynamics.

CHAPTER 6

Effect of nuclear spin in exchange of ¹⁷O in CO₂- O(¹D) system: Model calculation of Laboratory data.

6.1 Motivation

The oxygen isotopic composition of stratospheric CO_2 is anomalously enriched in heavy oxygen isotopes compared to the tropospheric CO₂. The mean δ^{18} O value of tropospheric CO₂ is about 41‰ (relative to VSMOW) with only small (less than 4‰) seasonal and geographical variations [Farquhar et al., 1993] and an annual average North Pole-South Pole difference of 2‰ [Trolier et al., 1996]. The first measurement of oxygen isotopic composition of stratospheric CO₂ was done by *Gamo et al.* [1989] which showed highly anomalous enrichment. Several other subsequent measurements of stratospheric CO₂ samples collected by aircraft [Thiemens et al., 1991, 1995a], balloon [Gamo et al., 1995; Alexander et al., 2001; Lammerzahl et al., 2002; Bhattacharya et al., 2006a] rocket [Thiemens et al., 1995b; Zipf and Erdman, 1994] Nasa ER-2 aircraft [Boering et al., 2004] not only confirmed the enrichment but also showed that the enrichment in ¹⁷O is greater than that of ¹⁸O by a factor of 1.2 to 2.1. It is also seen that the enrichment in ¹⁸O and ¹⁷O increases with increase in altitude while the value of the slope relating the two enrichments ($\Delta(\delta^{17}O)$ vs. $\Delta(\delta^{18}O)$) decreases. Yung et al. [1991] was the first to propose that the enrichment in CO_2 is due to an isotope exchange reaction between CO_2 and $O(^1D)$, the latter being produced by UV dissociation of ozone. It is known that the stratospheric ozone is unusually enriched in heavy oxygen isotopes relative to the ambient oxygen from which it is produced [Mauersberger et al., 1981,

1987, 2001; *Rinsland et al.*, 1985; *Abbas et al.*, 1987; *Schueler et al.*, 1990; *Meier and Notholt*, 1996; *Irion et al.*, 1996; *Lammerzahl et al.*, 2002] with enrichment in ¹⁸O and ¹⁷O varying from 70 to 130 ‰. As O(¹D) is derived from ozone it also possesses this anomalous enrichment and transfers its heaviness to other oxygen bearing species (like N₂O, CO₂, CO, sulfate aerosol etc.) during its interaction with them. The collision of O(¹D) and CO₂ produces a short -lived collision complex CO₃* which dissociates into CO₂+O(³P) [*Perri et al.*, 2003]. Since the production of O(¹D) from ozone occurs only in stratosphere, this strange effect is associated with stratospheric CO₂ only. The exchange mechanism as proposed by *Yung et al.* [1991] is given by:

$$O_3 + h\nu \to O_2 + O(^1D) \tag{6.1}$$

$$CO_2 + Q(^1D) \rightarrow COOQ^*$$
 (6.2)

$$COOQ^* \to COQ + O(^{3}P)$$
 (6.3)

The quenching of $O(^{1}D)$ by CO_{2} (reaction 6.2 and 6.3) is a spin forbidden reaction as it involves transition from singlet state to triplet state (total spin of reactants= 0: Singlet and total spin of products=1: Triplet) but it proceeds at quite fast rate 1.1×10^{-10} cm³s⁻¹ at 298 K. A recent study by Perri et al. [2003] has showed that the above isotope exchange reaction can occur via two different channels. The major channel is electronic quenching of $O(^{1}D)$ to $O(^{3}P)$ ($CO_{3}^{*} \rightarrow CO_{2} + O(^{3}P)$). In other channel, exchange occurs without quenching (i.e., no crossing to the triplet surface, $CO_3^* \rightarrow CO_2 + O(^1D)$). The branching ratios of these two channels are: (68%, 32%) and (84%, 14%) at the collision energy 7.7 kcal/mol and 4.4 kcal/mol respectively. The life time of CO_3^* complex is sufficiently high, between 1 to 10 ps [Baulch and Breckenridge, 1966] so that both isotope exchange and curve crossing from singlet to triplet surface can occur [Perri et al., 2003]. It is also noted that the oxygen isotope exchange proceeds at nearly statistical rate i.e., the probability that a reactant oxygen atom is incorporated into the product CO₂ molecule is close to 2/3 [Baulch and *Breckenridge*, 1966]. This can also be explained by a long life time of CO_3^* which allows a faster redistribution of intramolecular vibrational energy whereby all the three oxygen atoms become equivalent.

To explain quantitatively the anomalous oxygen isotopic composition of stratospheric CO₂, several models have been proposed [*Yung et al.*, 1991, 1997; *Barth and Zahn*, 1997; *Johnston et al.*, 2000; *Liang et al.*, 2006] but all of them had difficulty to explain the high value of

the slope. The model calculations for ¹⁸O enrichment in CO₂ by *Yung et al.* [1991] simply reflected the ¹⁸O enrichment in ozone. *Barth and Zahn* [1997] showed that stratospheric CO₂ enrichment cannot be explained by simple mixing of ozone and CO₂. They suggested an additional fractionation during the formation of the CO₃* complex that depends on the mass of the involved oxygen isotopes. Using this adhoc fractionation, they could reproduce the atmospheric observations. *Johnston et al.* [2000] also drew a similar conclusion and supported an additional mass dependent fractionation in dissociation of CO₃* complex. *Liang et al.* [2006] have shown that mass independent fractionation of oxygen in CO₂ can be satisfactorily explained by the exchange reaction with O(¹D). To explain the middle atmospheric CO₂ data, they considered an additional source of O(¹D) produced from O₂ dissociation by solar Lyman α in their model.

A recent study by *Mebel et al.* [2004] argued for a conventional isotope effect in CO_3^* dissociation process. They calculated the ratio of ${}^{16}O/{}^{18}O$ in ejected O-atoms based on theoretical considerations and derived a small deviation from the pure statistical probability of 2/3 in dissociation of $C^{16}O^{16}O^{18}O^*$ transient molecule. They also suggested the possibility of an unconventional isotope effect (non-RRKM effect) causing anomalous enrichment in ${}^{17}O$ and ${}^{18}O$ which could arise due to the breakdown of symmetry of transient CO_3^* complex (when one of the three atoms is a heavy isotope) as observed in case of O_3^* . On the whole, it is still not clear if the $O({}^{1}D)$ -CO₂ exchange process is a simple transfer of the isotope anomaly from ozone to CO_2 or involves some other anomalous isotope effect associated with CO_3^* formation/dissociation.

An important issue not considered in the earlier models is the internal distribution of ${}^{17}\text{O}$ and ${}^{18}\text{O}$ in ozone molecule. During ozone dissociation process, emission of the base atom is expected to be easier and more frequent than the apex atom emission. Indeed, an earlier trajectory calculation using a reliable potential energy surface predicts low (9%) emission probability of the apex atom [*Sheppard and Walker*, 1983]. It is therefore usually assumed that the O(${}^{1}\text{D}$) produced in ozone photodissociation comes mainly from the base position of the triangular ozone molecule. Due to intramolecular isotopic variation in ozone the abundances of heavy oxygen isotopes at the base (two possible positions) and apex position (one possible position) are different (i.e., not in random-case ratio of 2:1). Therefore, the isotopic composition of O(${}^{1}\text{D}$) depends not only on the composition of ozone as a whole but also on the composition of the base atoms and, therefore, a knowl-

edge of the internal distribution of heavy oxygen isotopes in ozone is required. Recent studies by *Janssen* [2005] and *Bhattacharya et al.* [2006b] provide a relationship between the enrichment of ¹⁸O (and ¹⁷O) at base position and corresponding total enrichment in ozone (see Chapter 5). *Bhattacharya et al.* [2006b] have also shown that in ozone molecules base position is relatively more enriched in ¹⁷O than ¹⁸O for same level of total ozone enrichment in two cases. In all earlier simulation studies, the enrichment in ¹⁷O was assumed to be same as that of ¹⁸O which is not correct.

Several controlled experiments have been done in the laboratory to study the CO₂- $O(^{1}D)$ isotope transfer mechanism with an aim to understand the enrichment phenomenon of stratospheric CO₂. [Wen and Thiemens, 1993; Johnston et al., 2000; Chakraborty and Bhattacharya, 2003d; Shaheen et al., 2006]. Wen and Thiemens [1993] photolysed O₃ (δ^{18} O= 44.4‰ and $\delta^{17}O = 22.9\%$ relative to VSMOW) and CO₂ mixture in UV and visible light. In their experiments ozone was mass dependently enriched in heavy oxygen isotope contrary to what is found in stratosphere. The isotopic composition of CO₂ was not directly measured but calculated from mass balance. Johnston et al. [2002] photolysed O₂ and CO₂ mixture of known isotopic composition. They measured both δ^{18} O and δ^{17} O of the final CO_2 in cases where CO_2/O_2 ratio was high (0.336 to 3.94) whereas in cases of low $\rm CO_2/O_2$ ratio (1/1000), only $\delta^{18}\rm O$ of $\rm CO_2$ was measured. The slope obtained in case of high CO_2/O_2 ratio was 0.74 to 1.11 (average 0.92 \pm 0.09) omitting two deviant values (1.59) and -4.54). However, experiments with high CO_2/O_2 ratio do not apply directly to stratospheric case. Shaheen et al. [2006] photolysed ozone and isotopically enriched CO₂ mixture and thus obtained different slope values. These laboratory experiments could not generate slope higher than one due to adoption of experimental conditions widely different from that of stratosphere. The results reported by Chakraborty and Bhattacharya [2003d] are the only one which showed a slope 1.8 relating $\Delta(\delta^{17}O)$ vs. $\Delta(\delta^{18}O)$ as observed in stratosphere. However, Chakraborty and Bhattacharya did not attempt to explain their data by a realistic chemical reaction kinetic model and address the issue of higher-than-one slope in stratosphere on a molecular level.

In the present study, a chemical reaction model is used to simulate the experimental data of *Chakraborty and Bhattacharya* [2003d] to understand the molecular level details of the heavy oxygen isotope transfer from ozone to CO_2 .

6.2 Laboratory experiment

In the experiment of *Chakraborty and Bhattacharya* [2003d], ozone was produced in a 5 liter chamber fitted with a MgF₂ window by irradiating ultra pure oxygen at 665 mbar with UV generated by a Hg resonance lamp (185 nm and 254 nm) driven by a micro-wave generator. The irradiation time and other parameters were kept fixed to produce nearly same amount of ozone with nearly constant isotopic composition (~ 800 μ mol with δ^{18} O= 125 ‰ and δ^{17} O = 106‰ with respect to VSMOW). Ozone was cryogenically separated from the left over oxygen. Next, about 100 μ mol of CO₂ was introduced into the chamber. The mixture was brought into gaseous phase and then photolyzed by UV light for various time periods to generate different enrichments in the final CO₂.

The isotopic composition of ozone was kept constant in all the experiments [*Chakraborty and Bhattacharya*, 2003d, Table 2] while CO₂ of three different oxygen isotopic composition (δ^{18} O, δ^{17} O) was used in three different sets of experiments, namely, Set 1 SM- CO₂: (39.3, 20.4); Set 2 SP- CO₂: (4.1, 2.2) and Set 3 SL- CO₂: (-10.9 and -5.6). The photolysis time was varied from 9 min to 25 min. After photolysis, CO₂ was separated from the product oxygen and left over ozone and its oxygen isotopic composition was measured by mass spectrometer. It was observed that the product CO₂ is enriched in heavy oxygen isotopes with ¹⁷O being more enriched than ¹⁸O. The values of slope relating the two enrichments ($\Delta(\delta^{17}\text{O})$ and $\Delta(\delta^{18}\text{O})$) obtained in these three sets are: 1.79, 1.52 and 1.29 for SM-CO₂, SP-CO₂ and SL-CO₂ respectively. To analyze these interesting data, we used the chemical reaction model (KINTECUS), described before, to simulate the results given in Table 2 and Figure 1 of *Chakraborty and Bhattacharya* [2003d] (i.e., for each of the three sets, Set 1 (SM-CO₂), Set 2 (SP-CO₂) and Set 3 (SL-CO₂)).

6.3 Model Input

All the basic reactions as well as isotopic exchange reactions involving isotopes and isotopomers of O, O_2 , O_3 and CO_2 (a total of 91 reactions) were included in the KINTECUS model (Table 6.1). The details of the reaction rates are described in Chapter 3.

As mentioned before, we assume that during ozone photolysis the O atom is derived only from the base position. Several studies [*Anderson et al.,* 1989; *Larsen et al.,* 1994, 2000; *Janssen,* 2005] have shown that abundance of heavy oxygen isotopes at base position is

	Reactions	Rate coefficient
	R1(Ozone photolysis: Singlet Products)	
R1	$OOO+h\nu \rightarrow O(^{1}D)+OO(^{1}\Delta)$	$k_1 = 6.5 \times 10^{-4}$
R2	$OOQ+h\nu \rightarrow O(^{1}D)+OQ(^{1}\Delta)$	k_2 =0.5× k_1
R3	$OOQ+h\nu \rightarrow Q(^{1}D)+OO(^{1}\Delta)$	$k_3 {=} 0.5 {\times} 0.983 {\times} k_1$
R4	$OQO+h\nu \rightarrow O(^{1}D)+OQ(^{1}\Delta)$	$k_4 = 0.983 \times k_1$
R5	$OOP+h\nu \rightarrow O(^{1}D)+OP(^{1}\Delta)$	$k_5=0.5 imes k_1$
R6	$OOP+h\nu \rightarrow P(^{1}D)+OO(^{1}\Delta)$	$k_6 {=} 0.5 {\times} 0.989 {\times} k_1$
R7	$OPO+h\nu \rightarrow O(^{1}D)+OP(^{1}\Delta)$	$k_7 = 0.989 \times k_1$
	R2(Ozone photolysis:triplet products)	
R8	$OOO+h\nu \rightarrow O+OO$	$k_8 = 7.2 \times 10^{-5}$
R9	$OOQ+h\nu \rightarrow O+OQ$	$k_9 = 0.5 \times k_8$
R10	$OOQ+h\nu \rightarrow Q+OO$	k_{10} =0.5×0.983× k_8
R11	$OQO+h\nu \rightarrow O+OQ$	k_{11} =0.983× k_8
R12	$OOP+h\nu \rightarrow O+OP$	$k_{12}=0.5 \times k_8$
R13	$OOP+h\nu \rightarrow P+OO$	k_{13} =0.5×0.989× k_8
R14	$OPO+h\nu \rightarrow O+OP$	k_{14} =0.989× k_8
	R3 (Oxygen photolysis)	
R15	$OO+h\nu \rightarrow O+O$	k_{15} =6.4×10 ⁻⁹
R16	$OQ+h\nu \rightarrow O+Q$	k_{16} =0.983× k_{15}
R17	$OP+h\nu \rightarrow O+P$	k_{17} =0.989× k_{15}
	R4 (O-O recombination)	
R18	O+O+A→OO+A	k_{18} =1.1×10 ⁻³³
R19	O+Q+A→OQ+A	k_{19} =0.972× k_{15}
R20	O+P+A→OP+A	k_{20} =0.985× k_{15}
	R5 (Isotopic exchange of O - atom with oxygen)	
R21	Q+OO→O+OQ	k_{21} =2.9×10 ⁻¹²
R22	O+OQ→Q+OO	k_{22} =1.34×10 ⁻¹²
R23	$P+OO \rightarrow O+OP$	k_{23} =2.9×10 ⁻¹²
R24	O+OP→P+OO	k_{24} =1.39 $ imes$ 10 ⁻¹²
	R6 (Ozone formation)	
R25	O+OO+M→OOO+M	k_{25} =6.0×10 ⁻³⁴
R26	O+OQ+M→OOQ+M	$k_{26} {=} 0.5 {\times} 1.45 {\times} k_{25}$
R27	O+OQ+M→OQO+M	$k_{27} {=} 0.5 {\times} 1.08 {\times} k_{25}$
R28	$Q+OO+M \rightarrow OOQ+M$	k_{28} =0.92× k_{25}
R29	Q+OO+M→OQO+M	k_{29} =0.006× k_{25}
R30	O+OP+M→OOP+M	$k_{30} {=} 0.5 {\times} 1.36 {\times} k_{25}$
R31	O+OP+M→OPO+M	$k_{31} {=} 0.5 {\times} 1.06 {\times} k_{25}$
R32	P+OO+M→OOP+M	k_{32} =0.98× k_{25}
R33	P+OO+M→OPO+M	k_{33} =0.006× k_{25}

Table 6.1: *List of various gas phase reactions along with the rate constants used in the kinetic model (KIN-TECUS) for simulation of* CO_2 - $O(^1D)$ *exchange.*

	Reactions	Rate coefficient
	R7 O(¹ D) Quenching)	
R34	O(¹ D)+OO→O+OO	k_{34} =8×10 ⁻¹²
R35	$Q(^{1}D)+OO \rightarrow Q+OO$	k_{35} =0.962× k_{34}
R36	$P(^{1}D)+OO \rightarrow P+OO$	k_{36} =0.980× k_{34}
	R8 (OO($^{1}\Delta$) quenching)	
R37	$OO(^{1}\Delta)+OO \rightarrow OO+OO$	k_{37} =1.5×10 ⁻¹⁸
R38	$OQ(^{1}\Delta)+OO \rightarrow OQ+OO$	$k_{38}=0.985 \times k_{37}$
R39	$OP(^{1}\Delta)+OO \rightarrow OP+OO$	$k_{39}=0.992 \times k_{37}$
	R9 (Ozone decomposition)	
R40	OOO+O→OO+OO	k_{40} =8.0×10 ⁻¹⁵
R41	OOO+Q→OO+OQ	k_{41} =0.957× k_{40}
R42	OOQ+O→OO+OQ	k_{42} =0.995× k_{40}
R43	OQO+O→OQ+OO	k_{43} =0.995× k_{40}
R44	OOO+P→OO+OP	k_{44} =0.978× k_{40}
R45	OOP+O→OO+OP	$k_{45}=0.997 \times k_{40}$
R46	OPO+O→OP+OO	k_{46} =0.997× k_{40}
R47	$OOO+O(^1D)\rightarrow OO+O+O$	$k_{47}=0.5\times1.2\times10^{-10}$
R48	OOO+O(¹ D)→OO+OO	$k_{48} = k_{47}$
R49	OOO+Q(¹ D)→OO+O+Q	$k_{49}=0.957 \times k_{47}$
R50	OOO+Q(¹ D)→OO+OQ	$k_{50} = k_{49}$
R51	$OOQ+O(^{1}D)\rightarrow OO+Q+O$	$k_{51}=0.5\times0.995\times k_{47}$
R52	$OOQ+O(^{1}D)\rightarrow OQ+O+O$	k_{52} = k_{51}
R53	$OOQ+O(^{1}D)\rightarrow OO+OQ$	k_{53} =0.995× k_{47}
R54	$OQO+O(^{1}D)\rightarrow OQ+O+O$	k_{54} =0.995× k_{47}
R55	$OQO+O(^{1}D)\rightarrow OQ+OO$	$k_{55}=k_{54}$
R56	$OOO+P(^{1}D) \rightarrow OO+O+P$	k_{56} =0.978× k_{47}
R57	$OOO+P(^{1}D)\rightarrow OO+OP$	$k_{57} = k_{56}$
R58	$OOP+O(^{1}D) \rightarrow OO+P+O$	k_{58} =0.997× k_{47}
R59	$OOP+O(^{1}D) \rightarrow OP+O+O$	$k_{59} = k_{58}$
R60	$OOP+O(^{1}D)\rightarrow OO+OP$	k_{60} =0.997× k_{47}
R61	$OPO+O(^{1}D)\rightarrow OP+O+O$	k_{61} =0.997× k_{47}
R62	$OPO+O(^{1}D) \rightarrow OP+OO$	$k_{62} = k_{61}$
R63	$OOO+OO(^{1}\Delta) \rightarrow OO+OO+O$	k_{63} =3.8×10 ⁻¹⁵
R64	$OOO+OQ(^{1}\Delta) \rightarrow OO+OO+Q$	k_{64} =0.5×0.982× k_{63}
R65	$OOO+OQ(^{1}\Delta) \rightarrow OO+OQ+O$	$k_{65} = k_{64}$
R66	$OOQ+OO(^{1}\Delta) \rightarrow OO+OQ+O$	k_{66} =0.992× k_{63}
R67	$OQO+OO(^{1}\Delta) \rightarrow OQ+OO+O$	k ₆₇ =k ₆₆
R68	$OOO+OP(^{1}\Delta) \rightarrow OO+OO+P$	k_{68} =0.5×0.991× k_{63}
R69	$OOO+OP(^{1}\Delta) \rightarrow OO+OP+O$	$k_{69} = k_{68}$
R70	$OOP+OO(^{1}\Delta) \rightarrow OO+OP+O$	k_{70} =0.996× k_{63}
R71	$OPO+OO(^{1}\Delta) \rightarrow OP+OO+O$	$k_{71} = k_{70}$

	Reactions	Rate coefficient
	R10 (Formation of COOO*)	
R72	O(¹ D)+COO→COOO*	k_{72} =1.1×10 ⁻¹⁰
R73	$Q(^{1}D)+COO \rightarrow COOQ^{*}$	k_{73} =0.958× k_{72}
R74	$O(^{1}D)+COQ\rightarrow COOQ^{*}$	k_{74} =0.994× k_{72}
R75	$P(^{1}D)+COO \rightarrow COOP^{*}$	k_{75} =0.978× k_{72}
R76	$O(^{1}D)+COP \rightarrow COOP^{*}$	k_{76} =0.997× k_{72}
R77	$O(^{1}D)+DOO \rightarrow DOOO^{*}$	k_{77} =0.997× k_{72}
R78	$O(^{1}D)+DOQ \rightarrow DOOQ^{*}$	k_{78} =0.994× k_{72}
R79	$Q(^{1}D)+DOO \rightarrow DOOQ^{*}$	k_{79} =0.958× k_{72}
R80	$O(^{1}D)+DOP \rightarrow DOOP^{*}$	k_{80} =0.997× k_{72}
R81	$P(^{1}D)+DOO \rightarrow DOOP^{*}$	k_{81} =0.978× k_{72}
	R11 (COOO* dissociation: triplet channel)	
R82	COOO*→COO+O	k_{82} =1.0×10 ⁸
R83	COOQ*→COQ+O	$k_{83} = (\frac{2}{3} + a) \times k_{82}$
R84	COOQ [∗] →COO+Q	$k_{84} = (\frac{1}{3} - a) \times k_{82}$
R85	COOP*→COP+O	$k_{85} = (\frac{2}{3} + b) \times k_{82}$
R86	$COOP^* \rightarrow COO+P$	$k_{86} = (\frac{1}{3} - b) \times k_{82}$
R87	DOOO*→DOO+O	k ₈₇ =k ₈₂
R88	DOOQ*→DOQ+O	$k_{88} = (\frac{2}{3} + a) \times k_{82}$
R89	DOOQ*→DOO+Q	$k_{89} = (\frac{1}{3} - a) \times k_{82}$
R90	DOOP*→DOP+O	$k_{90} = (\frac{2}{3} + b) \times k_{82}$
R91	$DOOP^* \rightarrow DOO+P$	$k_{91} = (\frac{1}{3} - b) \times k_{82}$

higher than that of apex position and is significantly different from that of the total ozone. Recently *Janssen* [2005] and *Bhattacharya et al.* [2006] (see Chapter 5) have given formulae relating the enrichment in ¹⁸O and ¹⁷O in asymmetric species with enrichment in total ozone as:

$$E^{50}(asymmetric) = -1.7 + 1.33E^{50}_{total} - 3.81 \times 10^{-4} (E^{50}_{total})^2$$
(6.4)

$$E^{49}(asymmetric) = 3.12 + 1.22E^{49}_{total} - 3.19 \times 10^{-4} (E^{49}_{total})^2$$
(6.5)

Using these two equations, the enrichment of heavy oxygen isotopes at base position (asymmetric species) corresponding to a given total ozone enrichment was calculated. It is noted that for asymmetric species, enrichment in ¹⁷O is more than that of ¹⁸O which is contrary to earlier assumptions.

Since the bond energies of O-Q and O-P are slightly more than that of O-O bond, it is relatively more difficult to break O-Q and O-P bonds in dissociation of ozone which leads to fractionation factors of 0.983 and 0.989 [*Chakraborty and Bhattacharya*, 2003b] in the model for O-Q and O-P bond dissociation (relative to O-O bond dissociation) in corresponding isotopologues of ozone. Recently, *Cole and Boering* [2006] have estimated the ozone dissociation rate constant for the experimental set up of *Chakraborty and Bhattacharya* [2003b] where ozone was dissociated in presence of UV and visible light. Since the same experimental setup was used for the CO_2 -O(¹D) experiment [*Chakraborty and Bhattacharya*, 2003d], the ozone dissociation rate constant is initially taken to be the same as derived by *Cole and Boering* [2006].

The rate of formation (k_{72}) of CO₃* intermediate due to quenching of O(¹D) with CO₂ was taken from *DeMore and Dede* [1970]. As discussed above, the intermediate CO₃* can dissociate into two channels, CO₂ +O(³P) (major) and CO₂+O(¹D) (minor). For simplicity, only the major dissociation channel i.e., electronic quenching of O(¹D) to O(³P) channel was included. The effect of neglecting the minor channel on the final CO₂ composition is less than 1‰. The dissociation rate (k_{77}) was taken from *DeMore and Dede* [1970]. As mentioned before, since the intermediate CO₃* has a reasonably long life time as shown experimentally by *Baulch and Breckenridge* [1966] one could argue that the complex can randomize its energy among all available vibrational/rotational mode before predissociating to CO₂ and O(³P). This enhances the probability that all oxygen atoms are equivalent and

have a nearly equal chance of becoming the product oxygen atom. However, one would expect a slight preference for lighter isotope being emitted. *Mebel et al.* [2004] argued that the ¹⁶O emission would be greater than statistical probability of 2/3 (for C¹⁶O¹⁶O¹⁸O type molecule) due to the conventional isotope effect. The vibrational frequencies of C-O bond are relatively higher than those of C-Q which results in slightly stronger C-Q bond. Therefore, during CO₃* dissociation, a ¹⁶O atom would come out preferentially compared to a heavy oxygen isotope (due to difference in zero point energies of the bonds). They calculated the ejection rate of O-atom from CO₃* and showed that the probability of ¹⁶O being ejected from CO₃* complex is slightly greater than the statistical value of 2 (relative to ¹⁷O and ¹⁸O) for both the channels. The value of this ratio is 2.014 for the quenching channel (CO₃*→ CO₂+O(³P)) at a collision energy of 4.2 kcal/mol. With this consideration, the rate k₈₃ and k₈₄ of the dissociation channels of COOQ* was multiplied by ($\frac{2}{3}$ +a) and ($\frac{1}{3}$ -a) respectively where the value of 'a' is 0.001548 which is calculated as:

$$\frac{\frac{2}{3} + a}{\frac{1}{3} - a} = 2.014$$
$$a = \frac{0.014}{3 \times 3.014} = 0.001548$$

Similarly in case of COOP^{*}, the rate k_{85} and k_{86} was multiplied by $(\frac{2}{3}+b)$ and $(\frac{1}{3}-b)$ respectively. The value of 'b' is taken to be 0.00078 using the standard mass dependent rule.

The abundance of various ozone species were calculated using the formulae given in Chapter 3. The abundance of CO_2 isotopomers were calculated as follows:

The absolute abundances of ¹⁸O, ¹⁷O and ¹³C of the starting CO₂ (x_4 , y_4 and z_2) and its total amount (t_4) can be expressed as:

$${}^{18}R_{O_2} = x_4 = \frac{[COQ] + [DOQ]}{2 \times [COO] + 2 \times [DOO] + [COQ] + [DOQ] + [COP] + [DOP]}$$
(6.6)

$${}^{17}R_{O_2} = y_4 = \frac{[COP] + [DOP]}{2 \times [COO] + 2 \times [DOO] + [COQ] + [DOQ] + [COP] + [DOP]}$$
 (6.7)

$$\frac{[\text{DOO}]}{[\text{COO}]} = \frac{[\text{DOQ}]}{[\text{COQ}]} = \frac{[\text{DOP}]}{[\text{COP}]} = z_2$$
(6.8)

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$$t_4 = [COO] + [DOO] + [COQ] + [DOQ] + [COP] + [DOP]$$
 (6.9)

Using these equations, the abundances of various CO₂ isotopologues were calculated:

$$[COQ] = \frac{2t_4 x_4}{(1+z_2)(1+x_4+y_4)}$$
(6.10)

$$[DOQ] = z_2[COQ] \tag{6.11}$$

$$[COP] = \frac{2t_4y_4}{(1+z_2)(1+x_4+y_4)}$$
(6.12)

$$[DOP] = z_2[COP] \tag{6.13}$$

$$[\text{COO}] = \frac{t_4(1 - x_4 - y_4)}{(1 + z_2)(1 + x_4 + y_4)}$$
(6.14)

$$[DOO] = z_2[COO] \tag{6.15}$$

The abundances of various ozone and CO_2 species were calculated and the model was run to match the observed ¹⁸O enrichments for Set 1, Set 2 and Set 3 respectively. The results are summarized in Table 6.2

6.4 Model Result and Discussion

The model predicted isotopic composition (¹⁸O, ¹⁷O) of the final CO₂ in Set 1: SM-CO₂ are: (46.7, 27.9), (48.2, 29.4), (49.2, 30.4) and (51.0, 32.2) in 9, 12, 15 and 25 mins of model run respectively whereas the corresponding values as observed in the experiment are (43.1, 27.9), (45.1,31.0), (47.3, 35.3) and (51.1, 41.4) respectively. Similarly, the isotopic composition (¹⁸O and ¹⁷O) of SP- CO₂ (Set 2) as predicted by the model are: (11.3, 8.7), (12.2, 9.5), (14.5, 11.6) and (22.7, 18.2) and in case of SL-CO₂ (Set 3): (2.4, 5.9), (4.9, 8.0) and (10.3, 12.1). It is noted that in most of the cases, the model predicts higher enrichment in ¹⁸O as compared to the observed value. This discrepancy could be due to the assumed value of the ozone dissociation rate (k₁) adopted from *Cole and Boering* [2006]. A higher value of k₁

Table 6.2: $experiment$ $expriment$ in the prese 17 O is intro	Model res , ozone ana ent study tu oduced whi	ults to rep I CO ₂ mixt 5 simulate ch makes it	produce 1 ture was these dat t possible	he oxyger photolyser a points. to match	n isotopic cc d by UV lig) To increase the three slo	mposition ht and the the exchar, pes.	t of CO ₂ i n CO ₂ wa ige rate of	n experin s separateu ¹⁷ O(¹ D)	tent of Chak I for isotopic relative to ¹⁵	raborty an measuren ⁸ O(¹ D) an	id Bhattachan uents. KINTE extra factor u	ya [2003d]. :CUS model iue to nucle	In their was used ar spin in
Sample	Photo	Obsei	rved	Enrie	chment	Mc	del	Enric	shment	Model	predicted	Enrich	ument
•	lysis	CC	O_2			predict	ed CO ₂	ц.	CO_2	CO ₂ (s)	pin factor)	in (0_2
	time	compo	sition			no spiı	1 factor	ids ou	in factor	=J	1.117	with spi	n factor
	(min)	δ^{18} O	$\delta^{17}O$	$\Delta(\delta^{18}\zeta)$	$O)\Delta(\delta^{17}O)$	$\delta^{18}O_{\delta}$	0,17	$\Delta(\delta^{18}\overline{C}$	$O(\delta^{17}O)$	$\delta^{18}O$	$\delta^{17}O$	$\Delta(\delta^{18}O)$	$\Delta(\delta^{18}O)$
						SM-CC	² (39.3, 2	.0.4)					
-	6	43.1	27.9	3.7	7.3	44.8 2	.0.9	5.5	5.6	44.8	31.0	5.5	10.6
2	12	45.1	31.0	5.6	10.4	46.1 2	27.4	6.8	7.0	46.1	33.4	6.8	13.0
С	15	47.3	35.3	7.7	14.6	47.3 2	28.5	8.0	8.1	47.3	35.2	8.0	14.8
4	25	51.1	41.4	11.4	20.5	49.7 3	9.08	10.4	10.5	49.7	38.8	10.4	18.4
Ŋ	130	44.5	29.9	5.0	9.3	1		ı	ı	ı	,	ı	ı
9	360	47.4	35.5	7.7	14.8	1		ı	ı	ı	ı	ı	ı
		Slope(c	observe	d)=1.78	±0.05					Slope(model)=1.7	9±0.07	
						SP-C(O ₂ (4.1, 2	.2)					
-	9	8.2	10.5	4.1	8.3	<u>9.2 (</u>	6.9	5.1	4.7	9.2	10.6	5.1	8.4
2	7	9.0	11.4	4.9	9.2	10.0 7	.5	5.9	5.3	10.0	11.7	5.9	9.5
ю	10	10.9	14.4	6.8	12.2	11.9 5	0.3	7.8	7.1	12.0	14.7	7.9	12.5
4	23	25.1	35.0	20.9	32.7	19.7 1	5.6	16.5	13.4	19.7	27.1	15.6	24.9
		Slope(c	observe	d)=1.52	±0.06					Slope(model)=1.5	9±0.01	
						SL-CO	2 (-10.9, -	5.6)					
-	13	1.8	11.2	12.7	16.8	-0.4 3	.5	10.5	9.1	-0.4	9.7	10.5	15.3
7	20	4.6	14.5	15.5	20.1	2.6 £	0.0	13.5	11.6	2.6	13.5	13.5	19.1
3	26	11.7	23.6	22.6	29.2	7.3 5	.5	18.2	15.1	7.3	21.5	18.2	27.1
		Slope(c	observe	d)=1.29_	±0.01					Slope(1	model)=1.4	7土0.04	

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would produce more $Q(^{1}D)$ which would lead to higher enrichment of ^{18}O in CO_{2} after exchange. We adjusted the dissociation rate by trial-and-error method for each case so that individual data matches the model predicted enrichment in ^{18}O . The dissociation rate (k₁) was required to be reduced by a factor between 0.45 to 0.92 except in three cases (4th data of Set 1, 2 and 3rd data of Set 3 where the required factor was larger, having values of 1.05 and 1.5 and 1.24 respectively).

The problem of exact matching of ¹⁸O values may also be due to unaccounted variation in lamp output, unknown flux reduction by air-gap between UV lamp window and chamber window or limitation of the model when applied to a finite size chamber of 5 l. The adjustment factor is however close to one (ranging from 0.45 to 1.5). For further discussion, the ozone dissociation rate was reduced by a constant factor of 0.67 (average value neglecting the higher values) in the model since our main purpose was to determine the relative variation between ¹⁷O and ¹⁸O enrichments. To show the effect of this factor on CO_2 slope, calculations were done for SM-CO₂ (Set 1) and the results are shown in Figure 6.1 and 6.2.

In Figure 6.1 the ozone dissociation rate was reduced by a constant factor of 0.67 (average value, as discussed above) whereas in Figure 6.2 dissociation rate was adjusted to match the exact ¹⁸O enrichment in each case. It is noted that the CO₂ in both the cases exhibits the slopes which agree within error $(1.79\pm0.07, 1.01\pm0.01)$ and $(1.73\pm0.08, 1.01\pm0.01)$ respectively (Figure 6.1 and 6.2). This comparison shows that the introduction of a constant factor has only a small effect on the slope values.



Figure 6.1: The oxygen isotopic composition of CO_2 observed in SM- CO_2 (Set 1) in the experiment done by Chakraborty and Bhattacharya [2003d, Table 2]. The enrichment in CO_2 is due to its interaction with $O(^1D)$ derived from ozone photo dissociation. The ozone dissociation rate was reduced by a factor of 0.65 (see text). The model reproduces both the enrichment and slope (shown by solid line) once the effect of spin orbit coupling due to the presence of nuclear spin (5/2) in case of ^{17}O is taken into consideration.



Figure 6.2: The ozone dissociation rate was adjusted in the model to reproduce the ¹⁸O enrichment as observed in case of SM-CO₂ (Set 1) Chakraborty and Bhattacharya [2003d]. The value of slope obtained is same as in Figure 6.1 where dissociation rate was reduced by a constant factor of 0.67 which shows that reducing the rate by a small factor has no significant effect on the slope values (see text for details).

The isotopic composition of the final product CO_2 after exchange as predicted by the model is given in Table 6.2. The results obtained from model simulation are compared to the experimental value in Figure 6.1 and Figure 6.3. The enrichment in ¹⁸O and ¹⁷O varies from SM-CO₂ (Set 1): (5.5 to 10.4) and (5.6 to 10.5), SP- CO₂ (Set 2): (5.1 to 16.5) and (4.7 to 13.4) and SL-CO₂ (Set 3): (10.5 to 18.2) and (9.1 to 15.1) respectively. The model predicts slopes (relating δ^{18} O vs. δ^{17} O) of 1.01, 0.86 and 0.84 for SM-CO₂, SP- CO₂ and SL- CO₂ respectively (shown by dashed lines in Figure 6.1 and 6.3).



Figure 6.3: The isotopic composition of Set 2 (SP-CO₂) (*a*) and Set 3 (SL-CO₂) (*b*) as obtained by model. The ozone dissociation rate was reduced by a constant factor of 0.67.

It is noted that the model predicts less enrichment of ${}^{17}\text{O}$ in CO₂ for all the three sets as compared to the observed values. This comparison shows that the experimentally observed enrichment in CO₂ cannot be explained by a simple exchange model of anomalously enriched ozone and normal CO₂. To explain the observed data it is necessary to invoke a mechanism which can enhance ${}^{17}\text{O}({}^{1}\text{D})$ exchange rate relative to ${}^{18}\text{O}({}^{1}\text{D})$ and ${}^{16}\text{O}({}^{1}\text{D})$ to reproduce firstly the enrichment in ${}^{17}\text{O}$ and secondly the slopes as observed in the experiment. There is one possible mechanism by which this can be achieved as explained below.

6.5 Nuclear spin effect on chemical reaction

It is known that many subatomic particles (electrons, protons and neutrons) possess a quantity called spin which can be imagined as equivalent to a "rotation" around its own axis. In many atoms (in case of 12 C, 16 O), these spins are paired against each other and the nucleus of the atom has no overall spin. Whereas in some atoms (¹H and 13 C) the nucleus contains unpaired nucleons and thus possess an overall spin.

The rules for determining the net spin of a nucleus are as follows:

- 1. If the number of neutrons and the number of protons are both even, then the nucleus has no spin (I=0).
- 2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half integer spin (i.e. I = 1/2, 3/2, 5/2).
- 3. It the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. I= 1, 2, 3).

Nuclear spin is associated with a nuclear magnetic moment which produces magnetic interactions with other nuclear magnetic moments, electron magnetic moments and orbital magnetic moments. These interactions may sometimes influence the chemical reaction rate.

It is known that the transition of electrons between electronic energy levels are governed by some selection rules as given below:

- 1. The orbital rule ($\Delta l = \pm 1$): if the molecule has a center of symmetry, transition within a given set of p or d orbitals (i. e., those which involve a redistribution of electrons within a given subshell) are forbidden.
- 2. The spin rule (Δ S =0): allowed transition must involve the promotion of electrons without a change in their spin.

Therefore, all chemical reactions are spin selective, i.e., they are allowed only for such spin states of products whose total electron spin is identical to that of reactants and are forbidden if they require a change of spin. However, relaxation of the selection rules can occur through spin-orbit coupling, spin-spin coupling. Spin-orbit coupling is a weak magnetic interaction of the particle spin and the orbital motion of this particle, e.g. the electron spin and its motion around an atomic nucleus. Spin-spin coupling is a kind of weak interaction between the spin of a nucleus and the spins of nearby nuclei and electron spin. Therefore, if a nucleus has unpaired nucleon, it can interact with other nuclear magnetic moments, electron magnetic moment, orbital magnetic moment and can affect the behavior of the electron spin through hyperfine magnetic interaction by changing electron spin and transforming nonreactive, spin forbidden states into reactive, spin allowed ones.

The rate of spin conversion (P) is a function of magnetic field H, hyperfine coupling constant a, nuclear spin I, and nuclear magnetic moment μ_n , nuclear spin projection m_l , resonance frequency ω and amplitude H_l of microwaves, the exchange interaction J between unpaired electrons of the radical partners (if present)

$$P = f[H, a, \mu_n, I, m_l, H_l, \omega, J]$$
(6.16)

This shows that the reaction rate depends on the nuclear spin, magnetic moment, hyperfine and electron-nuclear interaction. Therefore, presence of nuclear spin of an isotope involved in a chemical reaction may enhance its rate and cause isotopic fractionation. Nuclear mass selectivity of reactions results in classical isotope effect (CIE) which is governed by chemical energy of the starting and transition states of reactant molecule. Nuclear spin selectivity of chemical reactions results in magnetic isotope effect (MIE), which depends on the nuclear spin and nuclear magnetic moment of the reactants. This kind of fractionation has been observed in many cases [*Buchachenko et al.*, 1976, 1991a, 1991b, 1994, 1995, 2000, 2001, *Sagdeev et al.*, 1977; *Turro et al.*, 1985, 1995; *Tarasov et al.*, 1991; *Step*, 1990; *Wakasa et al.*, 1993a, 1993b]. For example,

1. MIE in Carbon 13

Sorting of isotope based on its nuclear spin was first observed in case of carbon isotopes (¹³C, nuclear spin 1/2) during photolysis of dibenzyl ketone (DBK) by Buchachenko [1976]. He observed that the left over DBK is anomalously enriched in 13 C by about ~ 100‰. In the photodecomposition of DBK in benzene, 13 C isotope enrichment of left over DBK is seen to increase as the chemical conversion of DBK increases. It was also seen that this effect depends on the magnetic field which is the direct evidence of its magnetic nature. In another experiment, nuclear spin effect of ¹³C was seen on triplet sensitized photolysis of benzoyl peroxide which produces phenyl benzoate enriched in ¹³C by ~60‰. The photolysis of DBK occurs via fragmentation of a triplet molecule and generation of triplet radical pair. Triplet-Singlet conversion of magnetic pairs (with ¹³C) is much faster than that of nonmagnetic pairs (with ¹²C nuclei), so that magnetic pairs predominantly recombine and regenerate the starting ketone molecules, while the slower T-S conversion of ¹²C pairs favors their dissociation and transformation into reaction products. As a result, the regenerated ketone molecules accumulate ¹³C nuclei. Due to difference in the rates of T-S conversion, radical pair sorts the nuclei according to their magnetic moments and dispatches magnetic and non-magnetic nuclei into different reaction products.

2. MIE in Oxygen 17

The effect of nuclear spin in ¹⁷O was observed in 1978 [*Belyakov*, 1978] in the liquid phase oxidation of ethylbenzene by molecular oxygen. The left over molecular oxygen was enriched in ¹⁷O (by ~120‰) relative to ¹⁸O. This result was confirmed by *Buchachenko et al.*, [1995] in chain oxidation of polymers and hydrocarbons by molecular oxygen. Here also the nuclear spin effect arises in the triplet-singlet spin conversion of the long living triplet pairs. The recombination probability of peroxy radicals with terminal magnetic ¹⁷O nuclei is higher than that of radicals with nonmagnetic ¹⁶O and ¹⁸O nuclei. As a result, peroxy radicals carrying ¹⁷O nuclei predominantly

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recombine into unstable tetraoxide, which decomposes and regenerates molecular oxygen enriched in ¹⁷O.

3. MIE in Silicon 29

MIE was seen in case of ²⁹Si during the photolysis of ketone $PhCH_2COSi(CH_3)_2Ph$) in SDS micelles. The magnetic isotope ²⁹Si is accumulated in the starting, regenerated ketone whereas nonmagnetic nuclei ²⁸Si and ³⁰Si are passed into the reaction products.

4. MIE in Sulfur 33

Photolysis of sulfur -containing ketone produces triplet radical pairs which sort isotopic nuclei so that ³³S undergoes fast T-S conversion and recombine carrying magnetic ³³S nuclei into the starting ketone [*Step et al.,* 1990].

5. MIE in Germanium 73

Photolysis of methyltriphenylgermane in Brij35micellar solution produces a triplet radical pair which selects radicals with ⁷³Ge magnetic nuclei and directs them into the starting molecule so that regenerated Ph₃GeCH₃ accumulates ⁷³Ge nuclei [*Wakasa et al.*, 1993].

6. MIE in Uranium 235

The photo induced reaction of uranyl nitrate (singlet ground state) with p-methoxyphenol shows a nuclear spin effect involving ²³⁵U. The reaction product UF₄ is depleted in magnetic ²³⁵U nuclei by 50‰ with respect to the starting uranyl. The presence of nuclear spin in ²³⁵ U nucleus stimulates the T-S conversion of the intermediate triplet ion-radical pair due to hyperfine coupling and gets accumulated in the left over UO_2^{2+} whereas ²³⁸ U nuclei (no nuclear spin) gets dissociated and produces UF₄.

7. MIE in photodissociation of CO_2

The effect of nuclear spin on the dissociation rate of CO_2 was studied by Bhattacharya et al. [2000]. The photodissociation of CO_2 by UV light produces CO and O_2 . It was observed that both the products CO and O_2 were anomalously enriched in ¹⁷O by ~100‰ whereas the enrichment in ¹⁸O was very small. While trying to explain this surprising result it was noted that dissociation of CO_2 take place through a
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spin forbidden process during transition from a singlet state to a triplet state (equation 6.18).

$$CO_2 + h\nu(185nm) \to CO_2(^1B_2)^*$$
 (6.17)

$$\operatorname{CO}_2({}^1\mathrm{B}_2)^* \leftrightarrow \operatorname{CO}_2({}^3\mathrm{B}_2)^* \tag{6.18}$$

$$CO_2(^{3}B_2)^* \to CO + O(^{3}P)$$
 (6.19)

The ¹⁷O enrichment is associated with this transition and is thought to be due to participation of nuclear spin of ¹⁷O in spin-orbit coupling. Recent experiments have confirmed this explanation. It is found that the product CO is also enriched in ¹³C but the enrichment is less than that of ¹⁷O because the nuclear spin of ¹⁷O (5/2) is higher than that of ¹³C (1/2) [*Bhattacharya and Mahata*, 2006].

6.6 Proposed mechanism

It is known that the quenching of $O(^1D)$ by CO_2 is a spin forbidden reaction, but in case of dilute concentration the presence of a spin-orbit coupling makes this reaction possible with fairly large rate coefficient. The required spin-orbit coupling arises when the total spin of the electrons interact with the magnetic moment associated with the orbital motion of the electrons. It is likely that the nuclear spin in ¹⁷O interacts with the electronic orbital motion and enhances the effect of spin orbit coupling. This would increase the exchange rate of ¹⁷O(¹D) as compared to ¹⁸O(¹D) and ¹⁶O(¹D). As a result, CO₂ after exchange would be relatively more enriched in ¹⁷O than ¹⁸O.

To take this proposed spin effect into account, the formation rate of COOP* and DOOP* was enhanced relative to that of COOQ* and DOOQ* (all measured relative to COOO* and DOOO*). The value of the enhancement factor 'f' was required to be varied from 1.089 to 1.158 (except in one case where it was 1.185) to reproduce the experimental data. A spin effect would, of course, be constant and should not vary from one experiment to another. The required variation is therefore attributed to the limitation in determining δ^{17} O value precisely in the experiment of *Chakraborty and Bhattacharya* [2003d] since it involved separation of CO₂ from ozone. For simplicity, the formation rate k₇₅ and k₈₁ was enhanced by an average factor f =1.117 for comparison with observed data in Figure 6.1 and Figure

6.3. The enrichments in ¹⁷O as predicted by the model then increase from (10.6 to 18.4), (8.4 to 24.9) and (15.3 to 27.1) for SM-CO₂, SP-CO₂ and SL-CO₂ respectively (Table 6.2). Using this factor, the model predicted CO₂ compositions fall on a line with slope 1.79 ± 0.07 , 1.59 ± 0.01 and 1.47 ± 0.01 for SM-CO₂, SP-CO₂ and SL-CO₂ respectively (shown by solid lines in Figure 6.1 and 6.3). The slopes obtained in Set 1 and Set 2 match quite well (within error) whereas in case of Set 3 the model predicted slope (1.47) is slightly higher than the observed value (1.29).

6.7 Conclusion

Both atmospheric results and laboratory simulation indicate that the isotopic exchange between $O(^1D)$ (derived from ozone dissociation) and CO_2 is responsible for isotopic enrichment in CO_2 . The exchange rate is faster for ¹⁷O than that of ¹⁸O yielding a slope relating the two enrichments having a value greater than one. It is clear from the model that neither the enrichment in CO_2 nor the slope can be explained by simple mixing of ozone with CO_2 . A mass dependent fractionation was considered in dissociation of $COOO^*$ which slightly favors ¹⁸O and ¹⁷O in the product CO_2 but this modification cannot explain the observed data. To explain the results we propose an explanation based on nuclear spin of ¹⁷O. Under this hypothesis, the magnetic moment due to nuclear spin (5/2) of ¹⁷O interacts with other spin and magnetic moments and enhances the spin orbit coupling which results in higher exchange rate of ¹⁷O(¹D) relative to ¹⁸O(¹D). Enhancement of ¹⁷O(¹D) exchange rate by a factor of 1.117 can explain the observed data and reproduce the higher than one slope as observed in the experiment of *Chakraborty and Bhattacharya* [2003d] as well as stratosphere.

Summary and Scope for Future Work

The objective of the present thesis was to explore the mechanism governing the mass independent fractionation process associated with photochemical reactions. Even after 25 years of discovery, the unusual isotope effect in the formation of ozone is not yet completely understood even though the influence of molecular symmetry on isotopic fractionation is recognized to be the principal cause. The major part of this research work was devoted to understand the role of molecular symmetry in anomalous isotope fractionation processes by studying a reaction $O+CO\rightarrow CO_2$ which is similar to the ozone formation. The various experimental parameters like CO pressure, exposure time, isotopic composition of O-atom and the source from which it is derived were varied to see their effect on the isotopic composition of the product CO_2 . A chemical reaction model KINTECUS was used to simulate the experimental conditions to calculate the expected isotopic composition of the product CO_2 . A detailed molecular level investigation of this reaction can further clarify the process of mass independent fractionation in oxygen isotopes of symmetric molecules.

The results of this study can also be used in understanding the consequences of various chemical reactions which occur in the Martian atmosphere. It is known that the Martian atmosphere is predominantly CO₂. The dissociation of CO₂ by solar photons to CO and O(³P) and its subsequent recombination to produce CO₂ can make it anomalously enriched in heavy oxygen isotopes. The interaction between atmospheric CO₂ and H₂O in the Martian Regolith can transfer the anomalous isotopic signature from CO₂ to H₂O and carbonate reservoirs [*Farquhar et al.*, 2001]. Such a process was invoked by *Farquhar et al.* [1998] to explain the occurrence of mass independently fractionated oxygen isotopes ($\Delta^{17}O\neq 0$) in carbonates from ALH 84001 and H₂O extracted from SNC meteorites (Martian meteorites)

[Karlsson et al., 1992].

Another important issue is the internal distribution of heavy oxygen isotopes in ozone molecule. This subject is of great importance as anomalous isotopic signature gets transferred by interaction of ozone with other trace gases in the stratosphere. The anomalous enrichment in the trace gases provides tracers for studying stratospheric transport processes and/or tropospheric oxidation reaction pathways. Several attempts have been made to measure the internal distribution of ¹⁸O in ozone molecule using remote sensing, TDLAS, FTAS techniques but with large uncertainty in measurement owing to small abundance of ¹⁸O. There is no study for the internal distribution of ¹⁷O whose abundance is still lower. We devised a new method to determine the internal distribution of ¹⁷O in ozone using reaction of ozone with metallic silver and analyzing the product gases using mass spectrometric technique.

This study is useful for calculating the isotopic composition $O(^1D)$ which is derived from ozone dissociation and is responsible for transfer of isotope anomaly to other species.

Finally we applied the information of intramolecular isotopic distribution in ozone to explain the transfer of heavy oxygen isotopes from ozone to CO_2 (with particular reference to the case of stratospheric CO_2). This study was aimed to provide the molecular level details of the isotopic exchange between $O(^1D)$ - CO_2 . Resolving this issue is not only of fundamental chemical interest but may allow measurements of the anomalous isotopic composition of CO_2 to be used as a unique tracer of stratospheric chemistry and transport on time scales of several years and a means to quantify gross carbon fluxes to and from the biosphere on annual to millennial time scales.

Important results obtained from the present study

- The isotopic composition of CO₂ produced from O+CO reaction is found to be anomalously enriched in heavy oxygen isotopes relative to that expected based on standard isotope chemistry as given by the simulation result. The enrichment in heavy oxygen isotopes of CO₂ varies from 65 to 107 and 41 to 82‰ in ¹⁸O and ¹⁷O respectively. Anomalous and mass independent enrichment seen in O+CO →CO₂ is similar to that of ozone produced from O+O₂.
- The enrichment in the product CO₂ does not depend on the isotopic composition of O atom used for the reaction. It is also independent of the O-atom sources from which

it is produced. This is due to the fast isotopic exchange between O-O₂ and O-CO, which changes the isotopic composition of O-atom significantly before it recombines with CO to produce CO₂. Due to fast exchange, the O-atom looses memory of its source and initial composition. The exchange is fast was known earlier but its effect on a O-atom induced reaction is now clearly demonstrated.

- The enrichment observed in case of asymmetric CO₂ species produced from O+CO reaction is less than that of asymmetric O₃ species produced from O+O₂ reaction. This is explained by the presence of relatively larger density of states in CO₂ near the threshold of dissociation as compared to ozone. Since the enrichment is expected to be a function of the difference between the density of states of asymmetric and symmetric species, a smaller value of this ratio (in case of CO₂) means less discrimination and lower enrichment.
- It is noted that there is no anomalous enrichment in carbon isotope since carbon being the central atom in CO₂ molecule is not affected by the symmetry related part of the total fractionation process. However, a small negative δ^{13} C value is observed due to the mass dependent fractionation associated with the reaction. This is an experimental demonstration of the hypothesis of mass dependence in collision induced reactions.
- It is demonstrated for the first time that the distribution of ¹⁷O and ¹⁸O inside ozone molecule are different. The difference between terminal and central position enrichments is more in case of ⁴⁹O₃ than in case of ⁵⁰O₃. For both ⁵⁰O₃ and ⁴⁹O₃, the difference between the two enrichments is not constant but decreases with increase in the total ozone enrichment.
- The value of r⁵⁰ and r⁴⁹ increases with the increase in total ozone enrichment. The value of r⁴⁹ is higher that that of r⁵⁰ by an amount of 0.06 which can be explained by the zero point energy(ZPE) difference of the relevant species.
- In case of zero-enriched ozone, the symmetric species is more enriched in ¹⁸O and ¹⁷O as compared to asymmetric species which is opposite to what is observed in case of enriched ozone samples. This is because symmetric ozone has the heavy isotope located in more tightly bound position and is more preferred as compared

to the purely statistical distribution. For zero enriched ozone, the value of r^{50} and r^{49} is always less than two. The r^{50} value is within (1.76 to 1.88) whereas the r^{49} value is within (1.88 to 1.99). The exact value cannot be derived due to limitation in knowledge of fractionation correction.

- The oxygen isotopic enrichment in CO₂ due to isotopic exchange between O(¹D) and CO₂ cannot be explained by a simple exchange model.
- It is known that the O(¹D)-CO₂ exchange is a spin forbidden reaction but takes place due to spin-conserving interactions (like spin-orbit interaction). We propose that the nuclear spin of ¹⁷O adds an extra component in the total spin-orbit coupling term enhancing the exchange rate of ¹⁷O(¹D). The data require a nuclear spin effect of nearly 12% relative to ¹⁸O to give agreement with observed data. This is the first experimental demonstration of nuclear spin effect in isotope exchange.

The future scope of the present work

- We have shown that the enrichment observed in CO₂ produced from O+CO reaction supports the hypothesis that molecular symmetry plays a major role in anomalous isotopic enrichment. But the cause for the variation observed in CO₂ enrichment is still not clear. To resolve the issue, controlled experiments should be done to investigate the effect of pressure, temperature and nature of bath gas molecules on enrichment in the product CO₂.
- We studied surface oxidation reaction of ozone with silver to determine the value of r⁵⁰ and r⁴⁹. It is known that ozone oxidizes NO to NO₂ which is a gas phase reaction. It would be interesting to calculate the value of r⁵⁰ and r⁴⁹ by reacting O₃ with NO which is similar to O₃-Silver reaction. This will provide an opportunity to confirm the values of r⁵⁰ and r⁴⁹ obtained by O₃-Silver reaction and to test the assumptions made in calculating r-values.
- It has been proposed recently [*Mebel et al.*, 2004] that hyperthermal O(³P) atom can combine with CO₂ to form CO₃* which could be an additional source of enrichment

of ¹⁷O and ¹⁸O in CO₂. It is known that ozone dissociation in UV light produces hyperthermal O(³P). It would be interesting to see its effect on the CO₂ enrichment.

A.1 Calculation of (18 O and 17 O) exchange rate in reaction of O with O₂ and CO

Consider a isotopic exchange equilibrium reaction:

$$A^* + AB \rightleftharpoons A + A^*B \tag{1.1}$$

where A and A^{*} indicate the light and heavy isotope of the same element respectively. The equilibrium constant (K_{eq}) for this exchange reaction can be written as:

$$K_{eq} = \frac{k_f}{k_b}$$
(1.2)

where k_f and k_b are the rate of forward and backward reaction respectively. It is possible to calculate the value of K_{eq} using statistical mechanics under the rigid rotor harmonic oscillator approximation [*Bigeleisen and Mayer*, 1947; *Urey*, 1947; *McQuarrie*, 1976].

The equilibrium constant can be expressed in terms of ratio of atomic and molecular partition functions of products and reactants as:

$$K_{eq} = \frac{Q_A \times Q_{AB}^*}{Q_A^* \times Q_{AB}}$$
(1.3)

It is known that the total partition function is a product of the translational, rotational and vibrational partition functions. The electronic partition function can be ignored as the electronic configurations and energies of atoms are unaffected by the isotopic differences.

$$Q_{\text{total}} = Q_{\text{trans}} \times Q_{\text{rot}} \times Q_{\text{vib}}$$
(1.4)

The partition function for translational motion is given by:

$$Q_{\rm trans} = \left(\frac{2\Pi \ \mathrm{m \ k \ T}}{\mathrm{h}^3}\right)^{\frac{3}{2}} \tag{1.5}$$

where 'm' is atomic mass (or reduced mass in case of molecule).

The rotational partition function is:

$$Q_{\rm rot} = \frac{T}{\Theta \sigma} \tag{1.6}$$

where Θ and σ are the rotational constant (expressed in ^oK) and symmetry number respectively.

 Θ can be expressed in different unit as,

$$\Theta = \frac{B_{e}h c}{k}$$
(1.7)

where B_e is also a rotational constant but expressed in cm⁻¹.

The vibrational partition function has a form:

$$Q_{\rm vib} = \exp\left(\frac{-\mathrm{h}\,\mathrm{c}\,\nu}{2\,\mathrm{k}\,\mathrm{T}}\right) \tag{1.8}$$

The contribution of the vibrational terms comes only from the zero-point energy difference of involved species. ν is the ground state vibrational frequency and 'h' is Plancks constant.

The total partition function (equation 1.4) is:

$$Q_{total} = \left(\frac{2\Pi \ m \ k \ T}{h^3}\right)^{\frac{3}{2}} \times \left(\frac{T}{\Theta \ \sigma}\right) \times \exp\left(\frac{-h \ c \ \nu}{2 \ k \ T}\right)$$

Since the expression of equilibrium constant contains ratio of the partition functions of the atomic and molecular species of the reactants and the products (equation 1.3), so K_{eq} becomes:

$$K_{eq} = \frac{Q_A(\text{trans}) \times Q_{AB}^*(\text{trans}) \times Q_{AB}^*(\text{rot}) \times Q_{AB}^*(\text{vib})}{Q_A^*(\text{trans}) \times Q_{AB}(\text{trans}) \times Q_{AB}(\text{rot}) \times Q_{AB}(\text{vib})}$$
(1.9)

$$= \frac{\mathbf{m}_{\mathrm{A}} \mathbf{m}_{\mathrm{AB}}^{*}}{\mathbf{m}_{\mathrm{A}}^{*} \mathbf{m}_{\mathrm{AB}}} \times \frac{\sigma_{AB} \Theta_{AB}}{\sigma_{AB}^{*} \Theta_{AB}^{*}} \times \exp\left[\frac{-\mathrm{h} \mathrm{c}\left(\nu_{\mathrm{AB}}^{*} - \nu_{\mathrm{AB}}\right)}{2 \mathrm{k} \mathrm{T}}\right]$$

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The method of calculation is illustrated here by taking the exchange reaction between O-atom and O_2 molecule in case of ¹⁸O isotope which is written as:

$${}^{18}\text{O} + {}^{16}\text{O}{}^{16}\text{O} \rightleftharpoons {}^{16}\text{O} + {}^{16}\text{O}{}^{18}\text{O} \tag{1.10}$$

Contribution from translational part $C_{\rm t}$

The contribution from the translational terms to the equilibrium constant is,

$$C_{t} = \left(\frac{16 \times 34}{18 \times 32}\right)^{\frac{3}{2}} = 0.918$$

Contribution from rotational part $C_{\rm r}$

For ${}^{32}O_2$, the value of rotational constant (B_e) is 1.44566 cm⁻¹ [*Herzberg*, 1950].

Putting the value of $B_{\rm e}$ in equation (1.7), the value of Θ is calculated as,

$$\Theta(^{32}O_2) = \frac{1.44566 \times 6.626 \times 10^{-27} \times 3 \times 10^{10}}{1.3807 \times 10^{-16}} = 2.0813^{\circ}K$$

where,

k= Boltzmann constant = 1.3807×10^{-16} erg/degree

- h= Planck's constant= 6.626×10^{-27} erg sec
- c= speed of light= 3.0×10^{10} cm/sec

 $\Theta(^{34}O_2)$ is obtained from $\Theta(^{32}O_2)$ by using the ratio of the reduced masses of $^{34}O_2$ and $^{32}O_2$.

$$\Theta(^{34}O_2) = \rho^2 \times \Theta(^{32}O_2) \tag{1.11}$$

where

$$\rho = \sqrt{\frac{\mu_{32}}{\mu_{34}}} = 0.94451$$
$$\Theta(^{34}O_2) = 0.94451 \times 2.0813 = 1.9658^{\circ}K$$

Since ${}^{32}O_2$ is a homonuclear diatomic molecule, it has a symmetry number, $\sigma = 2$ whereas $\sigma({}^{34}O_2) = 1$ as ${}^{34}O_2$ is a hetronuclear molecule.

The contribution from the rotational terms is:

$$C_{\rm r} = \frac{2 \times 2.0813}{1 \times 1.9658} = 2.1175$$

Contribution from vibrational part C_v

The vibrational frequency for ${}^{32}O_2(\nu)$ is 1580.4 cm⁻¹ [*Herzberg*, 1950]. The value of $\nu({}^{34}O_2)$ is obtained by considering reduced masses of ${}^{32}O_2$ and ${}^{34}O_2$.

$$\frac{\nu_{32}O_2}{\nu_{34}O_2} = \frac{\mu(^{32}O_2)}{\mu(^{34}O_2)}$$

So the value of ν (³⁴O₂) is 1580.4/1.029= 1535.9 cm⁻¹.

The contribution from the vibrational terms is:

$$C_{\rm v} = \exp\left(\frac{-{\rm h}\,c\{1535.9 - 1580.4\}}{2\,{\rm k}\,{\rm T}}\right) = \exp\left(\frac{32}{{\rm T}}\right)$$

The equilibrium constant is,

$$K_{eq} = C_t \times C_r \times C_v = 0.918 \times 2.1175 \times \exp\left(\frac{32}{T}\right) = 1.94 \exp\left(\frac{32}{T}\right)$$

The value of the forward rate, $k_f = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (at T =298 °K) is given by *Anderson et al.* [1985]. The backward rate (k_b) at 298 °K was calculated as,

$$k_{\rm b} = k_{\rm f}/K_{\rm eq} = \frac{2.9 \times 10^{-12}}{1.94 \exp(\frac{32}{T})} = 1.34 \times 10^{-12} {\rm cm}^3 {\rm molecule}^{-1} {\rm sec}^{-1}$$

Similarly, the value of K_{eq} for other isotopic exchange reactions are calculated and are shown in Table 1.1. The value of rotational constants (B_e and Θ), vibrational frequencies (ν_e) which are used for calculating C_t , C_r and C_v are listed in Table 1.2.

Table 1.1: The backward reaction rate (k_b) for various exchange reactions are calculated using the equilibrium constant (K_{eq}) and the forward reaction rate (k_f). C_t , C_r and C_v are the contribution from translational, rotational and vibrational terms to the partition function or the equilibrium constant (as discussed above). The equilibrium constant (K_{eq}) is defined as: $K_{eq} = C_t \times C_r \times C_v$. The value of k_f is taken form Anderson et al. [1985] and Jaffe and Klein [1966] for O-O₂ and O-CO exchange reactions.

Exchange reaction	\mathbf{k}_{f}	Ct	Cr	C _v	K _{eq}	k _b
$^{18}O + ^{16}O^{16}O \rightleftharpoons ^{16}O + ^{16}O^{18}O$	2.9×10^{-12}	0.918	2.118	1.113	2.16	1.34×10^{-12}
$^{17}\text{O} + ^{16}\text{O}^{16}\text{O} \rightleftharpoons ^{16}\text{O} + ^{16}\text{O}^{17}\text{O}$	2.9×10^{-12}	0.956	2.061	1.058	2.084	1.39×10^{-12}
$^{18}O + {}^{12}C^{16}O \rightleftharpoons {}^{16}O + {}^{12}C^{18}O$	8.3×10^{-16}	0.929	1.050	1.133	1.105	7.51×10^{-16}
${}^{17}\text{O} + {}^{12}\text{C}{}^{16}\text{O} \rightleftharpoons {}^{16}\text{O} + {}^{12}\text{C}{}^{17}\text{O}$	8.3×10^{-16}	0.962	1.026	1.068	1.055	7.87×10^{-16}
$^{18}O + ^{13}C^{16}O \rightleftharpoons ^{16}O + ^{13}C^{18}O$	8.3×10^{-16}	0.926	1.073	1.196	1.188	6.99×10^{-16}
${}^{17}\text{O} + {}^{13}\text{C}{}^{16}\text{O} \rightleftharpoons {}^{16}\text{O} + {}^{13}\text{C}{}^{17}\text{O}$	8.3×10^{-16}	0.961	1.047	1.126	1.133	7.33×10^{-16}

Table 1.2: The value of rotational constants (B_e), symmetry numbers(σ) and the ground state vibrational frequencies (ν_e) are given for different molecular species. These values were used to calculate C_t , C_r and C_v (see Table 1.1). The values of B_e and ν_e are taken from Herzberger [1950]. Θ is rotational constant expressed in °K and is related to B_e as: $\Theta = \frac{B_e \ h \ c}{k}$

Molecular species	$B_e(cm^{-1})$	$\Theta(^{o}K)$	σ	$\nu_{\rm e}({\rm cm}^{-1})$
¹⁶ O ¹⁶ O	1.446	2.081	2	1580.4
$^{16}O^{18}O$	1.366	1.966	1	1535.9
$^{16}O^{17}O$	1.403	2.020	1	1557.0
$^{12}C^{16}O$	1.931	2.781	1	2170.2
$^{12}C^{18}O$	1.839	2.648	1	2117.9
$^{12}C^{17}O$	1.882	2.710	1	2142.8
$^{13}C^{16}O$	1.882	2.710	1	2142.8
$^{13}C^{18}O$	1.755	2.526	1	2068.4
$^{13}C^{17}O$	1.798	2.588	1	2093.8

A.2 Fractionation associated with catalytic decomposition of ozone by silver oxide

A set of experiments were done to determine whether catalytic decomposition of ozone by silver oxide modifies the oxygen isotopic composition of silver oxide itself. In the experiment, few strips of silver foil were put in two identical chambers ('A' and 'B') both of which were connected to another chamber where ozone was made by Tesla discharge of oxygen. After the discharge, ozone was separated from left over oxygen and was brought to gaseous phase and then allowed to react with silver foils kept in Chambers 'A' and 'B'. The idea was to expose silver in Chamber 'A' single time and Chamber 'B' multiple times

to ozone samples having nearly same amount and isotopic compositions and then compare the isotopic compositions of Ag₂O produced in the two cases. Any difference in the δ -values of Ag₂O from the two chambers will help in quantifying the net effect of catalysis on Ag₂O composition. Two sets of experiments were done X (Chamber 'A': single exposure and Chamber 'B': double exposure) and Y (Chamber 'A': double exposure and Chamber 'B': triple exposure) to determine the change in isotopic composition of Ag₂O by catalytic decomposition of ozone.

Experiment 'X': (Chamber A: single exposure, Chamber B: double exposure)

Ozone with isotopic composition X_1 ($\delta^{18}O = 29.6$, $\delta^{17}O = 28.9$) was made and allowed to react with silver foil in Chambers 'A' and 'B'. When the reaction was over, left over oxygen was pumped out from both the chambers. Silver oxide from Chamber 'A' was heated separately to release the locked oxygen which was collected in sample bottle containing molecular sieve for amount and isotope measurements. Silver in Chamber 'B' was again exposed to ozone having slightly different isotopic composition X_2 ($\delta^{18}O = 22.0$, $\delta^{17}O = 22.8$). After pumping out the left over oxygen, silver oxide in Chamber 'B' was heated separately to release the oxygen for isotope measurements.

The oxygen isotopic compositions of silver-bound oxygen from Chamber 'A' (7 μ mol) and Chamber 'B' (12 μ mol) were (δ^{18} O, δ^{17} O): (19.4, 38.3) and (18.4, 37.4) (see Table 1.3). When the difference in δ^{18} O of the ozone used for the reaction in two cases (X₁-X₂) is 7.6‰ the difference between δ^{18} O values in Ag₂O from Chamber 'A' and 'B' is 1.0‰.

Experiment 'Y': (Chamber A: double exposure, Chamber B: triple exposure)

Silver in both the Chambers 'A' and 'B' was exposed twice to two ozone samples having isotopic composition Y₁ (26.0, 27.3) and Y₂ (26.0, 28.6). After each reaction, left over oxygen was pumped out. Silver oxide from Chamber 'A' (double exposure) was heated and the isotopic composition of the released oxygen was measured. Silver in Chamber 'B' was again exposed to ozone having different composition, Y₃ (30.1, 30.7). The left over O₂ was pumped out and silver oxide was heated to release the oxygen. The isotopic composition of silver oxide from Chamber 'A' (11.4 μ mol) and Chamber 'B' (16 μ mol) were (δ^{18} O, δ^{17} O): (16.7, 37.4) and (16.4, 38.1) (see Table 1.3). When the difference in δ^{18} O of the ozone sample used for first two reactions is 4‰ the difference between the δ^{18} O values in Ag₂O from Chamber 'A' and 'B' is 0.3‰.

The above experiments show that when ozone used for second phase of reaction +

catalysis differs from that used for the first phase there is a change in δ^{18} O of Ag₂O which depends on the isotope difference between the two ozone samples; when the difference is +7.6‰ (Expt. X) the effect is + 1‰ change. If the difference reduces to +4‰ (Expt. Y) the effect goes down to ~ +0.3‰. This suggests that when both catalysis and reaction are induced by the same ozone (as happens in the experiments described in the paper) there should not be any extra fractionation by catalysis. In other words, the fractionation involved in catalysis is same as that of the fractionation associated with the ozone-silver reaction.

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Effect of catalysis	(difference in	δ^{18} O of Ag ₂ O in	A and B) b (‰)	19.4-18.4 =1.0				16.7-16.4 =0.3								
Difference in	ozone $\delta^{18}O^a$	(%) (%)				29.6-22.0 =7.6							30.1-26.1=4		_	
		$\delta^{17}O$	(‰)		ı			37.4		I			ı			38.1
	Ag_2O	$\delta^{18}O$	(%)		ı			18.4		I			I			16.4
Chamber B		Amount	(μmol)		ı			12		ı			ı			16
		Exposure		# 1 Ozone X ₁	X ₁ : (29.6 , 28.9)	+	# 2 Ozone X_2	X ₂ : (22.0 , 22.8)	# 1 Ozone Y_1	Y ₁ : (26.0 , 27.3)	+	# 2 Ozone Y_2	Y ₂ : (26.2 , 28.6)	+	# 3 Ozone Y_3	Y ₃ : (30.1 , 30.7)
	Ag_2O	$\delta^{17}O$	(% o)		38.3					ı			37.4			
		$\delta^{18}O$	(%o)		19.4					ı			16.7			
Chamber A		Amount	(μmol)		7					ı			11			
		Exposure		#1 Ozone X_1^c	X ₁ : (29.6, 28.9)				# 1 Ozone Y_1	Y ₁ : (26.0, 27.3)	+	# 2 Ozone Y_2	Y ₂ : (26.2, 28.6)			
	Expt X ^d								Y^e							

^{*a*}Difference in δ^{18} O values of two consecutive batch of ozone used for reacting silver in Chamber B

 9 Difference in δ^{18} O values of Ag₂O after single and double exposure (in case of experiment X) and after single and triple exposure (in case of experiment Ξ

^cThe isotopic composition expressed relative to the working gas (δ^{18} O: 24.6, δ^{17} O: 12.5 relative to VSMOW). The amount of ozone (expressed in ^dSilver in Chamber A was exposed to ozone X₁ whereas silver in Chamber B was exposed to ozone X₁ followed by ozone X₂. X₁ and X₂ are the isotopic equivalent O_2) made in each case (X₁, X₂, Y₁, Y₂ and Y₃) was typically ~134 μ mol; nearly half of this was made to react with silver in each chamber.

compositions of ozone. The delta values of Ag_2O from both the Chambers were measured and compared. ^{*e*}Silver in Chamber A was reacted with ozone Y_1 followed by Y_2 and silver in Chamber B was exposed to ozone Y_1 , Y_2 and Y_3 in succession

A.3 Estimation of the values of r⁵⁰ and r⁴⁹ from known reaction rates

The values of rate coefficients at a given temperature and total enrichment available for both asymmetric and symmetric ozone formation channels ((k_1 to k_9),equation 5.6 to 5.14, see Chapter 5, section 5.3.2) in a specific case of total enrichment are used here to first calculate the enrichments in asymmetric and symmetric species of ⁵⁰O₃ and ⁴⁹O₃ at 300 K and then determine the values of r⁵⁰ and r⁴⁹ applicable in that case. In a scrambled system, ozone is made by photolysis of molecular oxygen. By definition,

$$\frac{[{}^{16}O{}^{18}O]}{[{}^{16}O{}^{16}O]} = 2f$$
(1.12)

where 'f' is $\frac{^{18}O}{^{16}O}$ atomic ratio. If a statistical distribution of heavy oxygen isotope in ozone is assumed then,

$$\frac{[{}^{16}O^{18}O^{16}O] + [{}^{18}O^{16}O^{16}O]}{[{}^{16}O^{16}O^{16}O]} = 3f$$
(1.13)

Similarly, in case of ¹⁷O,

$$\frac{[{}^{16}\mathrm{O}{}^{17}\mathrm{O}]}{[{}^{16}\mathrm{O}{}^{16}\mathrm{O}]} = 2\mathrm{g} \tag{1.14}$$

$$\frac{[{}^{16}\mathrm{O}{}^{17}\mathrm{O}{}^{16}\mathrm{O}] + [{}^{17}\mathrm{O}{}^{16}\mathrm{O}{}^{16}\mathrm{O}]}{[{}^{16}\mathrm{O}{}^{16}\mathrm{O}{}^{16}\mathrm{O}]} = 3\mathrm{g}$$
(1.15)

The atomic oxygen generated during O₂ photolysis undergoes a fast isotopic exchange with O₂ which depletes the O atom pool in ¹⁸O and ¹⁷O by ~75 and 39‰ respectively [*Anderson et al.*, 1985]. Therefore, the isotopic ratio $\frac{^{18}O}{^{16}O}$ and $\frac{^{17}O}{^{16}O}$ of the O atom pool is less than 'f' and 'g' and we have,

$$\frac{{}^{18}\text{O}}{{}^{16}\text{O}} = 0.924 \times \text{f} \tag{1.16}$$

$$\frac{170}{160} = 0.961 \times g$$
 (1.17)

Following the definition given below, the total enrichment in ozone can be calculated as,

$$\left(1 + \frac{E_{\text{total}}^{50}}{10^3}\right) = \frac{\frac{\{\frac{1}{2}(k_2 + k_3)[{}^{16}\text{O}][{}^{16}\text{O}{}^{18}\text{O}] + (k_4 + k_5)[{}^{18}\text{O}][{}^{16}\text{O}{}^{16}\text{O}]\}}{k_1[{}^{16}\text{O}][{}^{16}\text{O}{}^{16}\text{O}]}}\right)} \tag{1.18}$$

$$=\frac{\frac{1}{2}(k_2+k_3)\frac{|^{16}O^{16}O|}{|^{16}O^{16}O|} + (k_4+k_5)\frac{|^{16}O|}{|^{16}O|}}{3f \times k_1} = \frac{(k_2+k_3) + (k_4+k_5) \times 0.924}{3k_1} = 1.1285$$

Using the rate coefficients at 300 K given by *Janssen et al.* [2001] (equation 5.6 to 5.14) we thus get 128.5‰ for E_{total}^{50} . For calculating the enrichment in asymmetric ozone species, only those channels need to be considered which lead to the formation of asymmetric ozone.

$$\left(1 + \frac{E_{asy}^{50}}{10^3}\right) = \frac{\frac{\{\frac{1}{2}(k_2)[{}^{16}O][{}^{16}O]^{18}O] + (k_4)[{}^{18}O][{}^{16}O]{}^{16}O]^{8}}{k_1[{}^{16}O][{}^{16}O]^{6}O]}}{2f}$$
$$= \frac{\frac{1}{2}(k_2)[{}^{16}O^{18}O]}{[{}^{16}O^{16}O]} + (k_4)[{}^{18}O]}{2f} = \frac{k_2 + k_4 \times 0.924}{2k_1} = 1.150$$

 $E_{asy}^{50} = 150\%$. Similarly, the enrichment in symmetric ozone is calculated as,

$$\left(1 + \frac{\mathrm{E}_{\mathrm{sym}}^{50}}{10^3}\right) = \frac{\frac{\{\frac{1}{2}(\mathrm{k}_3)[{}^{16}\mathrm{O}][{}^{16}\mathrm{O}]{}^{18}\mathrm{O}][{}^{16}\mathrm{O}]{}^{18}\mathrm{O}][{}^{16}\mathrm{O}]{}^{16}\mathrm{O}]{}^{16}\mathrm{O}]}{\mathrm{f}}}{\mathrm{f}}$$
(1.19)
$$= \frac{\frac{1}{2}(\mathrm{k}_3)\frac{[{}^{16}\mathrm{O}{}^{18}\mathrm{O}]}{[{}^{16}\mathrm{O}{}^{16}\mathrm{O}]} + (\mathrm{k}_5)\frac{[{}^{18}\mathrm{O}]}{[{}^{16}\mathrm{O}]}}{\mathrm{f}} = \frac{\mathrm{k}_3 + \mathrm{k}_5 \times 0.924}{\mathrm{k}_1} = 1.0855$$

 $E_{sym}^{50} = 85.5\%$. Therefore, the r-value is:

=

$$\mathbf{r}^{50} = \frac{\left(1 + \frac{\mathbf{E}_{asy}^{50}}{10^3}\right)}{\left(1 + \frac{\mathbf{E}_{sym}^{50}}{10^3}\right)} = 2.12 \tag{1.20}$$

Similar calculations can be done for ¹⁷O and we get,

$$\left(1 + \frac{\mathbf{E}_{\text{total}}^{49}}{10^3}\right) = \frac{(\mathbf{k}_6 + \mathbf{k}_7) + (\mathbf{k}_8 + \mathbf{k}_9) \times 0.961}{3\mathbf{k}_1} \tag{1.21}$$

$$\left(1 + \frac{\mathbf{E}_{asy}^{49}}{10^3}\right) = \frac{\mathbf{k}_6 + \mathbf{k}_8 \times 0.961}{2\mathbf{k}_1} \tag{1.22}$$

$$\left(1 + \frac{\mathrm{E_{sym}^{49}}}{10^3}\right) = \frac{\mathrm{k_7 + k_9 \times 0.961}}{\mathrm{k_1}} \tag{1.23}$$

These show that a total enrichment (E_t^{49}) of 122.5 corresponds to an enrichment of 150.9 ‰ in E_a^{49} and 65.8 ‰ in E_s^{49} . The value of r^{49} is thus 2.16 which is higher than that of $r^{50}O_3$ by 0.04. The same value of r^{49} is obtained from a projection of the equation relating r^{49} with total enrichment (see Figure 5.7). As can be seen from the formulae (A2 and A5) given above, the difference arises mainly due to mass dependent exchange of atomic oxygen which favors ¹⁷O relative to ¹⁸O resulting in higher enrichment in asymmetric species for ⁴⁹O₃ than that of ⁵⁰O₃.

A.4 Estimation of total error in r⁴⁹ value

We have used the value of r^{50} , derived from *Janssen*[2005] equation, to determine the fractionation factor for ¹⁸O and ¹⁷O and then calculate the value of r^{49} in each case. So any error associated with r^{50} measurement gets reflected in r^{49} values. *Janssen* [2005, Table 1] has compiled the error in r^{50} which varies from 0.08 to 0.03 depending on the total ozone enrichment. Using these values we calculated the error in fractionation factors (α (¹⁸O) and α (¹⁷O)) and then in r^{49} values (Error # 1 (σ_1)).

A second source of error in r⁴⁹ arises due to variation or spread in δ^{18} O and δ^{17} O values of Ag₂O. At a fixed ozone composition, we expect no change in Ag₂O composition. But that is not true as evident from Figure 5.2. This variation is possibly due to the dynamics associated with the ozone-silver reaction such as diffusion of ozone molecules, kinetic fractionation associated with the formation of silver oxide and effect of catalysis. Since the Ag₂O-delta values were used to calculate the fractionation factor, any spread in δ^{18} O and δ^{17} O values of Ag₂O will introduce uncertainty in alpha values (α (¹⁸O) and α (¹⁷O)) and finally in r⁴⁹ values. To take this into account, we estimated the uncertainties in alpha based on the spread observed in δ^{18} O (Error # 2 (σ_2)) and then in δ^{17} O of Ag₂O (Error # 3 (σ_3)). The total error in r⁴⁹ was finally estimated as: $\sigma = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}$ and are listed in Table 1.5. The error associated with r⁴⁹ values varies from 0.06 to 0.04 corresponding to errors in r⁵⁰ from 0.08 to 0.03.

Table 1.4: Total error estimated in r^{49} values (PRL data). The value of r^{50} was calculated using Janssen equation. [Janssen, 2005]. Total error in r^{50} in given as reported by Janssen [2005]. The values of r^{49} were calculated using Ag_2O delta values (see text). Error # 1 (σ_1) in r^{49} is due to the error in r^{50} as reported by Janssen. Error # 2 (σ_2) and Error # 3 (σ_3) are due to variation observed in $\delta^{18}O$ and $\delta^{17}O$ of silver-bound oxygen (Ag_2O). Total error (σ) is calculated as: $\sigma = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}$

Sample	r^{50}	Total error	r ⁴⁹	Error #1	Error # 2	Error #3	Total error
1		in r 50		σ_1	σ_2	σ_3	in r $^{49}(\sigma)$
P-1	1.927	0.08	2.043	0.044	0.023	0.033	0.06
P-2	1.936	0.08	2.036	0.044	0.022	0.033	0.06
P-3	1.943	0.07	2.066	0.038	0.023	0.033	0.05
P-4	1.964	0.07	2.074	0.037	0.022	0.032	0.05
P-5	1.965	0.07	2.041	0.037	0.022	0.032	0.05
P-6	1.976	0.07	2.083	0.037	0.022	0.032	0.05
P-7	1.980	0.07	2.059	0.037	0.021	0.032	0.05
P-8	1.983	0.07	2.090	0.036	0.022	0.032	0.05
P-9	1.986	0.06	2.094	0.031	0.022	0.032	0.05
P-10	1.987	0.06	2.101	0.031	0.022	0.032	0.05
P-11	1.991	0.06	2.078	0.031	0.022	0.032	0.05
P-12	1.994	0.06	2.059	0.030	0.021	0.031	0.05
P-13	1.994	0.06	2.055	0.030	0.021	0.031	0.05
P-14	1.995	0.06	2.076	0.031	0.021	0.032	0.05
P-15	1.999	0.06	2.051	0.031	0.021	0.031	0.05
P-16	2.002	0.06	2.082	0.030	0.021	0.031	0.05
P-17	2.006	0.06	2.071	0.031	0.021	0.031	0.05
P-18	2.012	0.06	2.079	0.030	0.021	0.031	0.05
P-19	2.020	0.06	2.113	0.031	0.022	0.032	0.05
P-20	2.022	0.05	2.113	0.026	0.022	0.032	0.05
P -2 1	2.022	0.05	2.119	0.026	0.021	0.032	0.05
P-22	2.026	0.05	2.118	0.026	0.021	0.032	0.05
P-23	2.028	0.05	2.076	0.026	0.021	0.031	0.05
P-24	2.035	0.05	2.121	0.025	0.021	0.031	0.05
P-25	2.037	0.05	2.117	0.025	0.021	0.031	0.05
P-26	2.041	0.05	2.102	0.026	0.021	0.031	0.05
P-27	2.054	0.04	2.113	0.020	0.021	0.031	0.04
P-28	2.057	0.04	2.108	0.020	0.021	0.031	0.04
P-29	2.064	0.04	2.093	0.020	0.021	0.031	0.04
P-30	2.071	0.04	2.112	0.019	0.020	0.030	0.04
P-31	2.071	0.04	2.139	0.020	0.021	0.031	0.04
P-32	2.071	0.04	2.105	0.020	0.021	0.031	0.04
P-33	2.074	0.04	2.109	0.020	0.020	0.030	0.04
P-34	2.075	0.04	2.110	0.020	0.021	0.031	0.04
P-35	2.084	0.03	2.145	0.015	0.021	0.031	0.04
P-36	2.085	0.03	2.132	0.015	0.020	0.030	0.04
P-37	2.089	0.03	2.144	0.015	0.021	0.031	0.04

 r^{50} r^{49} Sample Error # 2 Error #3 Total error Error #1 Total error in $r^{49}(\sigma)$ in r^{50} σ_1 σ_2 σ_3 L-1 1.922 0.08 0.043 0.022 0.032 0.06 2.030 1.940 0.022 0.032 0.05 L-2 0.07 2.041 0.038 L-3 1.953 0.07 2.046 0.038 0.022 0.032 0.05 L-4 1.9740.07 2.056 0.037 0.022 0.032 0.05 L-5 1.985 0.07 2.062 0.022 0.032 0.05 0.037 1.995 L-6 0.06 0.022 0.032 0.05 2.066 0.032 L-7 1.997 0.06 2.069 0.022 0.032 0.05 0.031 L-8 2.010 0.06 2.066 0.031 0.021 0.031 0.05 L-9 2.016 0.06 2.090 0.031 0.021 0.032 0.05 L-10 2.097 0.021 2.034 0.05 0.025 0.031 0.05 L-11 2.045 0.05 2.105 0.025 0.021 0.031 0.05 L-12 0.05 2.044 0.05 2.100 0.025 0.021 0.031 L-13 0.025 2.049 0.05 2.085 0.020 0.030 0.05 L-14 2.065 0.04 2.113 0.019 0.020 0.030 0.04 L-15 2.077 0.03 2.128 0.0140.020 0.030 0.04

Table 1.5: Total error estimated in r^{49} values (LGGE data).

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List of Publications

I. In Refereed Journals:

- Pandey Antra and S. K. Bhattacharya (2006), Anomalous oxygen isotopic enrichment in CO₂ produced from O+CO: Estimates based on experimental results and model predictions, *J. Chem. Phys.*, 124, 234301.
- Bhattacharya S. K., Antra Pandey and J. Savarino (2006), Determination of intramolecular isotopic distribution of ozone by oxidation reaction with silver, submitted to *J. Geophys. Res.*
- Pandey Antra, S. K. Bhattacharya and S. Chakraborty (2006), Effect of nuclear spin in enhancing exchange of ¹⁷O by spin-orbit interaction in CO₂- O₃ system: Model calculation for Stratosphere, *J. Geophys. Res.* (in preparation).
- II. In Proceedings/Abstracts of Symposium/Conference:
 - Pandey Antra and S. K. Bhattacharya, Intramolecular isotopic variation in ozone, 11th Indian Society of Mass Spectometry-Work Shop 2004, Shimla,7-12 October, 2004.
- Pandey Antra and S. K. Bhattacharya, Intramolecular isotopic variation in ozone, XVth National Conference on Atomic and Molecular Physics, Physical Research Laboratory, Ahmedabad, 20- 23 December, 2004.
- Pandey Antra and S. K. Bhattacharya, Anomalous oxygen isotope enrichment in CO₂ produced from O+CO, *Third International Symposium on Isotopomers-2006*, San Diego, 27-31 August, 2006.