ANOMALOUS FRACTIONATION OF OXYGEN ISOTOPES IN PHOTOCHEMICAL REACTIONS

A THESIS SUBMITTED TO GUJARAT UNIVERSITY AHMEDABAD

For The Degree Of **Doctor Of Philosophy In Physics**

By

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November 2002

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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Dedicated to My Parents

..... Their dreams are my strength

Acknowledgements

The four year long voyage through the rough seas of research has come to an end. Unforgettable moments of agony and ecstasy, anguish and elation. Everything molded into a sense of success and accomplishment. It is a pleasant aspect that I have now the opportunity to express my gratitude for all who made this journey smooth and enjoyable.

The "Planetary and Geosciences Division", an organized research group, specialized in geo-cosmo-chemistry within Physical Research Laboratory, provided an unparalleled research environment and ambience needed for a balanced development of one's research aptitude and acumen. I feel privileged to be a part of this esteemed institution during my formative period.

Financial assistance in the form of fellowship and research grants from the Department of Space (DOS) is sincerely acknowledged.

I express my sincere gratitude to my mentor, Prof. S.K. Bhattacharya. His overly enthusiasm coupled with an integral view on research and an everlasting smile has made a deep impression on me. I am indebted to him for the encouragement and the freedom I enjoyed throughout. He has given my career in science a purpose and a meaning full direction.

I am grateful to Prof. Krishnaswami for correcting some of the manuscripts and sharing his critical comments and suggestions, which helped to make further improvements. Besides, I would like to thank Profs. Soma, Prof. Goswami, Prof. Ramesh, Prof. Sarin, Dr. Murty and Dr. Kanchan for their constructive inputs at different stages of my research. I have deep appreciation for Dr. P.N. Shukla and Dr. G. Srinivasan for their concern and encouraging words.

Sincere thanks are due to Prof. Sheorey, Dr. P. Sharma and other academic committee members who spent their time to critically review my work from time to time.

I would like to express my sincere thanks to Jani_ji and Rao_ji for their support, encouragement and assistance. My heartfelt thanks are due to Ravi Bhusan and R.D. Deshpandey for proof reading this thesis.

No amount of word is enough to express my regards for Shiva and Kurup for their help in building the vacuum line for my experimental work. I am also grateful to the staffmembers of Library, Computer center, Workshop, Maintenance and Liquid Nitrogen facilities of PRL for their promptness and friendly attitude.

It's a golden opportunity to remember my STAILIAN (members of STAIL) brothers: Ghosh (who taught me how to handle vacuum-line and showed me the path of hard work), Ashish_da (for his sincere advise whenever I needed), Supriyo_da (for fruitful scientific discussions), Aninda (who taught me: "think big, dream big"), Rajesh

and Prasanta. I am indebted to all these people for creating a jovial atmosphere in the lab.

I cherished every moment of my stay with JAPS (Jitti-Aninda-Pradeep) group with whom I shared my dreams. I am thankful to the PRL student-family for creating a 'home away from home' for me. I feel blessed to have such friends like you. I also extend my gratitude towards the members of PRL Soccer Club, who added an extra color to my life every weekend.

I am at dearth of words to express my gratitude to my parents and family members, who have been patient, supportive and caring. This thesis is indeed a realization of their dream.

Needless to say that there were times of hard feeling and war of words too. But it only taught me to be more patient, considerate and shaped me to face the more difficult challenges in future.

I end these dry words of appreciation with a deep sense of gratitude and obligation, and with a hope to reciprocate in due course.

Thanks Subrata Chakraborty 20th November 2002

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CHAPTER I

INTRODUCTION

1.1 ISOTOPIC FRACTIONATION

The partitioning of isotopes of an element in two or more phases by different physico-chemical processes is called isotopic fractionation. There are two major classes of processes (i) isotopic exchange reactions (equilibrium process) and (ii) kinetic processes (such as diffusion, condensation, evaporation etc.) responsible for the isotopic fractionation in nature. The theoretical basis for estimating the magnitude of fractionation for each of these processes differ, but the underlying principle for each is that the effects are dependent on mass.

The mass-dependent isotopic fractionation obeys a simple rule. For example, for three oxygen isotopes (^{16}O , ^{17}O and ^{18}O) we have,

$${}^{17}R_{A}/{}^{17}R_{B} = \left({}^{18}R_{A}/{}^{18}R_{B}\right)^{\beta}$$
(1.1)

where, ${}^{17}R_A$ and ${}^{17}R_B$ are the abundance ratios ${}^{17}O / {}^{16}O$ and ${}^{18}R_A$ and ${}^{18}R_B$ are the abundance ratios ${}^{18}O / {}^{16}O$ in phases A and B respectively. The exponent β depends on the mass of the isotopes and differs slightly for different processes. It is a common practice to denote the isotopic ratios in δ -notation, where δ (in per mil) is defined by,

$$\delta(\%_{0}) = \left(\frac{R_{sample}}{R_{std}} - 1\right) \times 1000$$
(1.2)

 R_{sample} and R_{std} are the isotope ratios (¹⁷O / ¹⁶O or ¹⁸O / ¹⁶O) of a sample and a standard material respectively. The non-linear fractionation curve of Eqn. 1.1 can be approximated in δ -notation as a straight line in the three-isotope space with a slope β :

$$\delta^{17}O = \beta \left(\delta^{18}O \right) \tag{1.3}$$

A fractionation process can be comprehensively studied if it involves an element with three or more isotopes. The best examples are oxygen (¹⁶O, ¹⁷O and ¹⁸O), sulfur (³²S, ³³S, ³⁴S, ³⁶S), Mg (²⁴Mg, ²⁵Mg and ²⁶Mg) etc. The calculated β for oxygen is nearly 0.5 (ranging from 0.51 to 0.52 depending upon the particular process involved) (Urey, 1947; Craig, 1957; Matsuhisa et al., 1978; Young et al., 2002). Therefore, for oxygen, Eqn. 1.3 is generally written as,

$$\delta^{17}O = 0.52(\delta^{18}O) \tag{1.4}$$

Experimentally, the oxygen isotopic composition of most of the terrestrial, lunar and some meteoritic materials lie on a line with a slope (~ 0.5) in a three-isotope plot as shown in Figure 1.1.



Figure 1.1. Three-isotope plot of the oxygen isotopic compositions of various terrestrial materials, which define a mass dependent fractionation line known as terrestrial mass fractionation line. Along with the Allende CAI line, the compositions of three classes of chondritic meteorites (L, LL and H) and the Lunar rocks are shown in the diagram. SMOW represents standard mean ocean water, a reference for all oxygen isotopic measurements.

1.1.1 Mass Independent Isotopic Fractionation

Though rare, there are processes in nature, which do not follow the above massdependent fractionation rule. These processes display mass independent or non-mass dependent isotopic fractionation. For oxygen isotopes, the mass independent fractionation is readily apparent when,

$$\delta^{17}O \neq 0.52(\delta^{18}O)$$
 (1.5)

And the degree of mass independent fractionation is denoted by

$$\Delta^{17}O = \delta^{17}O - 0.52(\delta^{18}O) \tag{1.6}$$

There are two natural systems where mass independent isotopic fractionations have been observed are described below.

1.1.2 The Early Solar System

The first mass independent oxygen isotopic anomaly was discovered in CAIs (calcium-aluminium rich inclusion) in Allende meteorite (Clayton et al., 1973) and was used as an indicator for nucleosynthetic anomaly. The ¹⁶O enrichment in these refractory objects was explained by invoking addition of nearly pure ¹⁶O component to the protosolar cloud from a nearby supernova (Clayton et al., 1973). After more than 25 years of measurements, meteoritic oxygen isotope anomalies have not been observed to correlate with anomalies of any other isotopes such as silicon or magnesium (Thiemens, 1999). Moreover, oxygen isotopic investigations of individual pre-solar grains have not detected any evidence for ¹⁶O carriers (Hutcheon et al., 1994; Huss et al., 1994). In fact, corundum grains from Bishunpur (Huss et al., 1994) and Orgueil (Hutcheon et al., 1994) show large ¹⁷O enrichment. Nittler et al. (1994) have reported 21 interstellar oxide grains (Al₂O₃) from the Tieschitz meteorite and concluded that they have not found any grain with large ¹⁶O enrichment, which would be consistent with the notion of a ¹⁶O carrier. Thus, "while there is unmistakable evidence for interstellar grains carrying anomalous oxygen, their oxygen isotopic composition does not support the notion of admixture of pure ¹⁶O component" (Thiemens, 1996). Therefore, the process responsible for the generation of these isotopic compositions is still not clear and more study is required to put constraints on various models.

1.1.3 Earth and Other Planetary Atmosphere

Stratospheric ozone is found to be enriched in both the heavy oxygen isotopes ¹⁸O and ¹⁷O and the enrichment is predominantly mass independent (Mauersberger, 1981, 1987; Mauersberger et al., 2001; Schueler et al., 1990; Krankowsky et al., 2000). Mass independent isotopic compositions were also found in a number of atmospheric species, such as stratospheric and mesospheric CO₂, atmospheric CO and N₂O (Thiemens et al., 1991, 1995; Rahn and Wahlen, 1997; Yung and Miller, 1997; Cliff and Thiemens, 1997; Huff and Thiemens, 1998; Röckmann et al., 1998; Weston, 1999).

Mass independent oxygen isotopic composition is not limited to the Earth's atmosphere, but is also found in the water extracted from hydrated minerals and CO₂ extracted from carbonates of SNC group of Martian meteorites (Karlsson et al., 1992; Farquhar et al., 1998)

1.1.4 Laboratory Observations

It was shown by a novel laboratory experiment (Thiemens and Heidenreich, 1983) that chemical processes could generate mass independent isotopic fractionation. Ozone formed from molecular oxygen by electric discharge has extremely enriched heavy oxygen isotopes and surprisingly has $\delta^{17}O = \delta^{18}O$ instead of $\delta^{17}O \sim 0.5 \ \delta^{18}O$. Subsequently the potential of the photochemical /chemical processes in generating mass independent isotopic fractionation has been shown in various laboratory studies (O + CO \rightarrow CO₂; SF₅ + SF₅ \rightarrow S₂F₁₀; isotopic exchange O(¹D) + CO₂ \rightarrow O(³P) + CO₂; OH + CO \rightarrow CO₂ + H) (Bhattacharya and Thiemens, 1989; Bains and Thiemens, 1989; Wen and Thiemens, 1993; Röckmann et al., 1998; Johnston et al., 2000).

Based on these laboratory experiments, it was argued that certain photochemical/ chemical processes have the potential to explain the mass independent isotopic fractionations observed in the atmosphere. Similar kind of photo-induced chemical processes can be invoked in a nebular environment to explain the isotopic anomaly observed in early solar system solids (Thiemens, 1999).

1.1.5 Accurate Expressions of Isotopic Fractionation

Equations 1.3 through 1.6 are the simplified approximation of equation 1.1. Recently, in few publications (Miller, 2002 and reference therein) these relations are presented in accurate form, showing non-linearity in a three-isotope plot between $\delta^{18}O$ and $\delta^{17}O$ for the cases where the sample data set includes points with greater $|\delta^{17}O|$ and $|\delta^{18}O|$. These non-linear expressions may be important for interpreting the data set, where the isotopic compositions marginally deviate from the terrestrial silicate composition (as for example, atmospheric oxygen). Moreover, in the case of oxygen from extraterrestrial reservoirs, where mass dependent fractionation line may be off-set parallel to that of the bulk silicate Earth, an extra term is necessary in equation 1.1 to quantify the off-set (Miller, 2002). Depending on these advancements, high precision data sets reported on the basis of $\delta^{18}O$ versus $\delta^{17}O$ plot need to be reassessed. However, the study presented in this thesis does not use directly any of these relationships to interpret the data, therefore, are not elaborated here.

1.2 OBJECTIVE OF THE PRESENT STUDY

The objective of this thesis is to explore the basic processes of mass independent fractionation based on laboratory investigation of oxygen isotopic fractionation in some photochemical/chemical processes.

To study the mass independent fractionation process in the laboratory, ozone is an attractive molecule since large mass independently fractionated ozone can be easily generated in the laboratory. Moreover, in the stratosphere, ozone is mass independently enriched in heavy oxygen isotopes (as mentioned earlier) and controls the oxygen isotopic distribution among other oxygen containing stratospheric trace species. Therefore, some results of the laboratory-based investigations related to ozone can be directly applied to the stratosphere for better understanding of the stratospheric isotope chemistry.

There are number of laboratory studies related to mass independent oxygen isotopic fractionation in ozone (Thiemens and Jackson, 1987, 1988; Morton et al., 1990; Wen and Thiemens, 1991; Mauersberger et al., 1999). Still there are several basic questions unanswered regarding origin of mass independent isotopic anomaly during ozone formation and dissociation. In addition, there are unsettled issues pertaining to stratospheric ozone isotopic anomaly and transfer of oxygen isotopic anomaly from ozone to other stratospheric molecules.

A number of laboratory experiments were devised in the present study to cover these aspects. The specific studies undertaken are:

- (i) Investigation of pressure dependence of heavy oxygen isotope enrichment in ozone in the pressure range 600 to 8 torr with a fine resolution.
- (ii) Investigation of isotope enrichment variation in ozone with the amount of ozone produced.
- (iii) Isotopic effect in photo-dissociation of ozone in Hartley and Chappuis band.
- (iv) Isotopic effect during ozone dissociation by interaction with a surface.
- (v) Isotopic fractionation during $O(^{1}D) CO_{2}$ isotopic exchange reaction.

A schematic representation of the present study, showing the objective and specific investigations, is shown in Figure 1.2

In the following section, a brief summary of the various aspects relevant to our understanding of the origin of mass independent fractionation in ozone and a summary of stratospheric observations are presented.



Figure 1.2. A schematic representation of the present study showing the objective and specific investigations carried out.

Introduction

1.3 OZONE FORMATION MECHANISM

According to Chapman mechanism, ozone is formed through the photolysis of oxygen below 185 nm followed by third body recombination of ground state O-atoms with O_2 molecules to form O_3 .

$$O_2 + h\nu \rightarrow O + O \ (\lambda < 185 \text{ nm}) \tag{1.7}$$

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

The photo-dissociation coefficient of eqn. 1.7 is 1.2×10^{-12} /sec in Earth's atmosphere at 25 km and the rate coefficient of eqn. 1.8 is 6×10^{-34} cm⁶ mol⁻² sec⁻¹ (at 300 K). Ozone so formed is dissociated by visible and UV wavelengths and by O-atoms,

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

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

The photo-dissociation coefficient of eqn. 1.9 is 2.1×10^{-4} /sec in Earth's atmosphere at 25 km and the rate coefficient of eqn. 1.10 is 8×10^{-15} cm³ mol⁻¹ sec⁻¹ (at 298 K). The photo-dissociation coefficients and rate constants are from DeMore et al. (1997). The cycle is shown pictorially in Figure 1.3.



Figure 1.3. Schematic reaction scheme of ozone formation by oxygen photolysis. The primary and secondary processes are shown separately. The conversion between O_3 and O is fast (relative to the primary process) and together they are called the odd oxygen.

1.3.1 Isotopic Enrichment in Ozone

The formation of ozone in the laboratory is always associated with heavy oxygen isotopic enrichment (mass independent) relative to the initial oxygen composition. The enrichment is almost equal in both ¹⁷O and ¹⁸O. The relative enrichment is more (about 100 ‰) when ozone is formed by the above mentioned reaction chain (Thiemens and Jackson, 1987, 1988) compared to the formation by electric discharge in molecular oxygen (Thiemens and Heidenreich, 1983). The latter results in an enrichment of about 30 ‰.

To explain this heavy isotopic enrichment, Heidenreich and Thiemens (1986) suggested a symmetry-selective process in the formation reaction. For ozone species $^{49}O_3$ and $^{50}O_3$, about one-third of all the molecules are symmetric (for example, $^{16}O^{18}O^{16}O$), and two-thirds are asymmetric (for example, $^{16}O^{16}O^{18}O$). It was proposed that the asymmetric reaction intermediate in the O + O₂ collision has a longer lifetime than the symmetric reaction intermediate, which results in an efficient quenching to ground state ozone (Heidenreich and Thiemens, 1986).

The apparent role of symmetry was found during the measurements of the distribution of all ozone isotopomers. A slight depletion of heavy symmetric isotopomers ${}^{17}O^{17}O^{17}O$ and ${}^{18}O^{18}O$ was observed along with an enrichment (~ 18 %) of the asymmetric combination ${}^{16}O^{17}O^{18}O$. The enrichment in all other isotopomers was found to be about one-third less compared to that of ${}^{16}O^{17}O^{18}O$ (Krankowsky and Mauersberger, 1996).

Gellene (1996) proposed a mechanism based on nuclear symmetry to model the above observations. According to this approach, symmetry restriction arises for homonuclear diatomics (${}^{16}O{}^{16}O$ and ${}^{18}O{}^{18}O$) involved in the O + O₂ collision because a fraction of their rotational states correlate with those of corresponding ozone molecule. On the other hand, for heteronuclear molecules (${}^{16}O{}^{18}O$), all their rotational states correlate with those of the resulting ozone molecule. This model can reproduce the general features of the observation by Krankowsky and Mauersberger (1996), but cannot be satisfactorily applied for the other laboratory studies (Thiemens and Jackson, 1987, 1988; Morton et al., 1990).

1.3.2 Relative Rate Coefficient of Different Ozone Formation Channels

Determination of the rate coefficient of different ozone formation channels (Anderson et al., 1997; Mauersberger et al., 1999; Janssen et al., 1999) clarified the role

of symmetry. The reaction channels 1, 12 and 36 (shown in Table 1.1) show nearly the similar rate whereas the channel 24 shows an advantage of 50 %. The channels 12 and 24 produce mainly asymmetric molecules (colliding atom becoming the end member), ¹⁸O¹⁶O¹⁶O and ¹⁶O¹⁸O¹⁸O respectively. The difference in the rate coefficients of these two reactions indicates that symmetry plays a complex role in the isotope enrichment process (Anderson et al., 1997).

The reactions 12 and 13 of Table 1.1 are indeed end-on process without forming symmetric molecules whereas the heteronuclear oxygen reactions (reactions 10 and 11) for the same isotopomers (${}^{18}O^{16}O^{16}O$ and ${}^{16}O^{18}O^{16}O$) show a pronounced difference in the formation rates of the symmetric and asymmetric species (1.45 and 1.08 respectively). These two are exclusively responsible for the enrichment in ${}^{50}O_3$, making an over all rate of 1.27 for the ${}^{16}O + {}^{16}O^{18}O$ channel (Janssen et al., 1999).

At present the rate constant investigation study is not complete. Specifically, the investigations involving the rare isotope ¹⁷O (which make the experiments more challenging) distribution in ozone isotopomers has to be carried out.

1.3.3 Non-RRKM Based Model

In a series of recent publications (Hathorn and Marcus, 1999, 2000; Gao and Marcus, 2001, 2002; Marcus and Gao, 2001), Marcus and his co-workers (at CalTech) developed a model to explain the anomalous oxygen isotopic composition during ozone formation. Their work is based on the statistical theory developed by Rice, Ramsperger, Kassel and Marcus over a long period and known as RRKM theory of unimolecular dissociation/ bimolecular recombination in its vibrational form (Marcus, 1952a, 1952b, 1968). It involves the formation of vibrationally excited ozone isotopomers from the recombination of O and O_2 with a hindered-rotor transition state.

In RRKM theory, for a bimolecular recombination, $X + YZ \rightarrow XYZ^*$ (^{**}, denoting vibrationally excited molecule), the vibrational-rotational energy is supposed to be statistically distributed among its vibrational-rotational modes. This excited molecule can redissociate, $XYZ^* \rightarrow (X + YZ)$ or (XY + Z) or lose its energy by collision to form a stable XYZ molecule. The unimolecular dissociation rate constant for a vibrationally excited molecule of vibrational-rotational energy *E* and total angular momentum *J* is given by,

$$K_{EJ} = N_{EJ}^+ / h \rho_{EJ} \tag{1.11}$$

 N_{EJ}^{+} is the number of quantum states accessible to the 'transition state' for dissociation for the given *E* and *J* and ρ_{EJ} is the density (number per unit energy) of quantum states of the vibrationally excited molecule.

Table 1.1. Reaction channels of all possible oxygen combinations leading to ozone molecules with the exit channel specific rate coefficient. The rate coefficients are relative to the standard rate for ${}^{16}\text{O} + {}^{16}\text{O}{}^{18}\text{O} + \text{M}$ of $6.05 \times 10^{-34} \text{ cm}^{6} \text{ sec}^{-1}$ [Janssen et al., 1999 and the references therein].

Mass	Reaction channel no.	Reaction	Relative rate
			coefficient
48	1	$^{16}O + ^{16}O^{16}O \rightarrow ^{16}O^{16}O^{16}O$	1.00
49	2	${}^{16}\text{O} + {}^{16}\text{O}{}^{17}\text{O} \rightarrow {}^{16}\text{O}{}^{16}\text{O}{}^{17}\text{O}$	
	3	\rightarrow ¹⁶ O ¹⁷ O ¹⁶ O	
	4	$^{17}\text{O} + ^{16}\text{O}^{16}\text{O} \rightarrow ^{17}\text{O}^{16}\text{O}^{16}\text{O}$	1.03
	5	$\rightarrow {}^{16}\mathrm{O}{}^{17}\mathrm{O}{}^{16}\mathrm{O}$	
50	6	${}^{16}\text{O} + {}^{17}\text{O}{}^{17}\text{O} \rightarrow {}^{16}\text{O}{}^{17}\text{O}{}^{17}\text{O}$	1.23
	7	\rightarrow ¹⁷ O ¹⁶ O ¹⁷ O	
	8	$^{17}\text{O} + ^{16}\text{O}^{17}\text{O} \rightarrow ^{17}\text{O}^{16}\text{O}^{17}\text{O}$	
	9	\rightarrow ¹⁷ O ¹⁷ O ¹⁶ O	
	10	$^{16}O + ^{16}O^{18}O \rightarrow ^{16}O^{16}O^{18}O$	1.45
	11	\rightarrow ¹⁶ O ¹⁸ O ¹⁶ O	1.08
	12	$^{18}\text{O} + ^{16}\text{O}^{16}\text{O} \rightarrow ^{18}\text{O}^{16}\text{O}^{16}\text{O}$	0.92
	13	\rightarrow ¹⁶ O ¹⁸ O ¹⁶ O	0.006
51	14	$^{17}O + ^{17}O^{17}O \rightarrow ^{17}O^{17}O^{17}O$	1.02
	15	${}^{16}\text{O} + {}^{17}\text{O}{}^{18}\text{O} \rightarrow {}^{16}\text{O}{}^{17}\text{O}{}^{18}\text{O}$	
	16	\rightarrow ¹⁶ O ¹⁸ O ¹⁷ O	
	17	$\rightarrow {}^{17}\mathrm{O}{}^{16}\mathrm{O}{}^{18}\mathrm{O}$	
	18	$^{17}\text{O} + ^{16}\text{O}^{18}\text{O} \rightarrow ^{17}\text{O}^{16}\text{O}^{18}\text{O}$	
	19	$\rightarrow {}^{17}O{}^{18}O{}^{16}O$	
	20	$\rightarrow {}^{16}O{}^{17}O{}^{18}O$	
	21	$^{18}O + {}^{16}O^{1}O \rightarrow {}^{18}O^{16}O^{1}O$	
	22	$\rightarrow \frac{18}{10} O_{10}^{17} O_{16}^{16} O_{17}^{16} O_{1$	
	23	$\rightarrow {}^{16}O{}^{18}O{}^{17}O$	
52	24	$^{16}O + {}^{18}O{}^{18}O \rightarrow {}^{16}O{}^{18}O{}^{18}O$	1.50
	25	$\rightarrow {}^{18}O_{10}^{16}O_{10}^{18}O_{10}$	0.029
	26	$^{18}O + ^{16}O^{18}O \rightarrow ^{18}O^{16}O^{18}O$	1.04
	27	$\rightarrow {}^{18}O_{17}^{18}O_{10}^{16}O_{10}^{10}$	0.92
	28	$^{17}O + ^{17}O^{18}O \rightarrow ^{17}O^{17}O^{18}O$	
	29	$\rightarrow {}^{1/}O{}^{18}O{}^{1/}O$	
	30	$^{18}\text{O} + ^{17}\text{O} ^{17}\text{O} \rightarrow ^{18}\text{O} ^{17}\text{O} ^{17}\text{O}$	1.03
	31	$\rightarrow {}^{1/}O{}^{18}O{}^{1/}O$	
53	32	$^{1}O^{1}O^{18}O^{18}O \rightarrow ^{1}O^{18$	1.31
	33	$\rightarrow {}^{18}\text{O}{}^{17}\text{O}{}^{18}\text{O}$	
	34	$O^{10}O^{11}O^{10}O^{1$	
	35	$\rightarrow {}^{18}O{}^{18}O{}^{10}O{}^{10}O$	
54	36	$O^{10}O^{10}O^{10}O \rightarrow O^{10}$	1.03

This theory considers (i) an " η -effect", which can be interpreted as a small deviation from the statistical density of states for symmetric isotopomers, compared with the asymmetric isotopomers, (ii) weak collisions for deactivation of the vibrationally excited ozone molecule, and (iii) a partitioning effect ("Y -effect") which controls the recombination rate constant ratios. It arises from small differences in zero point energies of the two exit channels of dissociation of an asymmetric ozone isotopomer, which are magnified into large differences in numbers of states in the two competing exit channel transition state. The considerations (i) and (iii) can be regarded as "symmetry driven" isotope effect. The above-mentioned points are briefly discussed below.

1.3.3.1 Non-Statistical η-Effect

As a modification of classical RRKM theory, it is argued that the effective ρ_{EJ} in Eqn.1.11 might be less than the statistical value and more so for the symmetric isotopomers XYX^{*} than for XYZ^{*}. This ρ_{EJ} should only be the density of the quantum states of the triatomic molecule that are sufficiently dynamically coupled to the two exit channels so that they can lead to the dissociation of the molecule in its typical life-time. 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 lifetime of the molecule (the non-RRKM effect). The ρ_{EJ} of Eqn.1.11 should only refer to the quantum states, which have been intra-molecularly equilibrated. As there are fewer dynamical coupling terms in the symmetric XYX than in the asymmetric XYZ, some terms being forbidden by the symmetry, it was suggested that this non-RRKM effect for ρ_{EJ} is expected to be greater for XYX than for XYZ. The consequence of this non-statistical effect leads to the non-mass dependent isotopic fractionation.

The above situation is shown pictorially in Figure 1.4. During the typical lifetime of the dissociating ozone, the shaded regions indicate the ozone quantum states sufficiently strongly coupled dynamically to the exit channels so as to contribute to ρ_{EJ} during that lifetime. The shaded region for the asymmetric molecules is shown as a greater fraction of the total region than that of symmetric molecule since there are fewer dynamical coupling terms in the symmetric than in the asymmetric molecule. The ratio of

the fraction of shaded to total region for the asymmetric molecule to the same fraction for the symmetric molecule is denoted by η .



Figure 1.4. Schematic diagram for XYX and XYZ of differences in ratios of rotationalvibrational states of ozone strongly coupled (shaded region) to the two dissociation exit channels of ozone and those that weakly coupled (unshaded region) to the exit channels [reproduced from Gao and Marcus, 2001].

1.3.3.2 Weak Collisions for Deactivation

During the stabilization of vibrationally hot molecule (XYZ^{*}), energy is transferred between excited ozone molecule and a bath gas molecule. The weak collision model assumes that the average energy lost by the vibrationally hot molecule (XYZ^{*}) in downward collisions and the energy gain in the upward collisions is relatively small. For simplicity, a step-ladder model, in which energy is transferred in discrete steps of ΔE per collision was considered.

1.3.3.3 Partitioning Effect in Dissociation Channels

The reaction scheme of ozone formation includes a redissociation step consisting of two channels, (a) $XYZ^* \rightarrow X + YZ$, and (b) $XYZ^* \rightarrow XY + Z$ when $Z \neq X$. Due to the difference in zero point energy of the product diatomic molecule, the rate constants of these two channels are different and hence, the net bimolecular rate constant of the reaction $X + YZ \rightarrow XYZ$, is dependent on the dissociation channel it follows. So, the dissociation fate of XYZ^* is partitioned into two dissociation channels due to the zero point energy effect. This partitioning effect is denoted by "Y" $(Y_a = N_{EJ}^{a+}/(N_{EJ}^{a+} + N_{EJ}^{b+}))$ and $Y_b = N_{EJ}^{b+}/(N_{EJ}^{a+} + N_{EJ}^{b+})$ in this model.

1.3.4 Interlink Between RRMK Based Theory and Rate Constants

With this non-statistical approach, Gao and Marcus (2001) tried to explain the results of different laboratory experiments (Thiemens and Jackson, 1990; Morton et al, 1990; Anderson et al., 1997; Mauersberger et al., 1999; Janssen et al., 1999). They observed that each model parameter (η , Y, ΔE) influences the calculated result of different experiments to different extent, i.e., the calculated results of different experiments are sensitive to different model parameters (see Table 1 of Gao and Marcus, 2001).

The calculated low-pressure rate constants at 300 K of individual channels for the formation of XYZ molecules (using η = 1.18 and ΔE = 210 cm⁻¹) agree well with that of the experimental values (Janssen et al., 1999). The computed isotopic enrichment at low pressure for "scrambled" systems, using these individual rate constants, also agrees with the experimental data of Mauersberger et al. (1999).

In view of the experimental and theoretical studies, the observed anomalous isotopic fractionation in ozone can be explained by sum of the effects arising out of different rate constants of different ozone forming channels. We note that the Gao-Marcus model is restricted to the formation of ozone and does not directly apply to photo-dissociation of ozone. However, the basic idea of departure from a statistical distribution of states can be useful in interpretation of photo-dissociation results.

1.4 ISOTOPIC MEASUREMENTS OF STRATOSPHERIC OZONE

Two types of techniques have been employed for ozone isotopic measurements in the stratosphere: the mass-spectrometric method (*in-situ* and return sample measurement) and the spectroscopic method. The first *in-situ* stratospheric ozone isotopic measurements were performed by Mauersberger (1981). He showed that stratospheric ozone is enriched in ¹⁸O ($^{50}O_3 \equiv {}^{16}O^{18}O^{16}O$ and ${}^{16}O^{18}O$) relative to the ambient oxygen from which it is formed. The enrichment is not constant all through the altitude, but shows a peak at around 32 km (with a relative enrichment of 400 ‰). In a later work Mauersberger (1987) showed that the enrichment is not constant, but also varies with the sampling latitude. In

the same study he also showed that for a few altitudes ${}^{49}O_3$ is also enriched (with large uncertainty) similar to that of ${}^{50}O_3$.

Schueler et al. (1990) measured the isotopic composition of stratospheric ozone (of collected samples) and found that the enrichment was in the range of 120-160 % for ${}^{50}O_3$ and 90-110 % for ${}^{49}O_3$. The nature of the isotopic enrichment was thus found to be mass independent.

Recently Krankowsky et al. (2000) measured the O₃ isotopic composition of a large number of stratospheric samples collected by five different balloon flights during 1998 - 2000 up to an altitude of around 33 km. The maximum enrichment observed was about 110 ‰ at an altitude of 33 km in ⁵⁰O₃ and none of the samples showed very high level of enrichment (~ 400 ‰) observed by Mauersberger (1981). The observed enrichment in ⁴⁹O₃ (~ 95 ‰) is less than that of ⁵⁰O₃ (Mauersberger et al., 2001).

1.4.1 Spectroscopic (Optical) Measurements

Parallel to the mass-spectrometric measurements of stratospheric ozone samples, some workers (Rinsland et al., 1985; Abbas et al., 1987; Goldman et al., 1989; Meier and Notholt, 1996; Irion et al, 1996) have carried out both space and ground based spectral analysis of ozone isotopomers.

Based on spectroscopic parameters derived from laboratory spectra of ozone, Rinsland et al. (1985) determined the heavy ozone content of the total column of ozone from the measurements of three high-resolution solar absorption spectra. Their results indicate only statistically marginally significant enrichments in the column abundances of the heavy isotopomers, by a factor of 1.05 ± 0.07 for ${}^{16}O{}^{18}O{}^{16}O$ and by 1.11 ± 0.11 for ${}^{16}O{}^{16}O{}^{18}O$. Goldman et al. (1989) performed a similar kind of analysis of infrared solar absorption spectra with higher resolution and obtained the column-averaged isotopic enrichment ratio of 1.20 ± 0.14 and 1.40 ± 0.18 for ${}^{16}O{}^{16$

Abbas et al. (1987) obtained the distribution of stratospheric heavy ozone isotopomers by balloon based high-resolution thermal emission spectra on the far infrared. The ratio of total heavy ozone isotopomers ⁵⁰O₃ to normal ⁴⁸O₃ show an enrichment of 450 ‰ at 37 km, decreasing to a minimum of 130 ‰ at ~ 29 km and increasing to 180 ‰ at 25 km.

The vertical enrichment profiles of stratospheric ${}^{16}O^{18}O$ and ${}^{16}O^{18}O^{16}O$ have been derived from space based ATMOS (Atmospheric Trace Molecule Spectroscopy) FTIR spectrometer by Irion et al. (1996). They have found a column average enrichment of ${}^{50}O_3$ of (130 ± 50) ‰ with insignificant altitudinal variation.

1.5 SCOPE OF THE PRESENT THESIS

The present thesis investigates the phenomenon of mass independent fractionation in a series of laboratory experiments involving ozone and its interaction with other oxygen containing molecules like CO₂.

The investigation of pressure dependency of oxygen isotopic enrichment in ozone is presented in **Chapter II. Chapter III** deals with the experiments on dissociation of ozone by photolysis (in Hartley and Chappuis band) and surface interaction. The laboratory experiments for the investigation of isotopic exchange between ozone photolysis product $O(^{1}D)$ and CO_{2} are described in **Chapter IV**. Implication of some of these laboratory results towards understanding of oxygen isotopic composition in stratospheric ozone and other oxygen containing molecules along with a discussion of major areas of future research are presented in **Chapter V**.

CHAPTER II

OZONE FORMATION: PRESSURE DEPENDENCE

2.1 INTRODUCTION

The mass independent (anomalous) oxygen isotopic composition of stratospheric ozone was discovered in 1981 (Mauersberger, 1981). As stated earlier, in the last two decades many isotopic measurements of stratospheric ozone have been carried out in both *in-situ* and stratospheric return samples (Mauersberger, 1981; Mauersberger, 1987; Goldman et al., 1989; Schueler et al., 1990; Mauersberger et al., 1993, 2001; Krankowsky et al., 2000) as well as by spectroscopic means (Rinsland et al., 1985; Abbas et al., 1987; Meier and Notholt, 1996; Irion et al, 1996). A number of laboratory experiments were also performed by different groups (Thiemens and Heidenreich, 1983; Thiemens and Jackson, 1987, 1988, 1990; Morton et al., 1990; Mauersberger et al., 1999), to understand the anomalous behavior of oxygen isotopes in ozone. The present chapter deals with some of the basic aspects of isotopic enrichment in ozone during laboratory study of ozone formation.

2.1.1 Laboratory Experiments

The first laboratory experiment demonstrating heavy oxygen isotopic enrichment in ozone was by Thiemens and Heidenreich (1983). They showed that during the ozone formation by electrical discharge on molecular oxygen (at LN₂ temperature), large mass independent ($\delta^{17}O = \delta^{18}O$) isotopic enrichment (~ 80 ‰) takes place. Thiemens and Jackson (1987, 1988) later showed that ozone produced from UV photolysis of molecular oxygen also has a mass independent heavy isotopic composition. They reported an enhancement of ~ 90 ‰ in both ¹⁸O and ¹⁷O containing ozone isotopomers.

Morton et al. (1990) investigated the pressure (in the range 5 – 1000 torr) and temperature (in the range 127-360 K) dependence of the isotope ratio produced in the gas phase O (${}^{3}P$) + O₂ (${}^{3}\Sigma_{g}$) recombination reaction using visible light (500 – 700 nm) dissociation of ozone to supply O-atom in order to exclude any unknown isotope effect related to excited electronic states of oxygen. They found that the enrichment in ${}^{18}O$ and ${}^{17}O$ are approximately constant from 5 – 100 torr and decreases at higher pressures in a mass independent fashion ($\delta^{17}O \approx 0.9 \times \delta^{18}O$). Their study also shows that the enrichment increase with increasing temperature with ${}^{50}O_3$ showing a slightly faster rate of increase than ${}^{49}O_3$.

Thiemens and Jackson (1990) also investigated the pressure dependency of isotopic enrichment in ozone using UV photolysis of oxygen from 0.8 - 87 atm. They

noted an enrichment (in δ^{18} O) of 90 ‰ at a pressure of 0.8 atm to 10 ‰ at 35 atm. The effect of pressure is less in the range of 45 to 87 atmospheres. Their experiment differs from that of Morton et al. (1990) in the procedure of final ozone production since Morton et al. (1990) produced initial ozone in an electrical discharge, mixed it with oxygen and subsequently photolyzed the mixture in visible light. Figure 2.1 gives the variation of isotopic enrichment with pressure obtained by these two sets of studies (Thiemens and Jackson, 1988, 1990; Morton et al., 1990).



Figure 2.1. Pressure dependency of isotopic enrichment in ozone (compiled data from different laboratories).

2.1.2 Motivation Behind the Present Experiment

The present work was undertaken to further explore the ozone isotope enrichment phenomenon in UV photolysis of oxygen by varying ambient oxygen pressure in an effort to understand the variation in isotopic enrichment of stratospheric ozone as described in Chapter I (§ 1.4).

The experiments so far performed in different laboratories were with the basic goal of understanding the non mass-dependent effect itself (as described in § 2.1.1). None of the experiments were specifically planned to address the stratospheric case.

The present experiment was planned to mimic the stratospheric condition as close as possible. In the stratosphere, the photolysis of oxygen occurs in the Schumann-Runge band (175-200 nm) system, which is the first step of Chapman reaction to form ozone. An important phenomenon in the stratospheric scenario is the recycling (formation as well as dissociation) of ozone for a number of times. The photo-dissociation of ozone in this altitude is mainly by Hartley band (200 - 320 nm) of UV spectrum. It is true that Morton et al. (1990) considered ozone recycling in their laboratory studies. However, since their goal was to study the enrichment in ozone from recombination of ground state oxygen (molecular and atomic) species, they performed the experiment in the Chappuis band (500 - 700 nm). The dynamics associated with the ozone dissociation process in the Hartley band and Chappuis band are different (Valentini et al., 1987). With a motivation for stratospheric applications, the present experiment was carried out in the Hartley band.

In the altitude range of 22 to 33 km constituting the important zone of ozone formation, the total pressure variation is from about 36 to 6 torr (corresponding oxygen partial pressure variation is from about 8 to 1 torr), which is quite large compared to the temperature variation (220 - 228 K). Experimentally it is not feasible to perform the experiment in the pressure range similar to that of the stratospheric oxygen partial pressure due to limitations imposed by surface processes. Therefore, a high-resolution pressure dependence study was planned corresponding to the stratospheric total pressure regime. In this respect, this is the first experimental effort to study some relevant factors related to the stratospheric ozone enrichment phenomenon.

2.2 ABOUT THE EXPERIMENT

The previous experiments dealing with the pressure dependence of ozone isotopic enrichment were aimed at delineating the variation in the primary formation process. In the present case, the formation and dissociation were both permitted to operate simultaneously i.e. the product ozone was not isolated from the photolysis zone by freezing with LN_2 . Also, the UV photolysis was done using wavelengths close to the stratospheric window where ozone dissociation is most significant.

2.2.1 Experimental Configuration

Vacuum Manifold and Reaction Chamber:

Figure 2.2 shows the schematic diagram of the vacuum line setup. The line is made of pyrex tubing with greaseless glass stopcocks. A vacuum of < 1 mtorr was achieved by two stages of pumping: mechanical and diffusion pumps. A 5-liter spherical

pyrex chamber (made opaque with aluminum foil) with a MgF_2 side window (1 mm thick and 2 cm diameter) and a cylindrical cold trap at the bottom was used for making ozone from ultra-pure oxygen at different pressures.



Figure 2.2. Schematic diagram of the vacuum manifold and reaction chamber used in the experiment.

UV Light Source:

The UV light is generated by two different electrode-less low pressure (~ 5 torr) lamps, (i) Mercury (Hg), and (ii) Krypton (Kr), excited by a 200 Watt, 2450 MHz microwave generator (Opthos Inc., Model: MPG-4M) coupled to Broida and Evenson cavity respectively. The significant lines, within the UV window of interest, for Hg lamp are 184.9 (1000) and 253.7 (15000) nm and that of Kr lamp are 116.5 (200) and 123.6 (650) nm (the number in the parenthesis denotes the relative strength of each line). The 116 nm line of Kr falls in the fall-off region of transmission curve of MgF₂ window. So, for Kr lamp along with 123 nm, about 80 % of 116 nm enters the reaction chamber.

2.2.2 Experimental Procedure

Ozone dissociation is an integral part of ozone formation (Equations 1.7 to 1.10). To decouple these two effects two sets of experiments were carried out: firstly to study the combined effect of formation and dissociation and secondly to analyze the effect of UV dissociation alone.

In the first set (set 1) of experiment, ultra-pure oxygen (XL grade BOC Gas, 99.99% purity) was photolyzed at pressures from ~10 to 700 torr without removal of product ozone. In order to check the effect of photon energy on the fractionation processes, photolysis was done using two different UV sources, Hg and Kr resonance lamps. Oxygen pressure was monitored by a dial gauge (Figure 2.2). Photolysis was done

for duration of 60 to 1200 minutes depending upon the pressure to produce adequate amount of ozone for mass spectrometric measurement.

In all the second set (set 2) of experiments, ozone was initially formed by photolysis of oxygen at a pressure of 240 torr. Ozone was trapped by LN_2 at the bottom of the chamber and the oxygen pressure was reduced to 1/2, 1/4 and 1/8 in three different cases and the trapped ozone was released. Subsequently, photolysis of the mixture was carried out by the Hg lamp for 8 minutes.

In all cases, the ozone was separated by first condensing it with LN_2 and pumping away the oxygen until a few mtorr pressure was obtained. Subsequently, the LN_2 was removed and ozone was transferred to a second trap with molecular sieve cooled by LN_2 . Warming this trap to room temperature converted ozone to oxygen.

All the stable isotopic measurements were performed in VG 903 (Upgrade) and Europa Scientific GEO 20-20 isotope ratio mass spectrometers (IRMS). Ozone samples are converted to oxygen and measurements are done as oxygen. Unless otherwise stated, all the oxygen isotopic measurements reported here are with respect to a laboratory working gas (oxygen) with $\delta^{17}O = 12.48$ ‰ and $\delta^{18}O = 24.58$ ‰ with respect to SMOW with an overall estimated uncertainty (based on a few repeat measurements) of ± 0.1 and ± 0.2 ‰ respectively for $\delta^{18}O$ and $\delta^{17}O$.

To measure small amount of oxygen in VG 903 machine, a cold finger of 0.7 cc (made of stainless steel) with molecular sieve was added at the inlet. During measurement, oxygen samples were completely transferred to this finger from the sample bottle with LN_2 . The current in the mass-spectrometer was adjusted near the typical value ~ 10 nA by using different inlet volume of the mass-spectrometer.

To measure the yield of the product ozone (as oxygen), the major beam of the mass spectrometers was used. For GEO 20-20, beam 32 was calibrated with known amounts of oxygen taken in a sample bottle of 1 cc containing molecular sieve. The yield was estimated from the beam 32 strength (all the sample bottles are of the same volume of 1 cc) using the calibration curve. The procedure followed for VG 903 machine is the following: Beam 32 was calibrated with known amounts of oxygen transferred completely into the finger containing molecular sieve (with LN₂). The yield was estimated from the mass 32-beam strength using the calibration curve. To make sure that the calibration curve did not change, along with each sample set a known amount of tank

oxygen was measured and the current was noted after stabilization of the beam. No significant change in calibration was observed during the course of the experiment.

2.3 RESULTS

Experimental results for the first set showing pressure dependence of enrichment are given in Table 2.1 and 2.2 for Hg lamp and Kr lamp respectively. In Figure 2.3 and 2.4, δ^{18} O and δ^{17} O of ozone is plotted against the oxygen pressure for Hg and Kr lamp photolysis respectively. The plots show that initially the δ^{18} O and δ^{17} O increase gently with decreasing pressure till about 50 torr. Subsequent decrease of pressure is associated with a sharp increase of δ^{18} O and δ^{17} O leading to a peak value of 150.1 and 123.5 ‰ at 16 torr oxygen pressure for Hg lamp. Similar nature was observed for the Kr lamp photolysis with the peak values of 147.6 and 114.1 ‰ for δ^{18} O and δ^{17} O at 14 torr pressure.

Results for the second set of experiments, UV dissociation of ozone in the presence of oxygen as bath gas at different pressures, are shown in Table 2.3. The result shows that the photolysis of ozone enriches the leftover ozone pool as shown in Figure 2.5 (a). The ozone reservoir enriches by about 22 ‰ when the extent of dissociation is 66 %. In order to determine the fractionation factor α , we assume a Rayleigh model of the form $R = R_0 f^{(\alpha-1)}$.

Here R_o is the initial ¹⁸O/¹⁶O ratio of O₃ and R is the same at a given time; f is the fraction of O₃ left after dissociation at that time. Writing in δ notation and taking the natural logarithm we get the following equation:

$$\ln(1 + 0.001 \times \delta) = \ln(1 + 0.001 \times \delta_{o}) + (\alpha - 1)\ln(f)$$
(2.1)

Where δ_0 and δ are the δ^{18} O of initial ozone and that at a time t respectively.

Figure 2.5 (b) shows the plot of $\Delta \ln(1 + 0.001 \times \delta)$ against $\ln(f)$, where Δ is the difference of ln-functions consisting final and initial δ^{18} O (i.e. $\ln(1 + 0.001 \times (\delta^{18}\text{O})) - \ln(1 + 0.001 \times (\delta^{18}\text{O}))$). The best fit of all the data points gives the instantaneous fractionation factor, $\alpha = 1.0192$ for the left-over ozone.

Oxygen	Exposure	Ozone Yield	$\delta^{18}O$	$\delta^{17}O$	Production
Pressure	Time	$(\mu mole of O_2)$	(‰)	(‰)	Rate
(torr)	(min)				(µmole/min)
500.0	155	46.5	91.5	78.0	0.30
336.0	187	39.0	98.6	87.2	0.21
162.0	365	29.0	106.5	89.0	0.079
126.5	410	15.0	109.3	94.2	0.037
50.6	630	15.0	114.1	102.3	0.024
46.8	885	17.0	121.1	103.7	0.019
25.3	870	8.0	126.4	110.3	0.009
18.0	1102	3.4	142.3	118.9	0.003
16.0	1473	2.6	150.1	123.5	0.002
15.0	1140	1.4	134.2	115.5	0.001

 Table 2.1. Experimental parameters and results for Hg lamp photolysis (set 1)

 Table 2.2. Experimental parameters and results for Kr lamp photolysis (set 2)

Oxygen	Exposure	Ozone Yield	$\delta^{18}O$	$\delta^{17}O$	Production
Pressure	Time	$(\mu mole of O_2)$	(‰)	(‰)	Rate
(torr)	(min)				(µmole/min)
607.2	105	85.0	95.0	78.6	0.810
405.0	120	86.6	101.3	82.5	0.633
175.0	180	101.2	107.1	90.3	0.562
139.0	382	188.7	112.0	93.7	0.523
73.0	180	63.2	116.0	96.0	0.194
43.0	247	60.9	124.7	98.3	0.344
32.0	270	24.3	121.7	98.9	0.222
18.0	330	18.0	135.6	105.9	0.055
16.0	570	23.7	143.6	108.0	0.042
14.0	258	13.0	147.6	114.1	0.050
12.0	874	25.0	129.4	99.6	0.029
12.0	720	21.4	130.0	101.0	0.030
10.0	1920	17.0	136.2	105.9	0.009
8.0	1765	14.0	132.4	102.2	0.008



Figure 2.3. Variation of $\delta^{18}O$ (filled circle) and $\delta^{17}O$ (unfilled circle) of ozone with oxygen pressure from 10 to 550 torr for Hg lamp photolysis. He Error of individual data point is comparable to the size of the symbol.



Figure 2.4. Variation of $\delta^{18}O$ (filled square) and $\delta^{17}O$ (unfilled square) of ozone with oxygen pressure from 8 to 600 torr for Kr lamp photolysis. The error of individual data point is comparable to the size of the symbol.

Initial Ozone	Bath Gas	Left-over	δ^{18} O of Ozone	δ^{17} O of Ozone	Fraction
Amount	Oxygen	Ozone Yield	(‰)	(‰)	Left
$(\mu mole of O_2)$	Pressure (torr)	(μ mole of O ₂)			
45.0	120	29.8	106.6	112.2	0.66
50.0	60	24.9	111.6	104.7	0.50
56.0	30	21.0	122.0	123.2	0.38
Initia	al Ozone Compos	sition	99.0	95.3	

Table 2.3. Experimental parameters and results for UV dissociation of ozone in the presence of bath gas oxygen at different pressures (set 2).



Figure 2.5. Effect of dissociation on the enrichment process. (a) $\delta^{18}O$ of the leftover ozone after dissociation at three different bath gas oxygen pressures. The bath gas oxygen controls the extent of dissociation during the photolysis time of 8 minutes. Enrichment of 22 ‰ was observed at the dissociation level of 66 %. (b) Plot of Eqn. 2.1 (as described in the text) to calculate the fractionation factor of the dissociation process using a Rayleigh model. The instantaneous fractionation factor is calculated to be 1.0192 for leftover ozone.

2.4 DISCUSSION

The present results demonstrate that production of ozone through UV photolysis of oxygen is always associated with heavy isotope enrichment and confirm the earlier results (Thiemens and Jackson, 1987, 1988). The δ^{18} O is above about 80 ‰ for all three types of UV range investigated so far by different workers i.e. resonance Hg (184.9 and 253.7 nm) lamp, Kr lamp in 116 to 160 nm range and Xe continuum lamp in 155 to 180 nm range (present work and Thiemens and Jackson, 1987, 1988). For all the lamps the nature of pressure dependence of δ^{18} O and δ^{17} O is the same. This shows that the enrichment process is largely independent of energy of the dissociating photon.

The increase in enrichment with decrease in pressure (Figure 2.4 and 2.5) occurs differently over three pressure ranges: (I) 700 to 50 torr, where the increase of enrichment is gentle, (II) 50 to 15 torr, where the increase is sharp and a peak is observed, and (III) below 15 torr where the enrichment decreases sharply.

The photochemical processes involved in the experiments are as follows (similar to that expressed in 1.3): (1) primary processes,

$$O_2 + h\nu \to O + O \tag{2.2}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2.3}$$

and (2) secondary processes,

$$O_3 + h\nu \to O_2 + O \tag{2.4}$$

$$O + O_3 \rightarrow 2O_2 \tag{2.5}$$

In the pressure regime of 50 to 700 torr (Range I), the gentle increase of enrichment with lowering of pressure is also evident from previous laboratory experiments as described in § 2.1.1.

2.4.1 Pressure Dependence in Range I and Gao-Marcus Theory

The gentle increase in enrichment with decrease in pressure has been modeled by Gao and Marcus (2001, 2002) using a novel approach. They have shown that the lower density of states of symmetric molecules can make the collisional energy transfer less efficient and lead to faster dissociation of the symmetric transient ozone complex. Therefore, isotopic enrichment would have inverse pressure dependence. The results in the pressure range of 50 to 500 torr (Range I) can nicely be explained by this mechanism, which demonstrates that in this pressure range primary process of ozone formation
dominantly controls the isotopic enrichment in the product ozone compared to the secondary processes.

2.4.2 Significant Effect of Secondary Processes in Enrichment

The isotopic enrichment pattern in Range II is different from that of Range I (see Figures 2.3 and 2.4). We propose that an additional contribution from the secondary processes (i.e. dissociation of ozone) is responsible for the observed rapid rise in enrichment in the Range II. The additional increase in enrichment in the final product ozone due to dissociation alone is not dealt with by Gao-Marcus theory.

The proposition that dissociation of ozone is responsible for the rapid rise is confirmed by the next set (set 2) of experiments. In this set (set 2) of experiments, photolysis of ozone was carried out along with bath gas oxygen kept at three different pressures. The data shows that (Figure 2.5 (a)) as the bath gas pressure decreases, the extent of dissociation increases. As the other controlling factors which can govern the extent of dissociation, (e.g. photolysis time, amount of initial ozone) are kept constant, it can be argued that different bath gas pressures control the extent of ozone dissociation instead of taking any significant part in ozone formation process. So, during the photolysis time of 8 minutes, the primary process leading to ozone formation is negligible compared to the secondary process of ozone dissociation (since, considering the production rate of 0.037 µmole/min from Table 2.1 for 120 torr oxygen pressure, 8 minutes photolysis can contribute only 0.3 µmole of ozone for the first entry of Table 2.3). In other words, set 2 experiments provide the insight to the ozone dissociation processes. Figure 2.5 (a) shows that the isotopic enrichment increases with the magnitude of dissociation (calculated using the amount of ozone left and the initial amount). For example, if the left-over ozone is 34 % of the original, the isotopic enrichment is about 22 ‰. Applying the calculated fractionation factor (1.0192) to PRL data (experiments carried out at Physical Research Laboratory, India) (17.5 to 50 torr range (Range II) in set 1) it is estimated that 87 % loss of initial ozone is required to obtain an enhancement of the isotopic enrichment by 36 ‰ at 17.5 torr (over a value of 116 ‰ at 50 torr from where the influence of dissociation starts to increase rapidly) assuming no recycling of ozone.

Before discussing the PRL results in more detail it is worthwhile to describe and discuss the results from a similar set of experiments carried out at the University of

California, San Diego (UCSD). The UCSD results and the PRL results together clarify the underlying factors behind the pressure dependency in a complimentary way.

2.4.3 Experimental Results of UCSD

The UCSD experiments are similar to that of the first set (related to ozone formation) described in § 2.2. These experiment were performed in three different configurations. In the first configuration, abbreviated as config. I, ultra pure oxygen was photolyzed at pressures from 6 to 700 torr without removal of product ozone during photolysis; in config. II, product ozone was removed during photolysis (done only at oxygen pressures from 8 to 90 torr) by condensation in the trap; in config. III, a mixture of oxygen and nitrogen was photolyzed at a total pressure of 100 torr, but with variable ratios between them. According to this nomenclature, experiments under PRL set 1 category belong to config. I of UCSD.

Table 2.4. Experimental parameters and results for Hg lamp photolysis performed at UCSD for three different configurations as described in the text.

Oxygen	Exposure	Ozone Yield	δ^{18} O	$\delta^{17}O$	Production
Pressure	Time	$(\mu mole of O_2)$	(‰)	(‰)	Rate
(torr)	(min)				(µmole/min)
702.0	120	165.2	90.4	84.6	1.4
400.0	124	163.3	100.3	93.0	1.3
100.6	900	128.5	115.3	105.0	0.14
50.0	240	21.9	122.4	112.1	0.09
35.0	240	9.6	130.3	116.8	0.04
25.0	300	1.05	153.2	128.1	0.0035
20.0	240	0.21	169.9	134.7	0.0009
18.0	270	0.09	171.3	136.0	0.0003
17.5	810	0.62	180.7	140.7	0.0008
15.1	1045	0.17	152.0	125.5	0.0002
15.0	780	0.46	138.0	116.8	0.0006
10.0	360	0.56	138.8	116.3	0.0016
8.4	800	0.02	137.0	111.9	0.00002
6.7	765	0.05	115.4	95.4	0.00006

A. Config. I (without removing the product ozone during photolysis)

••••p)					
Oxygen	Exposure	Ozone Yield	$\delta^{18}O$	$\delta^{17}O$	Production
Pressure	Time	$(\mu mole of O_2)$	(‰)	(‰)	Rate
(torr)	(min)				(µmole/min)
7.9	300	12.8	126.6	113.8	0.90
18.3	180	29.9	115.4	107.6	0.93
25.0	230	38.6	123.3	103.6	0.84
50.7	112	11.2	120.3	109.4	0.91

B. Config. II (removing the product ozone during photolysis by LN_2 in the bottom trap)

C. Config. III (without removal of product ozone during photolysis with Nitrogen at 100 torr total pressure)

Oxygen	Exposure	Nitrogen	Ozone	$\delta^{18}O$	$\delta^{17}O$	Production
Pressure	Time	Pressure	Yield	(‰)	(‰)	Rate
(torr)	(min)	(torr)	(µmole			(µmole/min)
			of O ₂)			
5.0	1230	95.0	0.1	141.9	115.5	0.0001
7.5	1132	92.8	0.2	148.1	119.4	0.0002
10.0	840	90.0	0.4	176.3	133.9	0.0005
11.9	1060	88.1	0.8	167.3	130.3	0.0008
17.9	1110	82.1	6.8	135.5	115.1	0.0061
50.1	180	49.8	16.2	125.7	113.6	0.090



Figure 2.6. Variation of $\delta^{18}O$ of ozone with oxygen pressure from 6.7 to 700 torr for Hg lamp photolysis in three different configurations performed at UCSD (the symbols circle, square and triangle are for config. I, II and III respectively). Note the absence of peak in config. II experiment, where the formed ozone was trapped as soon as it formed in the bottom finger of the reaction chamber with LN_2 . The shift in peak from 17.5 torr to 10 torr is due to addition of nitrogen to the system.

The results of these experiments are given in Table 2.4. Figure 2.6 shows the variation of δ^{18} O with pressure from 6.7 to 700 torr. The pattern is similar to that of Figure 2.3 and 2.4 with three distinct pressure ranges. The peak value of enrichment was obtained at a pressure of 17.5 torr with a value of 180.7 ‰ for δ^{18} O. This value is about 30 ‰ higher compared to the peak values obtained in PRL experiments with Hg and Kr lamps (150.1 and 147.6 ‰ respectively). The reason for this apparent discrepancy is explained further on.

2.4.4 Dissociation Effect in the Pressure Range II

The major difference between the config. I and config. II experiments of UCSD is that both the primary and secondary processes are in operation in config. I whereas in config. II, mostly primary processes are operative. Figure 2.6 suggests that the peak in pressure range II vanishes when the secondary process, i.e. the dissociation process, is minimized by ozone absorption. Therefore, in the low pressure regime the dissociation processes act in tandem with the (primary) formation process and contribute significantly to the enrichment. The production rate plot (Figure 2.7) for pressure Range I, II and III (for PRL data) does not show uniform rate of increase with the increase of oxygen pressure; instead, the rate of increase of production rate is slower in Range II. This proves that the effect of dissociation in Range II is more important than Range I in a relative sense. In our experimental set-up, the Kr lamp was found to be more efficient probably due to generation of higher UV flux leading to higher dissociation of oxygen.

Figure 2.8 is the three-isotope plot between δ^{18} O and δ^{17} O, showing the slopes in three pressures ranges for both the lamps for PRL (set 1) experiments. The proposition that dissociation plays an important role in the 15 to 50 torr range (Range II) is corroborated by the slope values. The slopes in config. I in the pressure Range II for both the lamps are close to that of UV dissociation slope (slope = 0.6, see Chapter III), suggesting that the enrichment in this pressure range is controlled by the photodissociation process. The slopes for Ranges I and III show a value close to 1, which is a value for pure ozone formation only by the primary processes (Thiemens and Heidenreich, 1983). So, the enrichment noted above about 100 ‰ can be attributed to the effect of UV dissociation.



Figure 2.7. Pressure dependence of production rate for pressure Ranges I (50 to 500 torr), II (15 to 50 torr) and III (8 to 15 torr). The rate of production of ozone for all the ranges is larger for Kr lamp than the Hg lamp photolysis. The production rate increment pattern with increasing pressure for Ranges I and II are not same. The increase in rate is slower in Range II, compared to Range I. This establishes that dissociation of ozone is relatively more important to increase the isotopic enrichment in the low-pressure range.



Figure 2.8. Three-isotope plot of photolysis data for all the three pressure ranges with both the lamps. The slopes of ranges I and III are nearly same for both the lamps (due to less number of points, the data of Range III for Hg lamp photolysis was not plotted). The slopes for Range II for both the lamps have values close to that obtained from ozone dissociation alone.

2.4.5 Enrichment in Range III

At pressure Range III (below 15 torr) we obtained lower enrichments than the peak zone. Lower values of enrichment with decrease of pressure below ~ 15 torr was observed with a slope of ~ 0.9 , which is higher relative to its value (~ 0.6) in the neighboring 15 to 50 torr range (Range II). The cause for this turn-around is still to be explained. One of our recent studies (described in Chapter III) shows that dissociation of ozone on a glass surface enriches the left-over ozone pool in a mass independent (slope = 1) fashion. It is conceivable that in the low-pressure range, the ozone molecules can migrate to the wall of the reaction chamber where surface dissociation of ozone takes place and contributes to increase the slope. However, since surface dissociation is a less efficient process, the magnitude of enrichment is lower than the peak region.

2.4.6 Effect of Nitrogen in the system

In the context of dissociation, it is easy to see how the addition of nitrogen shifts the peak to lower pressures (config. III, UCSD data). As explained above, the peak is the result of significant UV dissociation of ozone in a dynamic sense. The net amount of ozone is determined by the integrated rate of production and destruction. At equilibrium, these two rates are equal and the reservoir amount is constant. The role of dissociation at this stage is essentially recycling the ozone at a fixed rate. The relative strength of the reservoir, vis-à-vis the dissociation rate, gives a measure of the turn-over time $(\tau = [O_3] / d[O_3]/dt$, where $[O_3]$ is the ozone amount at a given time and $d[O_3]/dt$ is the dissociation rate at that time), whose value determines the position of the peak i.e. the peak develops when the net amount of ozone over dissociation rate is below a critical level determined by UV flux, transmission and oxygen pressure. Addition of nitrogen increases the collision frequency and results in a larger amount of ozone being formed which has the effect of increasing the value of τ (relative to the case when only oxygen is present at the same partial pressure). Therefore, the same peaking effect is seen at lower oxygen partial pressure when the value of τ is reduced again below the critical level. This observation provides another support to our proposition involving the turn-over time.

2.4.7 Amount Dependence in Enrichment of Ozone

As mentioned before, the enrichment noted at UCSD with similar set-up and experimental configuration was higher compared to that of PRL in the pressure Range II.

We note that the ozone yield of UCSD experiments were below 1 μ mole in the pressure Range II whereas the yield of PRL experiments were around 10 μ mole or more (except for two data points of Hg lamp photolysis) in the same pressure range (compare Tables 2.1 and 2.2 with Table 2.4A). To explore the amount dependence of enrichment another set of experiments was performed.

Table 2.5. Experimental parameters and results showing amount dependence of enrichment. Table A and B are for Kr lamp photolysis for initial oxygen pressure of 74 and 32 torr and Table C is for Hg lamp photolysis at 200 torr initial oxygen pressure.

50	1	(1)		
Exposure	Ozone Yield	$\delta^{18}O$	$\delta^{17}O$	Production
Time	$(\mu mole of O_2)$	(‰)	(‰)	Rate
(min)				(µmole/min)
17	0.7	136.6	96.1	0.04
30	4.1	123.6	99.1	0.14
45	9.1	118.1	82.8	0.20
60	12.7	114.7	78.6	0.22
90	20.5	114.5	88.7	0.23
180	35.0	115.9	98.0	0.19
300	53.8	116.3	83.0	0.18

A. Initial oxygen pressure of 74 torr (Kr Lamp)

B. Initial oxygen pressure of 32 torr (Kr Lamp)

Exposure	Ozone Yield	δ ¹⁸ Ο	δ ¹⁷ Ο	Production
Time	$(\mu mole of O_2)$	(‰)	(‰)	Rate
(min)				(µmole/min)
30	2.6	139.1	101.9	0.09
45	8.0	123.5	85.7	0.18
90	13.4	122.0	79.6	0.15
270	60.0	121.7	98.9	0.22

C. Initial oxygen pressure of 200 torr (Hg Lamp)

Exposure	Ozone Yield	$\delta^{18}O$	$\delta^{17}O$	Production
Time	(μ mole of O ₂)	(‰)	(‰)	Rate
(min)				(µmole/min)
25	1.7	109.9	115.6	0.07
30	3.6	100.4	116.8	0.12
38	6.2	97.5	115.5	0.15
50	9.5	96.0	115.9	0.19
70	15.0	96.0	115.0	0.21
110	34.4	94.9	112.7	0.31

Ozone was formed by photolysis of oxygen kept at a fixed pressure. The photolysis time was varied and different amount of ozone was produced. Each time the product ozone was collected and its amount and isotopic composition were measured (procedure described in § 2.2). The experiment was done for 74 and 32 torr of oxygen pressure using Kr lamp and at 200 torr oxygen pressure with Hg lamp. The experimental results are given in Table 2.5.



Figure 2.9. Isotopic enrichment in ¹⁸O with the amount of ozone produced (by varying the photolysis time) for three different pressures. When the production is less that ~8 µmole, enrichment increases with decreasing amount for all the three pressures. Beyond 8 µmole the enrichment is almost constant. The uncertainty in each data point is comparable to the size of the symbol.

Figure 2.9 shows isotopic enrichment in ¹⁸O with the amount of ozone produced (by varying the photolysis time) for three different pressures. When the production is less than ~ 8 µmole, enrichment increases with decreasing amount for all the three pressures. In contrast, beyond an ozone amount of ~ 8 µmole, the δ^{18} O is almost constant. In the constant enrichment zone, the pressure dependence of enrichment is also evident. The enrichment for 32 torr is higher than the enrichment for 74 torr, which in turn is higher than that for 200 torr.

The amount dependency of enrichment can explain the discrepancy in the magnitude of enrichment in the peak zone between UCSD and PRL results. In the pressure Range II, for UCSD experiments, the yield of ozone was about one µmole or less (for 25 torr and below). This contributes additional enrichment due to the amount effect.

For PRL experiments, when Kr lamp was used for photolysis, the yield for the same pressure range was much more than the transition value of ~ 8 μ mole. For Hg lamp photolysis, in the same pressure range for two pressures 17.9 and 16.0 torr, the yield was ~ 3 μ mole and for others it was more than 8 μ mole. The enrichment noted for these two pressures also show little higher value compared to the enrichment observed for Kr lamp in the nearby pressures (Tables 2.1, 2.2 and 2.4A). In order to detect the pressure effect alone, it is therefore important to maintain the ozone yield above 8 μ mole as done for most of the PRL experiments.

2.5 CONCLUSION

The pressure dependency of enrichment of heavy oxygen isotopes in ozone was studied in the pressure zone relevant to stratospheric pressure with high resolution. Stratospheric conditions were maintained as close as possible regarding the UV energy window and ozone recycling (primary and secondary processes were allowed to take place simultaneously).

It is observed that depending upon heavy oxygen isotopic enrichment pattern, the examined pressure zone can be divided into three ranges. Beyond 50 torr pressure (Range I), the enrichment in ¹⁷O and ¹⁸O decreases gently with increasing pressure. Within 50 to 15 torr (Range II), enrichment increases sharply with decreasing pressure. Again below 15 torr (Range III), enrichment decreases with decreasing pressure. The three-isotope plot depicts different slopes (between δ^{17} O and δ^{18} O) in these three pressure ranges. The slopes in Ranges I and III are close to unity whereas the slope in Range II is close to 0.6. It was shown that dissociation of ozone (as a secondary process) plays an important role in pressure range II, which brings down the slope close to 0.6 from unity. Considering simultaneous formation and dissociation, a parameter called turn-over time (τ) is introduced to explain the enrichment pattern in pressure range II. The transition of slope from 0.6 to unity again in pressure range III is attributed to the surface effect. Some of these results can be applied to the stratosphere to explain the altitudinal variation of enrichment and will be discussed in Chapter V.

CHAPTER III

OZONE DISSOCIATION: PHOTO-DISSOCIATION AND SURFACE INDUCED DISSOCIATION

Ozone Dissociation

3.1 INTRODUCTION

Ozone dissociation is an integral part of ozone formation during UV photolysis. Therefore, in addressing the issue of isotopic enrichment of ozone (as described in Chapter II; Bhattacharya et al., 2002), it is important to characterize its different dissociation channels. The relevant dissociation pathways are: i) photo-dissociation, ii) thermal dissociation, iii) dissociation by chemical reactions and iv) dissociation through surface interaction. Among these four, thermal dissociation was studied in detail by Wen and Thiemens (1991) and Kim and Yang (1997). Their studies show some intriguing aspects during ozone dissociation in gas phase. Below 90°C, thermally dissociated ozone yields isotopically light oxygen and the left-over ozone is enriched in a mass-dependent fashion. Above 90°C, the isotopic behavior flips and the product oxygen becomes heavier in a mass independent fashion. The isotopic characteristic of thermal dissociation products is still an open question from theoretical point of view.

Dissociation of ozone by chemical reactions was studied recently (Chakraborty and Thiemens, Personal Communication). The left-over ozone shows a normal massdependent enrichment, as seen in most of the chemical reactions.

Among the other two dissociation pathways, two earlier studies dealt with photodissociation of ozone by UV and visible light (Bhattacharya and Thiemens, 1988; Wen and Thiemens, 1991), which showed slight deviation from mass dependence in the case of UV dissociation. The present chapter deals with these two pathways of ozone dissociation. In Part A, photo-dissociation will be discussed and in Part B, surface induced ozone dissociation will be covered.

3.2 PART A: PHOTO-DISSOCIATION OF OZONE

3.2.1 Motivation

The previous photo-dissociation experiments by Bhattacharya and Thiemens (1988) and Wen and Thiemens (1991) show that photo-dissociation of ozone produces isotopically light oxygen with respect to the initial ozone. Due to limited number of data points in the UV dissociation experiment of Bhattacharya and Thiemens (1988), the slope $(\Delta\delta^{17}O/\Delta\delta^{18}O)$ could not be firmly established to probe the isotopic behavior of ozone during UV dissociation. The results of photo-dissociation experiments using UV and visible light by Wen and Thiemens (1991) are quite interesting. They suggest that UV dissociation results in oxygen with mass independent character, whereas, dissociation in

visible wavelengths is strictly a mass dependent process. But detailed characterization of the mass independent fractionation in UV dissociation is still required to better comprehend the causative factors.

The motive behind the present experiments is two-fold: first, a better characterization of the fractionation in photo-dissociation of ozone in UV (Hartley band) and visible wavelengths (Chappuis band) and second, search for the cause behind the anomalous fractionation in UV photo-dissociation process from an experimental perspective.

3.2.2 Experimental Procedure

Photolysis of ozone was done using UV (184.9 and 253.6 nm from Hg resonance lamp) and visible (520 and 630 nm) wavelengths for various periods (from 2 to 12 minutes for UV light and 60 to 1500 minutes for visible light). In all the experiments, ozone was first produced in a 5-liter spherical chamber fitted with a MgF₂ window (experimental set-up same as described in § 2.2.1) by irradiating ultra-pure oxygen with UV generated by a Hg resonance lamp (184.9 and 253.6 nm) driven by a micro-wave generator. After irradiation, the product ozone was frozen by LN₂ in a cold finger attached with the flask and the oxygen pumped away till 2 mtorr pressure (vapor pressure of ozone at LN₂) was obtained.

Three sets of experiment were carried out. In set 1, ozone was produced at 500 torr oxygen pressure for 200 to 400 minutes. Each time, the isotopic composition of the product ozone was determined by taking an aliquot by equilibrating the ozone with a separate 1-liter chamber connected to the 5-liter chamber through stopcocks. Since the oxygen pressure was always 500 torr the isotopic composition of the ozone was reasonably constant within $\delta^{17}O = 93.7 \pm 1.5$ and $\delta^{18}O = 97.0 \pm 1.6$ ‰ (with respect to a laboratory working gas). The amount of ozone produced varied from 434 to 1025 µmole (oxygen equivalent) depending on the time of UV irradiation. The isotopically characterized product ozone was considered as the initial ozone and irradiated by UV photons from the Hg resonance lamp (184.9 and 253.7 nm) for 2 to 12 minutes to dissociate its different fraction.

In set 2, ozone was produced by irradiating ultra-pure oxygen at 500 torr pressure for \sim 120 minutes. As before, each time the isotopic composition of the product ozone was determined by taking an aliquot from the 5-liter chamber and the values were 95.2 ± 1 and 95.9 \pm 0.2 ‰ for δ^{17} O and δ^{18} O respectively. Next, ultra pure nitrogen was added in steps from 10 to 80 torr to the ozone within the 5-liter chamber in different experiments and irradiated by UV photons from a Hg resonance lamp (184.9 and 253.6 nm) for 3 to 4 minutes.

In set 3, ozone was produced at 240 torr oxygen pressure for 60 minutes (except for one case where the irradiation time was increased to 80 minutes). The amount of product ozone and its isotopic composition was determined once during this set of experiment. The irradiation protocol (60 minutes with input power 70 watts and reflected power 10 watts) was strictly maintained to ensure retrieval of the same amount and isotopic composition of ozone (~ $55 \pm 7 \mu$ mole with $\delta^{17}O = 104 \pm 3 \%$ and $\delta^{18}O = 106 \pm$ 2 ‰). The product ozone was irradiated by halogen filled tungsten lamp fitted with two different interference filters providing photons at wavelength range $520 \pm 2 \text{ nm}$ and $630 \pm$ 4 nm in two different sub-sets of experiment; irradiation was done for 60 to 1500 minutes to dissociate different fractions of ozone.

In all the three sets of experiment, after the irradiation, the left-over ozone was frozen by LN_2 in the bottom trap of the chamber and the product oxygen (formed by ozone dissociation) was collected in a sample bottle (1 cc) containing molecular sieve with LN_2 . After the collection of product oxygen, the left-over ozone was released and collected in another sample bottle (1 cc) containing molecular sieve in a similar way. Heating and refreezing for 3 to 4 times converted the ozone to oxygen.

Isotopic ratios and the yield of ozone (as oxygen) were measured using a GEO 20-20 (Europa Scientific) mass-spectrometer following the procedure described in § 2.2.2. Considering transfers of gases, aliquot separation and several freezing and thawing processes, the error in determining the isotopic ratio is slightly higher than the analytical error due to mass spectrometer alone. We estimate an overall uncertainty of 0.1 ‰ for δ^{18} O and 0.2 ‰ for δ^{17} O for the final data based on few repeat measurements.

3.2.3 Results

The results of the photo-dissociation experiments using UV and visible wavelengths (set 1 to 3) are given in Tables 3.1, 3.2 and 3.3 respectively and show that the left-over ozone is enriched in both ¹⁷O and ¹⁸O with respect to the initial ozone in all the three sets of experiments. On the other hand, the product oxygen (measured in set 1 and set 3 experiments) is depleted and the depletion increases with increasing irradiation

time, i.e. with increase of the extent of dissociation. For set 1 (UV dissociation), at 98 % dissociation level, the enrichments in ¹⁷O and ¹⁸O in the left-over ozone pool are about 50.1 and 79.5 ‰ respectively (Table 3.1). In contrast, for set 3 (visible light dissociation), at 81 % dissociation level, the enrichments in ¹⁷O and ¹⁸O are about 16.7 and 29.9 ‰ respectively (Table 3.3), which are much lower compared to the values in set 1 for equivalent dissociation level.

Figures 3.1a and 3.1b show the covariation plot between $\Delta\delta^{17}O$ and $\Delta\delta^{18}O$ for product oxygen and left-over ozone for set 1 and set 3 experiments. The slopes of the covariation plots for these two sets are different. The visible light dissociation of set 2 (Figure 3.1b) depicts a strictly mass dependent slope (0.54 ± 0.01), whereas the UV dissociation of set 1 (Figure 3.1a) shows an increased value of the slope (0.63 ± 0.01).

In order to determine the fractionation factor α for the dissociation processes described in sets 1 and 3, we assume that the progressive variation in fractionation follows a Rayleigh model of the form $R = R_0 f^{(\alpha-1)}$ (similar to § 2.3). Here R_0 and R are the initial and final ¹⁸O/¹⁶O ratios (of O₃) respectively and f is the fraction of O₃ left. Writing in δ notation and taking natural logarithm:

$$\ln(1 + 0.001 \times \delta) = \ln(1 + 0.001 \times \delta_0) + (\alpha - 1) \ln(f)$$
(3.1)

Where δ_0 and δ are the δ^{18} O of initial and final ozone respectively. Figures 3.2a and 3.2b show the plot of $\Delta \ln(1 + 0.001 \times \delta)$ (= $\ln(1 + 0.001 \times (\delta^{18}\text{O})) - \ln(1 + 0.001 \times (\delta^{18}\text{O})_0)$) against $\ln(f)$ for sets 1 and 3 respectively. A best-fit line through the points yields values for the instantaneous fractionation factor α , 1.0176 and 1.0151 for set 1 and 3 respectively. These values imply that for UV dissociation the ¹⁸O containing isotopomers of ozone dissociate with a rate 1.76 % lower compared to only ¹⁶O containing isotopomers. And for the visible light dissociation the same rate is lower by 1.51 %.

Amount	Initial	ozone	Amount	Product oxygen			1	Amount	Left-over ozone				
of			of					of					
initial	$\delta^{17}O$	$\delta^{18}O$	product	$\delta^{17}O$	$\delta^{18}O$	$\Delta \delta^{17} O$	$\Delta \delta^{18} O$	Left-over	$\delta^{17}O$	$\delta^{18}O$	$\Delta \delta^{17} O$	$\Delta \delta^{18} O$	Slope [*]
ozone	(‰)	(‰)	oxygen	(‰)	(‰)	(‰)	(‰)	ozone	(‰)	(‰)	(‰)	(‰)	$(\Delta \delta^{17} O / \Delta \delta^{18} O)$
(µmole)			(µmole)		. ,			(µmole)	· · ·				· · · ·
720	91.1	97.5	198	80.7	80.6	-10.4	-16.9	522	95.8	105.0	4.7	7.5	0.63
434	93.0	95.2	173	82.2	79.8	-10.8	-15.4	261	98.5	104.4	5.5	9.2	0.60
756	94.7	98.8	456	86.6	86.2	-8.1	-12.6	300	103.9	113.6	9.2	14.8	0.62
482	92.8	94.7	329	87.0	85.5	-5.8	-9.2	153	105.6	114.6	12.8	19.9	0.64
830	92.7	96.4	644	87.8	88.9	-4.9	-7.5	186	109.8	122.7	17.1	26.3	0.65
750	96.3	99.7	594	91.5	92.1	-4.8	-7.6	156	114.9	128.8	18.6	29.1	0.64
670	93.8	96.4	642	92.2	93.7	-1.6	-2.7	28	131.4	156.1	37.6	59.7	0.63
1025	95.0	97.3	1005	94.0	95.7	-1.0	-1.6	20	145.1	176.8	50.1	79.5	0.63

Table 3.1. Oxygen isotopic fractionation in products of UV dissociation of ozone using Hg Lamp

^{*} After propagation of errors, the uncertainty in individual slope value is about 10 %.

Amount	Ini ozo	tial one	Nitrogen	Amount Nitrogen of		Left-over ozone						
initial ozone (µmole)	δ ¹⁷ O (‰)	δ ¹⁸ O (‰)	pressure (torr)	Left-over ozone (µmole)	δ ¹⁷ O (‰)	δ ¹⁸ O (‰)	Δδ ¹⁷ Ο (‰)	Δδ ¹⁸ Ο (‰)	$\frac{\text{Slope}^*}{(\Delta\delta^{17}\text{O}/\Delta\delta^{18}\text{O})}$			
370	93.8	96.4	NIL	96	108.7	120.0	14.9	23.6	0.63			
345	95.2	95.2	20	107	101.1	105.3	5.9	9.5	0.62			
385	93.4	93.4	26	101	98.9	103.8	5.5	7.7	0.71			
173	96.0	96.0	30	73	101.4	103.1	5.4	7.1	0.76			
380	94.8	95.9	36	78	102.9	105.5	8.1	9.6	0.84			
302	95.8	95.8	40	55	108.7	108.8	12.9	13.0	0.99			
360	96.0	96.0	40	122	105.0	105.0	9.0	9.0	1.00			
285	95.1	95.6	60	77	105.3	105.9	10.2	10.3	0.99			
325	95.1	96.2	80	195	99.3	100.4	4.2	4.2	1.00			

Table 3.2. Oxygen isotopic fractionation in products of UV dissociation of ozone using Hg Lamp in presence of nitrogen at different pressures

^{*} After propagation of errors, the uncertainty in individual slope value is about 10 %.

Amount	Initia	l ozone	Amount	Product oxygen			Amount		Left-over ozone				
of			of					of					
initial	$\delta^{17}O$	$\delta^{18}O$	product	$\delta^{17}O$	$\delta^{18}O$	$\Delta \delta^{17} O$	$\Delta \delta^{18} O$	Left-over	$\delta^{17}O$	$\delta^{18}O$	$\Delta \delta^{17} O$	$\Delta \delta^{18} O$	Slope [*]
ozone	(‰)	(‰)	oxygen	(‰)	(‰)	(‰)	(‰)	ozone	(‰)	(‰)	(‰)	(‰)	$(\Delta \delta^{17} O / \Delta \delta^{18} O)$
(µmole)		. ,	(µmole)			· /		(µmole)			· · ·		、
White Lig	ght												
52.6	100.8	102.8	36.6	95.5	93.2	-5.3	-9.6	16.0	113.0	124.8	12.2	22.0	0.55
Red Light	$\pm (630 \pm 4)$	nm)											
62.2	100.3	103.0	8.6	87.2	79.3	-13.1	-23.7	53.6	102.4	106.8	2.1	3.8	0.55
52.2	102.0	104.8	11.0	90.0	83.1	-12.0	-21.7	41.2	105.2	110.6	3.2	5.8	0.55
41.7	102.6	105.2	20.2	95.2	90.7	-7.5	-14.5	21.5	109.6	118.8	7.0	13.6	0.51
67.7	110.9	107.1	54.9	107.0	100.1	-3.9	-7.0	12.8	127.6	137.0	16.7	29.9	0.56
Green Lig	ght (520 \pm	2 nm)											
55.1	103.8	108.8	10.9	91.6	87.1	-12.2	-21.7	44.2	106.8	114.2	3.0	5.4	0.56
48.5	104.5	107.3	17.0	95.4	90.3	-9.1	-17.0	31.5	109.4	116.4	4.9	9.1	0.54
45.0	105.3	105.3	17.0	95.5	86.0	-9.8	-19.3	28.0	111.2	117.1	6.0	11.7	0.51
50.6	104.2	107.6	29.3	96.9	94.3	-7.3	-13.3	21.3	114.2	125.8	10.0	18.2	0.55
80.7^+	106.3	104.3	62.2	102.2	96.7	-4.1	-7.6	18.5	119.9	129.8	13.6	25.5	0.53

Table 3.3. Oxygen isotopic fractionation in products of Visible light dissociation of ozone.

^{*} After propagation of errors, the uncertainty in individual slope value is about 10 %. ⁺ During the production of ozone, irradiation time was increased to 80 minutes



Figure 3.1. Covariation plot between $\Delta \delta^{17}O$ and $\Delta \delta^{18}O$ for the photo-dissociation experiments. (a) For UV dissociation (using a Hg lamp) the left-over ozone (the filled circles) is enriched with respect to the initial ozone and the product oxygen (unfilled circles) is depleted. The best-fit line gives a slope of 0.63 ± 0.01 reflecting that the UV dissociation of ozone has a significant mass-independent component. (b) For the visible light dissociation at 520 (circles) and 630 (squares) nm (filled and unfilled symbols are for the left-over ozone and product oxygen respectively). The best-fit line gives a slope of 0.54 ± 0.01 indicating that the visible light dissociation of ozone is a mass-dependent process. The error of each data point is comparable to the size of the symbol.



Figure 3.2. Plot to calculate the instantaneous fractionation factor (α) for dissociation using a simple Rayleigh model: $lnR = lnR_{0+}(\alpha-1) ln f$. The symbols are described in the text. (a) For UV dissociation, the best-fit line yields $\alpha = 1.0176$ for the left-over ozone. (b) For visible light dissociation (circles are for 520 and squares are for 630 nm light), the calculated α is 1.0151. The error of data point is comparable to the size of the symbol.

Results of dissociation of ozone in the presence of nitrogen (set 2) are shown in Table 3.2. Up to about 20 torr of nitrogen partial pressure, the slope $(\Delta \delta^{17}O)/\Delta \delta^{18}O)$ of the left-over O₃ has the same value (0.63) as obtained in set 1 (no nitrogen) experiment. However, the slope increases with the increase in nitrogen partial pressure after 20 torr

and attains a constant value (1.0) beyond 40 torr. The sharp transition of the slope from 0.63 to 1.0 corresponding to nitrogen pressure change (from 20 to 40 torr) is shown in figure 3.3.



Figure 3.3. Change in slope connecting $\delta^{17}O$ and $\delta^{18}O$ of the left-over ozone from 0.63 to 1.0 with increasing nitrogen pressure in the reaction chamber during UV photolysis of ozone (of ~ 2 torr). Up to 20 torr of nitrogen pressure the slope is almost constant at 0.63. Subsequently, a rapid increase in slope from 0.63 to 1.0 is observed with the increase of nitrogen pressure from 20 to 40 torr. Beyond 40 torr of nitrogen pressure, the slope remains constant at unity. The errors of the individual slope values are estimated by propagating the errors.

3.2.4 Discussion

3.2.4.1 Photo-induced kinetic isotope effect

There are several ways in which isotopic substitution can influence the process of molecular photo-dissociation. It can lead to a shift in the absorption spectra (variation of absorption cross-section with wavelength) of a molecule. Isotopic substitution can also remove the symmetry restriction on the molecular wave function, allowing for the occurrence of transitions, which is forbidden for the unsubstituted molecule. It is also noted that isotopic substitution can affect the line intensities in the absorption spectra. Kaye (1991) has presented a review on this subject with illustrations. Miller and Yung (2000) put forward a simple model to explain the photo-induced isotopic fractionation effect and provide a recipe to calculate fractionation resulting from photo-dissociation of

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molecules possessing continuous UV absorption spectra and unit photo-dissociation probability. This model is based on the premise that due to shift in the zero point energy between different isotopic species of a molecule, the absorption spectra of the heavy isotopomers are relatively blue shifted and this shift in absorption spectra results in isotopic fractionation in a given wavelength range. The generated isotopic fractionation by this process is not unidirectional. The fractionation is negative (for the left-over ozone) before the peak of the absorption spectra (lower λ side) and positive after the peak (higher λ side) as shown by Miller and Yung (2000) for the D/H ratio variation in the case of water molecule.

Following the Miller-Yung model, we selected the wavelengths 520 ± 2 and 630 ± 2 4 nm which are on two sides of the peak (600 nm) of the absorption cross-section in the Chappuis band of ozone and carried out ozone photo-dissociation was to detect possible fractionation difference. The isotopic fractionations can be calculated based on zero point energy difference between ${}^{48}O_3$ and ${}^{50}O_3$ using the vibrational frequencies of the O_3 isotopomers (Hathorn and Marcus, 2001) and the absorption cross-section of these two isotopomers at a particular wavelength. The zero point energy difference between the symmetric species (${}^{16}O{}^{18}O{}^{16}O$) and (${}^{16}O{}^{16}O{}^{16}O$) is 36.2 cm⁻¹ and between the asymmetric species (${}^{16}O{}^{16}O{}^{18}O$) and (${}^{16}O{}^{16}O{}^{16}O$) is 22.0 cm⁻¹. This leads to fractionations of -18.05 and -10.45 % respectively in the symmetric and asymmetric species of ${}^{50}O_3$ at 520 nm (using Miller-Yung formula and the absorption cross-section data (DeMore et al., 1997) around 520 nm). Considering the statistical abundances of symmetric and asymmetric species, the total expected fractionation in ${}^{18}O/{}^{16}O$ ratio at 520 nm is -13.0 ‰. A similar calculation yields fractionation of 23.18 and 14.9 ‰ respectively in the symmetric and asymmetric species of ${}^{50}O_3$ at 630 nm, which leads to a total expected fractionation of 17.7 ‰ in ¹⁸O/ ¹⁶O at 630 nm (see Appendix). However, these amounts of fractionation were not observed. In both cases the product oxygen was depleted and the left-over ozone was enriched (Table 3.3) with respect to the initial ozone with an instantaneous fractionation of about 15 ‰ (Figure 3.2b). Similar enrichment was observed for photodissociation with a white lamp, which covers the entire Chappuis band. For the UV photolysis with Hg resonance lamp which emits 184.9 and 253.7 nm photons, the 253.7 nm photons are mainly responsible for the photo-dissociation of ozone since the 184.9 nm line is about 15 times weaker and the absorption cross-section is about 10 times less. The

Miller-Yung model predicts negligible depletion of 0.06 ‰ (see Appendix) in the leftover ozone due to photo-dissociation at 253.7 nm since this wavelength lies near the peak of the absorption band.

3.2.4.2 Photo-dissociation in the Hartley band

In the Hartley band (<300 nm) the $2^{1}A_{1} / {}^{1}B_{2} \leftarrow X^{1}A_{1}$ transition takes place. Subsequently, a curve crossing between these two upper states and a repulsive state (Valentini et al., 1987; Batista and Miller, 1998) leads to the following two channels of dissociation (Matsumi et al., 2002):

$$O_3 + h\nu \rightarrow O(^1D) + O_2 (a^1\Delta_g)$$
(3.2)

$$O_3 + h\nu \rightarrow O(^{3}P) + O_2 (X^{3}\Sigma_g)$$
(3.3)

Both these channels are spin-allowed and have quantum yield of 0.9 and 0.1 respectively (Alder-Golden et al., 1982). Two important reactions follow the channel (3.2):

$$O(^{1}D) + O_{3} \rightarrow 2O_{2} \tag{3.4}$$

$$O(^{1}D) + O_{3} \rightarrow 2 O(^{3}P) + O_{2}$$
 (3.5)

with nearly equal rate coefficients of ~ 1.1×10^{-10} at 298 K (DeMore et al., 1997). The generated O(³P) from 3.3 or 3.5 can react with O₃ to produce O₂, but the rate coefficient of this reaction is too low (~8 × 10⁻¹⁵) compared to the rate coefficients of 3.4 and 3.5 (DeMore et al., 1997).

3.2.4.3 Photo-dissociation in the Chappuis band

For the Chappuis band, the *ab initio* calculations show that five electronic states are expected to be involved in that energy range (Arnold et al., 1994). Two of which are singlets (1 ${}^{1}A_{2}$ and 1 ${}^{1}B_{1}$) and three are triplets (1 ${}^{3}A_{2}$, 1 ${}^{3}B_{1}$ and 1 ${}^{3}B_{2}$). The visible spectra irregularities and diffuse vibrational structures in this band indicate severe predissociation in the transition (Anderson et al., 1991; Anderson and Mauersberger, 1995; Woywod et al., 1997). The absorption spectra in the Chappuis band is due to symmetry allowed ${}^{1}B_{1} \leftarrow X^{1}A_{1}$ transition and the vibronically allowed ${}^{1}A_{2} \leftarrow X^{1}A_{1}$ transition via the v₃ asymmetric stretch from the ground state (Arnold et al., 1994; Levene et al., 1987; Harold and Valentini, 1987). A conical interaction, which couples the bonded ${}^{1}B_{1}$ state to the dissociative ${}^{1}A_{2}$ state, is responsible for the diffusive nature of the absorption band (Braunstein and Pack, 1992; Waywod et al., 1997). The dissociation pathway is,

$$O_3 + hv \to O({}^{3}P) + O_2 (X^{1}\Sigma_{g}^{+})$$
 (3.6)

The basic assumption of Miller-Yung model is the existence of a continuous absorption spectra of the molecule in the wavelength range of interest. This criterion is not strictly valid for the Chappuis band since it has a fine structure. A theory of isotopic fractionation in photo-dissociation involving band structure is still not available but is expected to be quite complex due to combination of vibrational frequency differences among isotopomers, the zero point energy effect and Franck-Condon factor differences. The net result due to various integrating effects will be to reduce the simple Miller-Yung prediction based on zero point energy alone. This probably explains the discrepancy between the observed isotopic fractionation in photo-dissociation at the wavelengths 520 and 630 nm (on the two sides of the Chappuis band absorption peak ~ 600 nm) and the same calculated from the Miller-Yung model.

3.2.4.4 Mass independent isotopic fractionation during photo-dissociation in Hartley band

The covariation plot between $\Delta \delta^{18}$ O and $\Delta \delta^{17}$ O for product oxygen and left-over ozone for the photolysis of ozone in the Chappuis band (Figure 3.1b) reveals that the underlying process is strictly mass-dependent with a slope of 0.54. But the same plot for Hartley band photolysis (Figure 3.1a) yields a slope 0.63 having significant mass independent character. Considering the reactions 3.2 to 3.6, it appears that the crucial difference in ozone photolysis in the Hartley band and the Chappuis band is the presence of O(¹D) in the former case. Wen and Thiemens (1991) have also inferred about the possible role of the excited species O(¹D) and O₂(¹ Δ) in mass independent isotopic fractionation observed in UV dissociation.

Knowing that the $O(^{1}D)$ yield from ozone photolysis drastically goes down below 300 nm (Matsumi et al., 2002), we have performed ozone dissociation experiment (as a separate set) with different types of lamps (Cd, Hg, Kr) with a set of BK-7 filters (which essentially cuts down the wavelengths below 300 nm). The experimental configurations along with the observed slopes in the left-over ozone are given in Table 3.4. As the Cd lamp has strong lines mostly above 300 nm, the resultant slope is about 0.55 (using a

filter the slope reduces to 0.51). Kr lamp dissociation shows a significant change: 0.55 slope with filter and 0.60 slope without filter. For Hg lamp, the use of filter changes the slope slightly from 0.63 (as mentioned previously) to 0.59.

The results of this set of experiments are quite important since they show that the change in slope in the left-over ozone during ozone photolysis by a particular lamp can be effected only by changing the experimental configuration (by allowing or restricting the wavelengths below 300 nm to enter the chamber).

Table 3.4. Experimental configuration and results (slope in left-over ozone) for ozone photolysis performed for three different lamps and a set of BK-7 filters to cut-off the wavelengths below 300 nm.

				Extent of	
Lamp	Available wavelengths	Configuration	Atomic	dissociation	Slope [*]
	$(nm)^{\#}$		species	(%)	
			present		
Cd	228.8 (1500), 298.0	Without filter	$O(^{1}D), O(^{3}P)$	13.9	0.55
	(1000), 346.6 (1000),	Without filter	$O(^{1}D), O(^{3}P)$	70.6	0.54
	346.7 (800), 361.0	Without filter	$O(^{1}D), O(^{3}P)$	83.0	0.54
	(1000), 508.6 (1000),	Without filter	$O(^{1}D), O(^{3}P)$	86.2	0.53
	643.8 (2000)	One BK-7 filter	$O(^{3}P)$	44.0	0.51
			2		
Hg	184.9(1000),	One BK-7 filter	$O(^{3}P)$	35.6	0.59
	253.6(15000), 296.7	Three BK-7	$O(^{3}P)$	5.7	0.59
	(1200), 365.0(2800),	filters			
	404.7 (1800), 435.8				
	(4000), 546.1 (1100),				
	614.9 (1000)				
			- 1 3		
Kr	116.5 (200), 123.6	Without filter	$O(^{1}D), O(^{3}P)$	68.0	0.60
	(650), 427.4 (1000),	Without filter	$O(^{1}D), O(^{3}P)$	82.0	0.60
	431.9 (1000), 437.6	One BK-7 filter	$O(^{3}P)$	7.4	0.55
	(800), 446.4 (800),	One BK-7 filter	O('P)	11.4	0.55
	557.0 (2000), 587.0				
	(3000)				

Considering the totality of the reactions 3.2 to 3.5 and the results of the experiments described above, two dissociation channels needs to be discussed to decipher the source for the mass independent fractionation in case of Hartley band dissociation: (i)

[#] The figures inside the bracket denote the relative strengths of the lines.

^{*} After propagation of errors, the uncertainty in individual slope value is less than 10 %.

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Direct UV dissociation step (reaction 3.2), and (ii) $O(^{1}D)$ assisted O_{3} dissociation steps (reactions 3.4 and 3.5).

3.2.4.5 Source of mass independent isotopic fractionation in Hartley band photodissociation

Set 2 experiments were designed to address the question of mass independent fractionation since the presence of nitrogen with O_3 in the reaction chamber during UV photolysis provides a pathway for removal of $O(^{1}D)$. Nitrogen is an effective quencher of $O(^{1}D)$ with a rate constant ~ 2.6×10^{-11} cm³/molecule-sec (DeMore et al., 1997), which is five times less than that of the $O(^{1}D) + O_{3}$ reaction. Figure 3.3 shows the effect of nitrogen on the resultant slope during UV photolysis. There is a sharp change in the slope with increase in the nitrogen pressure, which can be interpreted in terms of $O(^{1}D)$ removal. The effective quenching of $O(^{1}D)$ is more with increase in concentration of nitrogen in the chamber, making the contribution of $O(^{1}D)$ in net O_{3} dissociation via reactions 3.4 and 3.5 less. This is evident from the gradual transition of the value of slope from 0.63 to 1.0 with increase in the nitrogen pressure from 20 to 40 torr. The slope attains a constant value of 1.0 for nitrogen pressure higher than 40 torr indicating a saturation effect in the quenching of $O(^{1}D)$ by nitrogen. This leads to the conclusion that O₃ dissociation at relatively high nitrogen pressure is only through R1, the direct dissociation pathway. This step then ought to represent a process characterized by pure mass independent fractionation with a slope of unity. This is the first experimental demonstration that pure UV dissociation of ozone bears a mass independent slope intriguingly similar to that obtained in its formation process. The observed slope of 0.63 without nitrogen quencher, therefore, has to result from a combination of the two dissociation pathways - the pure photo-dissociation and pure O(¹D) mediated dissociation.

The instantaneous fractionation factor for pure photo-dissociation calculated following Eqn. 3.1 (using 4 data points for nitrogen pressure from 40 to 80 torr having slope value of 1.0) gives a value 1.0071, which, as expected, is less than that of the no-nitrogen case (set 1: $\alpha = 1.0176$) combining the two channels of dissociation. The dissociation without nitrogen quencher can be thought of as a combination of the two processes each working independent of the other such that $\alpha_{total} = \alpha_{photo} + \alpha_{O(^1D)}$.

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Therefore, the effective fractionation factor for the $O(^{1}D)$ mediated dissociation is 1.0104. It is of interest to enquire about the underlying process responsible for 10.4 ‰ fractionation in the $O(^{1}D)$ reaction with O_{3} . Since lighter molecules collide more frequently due to their higher velocity and the collision rate ratio is proportional to the square root of the reduced mass ratio, one can estimate the isotopic fractionation arising out of this effect. This turns out to be about 5 % considering collision between ¹⁶O with $^{48}O_3$ and ^{16}O with $^{50}O_3$. The remaining 5 % seems to be contributed by the effect of zero point energy difference on the reaction rates. The dissociation of ozone by $O(^{1}D)$ is typical example of an 'abstraction reaction' and involves break-down of one O-O bond in the ozone molecule and formation of a new O - O bond between the incident $O(^{1}D)$ and the ejected atom. As in any abstraction reaction (Shiner, 1975), it is slightly easier to break bonds involving lighter isotopes compared to those involving heavier isotopes. As a result, the reaction rate is slightly higher for the lighter isotopomer. An exact calculation of this effect in the present case is difficult because stretching motions of the transition state is involved (Shiner, 1975). However, an idea of the magnitude of fractionation can be obtained by using the high temperature limit of the Bigeleisen-Wolfsberg formula for the kinetic isotope effect under the Harmonic Oscillator approximation as summarized by Van Hook (1970). The isotope effect is given by $(\mu_2/\mu_1)^{0.5}$, where μ refers to the reduced mass of the two approaching particles (¹⁶O atom and ozone molecule) and the subscripts 2 and 1 refer to the heavy and light isotopomers of ozone (Van Hook, 1970). This produces again 5 ‰ fractionation which is consistent with the required amount. The high temperature limit is justified because the colliding $O(^{1}D)$ imparts its large electronic energy of 1.97 eV to the transition state molecule during the collision.

3.2.4.6 Non-RRKM effect during O₃^{*} dissociation

To explore the reason behind the fractionations mentioned above, it would be important to consider why UV dissociation gives a mass independent slope, but the dissociation in the visible range does not. The first step of photo-dissociation dynamics of a molecule is the formation of electronically and vibrationally excited molecule. Interestingly, a similar excited intermediate also results during ozone formation by collision of O-atom with O₂-molecule. The excited molecule in both the cases can dissociate through different channels. As discussed in Chapter I, the mass independent isotopic fractionation during ozone formation has been explained by a novel approach by introducing a small departure from the complete statistical randomness of the standard RRKM method (Hathorn and Marcus, 1999, 2000; Gao and Marcus, 2001) (see Chapter I, § 1.3.3 for a brief discussion). The first step in this scenario is the formation of a short-lived O_3^* complex by $O - O_2$ collision. Subsequent redistribution of the total energy among the vibrational-rotational modes of this vibrationally excited transient molecule proceeds at some finite rate and may be incomplete during the typical life-time of this excited molecule (the non-RRKM effect). This non-statistical effect reduces the effective density of the available quantum states and consequently, the unimolecular dissociation rate ($k_{EJ} = N_{EJ}^+/h\rho_{EJ}$) increases. The reduction of the density of quantum states is more for the symmetric molecules than for the asymmetric molecules (since there are fewer dynamical coupling terms in the symmetric than in the asymmetric molecules).



Figure 3.4. Schematic diagram of the potential energy curves as a function of dissociation coordinate with the possible dissociation channels for the Hartley and the Chappuis band. Dissociation in Hartley band yields $O({}^{1}D)$, whereas the Chappuis band dissociation produces ground state oxygen atom $(O{}^{3}P)$.

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It was shown by detailed calculations that this small non-statistical effect amplifies as a large mass independent isotopic effect in stabilized ozone molecules. A similar situation may be applicable for the photo-dissociation of ozone because of the formation of the intermediate excited state (O_3^*) by absorbing photons (UV or visible). Absorption of photons in the Hartley band will lead to the formation of excited O_3^* species in the ¹B₂ (or 2¹A₁) electronic state (shown in Figure 3.4) similar to the formation of excited state during ozone formation in the X¹A₁ state (Hathorn and Marcus, 1999). A non-statistical energy distribution can take place within various modes of O_3^* , which may be incomplete within its typical life-time ultimately leading to a mass independent isotopic effect. However, for the Chappuis band, pre-dissociation (Anderson et al., 1991, 1995; Woywod et al., 1997) plays a dominant role. This implies a larger life-time during which the molecule gets enough time for randomization of energy. Therefore, a nonstatistical symmetry dependent effect would not take place.

3.2.5 Conclusion of Photo-dissociation Study

In photon interaction with ozone isotopically lighter isotopomers are preferentially dissociated resulting in the formation of lighter oxygen and enriched left-over ozone. However, photo-dissociation in the Hartley band (by UV light) and Chappuis band (by visible light) are characteristically different – the former produces oxygen which is mass-independently fractionated while the latter produces oxygen, which is lighter in strictly mass-dependent fashion.

The recent Gao-Marcus theory explains the mass-independent enrichment in ozone formation by involving incomplete randomization of energy among the various modes of the ozone complex (a non-RRKM effect) formed by collision of O-atom and O_2 -molecule. A similar situation seems to be operative in case of photo-dissociation but the energy is provided by photon absorption. Therefore, the same Gao-Marcus theory can explain the mass-independent dissociation in UV photolysis of ozone. However, for the Chappuis band, pre-dissociation is mainly responsible for the ozone destruction and this involves large life-time of the complex thereby minimizing the non-RRKM effect and resulting in a mass-dependent fractionation.

3.3 PART B: SURFACE INDUCED DISSOCIATION OF OZONE

3.3.1 Motivation

The present set of experiments was planned for the isotopic characterization of the dissociation process when ozone molecules strike a surface. In many laboratory experiments surface dissociation of ozone can be important. For example, it was observed that the anomalous isotopic enrichment in the oxygen formed by ozone photo-dissociation is substantially less than that for ozone formation from oxygen (Bhattacharya and Thiemens, 1988; Wen and Thiemens, 1990, 1991), though the source of the anomalous fractionation for both the cases can be traced to the formation of an activated complex involving vibrationally excited ozone molecule. The smaller enrichment in the dissociation process is presumably due to the interference by surface effects operating in the low-pressure dissociation experiments. Again, to explain the increase in enrichment with temperature during thermal dissociation it was proposed that increased collision rate at higher temperature results in more effective gas phase reaction. This implies a reduced role of surface interaction of ozone molecules and higher net enrichment at higher temperature. The need to test these propositions provided the motivation for our present study.

Another goal is to understand the mechanism of dissociative reactions on surface followed by chemi-adsorption, which are still modeled by empirical concepts without adequate microscopic picture of the underlying processes (Gregg, 1961). Isotopic fingerprints of the products can sometimes provide valuable insight. For example, Winter (1958) showed that oxygen adsorbed on metal oxide surfaces undergoes exchange with lattice oxygen through isotopic methods. Since ozone is highly reactive, its dissociation on glass surface provides an easy set up for such studies.

In the present experiment, dissociation of ozone on two different surfaces, pyrex and quartz was carried out and the isotopic fractionation between the left-over ozone and product oxygen was studied.

3.3.2 Experimental Procedure

Ozone was produced by UV photolysis of ultra-pure oxygen (99.99% purity) at pressure of 180 torr. The same 5-liter spherical Pyrex vessel described in §2.2.1 was used as the reaction chamber. A resonance Krypton lamp (116.5 and 123.6 nm) operated inside

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an Evenson cavity excited by a 120 watt, 2450 MHz microwave generator was used as the UV source.

Figure 3.5. Schematic diagram of the vacuum manifold used for surface dissociation study. The reaction chamber has a cold finger at the bottom and is fitted with a MgF_2 window. Ozone was made to pass through the spiral for effecting surface dissociation.

The photolysis time for all the experiments were kept constant at 180 minutes. The produced ozone was separated by first condensing it at the bottom trap with LN_2 and pumping the remaining oxygen till a few mtorr pressure (vapor pressure of liquid ozone) was obtained. For effecting dissociation at the inner surface of glass, the following steps were followed. LN_2 was removed and ozone was transferred to a chamber (volume ~10 cc) cooled by LN₂. The unfrozen residual gas amount for all the experiments were about 2 µmole. Two different spirals made of pyrex and quartz (each of them made from 2 meter long and 8 mm inner diameter tube) were used (Figure 3.5 shows the complete set-up of the experiment). The spiral as well as the manifold was kept opaque with aluminum foil wrapping. The liquid ozone was released by removing LN₂ and made to pass through the spiral by keeping another chamber (volume ~ 10 cc) cooled by LN₂ at the other end of the spiral. After passing through the spiral, the residual ozone gets collected in this second chamber. Sufficient time was given to get the residual ozone in the second chamber and the unfrozen fraction (supposed to be oxygen, produced from the breakdown of ozone by surface collision) was collected in a sample bottle with molecular sieve at LN₂ temperature. It was estimated that about 15 % of the initial ozone breaks down in the first pass. To get different fractions of product oxygen, ozone was passed through the spiral several times and each time residual ozone was collected first and then the product oxygen. As the number of passes increased the percentage breakdown of ozone decreased

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significantly. The residual ozone was finally collected in a sample bottle (volume = 1 cc) with molecular sieve at LN_2 temperature. Ozone was converted to oxygen by repeated freezing and heating of molecular sieve containing ozone.

Oxygen isotopic measurements were done on a triple collector mass spectrometer (model GEO 20-20 of Europa Scientific) with typical error of 0.2 ‰ and 0.1 ‰ for δ^{17} O and δ^{18} O respectively. The yield of ozone and product oxygen was estimated following the procedure described in § 3.2.2.

3.3.3 Results

The isotopic composition (δ^{17} O and δ^{18} O) of the left-over ozone and product oxygen along with their amount are shown in Table 3.5 for the pyrex and quartz spirals. The initial composition of ozone was calculated by mass balance, knowing the amount and composition of the left-over ozone and product oxygen. The amount of ozone initially produced (sum of the amount of left-over ozone measured as oxygen and product oxygen) by photolysis shows large variation (from about 23 to 57 µmole) due to variation in the output of the Kr lamp. However, the δ^{18} O of the initial ozone varied only by a small amount (mean ~104 \pm 2 ‰). $\Delta \delta^{17}$ O and $\Delta \delta^{18}$ O (Table 3.5) denote the enrichment or depletion with respect to the initial ozone composition. The data show that dissociation of ozone yields isotopically light oxygen, while enriching the left-over ozone pool. To increase the extent of fractionation, the ozone was passed through the spiral several times. With the increased amount of dissociation, the amount of left-over ozone decreased and gradually became isotopically heavier. Figure 3.6 shows the covariation plot between $\Delta \delta^{17}$ O and $\Delta \delta^{18}$ O. When the fractionation of the ozone reservoir is small (less than ~15 ‰ with respect to the initial composition), the slope of the covariation plot is about one and with the increase of fractionation the slope of the line decreases. Beyond 25 ‰, the points do not fall on the slope one line rather they yield a slope value of about 0.75. The isotopic behavior does not change significantly with the change of the spiral material from pyrex to quartz.

Table 3.5. Table showing results of the surface induced dissociation experiment. Results for the two different surfaces, made of pyrex glass and the quartz glass are shown separately. The amount of ozone is measured as oxygen after converting O_3 to O_2 (as described in the text). The initial composition of ozone was calculated from the mass balance of the two component (i) leftover ozone and (ii) product oxygen. $\Delta\delta^{17}O$ and $\Delta\delta^{18}O$ represent enrichment and depletion for ozone phase and oxygen phase respectively with respect to the initial composition.

Amount	Initial compo	ozone [*] osition	Amount of left- Amount		Left-over ozone [*]					Produc	t oxygen [*]	
ozone (µmole)	δ ¹⁷ O (‰)	δ ¹⁸ O (‰)	over ozone (µmole)	or product oxygen (μmole)	δ ¹⁷ O (‰)	δ ¹⁸ Ο (‰)	Δδ ¹⁷ Ο (‰)	Δδ ¹⁸ Ο (‰)	δ ¹⁷ O (‰)	δ ¹⁸ Ο (‰)	Δδ ¹⁷ Ο (‰)	Δδ ¹⁸ Ο (‰)
Pyrex Glas	S											
39.3	97.5	100.9	30.0	9.3	101.5	95.8	3.9	5.1	84.8	84.5	-12.7	-16.4
31.5	97.4	103.4	22.6	8.9	102.6	99.0	5.1	6.5	84.4	87.0	-13.1	-16.4
41.8	96.5	103.8	24.5	17.3	104.5	102.0	7.9	9.8	85.3	89.9	-11.2	-13.9
36.5	94.8	105.8	19.1	17.4	107.8	107.0	13.1	14.0	80.4	90.4	-14.4	-15.4
29.5	95.3	103.9	11.7	17.8	105.5	96.3	10.2	11.7	88.6	92.3	-6.7	-11.6
25.8	96.1	105.6	8.0	17.8	106.5	108.4	10.4	20.9	91.4	96.3	-4.7	-9.4
27.8	92.9	106.0	7.8	20.0	111.7	116.5	18.8	26.0	85.6	95.8	-7.3	-10.1
22.9	93.4	106.2	3.0	19.9	119.6	128.0	26.2	40.6	89.5	100.1	-4.0	-6.1
42.0	96.7	104.8	5.0	37.0	119.9	125.9	23.2	39.2	93.6	99.5	-3.1	-5.3
Quartz Gla	SS											
56.8	97.3	105.2	51.0	5.8	100.2	108.7	3.0	2.4	71.4	83.9	-25.9	-21.3
52.2	94.8	104.9	42.7	9.5	99.0	108.8	4.2	3.8	75.9	87.8	-18.9	-17.2
39.7	95.3	106.6	26.7	13.0	106.7	116.3	11.4	9.8	71.8	86.5	-23.5	-20.1
37.3	88.7	100.5	23.8	13.5	94.8	108.9	7.1	8.4	75.3	85.7	-12.5	-14.8

^{*} The errors in measurements of δ^{18} O and δ^{17} O (estimated from some repeat measurements) are 0.1 and 0.2 % respectively.



Figure 3.6. Covariation plot of $\Delta \delta^{18}O$ and $\Delta \delta^{17}O$ for surface induced dissociation process. The initial composition of ozone is calculated by mass balance of the two fractions (left-over ozone and product oxygen). The upper right quadrant represents the left-over ozone component (filled symbols) and the lower left quadrant the product oxygen (unfilled symbols), which is enriched in light isotope. The circles and the triangles represent the results for pyrex and quartz surfaces respectively. For small amount of fractionation, the slope is around unity. As the fractionation increases, the slope decreases. The two points (encircled squares) represent a different experimental condition effecting thermal dissociation as described in the text. The errors of the individual data points are comparable to the size of the symbols.

In order to determine the fractionation factor α , we assume a Rayleigh fractionation function of the form of Eqn. (3.1). Figure 3.7 shows the correlation diagram between Δ and ln(f). The best fit of all the data points gives the instantaneous fractionation factor for the left-over ozone as $\alpha_{\text{left-over ozone}} = 1.017$ indicating that the product oxygen is depleted by about 17 % relative to the initial ozone composition.



Figure 3.7. Plot for calculating the fractionation factor for the surface dissociation process using a Rayleigh model. X-axis represents the fraction left in the O_3 pool. Data plotted in the Y-axis are normalized to the initial composition of ozone. As the fraction in the O_3 pool decreases, the delta value increases accordingly giving a fractionation factor (α) of 1.017. The error of each data point is comparable to the size of the symbol.

3.3.4 Discussion

The dissociation of ozone yields isotopically light oxygen similar to that of the product of photo-dissociated ozone and thermally (< 90°C) dissociated ozone (Wen and Thiemens, 1990, 1991, Kim and Yang, 1997) but does not follow the conventional mass fractionation pattern (slope value of half). Instead, it gives rise to a slope value of unity in the covariation plot of $\Delta\delta^{17}$ O and $\Delta\delta^{18}$ O (Figure 3.6) surprisingly similar to the slope observed in case of formation of ozone (see initial ozone composition in Table 3.5).

Why the surface dissociation of ozone produces oxygen with mass independent fractionation is a puzzling question but one can invoke a scenario using the concepts of recently proposed Gao-Marcus theory (Gao and Marcus, 2001; see Chapter I, § 1.3.3 for a brief discussion), which explains the mass independence in case of ozone formation. Gao-Marcus theory proposes that during ozone formation by $O + O_2$ recombination reaction a short-lived O_3^* complex is formed. Subsequent redistribution of the total energy among the rotational-vibrational modes of this excited transient molecule proceeds at some finite rate and may be incomplete during the typical life-time of this complex (non-RRKM effect). This non-statistical effect reduces the effective density of the available quantum

states and consequently the unimolecular dissociation rate of the complex increases decreasing the probability of formation of a stable ozone molecule. The reduction of the density of states is more for the symmetric molecule (which has more share of lighter isotopes) than for the asymmetric molecules (since there are fewer dynamical coupling terms in the symmetric molecule). It was shown that this small non-statistical effect amplifies as a large mass independent isotope effect in stabilized ozone molecules.

For surface dissociation of ozone, the first step involves chemi-sorption of ozone molecule on the surface as it happens in the case of oxygen, which is slightly less reactive. We postulate that the ozone molecule forms an activated complex (Figure 3.8) with a reactive atom residing on the surface (Cristmann, 1991). This activated complex is a transient species and may dissociate after its typical lifetime in the following way,

$$O_3 + Surface (W) \to (O_3W)^* \to O({}^{3}P) + O_2 (X^{1}\Sigma_g^{+}) + W^*$$
 (3.7)

The ozone complex being confined to the surface has less degrees of freedom and can only have restricted rotational and vibrational motions. This reduces the density of states and makes the activated complex short-lived. We then can consider a non-statistical Gao-Marcus model, which favors the asymmetric molecules for its intra-molecular energy redistribution. This reduces the dissociation rate constant of the asymmetric molecules and results in mass independent isotopic enrichment in the left-over ozone. The product oxygen is correspondingly equally depleted in ¹⁷O and ¹⁸O. This explanation is at present speculative and needs to be tested experimentally and theoretically.

To achieve larger fractionation, the ozone had to go through the spiral many times. For example, to get around 25 ‰ enriched ozone, the required time was nearly 6 hours and some amount of thermal dissociation in this time cannot be avoided. Therefore, higher amount of fractionation (> 25 ‰) arises due to combination of two processes i.e. surface interaction and gas phase dissociation. The room temperature thermal dissociation yields a mass-dependent slope (~ 0.5) in contrast to the surface dissociation (slope ~1.0) and the admixture of these two components produces a resultant slope with value less than one. This explanation is supported by the thermal dissociation data (points encircled in Figure 3.6, representing the situation when the ozone was kept within the spiral for about 8 hours at room temperature). They define a slope of around half, which is expected in case of thermal decomposition at room temperature (Wen and Thiemens, 1990).

Recently Bhattacharya et al. (2002) (also see Chapter II) studied the pressure dependency of isotopic enrichment in ozone (produced from oxygen photolysis at different oxygen pressures ranging from 8 to 700 torr). They explained the observed enrichment pattern for pressure upto 15 torr by considering simultaneous formation and dissociation in gas phase. However, the enrichment pattern observed below 15 torr (equal enrichment in ¹⁷O and ¹⁸O with lower magnitude compared to that observed at 15 torr) did not fit with the proposed hypothesis. In that pressure range, the ozone production was less than 0.05 μ mole/min (Bhattacharya et al., 2002; Chapter II, § 2.3) and ozone decomposition by interaction with the surface was assumed to be significant. The results obtained in the present experiment provide support for this assumption.



Figure 3.8. Formation of an activated complex $(O_3W)^*$ by adsorption of ozone molecule on a surface (ΔE represents the heat of adsorption). The energy redistribution among all its rotational/vibrational states may be incomplete during its typical lifetime resulting in a mass independent isotopic effect in the products.

3.3.5 Conclusion of Surface Induced Dissociation Study

The isotopic behavior of ozone during dissociation on glass surface is anomalous. The process leads to faster dissociation of lighter isotopomers and surprisingly, the rate constant is equally less for ¹⁷O and ¹⁸O containing molecules. No noticeable variation was observed with the change in the surface material. As the experimental time increases, the
mass independent effect is reduced due to the admixture of products from thermally dissociated ozone.

It is postulated that the dissociation of ozone on a surface takes place by dissociative adsorption. In this mechanism, an activated complex $(O_3W)^*$ formed as an intermediate. The mass independent isotopic fractionation arises due to non-statistical (non-RRKM) energy randomization within the activated complex resulting in lesser dissociation rate of the asymmetric intermediates compared to the symmetric one.

CHAPTER IV

ISOTOPIC EXCHANGE: $CO_2 - O(^1D)$

4.1 INTRODUCTION

Ozone in the stratosphere is mass independently enriched in the heavy oxygen isotopes (¹⁷O and ¹⁸O) relative to the ambient oxygen from which it is formed (Krankowsky et al., 2000; Mauersberger et al., 2001). A detailed discussion about this mass independent enrichment is given in Chapter I of this thesis (§ 1.4). As ozone is a photochemically active species in the atmosphere, its mass independent signature can be transferred to other oxygen-containing molecules in the atmosphere (e.g. CO_2 , N_2O , CO, H_2O etc.). The present chapter deals with the mechanism involved in the isotopic exchange between CO_2 and ozone through a ozone dissociation product, $O(^1D)$.

4.1.1 Anomalous Oxygen Isotopic Composition of Stratospheric CO₂

Isotopic measurements of stratospheric CO₂ clearly show that it is enriched in heavy oxygen isotopes (Gamo et al., 1989, 1995; Thiemens et al., 1991, 1995) and this enrichment (both in ¹⁸O and ¹⁷O) increases with altitude (Lämmerzahl et al., 2002). Moreover, the enrichments in ¹⁷O and ¹⁸O are linearly related with slope 1.7 (Lämmerzahl et al., 2002). Following a different method, Bhattacharya et al. (Bhattacharya, S.K., R.J. Francey, C.E. Allison, I. Levin, U. Schmidt, and T. Gamo, Altitudinal variation in oxygen isotopic composition of the stratospheric carbon dioxide, paper under preparation for *J. Geophys. Res.*) also obtained a slope much higher than unity and showed that depending upon the sampling altitude it varies from 1.2 to 2.2. Further discussion about oxygen isotopic composition of stratospheric CO₂ is presented in Chapter V (§ 5.3).

4.1.2 Mechanism of the Isotopic Exchange Between CO₂ and O(¹D)

Yung et al. (1991) and Thiemens et al. (1991) proposed that stratospheric ozone is the real source of "heaviness" of the stratospheric CO_2 . The direct transfer of "heaviness" from the ozone pool to the CO_2 pool by the reaction,

$$CO_2 + O_2Q \rightarrow COQ + O_3 \tag{4.1}$$

where Q is the heavy oxygen isotopic species: 17 O or 18 O, is quite inefficient. Yung et al. (1991) proposed the transfer mechanism via O(1 D), a very reactive species, produced during UV photolysis of O₃. The reaction schemes are as follows,

$$O_3 + hv \rightarrow O(^1D) + O_2 \quad (\lambda < 315 \text{ nm})$$
 4.2a

or,
$$O_2Q + h\nu \rightarrow Q(^1D) + O_2 \quad (\lambda < 315 \text{ nm}) \qquad 4.2b$$

The quenching rate of $O(^{1}D)$ by CO_{2} is quite high (DeMore et al., 1997). The quenching rate coefficient at T = 298 K is ~ 1.1 x 10^{-10} cm³ s⁻¹ (the same for Ar and Kr are 7 × 10^{-13} and 8 × 10^{-12} cm³ s⁻¹ respectively). The high efficiency of the $CO_{2} + O(^{1}D)$ quenching is somewhat unusual given the fact that it is spin forbidden. So, the quenching mechanism is thought to be through an intermediate CO_{3}^{*} as follows:

$$\rm CO_2 + O(^1D) \rightarrow \rm CO_3$$
 4.3a

$$\mathrm{CO}_3^* \to \mathrm{CO}_2 + \mathrm{O}(^3\mathrm{P})$$
 4.3b

or,
$$\operatorname{CO}_2 + \operatorname{Q}({}^1\mathrm{D}) \to \operatorname{CO}_2\operatorname{Q}^*$$
 4.4a

$$\text{CO}_2\text{Q}^* \rightarrow \text{COQ} + \text{O}(^3\text{P})$$
 4.4b

Table 4.1. List of essential reactions involved in the mechanism of "heavy" isotope transfer from O_3 pool to CO_2 pool along with their reaction coefficients. The molecular kinetic data are taken from DeMore et al. (1997).

Reaction Pathway	Photo-dissociation Coefficients (s ⁻¹)
$O_3 + h\nu \to O(^1D) + O_2 \ (\lambda < 315 \text{ nm})$	$J_1 = 7.4 \times 10^{-5}$
$O_2Q + h\nu \rightarrow Q(^1D) + O_2 (\lambda < 315 \text{ nm})$	$J_2 = \frac{1}{2} J_1 = 3.7 \times 10^{-5}$
	Rate Constant ($\text{cm}^3 \text{ s}^{-1}$)
$O(^{1}D) + CO_{2} \rightarrow CO_{2} + O(^{3}P)$	$k_1 = 7.4 \text{ x } 10^{-11} \text{ e}^{120/\text{T}}$
$Q(^{1}D) + CO_{2} \rightarrow COQ + O(^{3}P)$	$k_2 = 2/3 k_1 = 4.9 x 10^{-11} e^{120/T}$
$O(^{1}D) + COQ \rightarrow CO_{2} + Q(^{3}P)$	$k_3 = 1/3 k_1 = 7.4 x 10^{-11} e^{120/T}$
$O(^{1}D) + O_{3} \rightarrow O_{2} + O_{2}$	$k_4 = 1.2 \text{ x } 10^{-10} \text{ e}^{80/\text{T}}$
$O(^{1}D) + O_{2} \rightarrow O_{2} + O(^{3}P)$	$k_5 = 3.2 \times 10^{-11} e^{67/T}$
$Q(^{1}D) + O_{2} \rightarrow O_{2} + Q(^{3}P)$	$k_6 = k_7 = 3.2 \text{ x } 10^{-11} \text{ e}^{67/\text{T}}$
$O + O_3 \rightarrow O_2 + O_2$	$k_8 = 8.0 \text{ x } 10^{-12} \text{ e}^{70/\text{T}}$

The existence of CO_3^* was first proposed by Katakis and Taube (1962). CO_3^* is a sufficiently long-lived species, with a life time of 10^{-11} to 10^{-12} seconds and it predissociates to $CO_2 + O(^{3}P)$. Low-temperature experimental studies (Jacox and Milligan, 1971; Moll et al., 1966; Weissberger et al., 1967) and *ab initio* calculations (Froese and Goddard, 1993) indicate that CO_3^* intermediate has C_{2v} symmetry with the structure shown in Figure 4.1. The transfer of "heaviness" from the O₃ to the CO₂ pool can also be imagined through $O(^{3}P)$, an ozone photolysis product at visible wavelength. However, the reactivity of this species is very low, and it was not considered effective for the isotopic transfer process. The reactions involved in the mechanism along with their rate coefficient are shown in Table 4.1.



Figure 4.1. Structure of CO_3^* intermediate with $C_{2\nu}$ symmetry (Froese and Goddard, 1993)

4.1.3 Previous Experimental Studies

So far, two experimental studies have been carried out (Wen and Thiemens, 1993; Johnston et al., 2000) to understand the isotopic exchange mechanism. In the first study, Wen and Thiemens (1993) photolyzed O_3 and CO_2 till most of the O_3 was decomposed to O_2 . They measured the isotopic composition of the final O_2 and inferred the composition of CO_2 assuming a mass balance. Based on these data they argued that the exchange does not occur through a simple statistical mixing between O-atom and CO_2 but involves a mass-independent fractionation presumably through CO_3^* . However, there were some limitations in the Wen and Thiemens (1993) experiments as far as application to stratosphere is concerned. The initial O_3 reservoir was not isotopically enriched and had a mass-dependent isotopic ratio contrary to what is observed in stratosphere. Also, the calculations were done assuming 100 % dissociation of O_3 , which was not strictly true (see Table 1 of their paper). Thus, even though their conclusions were correct one cannot use their data for quantitative derivation of $\delta^{17}O-\delta^{18}O$ slope in stratosphere.

In another set of experiments, Johnston et al., (2000) photolyzed O_2 and CO_2 of known isotopic composition with variable O_2/CO_2 reservoir ratio. They measured the two oxygen isotope ratios of the final CO_2 in cases where the CO_2/O_2 ratio was high (0.336 to 3.94). But they did not measure the $\delta^{17}O$ of CO_2 for those experiments where the ratio was low (~ 1/1000) as in the case of atmosphere. Moreover, in their experiments there was no O_3 at the beginning; the O_3 concentration built up slowly with corresponding increase in the extent of exchange of $O(^1D)$, derived from O_3 photolysis, with CO_2 . This

is unlike the case in stratosphere where there is always an ozone reservoir with enriched isotope ratios. Additionally, presence of oxygen reservoir introduces complications through its own quenching effect. Though the rate coefficient of quenching of $O(^{1}D)$ with O_{2} is 60 % of that with CO₂, since the O₂ reservoir was quite large, the quenching of $O(^{1}D)$ with O₂ became a major (unknown ?) factor in limiting the heavy oxygen isotope transfer to CO₂. In view of these uncertainties, it is not clear why the "high-CO₂" experiments of Johnston et al. (2000) did not reproduce the observed stratospheric $\delta^{17}O$ - $\delta^{18}O$ slope of more than one which prompted them to suggest that further experiments with "low-CO₂" are required to clarify the issue.

4.1.4 Numerical Model Studies

Two numerical model studies were carried by Yung et al. (1997) and Barth and Zahn (1997) to explain the laboratory data as well as stratospheric observations. Yung et al. (1997) applied a mixing model (first proposed by Yung et al., 1991) to explain the laboratory results of Wen and Thiemens (1993) following the chemical scheme given by the Equations 4.3 and 4.4. Yung et al. (1997) varied the isotopic composition of initial O₃ by 200 ‰ in their model and observed that at equilibrium the isotopic composition of O₂ reservoir varied only by 14 ‰. This insensitivity to the isotopic composition of the initial O_3 is attributed to the fact that the $O({}^1D)$, originating in O_3 photolysis, is guenched to $O({}^{3}P)$ during reaction with CO₂. This $O({}^{3}P)$ can either then react with O₃, forming two O₂ molecules, or it can combine with O₂, reforming O₃. Because the second reaction is orders of magnitude faster than the first, oxygen atoms cycle through O₃ many times before ending up as O₂. Yung et al. (1997) argued that this "wash-out" effect, combined with the fact that the CO₂ reservoir is much larger than O₂ reservoir (CO₂ : $O_2 = 20 : 1$), can explain the laboratory results of Wen and Thiemens (1993). Whereas the model is able to reproduce the experimental ¹⁸O results, it does not succeed in reproducing the ¹⁷O results. Incorporating the same enrichment mechanism into a 1-D atmospheric model Yung et al. (1997) predict a ¹⁸O enrichment profile in stratospheric CO₂; they found that, by doubling the eddy diffusion coefficient, the model predicted profile roughly matched the observations.

With different sets of assumptions Barth and Zahn (1997) tried to explain the laboratory data of Wen and Thiemens (1993) and the stratospheric data (Zipf and Erdman, 1994; Thiemens et al., 1995). As a first step, they constructed four different

vertical profiles (P1 to P4) of δ^{18} O of stratospheric ozone by using (i) the measured middle stratosphere profiles of Mauersberger (1981), (ii) setting the tropospheric value (δ^{18} O = 116 ‰) for the whole stratosphere, (iii) and (iv) using Irion et al. (1996) and Meier and Notholt (1996) data which show increasing δ^{18} O values in ozone above tropopause and reach a constant maximum value of δ^{18} O = 150 and 160 ‰ respectively above 40 km. Since little was known about the δ^{17} O in ozone, they assumed a fixed offset of $\Delta = \delta^{18}$ O – δ^{17} O = 34 ‰ using the tropospheric observations of Krankowsky et al. (1995). They justified this constant offset on the basis of laboratory data of Morton et al., 1990.

As the input of their model, they considered an enhanced isotopic composition of $O(^{1}D)$ compared to O_{3} since the isotopic composition of $O(^{1}D)$ produced by O_{3} photolysis should be modified by the mass dependent collision rates with N_{2} and O_{2} . They estimated 19 and 36 ‰ increase in $\delta^{17}O$ and $\delta^{18}O$ of $O(^{1}D)$ compared to the O_{3} composition for all the four profiles (P1 to P4).

They first run their model using the profiles P1 to P4 following the reaction scheme (given by Equations 4.3 and 4.4). While trying to match the measured altitudinal profile of δ^{18} O in CO₂, they realized the necessity of introducing an extra fractionation process in the model. They postulated that the isotopic exchange between O(¹D) and CO₂ operates faster for ¹⁷O than for ¹⁸O resulting in a fractionation. This fractionation (ϵ) was incorporated as a mass dependent fractionation during the formation of CO₃^{*}. Using the P4 profile and assuming $\Delta = 34$ ‰ and $\epsilon = (32 \pm 7)$ and (64 ± 14) ‰ for ¹⁷O and ¹⁸O respectively, they could reproduce the observations of Zipf and Erdman (1994) and Thiemens et al. (1995) for both δ^{18} O and δ^{17} O in stratospheric CO₂.

4.1.5 Motivation Behind the Present Work

The two aspects (isotopic enrichment and slope) of stratospheric CO_2 (as described in § 4.1.1) pose interesting challenge to atmospheric scientists. The motivation of the present work was to further constrain the factors affecting the isotope transfer in stratospheric CO_2 and especially check if the observed high slopes (Lämmerzahl et al., 2002) could be obtained in the laboratory using O_3 and CO_2 of relevant stratospheric isotopic composition. An important question is whether the proposed mechanism has the potential for preferential transfer of ¹⁷O relative to ¹⁸O from the ozone pool to the CO_2 pool.

4.2 ABOUT THE EXPERIMENT

The presence of a large oxygen reservoir in the experiments of Johnston et al. (2000) complicates the issue of isotopic transfer between CO_2 and O_3 pools through quenching of $O(^1D)$ by oxygen. Therefore, a simple experiment was designed to study oxygen isotope exchange process between CO_2 and $O(^1D)$ (derived from UV photolysis of ozone). Photolysis of a mixture of CO_2 (of mass dependent composition) and O_3 (of mass independent composition) was carried out for various periods (< 30 minutes) using appropriate UV wavelengths. The present experimental conditions are obviously not similar to that of stratosphere since a large oxygen reservoir is missing, but it was felt that the mechanism involved in the isotope transfer between these two stratospheric oxygen bearing species (O_3 and CO_2) can be better understood if other interfering effects are absent.

Two different sets of experiments were performed. In set I, photolysis of ozone of fixed isotopic composition with CO_2 of three distinctly different oxygen isotopic composition (in three different sub-sets) was done and, in set II, photolysis of CO_2 of fixed isotopic composition with ozone of nine different isotopic compositions was done.

4.2.1 Preparation of O₃ of fixed isotopic composition

Ozone was produced in a 5-liter spherical chamber fitted with a MgF₂ window by irradiating ultra-pure oxygen ($\delta^{18}O = 24.6 \%$, $\delta^{17}O = 12.5 \%$ with respect to V-SMOW) at 500 torr pressure with UV generated by a Hg resonance lamp (184 and 254 nm) driven by a micro-wave generator as described in Chapter II (§ 2.2.2). Photolysis was carried out for about six hours (irradiation time was decided based upon the previous experiments described in Chapter II (§ 2.2.2). After photolysis, the formed ozone was frozen by LN₂ and the oxygen pumped away till 2 mtorr pressure (vapor pressure of ozone at LN₂). A 1liter flask was connected to the 5-liter chamber and the formed ozone was equilibrated within the total volume (5 + 1 = 6 liters). After equilibration, the 5-liter chamber was isolated and the ozone within the 1-liter flask was collected in a molecular sieve with LN₂ and converted to oxygen (as described in § 2.2.2). The mass-spectrometric measurement of this aliquot of oxygen provides the isotopic composition of the ozone as well as the estimate of the remaining amount (see § 2.2.2 for more details) within the 5-liter chamber. The irradiation protocol (6 hrs with input power of 80 watts and reflected power 10 watts) was strictly maintained to ensure retrieval of essentially the same amount of ozone with nearly the same isotopic composition (~ 800 µmole with $\delta^{17}O = 110 \pm 4 \%$ and $\delta^{18}O = 124 \pm 2 \%$ wrt SMOW; the δ -values are always expressed wrt SMOW). Longer (~14 hrs) irradiation was done in two cases to get more amount of (~2000 µmole) ozone, the time being decided based on the production rate of ozone at 500 torr of O₂ pressure (2.5 µmole per min) for the particular experimental set up (see Chapter II for details).

4.2.2 Preparation of CO₂ and O₃ of different isotopic compositions

Four different isotopic compositions of CO₂ were used in the whole experiment. The primary CO₂ was a tank CO₂ (99.99 % pure) from Vadilal Gas Company, Ahmedabad (India) with isotopic composition of $\delta^{18}O = 17.40$ ‰ and $\delta^{17}O = 9.04$ ‰. This CO₂ was equilibrated with water of three different isotopic compositions: a) V-SMOW water ($\delta^{18}O = 0.0$ ‰ and $\delta^{17}O = 0.0$ ‰), b) South-Pole water ($\delta^{18}O = -45$ ‰ and $\delta^{17}O = -23.5$ ‰) and, c) SLAP water ($\delta^{18}O = -55$ ‰ and $\delta^{17}O = -28.5$ ‰). In each of the three cases, 1200 µmole of CO₂ was equilibrated for 2 days with 4 cc of water. After 2 days, CO₂ was extracted and cleaned by the usual procedure (passing repeated number of times through - 90°C slush). The three CO₂ gas samples made this way will be abbreviated as SM-CO₂, SP-CO₂ and SL-CO₂ respectively.

The strategy to produce ozone of different isotopic composition was based on the fact that UV dissociation of ozone (see Chapter III for more details) enriches the left-over ozone pool. The steps taken were as follows: the initial ozone was produced as described in the previous section (§ 4.2.1). This ozone was dissociated to the extent of 30 to 97 % by a Hg lamp and the left-over ozone was separated cryogenically from the product oxygen. The left-over ozone in the reaction chamber was treated as the initial ozone for the exchange with CO₂. The amount of ozone left in the chamber was, of course, not constant but decreased with increasing enrichment. The maximum enrichment observed was about 80 and 50 ‰ with respect to the initial ozone (124 and 110 ‰) in δ^{18} O and δ^{17} O respectively at the dissociation level of ~ 97 %, which reduces the ozone reservoir to about 20 µmole.

4.2.3 CO₂ – O(¹D) Isotopic Exchange

The isotopic exchange was carried out by photolysis of a $CO_2 - O_3$ mixture for a certain time. Two sets of experiments were performed. The first set of experiment

consisted of three subsets with ozone of fixed isotopic composition and CO₂ of three distinctly different compositions as follows: sub-set Ia: SM-CO₂ with $\delta^{17}O = 20.35 \%$ and $\delta^{18}O = 39.33 \%$, sub-set Ib: SP-CO₂ with $\delta^{17}O = 2.15 \%$ and $\delta^{18}O = 4.09 \%$, and sub-set Ic: SL-CO₂ with $\delta^{17}O = -5.55 \%$ and $\delta^{18}O = -0.91 \%$. In each case, 100 µmole of CO₂ was taken in the 5-liter chamber from the respective reservoirs and the same Hg lamp was used for photolysis of the mixture. The time of photolysis was varied (up to 25, 23 and 26 minutes for set Ia, Ib, and Ic respectively) to get a wide range of enrichment in CO₂.

In the second set of experiment, the amount (100 µmole) of CO₂ (called V-CO₂ hereafter) as well as its isotopic composition ($\delta^{18}O = 17.28$ ‰ and $\delta^{17}O = 8.98$ ‰) was kept constant. The isotopic composition of O₃ was varied by the process described in the previous section (§ 4.1.2) from 124 to 205.7 ‰ in $\delta^{18}O$. The corresponding change in the amount of O₃ was from 300 µmole to 30 µmole. Depending upon the initial O₃ amount, photolysis time (estimated beforehand) was varied in such a way that 80 to 90 % of O₃ dissociation occurs during the photolysis.

After photolysis of the $CO_2 - O_3$ mixture, the product O_2 , final CO_2 and left-over O_3 were separated following the procedure of Johnston et al (2000). CO_2 and left-over O_3 were trapped at the bottom of the reaction chamber by LN_2 and the product oxygen was collected in a sample bottle with molecular sieve with LN_2 . $CO_2 - O_3$ mixture was collected in a 50 cc bottle (containing nickel flakes, properly degassed beforehand at ~ 200° C) with LN_2 . After the total transfer, the nickel-containing bottle was closed and it was heated up mildly for about 20 minutes. Mild heating in the presence of Nickel decomposes O_3 to O_2 (Johnston et al., 2000). After 20 minutes, CO_2 and O_2 (from decomposed O_3) were collected cryogenically one after another.

4.2.4 Isotopic Measurement of Oxygen and CO₂

The isotopic measurements were done in GEO 20-20 (Europa Scientific) massspectrometer. For oxygen isotopic measurement, the sample bottle used to collect oxygen and ozone (converted to oxygen) samples were of 1 cc with few pellets of molecular sieve in it. The major beam (mass 32) was calibrated beforehand with different amounts of oxygen samples using the same sample bottles. The calibration was used to estimate the amount of sample (as described in § 2.2.2). The estimated uncertainty in δ -values is 0.1 ‰ for δ^{18} O and 0.2 ‰ for δ^{17} O based on a few repeat measurements. The oxygen isotopic (δ^{18} O and δ^{17} O) measurements of CO₂ are not straight forward due to the fact that the isotopomers with mass 45 represents ${}^{16}O{}^{13}C{}^{16}O$ as well as ${}^{17}O{}^{12}C{}^{16}O$. The $\delta^{17}O$ and $\delta^{18}O$ of the final CO₂ were determined using the value of $\delta^{45}R$ and $\delta^{46}R$ and assuming invariance of $\delta^{13}C$ before and after the photolysis since there is no loss or gain of carbon in the exchange process (Johnston et al., 2000). The measured ratios of the CO₂ isotopomers can be expressed in terms of the individual oxygen and carbon isotopic ratios as follows:

$$R^{45} = (\text{molecules with mass 45})/(\text{molecules with mass 44})$$

= ([¹⁶O¹³C¹⁶O] + [¹⁶O¹²C¹⁷O] + [¹⁷O¹²C¹⁶O])/ [¹⁶O¹²C¹⁶O]
= R¹³ + 2(R¹⁷) (4.5)

and,
$$R^{46} = (\text{molecules with mass 46})/(\text{molecules with mass 44})$$

= $(\Gamma^{16}O^{12}C^{18}O) + (\Gamma^{18}O^{12}C^{16}O) + \Gamma^{16}O^{13}C^{17}O) + \Gamma^{17}O^{13}C^{16}O) + \Gamma^{17}O^{12}C^{17}O)/(16)$

$$[^{16}O^{12}C^{16}O]$$

$$= 2(R^{18}) + 2(R^{13}R^{17}) + (R^{17})^2 \approx 2(R^{18})$$
(4.6)

(Note the symmetry factor 2 to convert atomic ratios to the molecular ratios)
so,
$$\delta_{std}^{45} X = (\mathbb{R}^{45X} / \mathbb{R}^{45std} - 1) \ge 10^3 = \{[(\mathbb{R}^{13} + 2\mathbb{R}^{17})^X / (\mathbb{R}^{13} + 2\mathbb{R}^{17})^{std}] - 1\} \times 10^3$$
 (4.7)
and, $\delta_{std}^{46} X = (\mathbb{R}^{46X} / \mathbb{R}^{46std} - 1) \ge 10^3 = \{[(2\mathbb{R}^{18})^X / (2\mathbb{R}^{18})^{std}] - 1\} \times 10^3$ (4.8)
By simple algebra,

$$\delta_{std}^{13} X = (1+2Z) \, \delta_{std}^{45} X + 2Z \, \delta_{std}^{17} X \tag{4.9}$$

where, $Z = (R^{17}/R^{13})^{std} = 15.38315937$ [for our tank CO₂, the mass-spectrometer standard]

and,
$$\delta_{std}^{18} X = \delta_{std}^{46} X \tag{4.10}$$

In the course of oxygen isotopic measurements in CO₂, δ_{std}^{45} and δ_{std}^{46} were measured and using equations (4.9) and (4.10) and considering no change in ¹³R in the process, δ^{17} O and δ^{18} O of the sample CO₂ were calculated.

For some cases, the isotopic ratios of all the three final products were measured to ensure the validity of the O-isotope mass balance. Considering transfers of gases, taking of aliquots, and several freezing and thawing the uncertainty in δ -values are little higher than that of direct oxygen measurements; we estimate an overall uncertainty of 0.2 ‰ for δ^{18} O and 0.5 ‰ for δ^{17} O for the final data based on a few repeat measurements.

4.2.5 Test of Recovery Yield of CO_2 and Blank $\delta^{13}C$

In view of the difficulties experienced by Johnston et al. (2000) in getting proper CO_2 yield in their "low- CO_2 " experiments; great care was taken to perform these experiments. All stopcocks were of "Viton" O-ring type and no grease was used. Three blank experiments were done where CO_2 and O_3 were mixed and separated after keeping for an hour without photolysis. The isotopic composition of this CO_2 (treated as blank) was determined and shown in Table 4.2.

Table 4.2. δ^{45} and δ^{46} of V-CO₂ and CO₂ from three blank experiments when V-CO₂ was mixed with ozone of enriched oxygen isotopic composition and separated without photolysis (see text for details). The analysis is done w.r.t. a machine CO₂ reference having $\delta^{17}O = 9.04$ ‰ and $\delta^{18}O = 17.40$ ‰ with respect to SMOW. The δ -value differences between the mean of the blanks values and V-CO₂ (i.e., $\Delta\delta^{45} = 0.122$ ‰ and $\Delta\delta^{46} = 0.410$ ‰) are added with all δ^{45} and δ^{46} measurements as blank corrections.

CO ₂ Samples	δ^{45}	δ^{46}
V-CO ₂	-0.037	-0.119
Blank-1	-0.138	-0.732
Blank-2	-0.113	-0.405
Blank-3	-0.226	-0.450
Mean	-0.159	-0.530
δ-difference	-0.122	-0.41

The blank data show that there is slight decrease in δ -values of CO₂ due to mixing with O₃ and subsequent cryogenic separation. This decrease does not show up in the yield value, which was always close to 100 % (within 1 to 2 % which is the estimated experimental uncertainty in the yield measurement from mass-44 beam current). A small positive correction was applied to the measured δ^{45} and δ^{46} based on the mean blank values, i.e., $\delta^{45} = 0.12$ and $\delta^{46} = 0.41$. These corrections are well within the experimental uncertainties in the δ -values of CO₂.

4.3 **RESULTS**

The results of the photolysis experiments pertaining to sets Ia, Ib and Ic are given in Table 4.3 and show that the final CO_2 is enriched in both ¹⁷O and ¹⁸O in all the cases

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and the enrichments increase with time of exposure. However, when the time is very large so that there is significant recycling of ozone the enrichment attains nearly steady value (see last two entries in set I, Table 4.3), which is reflected by the comparatively lower values of increase in ¹⁸O enrichment. We did not investigate whether in each individual set the steady state was achieved or not since our objective was to check the slope value and this was nearly independent of the photolysis time for a given set of CO₂ and O₃. Johnston et al. (2000) also found that the slope does not change even though the enrichment initially increases with time. The maximum ¹⁸O-enrichments obtained are 11.4, 20.6 and 22.2 ‰ respectively for the three sets of experiments whereas the respective enrichments in ¹⁷O are 19.3, 29.5 and 27.3 ‰. It is interesting to note that the enrichment in ¹⁷O is always more than that in ¹⁸O and this is clearly reflected in a plot of $\delta^{17}O$ vs. $\delta^{18}O$ (Figure 4.2).

In these experiments the isotopic composition of ozone is always kept constant (at $\delta^{17}O = 110.4$ and $\delta^{18}O = 124.9$ ‰) near the value observed in the stratosphere at the altitude of about 32 km (Mauersberger et al., 2001) (note that the values reported by Mauersberger et al., 2001 are with respect to atmospheric oxygen and the values reported here are with respect to SMOW). It is also seen that the slope relating $\Delta\delta^{17}O$ and $\Delta\delta^{18}O$ of the final CO₂ changes depending on the initial composition of CO₂. Slope values of 1.29 \pm 0.04, 1.52 \pm 0.04 and 1.81 \pm 0.06 are obtained for composition of SL-CO₂ (-5.55, -10.91), SP-CO₂ (2.15, 4.09) and SM-CO₂ (20.35, 39.33), respectively i.e. the slope increases as the δ -values of the initial CO₂ increase and get closer to that of the ozone. Interestingly, the slope obtained from set Ia (with SM-CO₂ of tropospheric composition) experiment is close to the observed stratospheric slope 1.71 (Lämmerzahl et al., 2002).

The results for the set II experiments are given in Table 4.4. They show that the isotopic composition of final CO₂ depends on the initial ozone composition; higher the enriched in the initial ozone, more is the enrichment in the final CO₂ (keeping the photolysis time constant at around 3 minutes). The initial ozone composition varied from 124.9 to 205.7 ‰ for δ^{18} O and from 110.4 to 159.4 ‰ for δ^{17} O. The two variations are related by a slope value of nearly 0.6. It is quite expected since the dissociation process results in such a slope for the left-over ozone (see chapter III; Chakraborty and Bhattacharya, 2002). On the other hand, this change in initial ozone composition results in a change of 9.8 ‰ in δ^{18} O and 18.5 ‰ in δ^{17} O of final CO₂. The isotopic composition

of final CO₂ shows a linear trend of increase with a slope ($\Delta \delta^{17}O/\Delta \delta^{18}O$) of 1.94 as shown in Figure 4.3.



Figure 4.2. The $\delta^{17}O-\delta^{18}O$ plot showing the evolution of isotopic composition of CO_2 as a result of exchange with $O({}^{1}D)$ derived from isotopically enriched ozone under UV exposure (initial compositions of both the gases are shown). With the increase in photolysis time the CO_2 gets more and more enriched in heavy isotope ratios but the change is higher in ${}^{17}O/{}^{16}O$ compared to ${}^{18}O/{}^{16}O$. The three different CO_2 gases (SM-CO₂, SP-CO₂ and SL-CO₂ corresponding to set Ia, Ib and Ic respectively) evolve along three enrichment lines with slopes 1.81 ± 0.06 , 1.52 ± 0.04 and 1.29 ± 0.04 respectively. The slope for SM-CO₂ (similar in composition to tropospheric CO_2) is close to the one (1.71) observed in stratosphere. The line labeled as MFL denotes the terrestrial mass fractionation line (slope 0.5). The error of each data point is comparable to its size.

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Table 4.3. Oxygen isotopic composition of CO_2 after exchange with $O(^1D)$ derived from UV photolysis of isotopically enriched O_3 in the set Ia, Ib and Ic experiments using three different initial CO_2 (SM-CO₂, SP-CO₂ and SL-CO₂) but same composition of O_3 . The amount of O_3 and CO_2 were 800 and 100 µmole respectively except in two cases as shown. The CO_2 gets enriched after exchange with slopes relating the two isotopic enrichments higher than one (see text). Set Ia yields slope value of 1.81 ± 0.06 (obtained from Figure 1), which is similar to that found in stratosphere.

	Initial CO ₂		Initial O ₃ ***		Amount	Amount	Photolysis	Final CO ₂ ^{##}		Enrichment in CO ₂		Slope ^{**}	Rate of
Set No.	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	of CO ₂	of O ₃	Time	$\delta^{17}O$	$\delta^{18}O$	$\Delta \delta^{17} O$	$\Delta \delta^{18} O$	$(\Delta \delta^{17} O/$	Increase in ¹⁸ O
	(‰)	(‰)	(‰)	(‰)	(µmole)	(µmole)	(t- min)	(‰)	(‰)	(‰)	(‰)	$\Delta \delta^{18}$ O)	Enrichment
	. ,								× /	. ,	~ /	,	$(\Delta^{18}O/t \%/min)$
					100	800	9	28.0	42.7	7.6	3.8	1.90	0.42
					100	800	12	31.2	44.8	10.8	5.8	1.86	0.48
Ia	20.35	39.33	110.4	124.9	100	800	15	35.5	46.8	15.1	8.0	1.83	0.53
$(SM-CO_2)$					100	800	25	41.6	50.7	21.2	11.8	1.79	0.47
					(180)•	800	130	30.0	44.1	9.6	5.2	1.83	$(0.04)^{\#}$
					100	800	360	35.7	46.9	15.3	8.1	1.85	$(0.02)^{\#}$
						800	6	10.5	9.6	8.4	5.5	1.52	0.92
Ib	2.15	4.09	110.4	124.9	100	800	7	11.5	10.2	9.3	6.1	1.52	1.33
$(SP-CO_2)$						800	10	14.5	12.4	12.3	8.3	1.48	1.23
						$(2000)^{*}$	23	35.2	25.8	33.1	21.7	1.52	0.94
						800	13	11.3	1.8	16.8	12.7	1.32	0.97
Ic	-5.55	-10.91	110.4	124.9	100	800	20	14.6	4.6	20.2	15.6	1.30	0.78
$(SL-CO_2)$						$(2000)^{*}$	26	23.7	11.7	29.3	22.7	1.29	0.87

^{***} The estimated uncertainty in δ -values of ozone is 0.2 % for δ^{18} O and 0.5 % for δ^{17} O based on few repeat measurements.

^{##} The estimated errors of oxygen isotopic measurement in final CO₂ are 0.5 and 1.0 ‰ in δ^{18} O and δ^{17} O respectively.

^{**} After propagation of error, the uncertainty in individual slope value is less than 10 %.

[•] In this case the initial amount of CO₂ was higher.

[#] In these cases the time was very large allowing for significant recycling of ozone.

^{*} In these cases the initial amount of ozone was higher.

Table 4.4. Experimental results for the exchange reactions between CO_2 and O_3 for the set II experiments. The CO_2 isotopic composition (V-CO₂) was kept constant whereas the isotopic composition of ozone was varied. The amount of CO_2 used for all the experiments was 100 µmole. The amount of ozone was not constant throughout but varied from 300 to 30 µmole depending upon its composition (higher the enrichment lower was the amount). All the oxygen isotopic data are expressed with respect to SMOW.

Initia	Initial CO ₂ Initial Ozone ^{**}		Photolysis	Product Oxygen**		Left-over	· Ozone ^{**}	Final CO ₂ [#]		
$\delta^{17}O$ (‰)	$\delta^{18}O(\%)$	δ ¹⁷ O (‰)	$\delta^{18}O(\%)$	Time (min)	δ ¹⁷ O (‰)	$\delta^{18}O$ (‰)	δ ¹⁷ O (‰)	$\delta^{18}O(\%)$	$\delta^{17}O(\%)$	$\delta^{18}O$ (‰)
8.98	17.28	110.4	124.9	3.0	92.0	109.0	118.0	137.1	18.3	21.4
8.98	17.28	112.2	131.5	3.5	102.7	118.4	125.4	152.8	21.2	22.4
8.98	17.28	109.5	132.2	3.5	101.4	118.3	120.1	149.3	32.8	29.1
8.98	17.28	117.7	141.0	4.0	108.9	128.2	128.1	158.4	33.8	29.4
8.98	17.28	119.4	142.0	3.0	107.2	125.9	128.1	156.0	26.8	25.0
8.98	17.28	123.7	150.3	3.5	114.0	136.3	134.5	167.2	24.2	24.0
8.98	1728	128.8	156.5	3.5	118.7	141.6	138.1	172.5	23.8	23.4
8.98	17.28	145.5	184.5	2.3	127.4	154.0	142.5	177.0	26.2	25.5
8.98	17.28	159.4	205.7	2.5	138.7	166.7	NM^*	NM^*	36.8	31.2

^{**} The estimated uncertainty in δ -values of ozone (measured as oxygen) is 0.2 % for δ^{18} O and 0.5 % for δ^{17} O based on few repeat measurements.

[#] The estimated errors of oxygen isotopic measurement in final CO_2 are 0.5 and 1.0 % in $\delta^{18}O$ and $\delta^{17}O$ respectively.

^{*} NM denotes not measured. As the amount was negligible it was not possible to measure the amount as well as the isotopic composition of the left-over ozone for that particular experiment.



Figure 4.3. A three-isotope plot showing changes in δ -values of a fixed CO_2 (V- CO_2) as a result of exchange with $O({}^{1}D)$ derived from ozone of different initial compositions. As the isotopic composition of initial ozone increases, the enrichment in corresponding final CO_2 also increases. The different ozone samples were taken in such a way that they lie along a line of slope 0.63 close to the value in ozone samples from various stratospheric levels. The corresponding CO_2 points lie along a line of slope 1.71 found in CO_2 samples obtained from various stratospheric levels. The line labeled as MFL denotes the terrestrial mass fractionation line (slope 0.52). The error of each data point is comparable to its size.

4.4 DISCUSSION

According to the proposed (Yung et al., 1991) pathway of isotopic transfer from the ozone pool to the CO_2 pool, the exchange takes place through $O(^1D)$, a UV dissociation product of O_3 . Therefore, to gain insight in the process, it is essential to estimate the isotopic composition of $O(^1D)$.

4.4.1 Isotopic Composition of O(¹D)

The isotopic composition of $O(^{1}D)$ is derived based on the assumption that only terminal atoms in the ozone molecule can be broken to form $O(^{1}D)$ during photodissociation of ozone. If ozone is isotopically enriched and the enrichment is mainly due to concentration of the heavy isotope in the asymmetric species it is apparent that the $O(^{1}D)$ reservoir would have enrichment higher than that of progenitor ozone since asymmetry is caused by placement of a heavy isotope in the terminal position. The derivation of the isotopic composition of $O(^{1}D)$ follows closely the steps outlined by Janssen et al. (2001) to calculate the enrichment in $^{50}O_{3}$ and is given in Chapter V (§ 5.4.1). Following the definition of enrichment, E (‰) = [($^{M}O_{3}/ {}^{48}O_{3}$) measured / ($^{M}O_{3}/ {}^{48}O_{3}$) calculated -1] × 1000 ‰, and the rate constants of different ozone forming channels, the isotopic composition of the asymmetric ozone is calculated and we assume that the $O(^{1}D)$ has the same composition as that of the asymmetric ozone.

It is seen that under the terminal atom source assumption $O(^{1}D)$ has an enriched composition ($\delta^{17}O = 150 \%$ and $\delta^{18}O = 150 \%$) relative to total initial oxygen (see Chapter V, § 5.4.1). For our experiment, the oxygen has the composition of $\delta^{17}O = 12.48$ ‰ and $\delta^{18}O = 24.58$ ‰ with respect to SMOW. Therefore, $O(^{1}D)$ will have the composition, $\delta^{17}O = 164.1 \%$ and $\delta^{18}O = 178.3 \%$ with respect to SMOW.

It is logical to assume that this transient reservoir of $O(^1D)$ is further modified by mass dependent collision rate of $O(^1D)$ atoms with CO₂ molecules. In a simple collision model the rate coefficient for a chemical reaction is inversely proportional to $\sqrt{\mu}$ (where μ is the reduced mass). For simplicity we can think of this as a combination of two effects arising from two types of collisions: (i) collision between dominant CO₂ species $(^{16}O^{12}C^{16}O)$ and ^{16}O , ^{17}O and ^{18}O isotopes and (ii) collision of ^{16}O atoms with CO₂ species of mass 44, 45 and 46. The first type would yield a modified $O(^{1}D)$ composition which is effective in collision with CO₂ while the second type would yield a modified CO₂ composition which is effective during collision with $O(^{1}D)$.

Following this argument, the calculated reaction rate ratios between the colliding pairs $CO_2 - {}^{16}O({}^{1}D)$ and $CO_2 - {}^{17}O({}^{1}D)$ and $CO_2 - {}^{18}O({}^{1}D)$ are 0.977 and 0.957 respectively. Therefore, the effective $O({}^{1}D)$ composition would be $\delta^{17}O = 138.1$ ‰ and $\delta^{18}O = 127.6$ ‰ with respect to SMOW. Similarly, the CO_2 composition will get modified by the factors 0.997 and 0.994 for ${}^{45}R$ and ${}^{46}R$ respectively.

4.4.2 Failure of Two-Component Mixing

A simple mixing of modified SM-CO₂ ($\delta^{17}O = 17.32$ ‰ and $\delta^{18}O = 33.29$ ‰) and modified O(¹D) composition ($\delta^{17}O = 138.1$ ‰ and $\delta^{18}O = 127.6$ ‰) representing the end members of set Ia experiment would result in slope value of 1.28 in the scrambled CO₃^{*}

(Figure 4.4). During formation of CO_2 and O-atom from CO_3^* , a mass dependent fractionation with lighter O-atom is expected. Therefore, the oxygen isotopic composition of the product CO₂ would lie over the secondary fractionation line (shown by the line BC in Figure 4.4) and hence, the slope value of the final CO₂ would be lower than 1.28 (the value for the scrambled CO_3^*). This limit of the slope value of 1.28 is drastically different from what is observed in set Ia experiment (1.81, Figure 4.2). A similar mixing calculation yields slopes of 1.07 and 1.02 for modified CO₂ compositions of set Ib ($\delta^{17}O$ = -0.62 ‰ and $\delta^{18}O$ = -1.75 ‰) and set Ic ($\delta^{17}O$ = -8.50 ‰ and $\delta^{18}O$ = -16.66 ‰) experiments. The corresponding observed slopes for set Ib and set Ic experiments are 1.52 and 1.29 clearly demonstrating preferential transfer of ¹⁷O (relative to ¹⁸O) to the CO₂ pool. It is also interesting to note that the value of the slope (1.81) obtained for typical stratospheric O₃ and CO₂ composition (set Ia) agrees well with the observed value (1.71) of Lämmerzahl et al. (2002). This agreement between the observed and experimental slopes is not accidental. The two end-member (CO_2 and $O(^{1}D)$) compositions along with the applicable fractionation related to isotopic transfer decides the slope of the final CO₂ evolution line. In the stratosphere, the CO_2 concentration is much higher than O_3 concentration and the interaction time is not only longer (year scale) but also cumulative as the CO₂ ascends upwards. Consequently, the isotopic enrichment increases continuously with altitude due to increase in the time of interaction. A similar effect of enrichment increase with irradiation time is seen in the present laboratory experiment.

A major difference between the stratosphere and the present laboratory condition is the possibility of additional quenching of $O(^1D)$ in stratosphere by other major species like N₂ and O₂. This quenching would diminish the available $O(^1D)$ reservoir and consequently the isotopic enrichment imparted to CO₂. However, this large magnitude of quenching in stratosphere is compensated by long interaction time (a few years) between CO₂ and ozone-derived $O(^1D)$ which makes it possible to achieve large isotopic enrichment in CO₂ from a rather small reservoir of ozone. On the other hand, reasonable enrichment in CO₂ could be attained in the laboratory in short time by having much larger amount of highly enriched ozone.



Figure 4.4. Schematic representation of two component mixing (for set Ia) using the effective $O({}^{1}D)$ composition as one end member and modified SM-CO₂ composition (point A) as other end member. B represents the composition of CO_{3}^{*} obtained by simple mixing of these two components. The slope of this mixing line (represented by AB) is 1.28. During the breakdown of CO_{3}^{*} product CO_{2} is expected to incorporate the heavy isotopes preferentially and fractionate along the secondary fractionation line. C represents the corresponding CO_{2} composition (assuming equilibrium fractionation) and AC represents the corresponding CO_{2} evolution trend with a slope less than that of the simple mixing line AB i.e., 1.28. In contrast, the observed trend is 1.81 demonstrating ¹⁷O preference to CO_{2} in such exchange process.

4.4.3 Previous Results in the Light of Present Experiment

A re-plot (Figure 4.5) of Wen and Thiemens (1993) data of final CO_2 compositions (see Table 1 of their paper) along with their initial CO_2 and O_3 compositions in the same format as in Figure 1 shows that the final CO_2 evolves along a line with a slope value of 0.97 during isotopic exchange. They used ozone and CO_2 of mass dependent composition and it can be assumed that the derived $O(^1D)$ from O_3 photolysis would be of the same composition as that of ozone (since the isotopic distribution within ozone molecule would be statistical in this case). Since the modification of the compositions of the two reservoirs due to collisional effect is mass

dependent, the effective $O(^{1}D)$ ($\delta^{17}O = -1.37$ ‰ and $\delta^{18}O = -3.47$ ‰) as well as the modified CO_{2} ($\delta^{17}O = 0.107$ ‰ and $\delta^{18}O = -0.76$ ‰) compositions would essentially lie over the mass fractionation line with a slope value of 0.52 (the modified $O(^{1}D)$ and CO_{2} compositions are calculated following the arguments of § 4.4.1). A simple mixing calculation (similar to that described for the present study in § 4.4.2), using these two end-member compositions, i.e., effective $O(^{1}D)$ and initial CO_{2} yields the same slope as that of mass fractionation line for the scrambled CO_{3}^{*} . Since the second stage of fractionation during separation of CO_{3}^{*} to form CO_{2} is also mass dependent, the composition of final CO_{2} would essentially lie over the same mass fractionation line. Therefore, this analysis reflects preferential transfer of ^{17}O to the CO_{2} pool in Wen and Thiemens' experiment as observed in the present experiments.



Figure 4.5. Three-isotope plot of the data from the experiment of Wen and Thiemens (1993) showing the compositions of initial CO_2 and O_3 and the progression of final CO_2 compositions (data taken from their Table 1 expressed with respect to SMOW) as a result of photolysis of $CO_2 - O_3$ mixture. The photolysis was done till O_3 was completely decomposed to O_2 . The expected slope based on similar considerations as in Figure 4.4 is 0.52 (i.e. mass-dependent) in contrast to the observed slope of 0.97 again indicating preferential ¹⁷O transfer in exchange of CO_2 with $O({}^1D)$.

For long UV exposure, Wen and Thiemens (1993) observed negligible change in the composition of product oxygen even with large variation in the initial ozone composition. This phenomenon was interpreted as a "wash-out" effect by Yung et al. (1997) signifying numerous recycling of oxygen atoms through ozone and oxygen molecular reservoirs in the presence of a large CO_2 reservoir, which destroys the isotopic signature of the original O_3 . In contrary, no such situation arises in the present experiment since the recycled ozone component is negligible. The recycle ozone component is estimated from the experimental results of Chapter II (§ 2.4.7), which shows that at the most 0.2 µmole of ozone can be regenerated from product oxygen photolysis due to short photolysis time (~ 25 minutes) (also see Bhattacharya et al., 2002).

4.4.4 Supportive Evidence for Preferential ¹⁷O Transfer

Another way to look at the results of the present study is to plot the compositions of the left-over ozone and product oxygen along with initial and final CO₂ compositions (Figure 4.6). The left-over ozone and the product oxygen follow two different slopes having values of 0.63 and 0.98 respectively (with respect to initial ozone composition), which indicates clearly the preferential transfer of ¹⁷O to CO₂. It is interesting to note that in the case of pure dissociation of ozone, the left-over ozone and product oxygen compositions lie along the same line in the three isotope plot i.e. they follow the same slope (due to mass balance), whereas in the presence of CO₂ the oxygen points deviate and plot along a line of higher slope due to depletion in ¹⁷O which end up in CO₂. This provides a supportive evidence for the preferential transfer of ¹⁷O from ozone pool to CO₂ pool. The slope (0.63) in left-over ozone has been explained in Chapter III, § 3.2.4 (also see Chakraborty and Bhattacharya, 2002) arising out of a combination of two effects: pure photo-dissociation of ozone (leading to a slope of 0.5).

4.4.5 Results of Set II Experiments: Connection to the Stratosphere

The data from the set II experiments also reflect the same ¹⁷O preference over ¹⁸O during isotopic exchange. In this set, nine identical samples of CO₂ (100 μ mole in size and having same isotopic composition) are made to exchange with nine different ozone samples having widely different isotopic composition but mutually connected along a line of slope 0.63. It is seen that the enrichment transferred to CO₂ reflects that in the

corresponding ozone. If the ozone is more enriched so is the corresponding CO_2 . Interestingly, all the CO_2 points (Figure 4.3) lie along a line of slope 1.94 with corresponding ozone points along a line of slope 0.63. These results cannot be directly compared with those of sets Ia, Ib and Ic, since it demonstrates a different experimental feature. While data from sets Ia, Ib and Ic show the time variation of enrichment with two fixed end members, set II data show the effect in enrichment with a fixed CO_2 end member and variable ozone composition.



Figure 4.6. A comprehensive three-isotope plot for set I experiment showing the interrelation among the compositions of CO_2 , O_3 and product O_2 . The left-over ozone and the product oxygen follow two different slopes 0.63 and 0.98 respectively (with respect to initial ozone composition), in contrast to the case of simple dissociation of ozone when the left-over ozone and product oxygen follow the same slope of 0.63. This demonstrates a clear depletion of ¹⁷O in the product oxygen and preferential transfer of ¹⁷O to the CO_2 after exchange with $O({}^{1}D)$. The error of each data point is comparable to its size.

In the stratosphere, with increasing altitude, oxygen isotopic enrichment in both CO_2 and ozone increases progressively (Lämmerzahl et al., 2002). Interestingly, the enrichment pattern has slope values of 1.71 and 0.62 respectively close to the pattern found in set II data and also in set Ia results. Though the initial CO_2 composition ($\delta^{17}O = 8.98 \%$ and $\delta^{18}O = 17.28 \%$) and the variation in initial ozone composition (124.9 to 205.7 ‰, i.e. about 80 ‰ in $\delta^{18}O$) in the laboratory experiment is not representative of

the stratospheric values (the isotopic composition of stratospheric ozone varies only by about 30 ‰ in δ^{18} O), the slope values observed in these experiments are quite similar to that of stratospheric values (compare stratospheric values with the slopes shown in Figures 4.3 and 4.6 for the laboratory results for set II and Ia respectively). This establishes an invariant isotopic relationship between these two interacting oxygen reservoirs (ozone and CO₂). The stratospheric situation can be envisaged as a combination of the effects arising out of the two types of experiments – one dealing with the time variation and the other dealing with the enrichment variation.

Though the oxygen isotopic composition of CO₂ used in set Ia ($\delta^{17}O = 20.35$ and $\delta^{18}O = 39.33 \%$) is heavier compared to that used in set II ($\delta^{17}O = 8.98$ and $\delta^{18}O = 17.28 \%$), the observed slope value of set Ia (1.81) is lower compared to set II (1.94). However, the initial ozone composition of set II (varied from 124.9 to 205.7 ‰ in $\delta^{18}O$, Table 4.4) is heavier than that of set Ia ($\delta^{18}O = 124.9 \%$, Table 4.3). Therefore, the noticeable point from the combined result of these two sets of experiments is that the slopes in final CO₂ increases with the increase in the initial ozone compositions. In the lower stratosphere the observed variation in isotopic composition of ozone is about 95 to 135 ‰ (in $\delta^{18}O$ with respect to SMOW) (Mauersberger et al., 2001), which is lower compared to that used in sets Ia and II. Hence, with this lower ozone composition, the lower stratospheric slope (1.71) can be reproduced with SM-CO₂ (equivalent to tropospheric CO₂). More discussion about this issue will be presented in Chapter V.

4.4.6 Preferential ¹⁷O Transfer to CO₂

The following scenario is envisaged to explain the observed anomalous ¹⁷O enrichment in CO₂ during exchange with O(¹D). The UV photolysis of the CO₂ – O₃ mixture for certain duration of time produces O(¹D) continuously. As the quantum yield of O₃ photo-dissociation (at < 315 nm) is unity (Matsumi et al., 2002), every photon, when absorbed, leads to one O(¹D) atom and one O₂ molecule. As O(¹D) is a very reactive species it quenches quickly to O(³P) soon after its formation by interaction with product O₂ and CO₂ with high rate coefficients (4.0 x 10⁻¹¹ cm³ s⁻¹ and 1.1 x 10⁻¹⁰ cm³ s⁻¹ respectively). Therefore, the CO₂ molecules continuously interact with newly formed O(¹D) atoms forming CO₃* complexes, which dissociate to CO₂ and O(³P) within its short lifetime (~10⁻¹¹ s) . It implies that a fraction of the CO₂ molecules in the system are continuously modified by this process and the total CO₂ is a mixture of the CO₂

molecules which interacted with $O(^{1}D)$ and those which did not. During the above mentioned processes, the oxygen isotopic composition of the final CO₂ is determined by that of $O(^{1}D)$ and fractionation associated with quenching of $O(^{1}D)$ by CO₂ through formation and dissociation of CO₃^{*}.

The reason for ${}^{17}O$ selectivity in CO₂ during quenching via CO₃^{*} formation/dissociation is not clear but can be speculated based on a few previous studies (Zahr et al., 1975; Harding et al., 1988; Bhattacharya et al., 2000). It is known that the quenching of $O(^1D)$ by di and tri-atomic molecules such as N_2 , O_2 , CO and CO_2 is extremely efficient. Collision of these molecules with $O(^{1}D)$ excites sufficient rotation and vibration in them on a strongly attractive singlet potential energy surface through formation of a collision complex. 1.97 eV energy of the $O(^{1}D)$ atom is transferred to the complex molecule by this process and it is converted to $O(^{3}P)$ on a dissociating triplet surface. The crossing for singlet to triplet surface is mediated by spin-orbit coupling which is normally weak. But in case of a collision complex with small but finite life-time the crossing point is traversed many times leading to sizeable quenching cross-section. For the present case, ab initio calculations (Froese and Goddard, 1993) predict existence of a low-lying bound region of the singlet potential energy surface (corresponding to $O(^{1}D) + CO_{2}$ collision), where the CO_{3}^{*} formation takes place. In this region, an intersystem crossing to the triplet surface may occur to form the $O(^{3}P) + CO_{2}$ as dissociation products. Since the vibrational frequencies of the isotopomers of CO₂ are different, it is possible to imagine that a ¹⁷O containing CO₂ molecule has a favorable disposition in the region of cross-over due to a combination of rotational and vibrational energies accounting for major part of the 1.97 eV energy of the O(¹D). In effect, this will result in slightly more rapid quenching of a 17 O containing CO₃^{*} when the 17 O goes to the CO₂ molecule in a process mimicking resonant absorption. A schematic diagram showing such a singlet-triplet transition with matching of vibrational levels is given in Figure 4.7 for illustration. A similar resonant process of ¹⁷O enrichment in product oxygen in dissociation of CO₂ by UV has been recently found by Bhattacharya et al. (2000). It is to be noted that such a near-resonance effect was also postulated by Harding et al. (1988) to explain the unusual efficiency of CO in quenching of $O(^{1}D)$. The 1.97 eV energy of $O(^{1}D)$ matches closely the energy required to excite v = 7, 8 vibrations of CO molecule through spin-orbit induced surface crossing of a long-lived complex CO₂* from ¹B₂ state to ${}^{3}B_{2}$ state.



Figure 4.7. A schematic of the lowest singlet and a typical triplet potential energy curves for $CO_2 - O({}^{l}D)$ system. The arrow depicts a collision of $O({}^{l}D)$ and CO_2 which results in rotational /vibrational excitation of the transient molecule (occurring predominantly at the inner classical turning point) to form a collision complex. It is proposed that a better matching of rovibrational levels of ${}^{17}O$ containing CO_2 with the cross-over zone favors its formation in quenching of $O({}^{l}D)$.

It is also possible that coupling by nuclear spin of ¹⁷O plays a role. Among the three isotopes of oxygen, only ¹⁷O has nuclear spin (5/2). Since the singlet-triplet transition is spin-forbidden it can only be affected by a spin-orbit interaction and an addition to the total perturbation from the nuclear spin of ¹⁷O may increase the quenching probability.

4.4.7 A Simple Box Model Calculation

Following the reaction sequence outlined above one can empirically derive the magnitude of the extra fractionation in ¹⁷O during CO_3^* formation/dissociation step from the experimental data. Keeping in mind the production of O(¹D) during the photolysis of $O_3 - CO_2$ mixture, an O(¹D) generator is assumed which continuously supplies O(¹D) into the system. The entire process (shown schematically in Figure 4.8) is thought to be

consisting of a large number of cycles. In each cycle, a small part of CO_2 interacts with $O(^1D)$ and forms CO_3^* complex. The isotopically modified CO_2 generated from CO_3^* decomposition mixes up with the rest of the CO_2 . In this process the oxygen isotopic composition of the total CO_2 changes. After a large number of similar cycles the oxygen isotopic composition of final CO_2 will be markedly different from that of the initial composition.



Figure 4.8. A schematic pathway of the box model showing a single cycle. In reality, this cycle operates large number of times to change the isotopic composition of the final CO_2 . No reservoir of $O({}^{1}D)$ was assumed, rather a constant source of $O({}^{1}D)$ was considered. In each cycle 5 % of reservoir CO_2 interacts with $O({}^{1}D)$ and mixes up with 95 % un-reacted CO_2 to change the isotopic composition of CO_2 reservoir.

To compute the modified composition of CO₂ in each step, the isotopic composition of CO₃^{*} was first calculated by two component (O(¹D) and CO₂) mixing. Next, a mass balance calculation (assuming 95 % original CO₂ and 5 % modified CO₂) yields the composition of the final CO₂. Since there is no time parameter in the model, 5 % modified CO₂ essentially represents the step size. A free parameter is introduced during CO₃^{*} formation/decomposition step through which an extra fractionation from CO₃^{*} decay can be added. The isotopic composition of O(¹D) is considered to be equal to that of asymmetric ozone modified for collision as mentioned before ($\delta^{17}O = 138.1 \%$ and $\delta^{18}O = 127.6 \%$) and the CO₂ composition is assumed to be the same as modified SM-CO₂ (applicable to set Ia experiment).

The model is run with the above parameters and compositions. It is seen that to generate a slope of 1.81 (for set Ia experiment) an extra fractionation of 16.5 ‰ in ¹⁷O needs to be introduced (through the free parameter mentioned above). Interestingly, with the same amount of extra fractionation in ¹⁷O, the model predicts slopes of values 1.46 and 1.36 when the initial CO₂ composition is changed to that of modified SP-CO₂ and modified SL-CO₂ respectively. These two slopes compare well (within errors) with the values (i.e. 1.52 and 1.29) obtained in experiments of set Ib and set Ic respectively. The consistency of the extra enrichment in ¹⁷O/¹⁶O ratio of the final CO₂ between the three sets is reassuring, since it shows that a fixed amount of fractionation is associated with CO₃^{*} formation / decomposition process, which favors ¹⁷O more than ¹⁸O in the final product.

4.5 CONCLUSION

The transfer of "heaviness" from the ozone pool to the CO₂ pool in UV-induced exchange reaction is not by simple mixing of CO_2 with $O(^1D)$ but has a component due to fractionation from intermediate CO_3^* , which favors ¹⁷O transfer relative to ¹⁸O. Present experiments were designed to provide further insight in this transfer mechanism and explain the data pertaining to the stratosphere. The evolution of the exchanged-CO₂ was examined by taking three different initial CO₂ compositions and a fixed ozone composition. The trend in final CO₂ was also investigated using a fixed CO₂ composition and varying initial ozone composition. Though the experimental set up does not exactly correspond to the stratospheric condition, the results bring out the essential feature of the stratospheric process governing the oxygen isotopic distribution among ozone and CO₂ reservoir in stratosphere. Analysis of the data suggests that the processes associated with formation/dissociation of the collision complex CO_3^* contribute an extra enrichment in 17 O to the product CO₂. We postulate that a process similar to resonant absorption takes place during the quenching of $O(^{1}D)$ by CO_{2} such that ^{17}O containing isotopomers of CO_{2} are favored during dissociation of the CO_3^* complex which takes place through transition from a singlet to triplet state.

CHAPTER V

STRATOSPHERIC IMPLICATIONS AND FUTURE DIRECTION

5.1 INTRODUCTION

The experimental studies discussed in the last three chapters (Chapter II, III, and IV) describe some physico-chemical processes, which can generate mass independent isotopic fractionation in the product phases. These experiments were designed keeping in mind the processes taking place in the stratosphere, where mass independent signatures in some trace molecules have been discovered (e.g. stratospheric ozone, CO_2 etc.). For most of the cases, the sources of these mass independent isotopic signatures are still to be deciphered. The present study is expected to be useful in this regard. This study can also lead us to speculate about some other stratospheric molecules where mass independent signature is expected to be present. The present chapter will deal with these aspects in some detail.

5.2 STRATOSPHERIC IMPLICATIONS

The mean ozone concentration in the stratosphere is calculated by the Chapman function, which involves product of molecular oxygen concentration, UV flux and the photolysis cross-section. Figure 5.1 shows the depth of solar energy penetration through the atmosphere and Figure 5.2 shows the photon absorption cross-sections of oxygen and ozone molecules. These two together determine the ozone concentration profile shown in Figure 5.3. It has a nearly symmetrical shape with the maximum occurring at about 27 km altitude (Banks and Kockarts, 1973; Seinfeld and Pandis, 1998). As it is well known, this profile is not invariant in space and time and at a given region the observed profile represents a balance between constant production of ozone (from oxygen) and dissociation of ozone by UV. Just as ozone concentration profile is determined basically by the product of oxygen concentration, the UV flux at a particular altitude, and the crosssection, the ozone dissociation profile is determined by the product of ozone concentration (Figure 5.3), absorption cross-section (Figure 5.2) and the UV flux and is shown in Figure 5.4. As a consequence, the dissociation profile is similar to the concentration profile in shape but the maximum is shifted upwards in altitude (Banks and Kockarts, 1973) and occurs between 30 to 40 km in mid-latitudes.



Figure 5.1. Depth of penetration of solar radiation through the atmosphere. Penetration altitude corresponds to an attenuation of the incident radiation by a factor of e (reproduced from Seinfeld and Pandis, 1998).





Figure 5.2. Wavelength dependent absorption cross-section of (a) oxygen and (b) ozone molecule [reproduced from Yung and DeMore, 1999].



Figure 5.3. Ozone molecular number density profile in the atmosphere showing a peak at an altitude of around 27 km. The corresponding concentration at the peak region is around 30 ppb. The concentration level goes down rapidly above and below this typical altitude, which varies depending upon latitude and season [reproduced from Seinfeld and Pandis, 1998].



Figure 5.4. Altitudinal variation of photo-dissociation rate of ozone in different state of O_2 and O [reproduced from Banks and Kockarts, 1973].

5.2.1 Isotopic Enrichment Profile ($\Delta \delta^{18}$ O) of Stratospheric Ozone

Though it is firmly established that the ozone in stratosphere is isotopically enriched, the nature of the variation of enrichment with altitude is not very clear. Since the ozone concentration is only about 30 ppb at the stratospheric peak (Figure 5.3), the isotopic measurements are difficult and have large uncertainties. Two types of techniques have been employed for this purpose: the mass-spectrometric methods and the spectroscopic methods (as described in Chapter I, § 1.4). The mass-spectrometric methods are presumably more accurate but initially the data were beset with unknown sources of error. Recent summary by Mauersberger et al. (2001) made a critical review of earlier measurements and showed that isotopic enrichment increases with altitude, initially slowly but sharply above about 30 km as shown in Figure 5.5 (the highest enrichment that was considered acceptable is about 110 ‰ at 33 km). Irion et al. (1996) reported integrated enrichment in ${}^{50}O_3$ of 130 % (with large error of 50 %) between 25 to 41 km based on ATMOS Infrared solar spectra. Meier and Notholt (1996) reported a similar level of enrichment with smaller error. Since the average itself is 130 ‰, it is expected that much higher level of enrichment would prevail at altitudes beyond 30 km taking mass-spectrometric values (Mauersberger et al., 2001) at the lower level as representative. The high values beyond 30 km are also supported by the studies of Goldman et al. (1989) and Abbas et al. (1987). The former showed column-averaged isotope enhancement (all in ‰) above 37 km to be 330 ± 160 and 220 ± 100 ‰ while the latter showed enrichment of 180 ± 140 ‰ at 25 km and 450 ± 140 ‰ at 37 km.



Figure 5.5. Compiled data of altitudinal variation of stratospheric ozone enrichment (a) enrichment in ${}^{18}O \ (\equiv {}^{50}O_3)$ and (b) enrichment in ${}^{17}O \ (\equiv {}^{49}O_3)$ [data from Mauersberger et al., 2001].

5.2.2 Altitudinal Variation: Previous Explanation and Present Proposition

Mauersberger et al. (2001) attempted to explain the altitude variations in ozone isotopic enrichments through temperature dependence. In stratosphere, as one goes up the temperature increases, from about 217.6 K at 21 km to about 231 K at 33 km. It was surmised that since the enrichment increases with increase in temperature, as observed by Morton et al. (1990), the stratospheric temperature increase can account for the altitude variation. However, there are some difficulties in accepting this explanation with temperature as the sole cause of observed increase, especially the high variability. The temperature coefficient determined by Morton et al. (1990) pertains to ozone recycling experiment using visible light as the dissociating agent (in the Chappuis band of 500 to 700 nm), which is not the major agent of dissociation in the stratosphere. It is also noted that the experimental data points show large scatter (Figure 3 from Morton et al., 1990) through which it is difficult to fit a well-defined line. Even if one neglects these points,

the total temperature change from 21 km to 33 km is only 13.4 K and assuming an average temperature coefficient (0.6 ‰ per K) from Morton et al. paper one would expect an increase of only about 8 ‰ which is far too small compared to the observed increase of about 30 ‰. The problem is more serious when one considers other spectroscopic data showing very high enrichments at high altitudes. Based on these considerations it is clear that temperature dependence can only account for a small part of the total increase in stratosphere.

On the contrary, the experimental results obtained in the present study (Chapter II) show that significant enrichments could be obtained in the laboratory if formation and dissociation are allowed to proceed within a certain pressure range where the turn-over time ($\tau = [O_3] / d[O_3]/dt$, where $[O_3]$ is the ozone amount at a given time and d $[O_3]/dt$ is the dissociation rate at that time) of the ozone reservoir is short (Chapter II, § 2.4.4; Bhattacharya et al., 2002). The stratospheric situation is, of course, not exactly similar to that of the experiment described in Chapter II, but the basic process regulating the enhancement of fractionation should be similar. Two major differences between stratosphere and laboratory experiments are readily apparent – presence of four times abundant nitrogen (helping in collisional deactivation of ozone complex) and the absence of a confining surface. Theis would result in higher relative production and increase the value of τ .

Figure 5.5 shows the variation of ozone isotopic enrichment with altitude in stratosphere as summarized by Mauersberger et al. (2001) and shows a fitted line to the data. It also shows the calculated turn-over time with pressure (or altitude) for stratospheric ozone (estimated using the data of Banks and Kockarts (1973) of ozone concentration and dissociation rate in the stratosphere as shown in Figures 5.3 and 5.4). For comparison, PRL config I profile (Chapter II, Figure 2.4) is given against the oxygen pressure. Lower limit estimates of τ for the PRL config I data in the peak zone are also indicated alongside the enrichment profile. To compare the stratospheric enrichment profile with the laboratory profile, we have to first correct the laboratory data for the temperature effect. The experiments were done at room temperature, at about 300 K, whereas the mean stratospheric temperature at 25 km is about 225 K. Assuming an increase of 0.6 ‰ per K increase we have to subtract about 45 ‰ from the laboratory data. It is interesting to note that, after this correction, the variation of enrichment with

pressure shows a similar trend as observed in the stratosphere and the values are also in the same range.



Figure 5.6. Comparison of variation of isotopic enrichment ($\delta^{l8}O$) as observed in the stratosphere and in the laboratory. The trend in enrichment variation with altitude (a fitted curve based on data from Mauersberger et al., 2001) and the variation of enrichment with pressure as obtained from the PRL experiment are shown. To compare the laboratory data with stratospheric data, the PRL profile has been corrected for lower stratospheric temperature. The PRL profile has τ values (which are approximate estimates) marked alongside. The variation of turn-over time τ as a function of altitude for stratosphere ozone is shown by the dotted line (upper scale). Note the inverse relation of τ with ozone isotopic enrichment in stratosphere allowing us to predict an enrichment variation with altitude beyond 33 km as shown (see text for explanation).

It should be mentioned here that it is difficult to calculate the turn-over time for the laboratory data points since the experiments were not designed to get steady state concentration or isotope ratios. During the photolysis time, the ozone builds up and dissociates simultaneously; therefore, the turn-over time varies systematically. Taking the end point when the photolysis is terminated we can only get a lower limit of turn-over time. These values are shown in Figure 5.6 and vary from about 300 to 30 sec in the peak region. It is seen that the enrichment increases with decrease in the turn-over time as expected. The turn-over time for stratospheric ozone based on Chapman model (Banks and Kockarts, 1973) range from about 2550 to 1250 sec in the height range of 20 to 33 km. These are much higher than the laboratory values indicating slower recycling in the
stratosphere. An important reason for the difference in the τ values is the wavelength used for the laboratory experiment. Since the Hg lamp has emission peak at 253.7 nm, which happens to be near the peak in absorption of ozone the dissociation is very effective in case of laboratory experiments. Whereas, in case of stratosphere the solar actinic flux has very different structure and is altitude dependent. Notwithstanding this complexity, the turn-over time variation with altitude seems to be reverse of the enrichment variation based on a smooth fitting of Mauersberger et al. (2001) data. The reverse pattern is consistent with the expected turn-over time dependence as predicted from the experimental data (PRL data). Since the turn-over time decreases further with height, we expect further enrichment in isotopic ratio with altitude, which is consistent with values based on the spectroscopic methods mentioned before.

5.2.3 Application of Altitudinal Variation of Isotopic Enrichment in ¹⁸O

The intimate relation of ozone isotopic composition and its dissociation in the stratosphere can have an interesting application. Since, absorption of UV by ozone and its dissociation is the major contributor for stratospheric heating, the altitudinal variation in isotopic enrichment of ozone could be used to monitor the heating rate variation. Only indirect methods are available so far for estimating this important parameter.

5.2.4 Altitudinal Variation in Slope of $\Delta \delta^{17}O - \Delta \delta^{18}O$ Correlation Plot

It is well known that dissociation of ozone is an important and continuous process in the stratosphere and both formation and dissociation play their role in determining the ozone concentration variation with altitude. It is also known that stratospheric ozone is enriched in heavy oxygen isotopes and the enrichment increases with altitude (§ 5.2.1). The proposition described in § 5.2.2 explains the altitudinal variation of δ^{18} O, but does not consider the relative change between δ^{17} O and δ^{18} O. Since numerous laboratory experiments have established that formation of ozone by UV photolysis of oxygen is associated with large mass-independent heavy isotope enrichment, stratospheric results are sought to be explained through formation process alone. But in view of the present experiments (Chapter II and III), which clearly show that photo-dissociation acts preferentially on the lighter isotopes and enriches the left-over ozone pool, it is pertinent to inquire about its role in modifying the ozone isotope ratios in the stratosphere.

The dissociation experiment (described in Chapter III) shows that photodissociation consists of two channels, i.e., pure photo-dissociation and $O(^{1}D)$ (ozone derived) mediated dissociation and these two channels produce different isotopic effects. Both the dissociation channels enrich the left-over ozone pool, but the former does not distinguish between ¹⁷O and ¹⁸O, whereas the latter discriminates them in a mass dependent way. These two effects together result in a slope of 0.63 in photo-dissociation.

In the lower stratosphere, ozone formation is relatively more important than photo-dissociation but with altitude photo-dissociation becomes more and more important resulting in reduction of ozone concentration. The process of ozone formation results in an ozone reservoir where both the heavy oxygen isotopes (¹⁷O and ¹⁸O) are equally enriched (Thiemens and Jackson, 1987, 1988). In photo-dissociation of ozone in the stratosphere, the first channel (i.e., the photon-induced dissociation) is mainly responsible for the dissociation since the product $O(^{1}D)$ is quenched rapidly by N₂ and O₂. Since this results in equal enrichment of the two heavy isotopes, it follows that the relative enrichment would still be the same for ¹⁷O and ¹⁸O in the stratosphere (i.e., the two delta variations would have a slope value of unity). However, the observed stratospheric slope (up to ~ 35 km) is 0.62 (Lämmerzahl et al., 2002), a value well below unity. The deviation of the observed stratospheric slope from the expected value is puzzling and needs further scrutiny. It is, of course, clear that the stratospheric processes are not so simple as described above. Oxygen isotopic exchange between ozone and CO₂ (via ozone dissociation product $O(^{1}D)$) may have a role in controlling the isotopic composition of the ozone reservoir and will be discussed later. Additionally, there are other dissociation processes besides the photo-dissociation, which are similar to simple chemical reactions and probably result in mass dependent fractionations. The net effect of these would be to reduce the slope value from unity.

5.3 OXYGEN ISOTOPIC COMPOSITION OF STRATOSPHERIC CO₂

The oxygen isotopic composition of tropospheric CO_2 is controlled by the oceans and the land biota. On a global scale, isotopic exchange with vegetation and respiration processes produce an isotopic enrichment in ¹⁸O, while exchange with soils acts to decrease the ¹⁸O content (Ciais et al., 1997). The mean δ^{18} O of tropospheric CO_2 is enriched by ~ 41.5 ‰ relative to oxygen isotopic composition of ocean water (i.e. SMOW), with an annual average difference of ~ 2 ‰ between the two poles (Trolier et al., 1996). The oxygen isotopic measurement (δ^{18} O) of stratospheric (from 19 to 25 km) CO₂ was first carried out by Gamo et al., (1989) over Japan (39°N, 142°E). They found that at 19 km δ^{18} O of CO₂ was enriched by ~ 2 ‰ relative to the tropospheric value and the enrichment increased with increasing altitude. In a later publication (Gamo et al., 1995) they showed that the enrichment increased up to 7 ‰ at 35 km. A new dimension was added to this subject with the simultaneous determination of δ^{18} O and δ^{17} O in stratospheric CO₂ (Thiemens et al., 1991, 1995). The samples collected over Palestine, Texas (32°N, 96°W), and Fort Sumner, New Mexico (34°N, 104°W), at altitude between 26 to 35.5 km (Thiemens et al., 1991) were enriched by 7.9 to 12.6 ‰ and 10.0 to 15.5 ‰ in δ^{18} O and δ^{17} O respectively compared to the tropospheric level. These samples bear a mass independent signature expressed as Δ^{17} O (= δ^{17} O - 0.52 * δ^{18} O) ranging from 5.2 to 9.5 ‰. The CO₂ collected over White Sands, New Mexico (32°N, 106.3°W) at altitudes between 29.3 to 60 km, showed higher enrichment of 4.1 to 14.5 ‰ with concomitant Δ^{17} O values ranging from 5.25 to 11.95 ‰ (Thiemens et al., 1995).



Figure 5.7. Compiled data of altitudinal variation in oxygen isotopic enrichment (wrt tropospheric composition) in stratospheric CO_2 ; (a) enrichment in ${}^{17}O/{}^{16}O$ and (b) enrichment in ${}^{18}O/{}^{16}O$. Circles are the data from Lämmerzahl et al., 2002, squares are from Alexander et al., 2001 and triangles are from Thiemens et al., 1995. The observations clearly show the altitudinal variation of enrichment in ${}^{17}O$ and ${}^{18}O$.

The most recent stratospheric measurements by Lämmerzahl et al. (2002) over northern Europe at altitudes between 10 to 35 km demonstrate enrichment values up to 11 ∞ in δ^{18} O and 19 ∞ in δ^{17} O. The stratospheric CO₂ data from the above papers are compiled in Figure 5.7. Figure 5.8 shows a covariation plot of δ^{17} O and δ^{18} O in stratospheric CO₂.



Figure 5.8. Three-isotope plot of compiled data showing the variation in ${}^{17}O/{}^{16}O$ enrichment against ${}^{18}O/{}^{16}O$ enrichment (w.r.t tropospheric composition) in stratospheric CO_2 . The circles are the data from Lämmerzahl et al., 2002, squares are from Alexander et al., 2001 and triangles are from Thiemens et al., 1995. A strong correlation between the $\delta^{18}O$ and $\delta^{17}O$ exist with a slope 1.71 for the enrichment up to 11 ‰ in $\delta^{18}O$ (for the data from Lämmerzahl et al., 2002). In the higher altitude where the enrichment is more than 11 ‰ (in $\delta^{18}O$) the same relationship does not hold; rather a lower slope (1.2) is observed.

5.4 ROLE OF O(¹D) IN THE STRATOSPHERE

Photochemistry is the main driving force behind most of the reactions of the stratosphere. It initiates a large number of chemical cycles; the ozone cycle is one of the well-known examples. The $O(^{1}D)$ is the most active photochemical product in the stratosphere. Depending upon the solar wavelength penetration (Figure 5.1) in the stratosphere, production of $O(^{1}D)$ by the photolysis of O_{2} , O_{3} , NO_{2} , CO_{2} , $N_{2}O$ is energetically possible (Okabe, 1978). Among these molecules, O_{3} photolysis is the major source of $O(^{1}D)$. Since the production of $O(^{1}D)$ by photolysis of different oxygen

containing molecules in the stratosphere is ceaseless during the day, a certain level of $O(^{1}D)$ is present throughout the stratosphere (the concentration profile of $O(^{1}D)$, similar to that of ozone photo-dissociation rate profile with a maximum at around 40 km) in the day time. After sunset (after ~ 100 sec) all the oxygen atoms in the stratosphere disappear since there is no photo-dissociation of ozone or other molecules (Banks and Kockarts, 1973).

As an important part of atmospheric transport, the tropospheric air enters the stratosphere predominantly at the topical tropopause and is then dispersed slowly upward and towards the poles (Volk et al., 1996). During this transport air molecules act as quencher for the stratospheric $O(^{1}D)$ (Tully, 1975).

The electronic energy of $O(^{1}D)$ is 1.967 eV above the ground state. Since transition to the ground state $O(^{3}P)$ is forbidden by spin conservation (Okabe, 1978), the fate of this singlet atomic species is physical and chemical quenching. The chemical quenching of this active species governs a number of chemical reactions in the atmosphere (as for example, reactions with H₂O, N₂O etc.) (Tully, 1975). The physical quenching, especially with oxygen containing molecular species, is of great interest. At the time of quenching, the $O(^{1}D)$ can take part in an isotopic exchange with the oxygen atom of that molecule.

5.4.1 Isotopic Composition of O(¹D)

The isotopic composition of the $O(^{1}D)$ derived from ozone photo-dissociation is not known. Previous studies (Barth and Zahn, 1997; Yung et al., 1991, 1997) assumed negligible fractionation during the O₃ photolysis reaction. Consequently, the isotopic composition of the $O(^{1}D)$ reservoir was thought to be equal to that of the ozone reservoir. However, the present study shows that pure photo-dissociation of ozone (Chapter III) enriches the left-over ozone pool in a mass independent way with an instantaneous fractionation factor of about 7 ‰. The model calculations of Johnston et al. (2000) also show slightly enriched $O(^{1}D)$ reservoir. Moreover, it is now known that isotopic enrichment in ozone occurs primarily in the asymmetric isotopomers of ozone. The kinetic studies of Janssen et al. (1999) show a rate coefficient advantage in the formation channel of the asymmetric ozone molecule ($^{16}O^{16}O^{18}O$). Since during photo-dissociation of ozone the product $O(^{1}D)$ is likely to be derived from the terminal atoms, it should have an enrichment similar to that of asymmetric ozone molecules. Janssen et al. (2001) calculated an enrichment of 129 ‰ in ⁵⁰O₃ using the relative rate coefficient of formation by different channels (given in Table 1.1, Chapter I). Following the definition of enrichment (Janssen et al., 2001), i.e., E (‰) = $[(^{M}O_{3}/ ^{48}O_{3})]_{measured}$ / $(^{M}O_{3}/ ^{48}O_{3})]_{calculated}$ –1] × 1000 ‰, and the rate constant of different ozone forming channels, the isotopic composition of the asymmetric ozone can be computed in the following way.

When oxygen and ozone molecules are formed from an isotopically scrambled O_2 molecule reservoir with atomic isotopic ratio $f = {}^{18}O/{}^{16}O$, we have by definition (statistically), $2f = [{}^{18}O^{16}O] / [{}^{16}O^{16}O]$ and $3f = [{}^{18}O^{16}O^{16}O + {}^{16}O^{16}O^{16}O] / [{}^{16}O^{16}O^{16}O]$ for the ratios of ${}^{34}O_2 / {}^{32}O_2$ and ${}^{50}O_3 / {}^{48}O_3$. For atomic oxygen the ratio of ${}^{18}O/{}^{16}O$ is given by $[{}^{18}O] / [{}^{16}O] = 0.924f$, where atomic oxygen is in isotopic equilibrium with molecular oxygen. Using these definitions, the enrichment in asymmetric ozone can be expressed (in per mil) as,

 $1 + E({}^{50}O_3)^{asy} / 1000 = [\{k_{12}[{}^{18}O][\;{}^{16}O{}^{16}O] / k_1[{}^{16}O][\;{}^{16}O{}^{16}O]\} + \{1/2 \; k_{10}[{}^{16}O][\;{}^{16}O{}^{18}O] / k_1[{}^{16}O][{}^{16}O{}^{16}O]\} / 2f$

where, k_1 , k_{10} and k_{12} are relative rate coefficient of channels 1 (${}^{16}O + {}^{16}O{}^{16}O \rightarrow {}^{16}O{}^{16}O{}^{16}O)$, 10 (${}^{16}O + {}^{16}O{}^{18}O \rightarrow {}^{16}O{}^{16}O{}^{18}O)$ and 12 (${}^{18}O + {}^{16}O{}^{16}O \rightarrow {}^{18}O{}^{16}O{}^{16}O)$ given in Table 1.1 (Chapter I) (In the denominator, (${}^{M}O_{3}/{}^{48}O_{3}$)_{calculated} is substituted by 2f since the asymmetric ozone species are only considered). Therefore, inserting the relative rate coefficient of channels 10 and 12 (1.45 and 0.95 respectively), we obtain, $E({}^{50}O_{3})^{asy} = 150$ ‰.

Unfortunately, there are limited studies regarding the distribution of ¹⁷O within the ozone isotopomers. Except channel 4 (¹⁷O + ¹⁶O¹⁶O \rightarrow ¹⁷O¹⁶O¹⁶O), the rate coefficients for the channels forming ⁴⁹O₃ are not known. To calculate the enrichment of asymmetric ⁴⁹O₃, the knowledge of rate coefficient of channel 2 (¹⁶O + ¹⁶O¹⁷O \rightarrow ¹⁶O¹⁶O¹⁷O) is specially required since similar kind of reaction channel (channel 10) forming asymmetric ⁵⁰O₃ shows very high relative rate. Considering a zero point energy difference of 11.6 cm⁻¹ between ¹⁶O¹⁶O and ¹⁶O¹⁷O (i.e. the isotopic exchange reaction corresponding to channel 2) and using the Δ (ZPE) vs. relative rate coefficient plot (Figure 1 of Janssen et al., 2001), a relative rate coefficient of 1.35 is obtained for channel 2. Following the steps similar to the calculation of E(⁵⁰O₃)^{asy}, we finally obtain, E(⁴⁹O₃)^{asy} = 150 ‰. Therefore, under the terminal atom source assumption O(¹D) has an enriched composition ($\delta^{17}O = 150 \%$) relative to the total initial oxygen. For our experiment the

oxygen has the composition of $\delta^{17}O = 12.48$ ‰ and $\delta^{18}O = 24.58$ ‰ with respect to SMOW. Therefore, O(¹D) will have the composition, $\delta^{17}O = 164.1$ ‰ and $\delta^{18}O = 178.3$ ‰ with respect to SMOW.

5.4.2 Interaction of O(¹D) With Other Oxygen Bearing Molecules

The physical quenching of $O(^{1}D)$ with oxygen bearing trace molecules result in isotopic exchange which alters the isotopic composition of those molecules. The alteration of isotopic composition of a molecule depends upon the nature of the exchange and in principle can take place in two different ways, (i) simple mixing of the two exchanging components and, (ii) isotope selective exchange.

The isotopic composition of CO₂ after isotopic exchange with O(¹D) can not be interpreted by a simple mixing of CO₂ and O(¹D) (as described in Chapter IV). An isotope selective exchange mechanism was hypothesized to explain the laboratory data, which reflects a slope ($\Delta\delta^{17}O/\Delta\delta^{18}O$) of about 1.8 in the exchanged CO₂, using the isotopic compositions of O₃ (the source of O(¹D)) and CO₂ similar to the atmospheric values. This slope is close to the value obtained recently in the stratospheric CO₂ (Lämmerzahl et al., 2002).

Even for the cases where simple mixing mechanism is operative during the isotopic exchange between $O(^{1}D)$ and a oxygen bearing molecule, a mass independent isotopic composition can be seen in the exchanged molecule if the $O(^{1}D)$ is derived from ozone since it bears mass independent signature.

Similar to the case of stratospheric CO_2 which inherits a mass independent signature due to the isotope selective exchange with $O(^1D)$, stratospheric CO is another potential candidate to look for a similar kind of effect since it has a similar quenching rate constant (7 × 10⁻¹¹ cm³/molecule-sec) as that of $O(^1D) - CO_2$ reaction (Heidner et al., 1972). Unfortunately, due to its very low stratospheric concentration (< 0.1 ppbv), it is difficult to investigate with present day facilities. However, these types of exchange reactions can be studied in the laboratory for better understanding of the transfer mechanism.

5.4.3 Importance of $CO_2 - O(^1D)$ Exchange

There are three significant oxygen reservoirs in the stratosphere. The major one is of course, the ambient oxygen. The other two are ozone and stratospheric CO₂. Two types

of oxygen atoms, i.e. $O({}^{3}P)$ and $O({}^{1}D)$ are the transient species and work as mediators between these three oxygen reservoirs. With increasing altitude, oxygen isotopic enrichment in both CO₂ and ozone increases progressively in stratosphere (Lämmerzahl et al., 2002) and the observed enrichment pattern relating $\delta^{17}O$ and $\delta^{18}O$ has slope values of 1.71 and 0.62 respectively. It is puzzling to see that the slope relating ozone isotopic enrichments is 0.62 despite the fact that both formation and photo-dissociation processes generate a slope of unity in laboratory studies. It is established from the present study as well as the earlier ones that the isotopic exchange between ozone and CO₂ via O(${}^{1}D$), transfers ${}^{17}O$ preferentially. This can make the stratospheric ozone pool relatively depleted in ${}^{17}O$ and result in a lower value of the slope.

The enrichment pattern found in set II data described in Chapter IV for CO₂ and initial ozone is of relevance at this point. Though the initial CO₂ composition ($\delta^{17}O = 8.98 \%$ and $\delta^{18}O = 17.28 \%$) and the variation in initial ozone composition (124.9 to 205.7 ‰ in $\delta^{18}O$) in the laboratory experiment are not representative of the stratospheric values (the isotopic composition of stratospheric ozone varies only by about 30 ‰ in $\delta^{18}O$), the relationship between the two slope values are quite similar and suggest intimate connection between these two interacting oxygen reservoirs.

In addition to the above exchange process, there are other processes influencing the ozone isotopic composition like catalytic ozone destruction cycles (namely by HO_X , NO_X , ClO_X cycles). The classical Chapman ozone cycle does not consider these destruction channels and thus predicts a higher ozone concentration (Seinfeld and Pandis, 1998). These destruction cycles are chemical processes and probably enrich the ozone reservoir in a mass dependent way since kinetic chemical reactions, in general, destroy lighter isotopes preferentially. Therefore, the exchange process with CO_2 and these destructive ozone cycles together can influence the relative enrichment between ¹⁷O and ¹⁸O in the stratospheric ozone to produce a net slope of 0.62.

5.5 FUTURE LABORATORY STUDIES

There are several exchange reactions, which can impart the mass independent signature of ozone to other oxygen containing atmospheric molecules. Recently Lyons (2001) has computed, using a photochemical equilibrium model, the expected mass independent fractionation in NO_X (and HNO_3), OH and ClO species due to such exchange. In this model, the number density profiles of O-containing short lived and

long-lived radicals were computed by balancing total chemical production and loss for each species at a given altitude. The predicted Δ^{17} O in HNO₃ is about 22 ‰, which agrees well with the observed 23 ‰ in the nitrates from tropospheric aerosols (Michalski and Thiemens, 2000). This model also predicts mass independent fractionation in stratospheric OH with a wide range of value (~ 2 to 45 ‰). Some of these predictions about the transfer of mass independent signature from ozone to other oxygen containing radicals can be tested in the laboratory in future. Such studies will not only constrain the model but also offer an opportunity for better understanding of the atmospheric isotope chemistry.

EPILOGUE

Despite of more than two decades of extensive research on oxygen isotopic fractionation in ozone isotopomers, there are still a number of unresolved problems related to fundamental fractionation mechanism during its formation and dissociation. Moreover, there are several unanswered issues regarding stratospheric ozone and its direct or indirect heavy isotope transfer to other oxygen containing stratospheric trace species.

The present thesis explores the phenomenon of mass independent fractionation in light of the several experimental processes involving ozone and its interaction with other oxygen containing molecules like CO_2 to throw light on some of these issues.

In the course of this work, a number of experiments were devised in a way such that some of the fundamental fractionation mechanisms related to ozone as well as some specific stratospheric issues (e.g. altitudinal variation of enrichment in stratospheric ozone, relative variation of enrichment in ¹⁷O and ¹⁸O of ozone in the upper stratosphere etc.) could be addressed. Some of the important findings of this study are the following:

Dissociation of ozone contributes significantly in the isotopic enrichment of ozone while recycling is allowed to take place during formation through oxygen photolysis at low pressure (< 50 torr). Over and above the dissociation effect, the amount of ozone produced has also a role in enrichment process. The data are explained easily by introducing a parameter called "turn-over time" ($\tau = O_3$ reservoir amount / rate of O_3 dissociation) which clarifies the role of dissociative enrichment from the perspective of a Rayleigh type of process. An effort is made to explain and predict the altitudinal enrichment variation of stratospheric ozone with the help of this parameter.

It is established that the isotopic fractionations during photo-dissociation of ozone in Hartley (peak around 254 nm) and Chappuis band (peak around 600 nm) are distinctly different. The former shows a mass independent character while the latter is strictly a mass dependent process. Further investigations on Hartley band dissociation decipher the fact that pure UV dissociation is a mass independent process, which proceeds with equal enrichment in ¹⁷O and ¹⁸O in the left-over ozone. An explanation for this dissociation process is presented in the context of Gao-Marcus theory. An interesting phenomenon is observed during ozone dissociation by its interaction with a surface. The origin of the mass independent character of this process is hypothesized by non-statistical breakdown of short-lived complex O_3^* (formed by adsorption of O_3 in the wall).

During the isotopic exchange between the ozone photolysis product $O(^{1}D)$ and CO_{2} , the $\delta^{17}O$ and $\delta^{18}O$ of evolved CO_{2} defines a line of slope 1.7 (with initial O_{3} and CO_{2} compositions identical to atmospheric composition) similar to the one observed for stratospheric CO_{2} . The slope of the line changes with the change of initial CO_{2} composition and establishes the fact that the isotopic transfer favors ¹⁷O relative to ¹⁸O. It is postulated that a process similar to resonant absorption affects the quenching of $O(^{1}D)$ such that ¹⁷O containing isotopomers of CO_{2} is favored during the singlet-triplet transition of the CO_{3}^{*} complex during its breakdown to O-atom and CO_{2} molecule.

In summary, this work is an effort to enhance our understanding of the mass independent isotopic fractionation processes.

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APPENDIX

Physical Data for Ozone as found in literature:

(Determined by microwave spectroscopy)

Table A1. Physical quantities of ozone molecule.

Quantity	Value
Density (Gas)	2.133 g/L at 273.15 K
Density (Liquid)	1.614 g/cm ⁻³ at 77.75 K
Melting Point	80.0 K
Boiling Point	161.80 K
Critical Temperature	261.05 K
Critical Pressure	53.8 atm
Critical Volume	$89 \text{ cm}^3/\text{mol}$
Heat of Formation	34.4 kcal/mole (298.15 K)
Heat of Vaporization	4.88 kJ/g
Bond Length	1.2716 Å
Molecular Angle	117.47 °
Point Group	C_{2v}



Figure A1. A schematic representation of three types of vibration in ozone molecule.

Isotonomors	Mass	Cal	culated (ci	n ⁻¹)	Me	easured (cn	n ⁻¹)
isotopoiners	Iviass	ν_1	v_2	v ₃	ν_1	v_2	v ₃
$^{16}O^{16}O^{16}O$	48	1103.9	701.3	1043.3	1103.1	700.9	1042.1
$^{17}O^{17}O^{17}O^{17}O$	51	1071.0	608.3	1012.2	1070.9		1012.2
$^{18}O^{18}O^{18}O$	54	1040.8	661.2	983.7	1041.6	661.5	984.8
$^{16}O^{16}O^{17}O$	49	1095.6	692.7	1037.0	1095.7	692.4	1035.7
$^{16}O^{17}O^{16}O$	49	1088.2	697.3	1025.0	1087.8	697.1	1024.4
$^{16}O^{16}O^{18}O$	50	1088.1	685.0	1031.4	1090.4	684.6	1028.1
$^{16}O^{18}O^{16}O$	50	1074.2	693.5	1008.4	1074.3	693.3	1008.4
$^{17}O^{17}O^{16}O$	50	1079.6	688.9	1018.6			
$^{17}O^{16}O^{17}O$	50	1087.2	684.0	1030.7			
$^{17}O^{17}O^{18}O$	52	1063.3	672.5	1006.4			
$^{17}O^{18}O^{17}O$	52	1056.5	676.7	995.4			
$^{18}O^{18}O^{16}O$	52	1057.5	677.7	996.1	1060.7	677.5	993.9
$^{18}O^{16}O^{18}O$	52	1072.3	667.9	1019.4	1072.2	668.1	1019.4
$^{18}O^{18}O^{17}O$	53	1048.7	669.0	989.5			
$^{18}O^{17}O^{18}O$	53	1055.6	664.5	1000.6			
$^{16}O^{17}O^{18}O$	51	1071.9	681.3	1012.9			
¹⁶ O ¹⁸ O ¹⁷ O	51	1065.4	685.2	1001.9			
¹⁷ O ¹⁶ O ¹⁸ O	51	1079.8	676.1	1025.1			

Table A2. The calculated and measured vibrational frequencies of different ozone isotopomers (taken from Hathorn and Marcus, 2001).

Calculated Fractionation of Ozone at Different Wave Lengths Following Miller-Yung Model

The absorption cross-sections of ${}^{48}O_3$ and ${}^{50}O_3$ are slightly different which can cause isotopic fractionation due to photo-dissociation. This can be calculated using Miller-Yung model (2000). First, the zero point energy difference (ΔZPE) between ${}^{48}O_3$ and ${}^{50}O_3$ (${}^{16}O^{18}O^{16}O + {}^{16}O^{16}O^{18}O$) is calculated using the vibrational frequencies of ozone isotopomers, where ΔZPE is given by:

 $(\Delta ZPE)_s = ZPE \ ({}^{16}O{}^{16}O{}^{16}O) - ZPE \ ({}^{16}O{}^{18}O{}^{16}O)$ and, $(\Delta ZPE)_a = ZPE \ ({}^{16}O{}^{16}O{}^{16}O) - ZPE \ ({}^{16}O{}^{16}O{}^{18}O)$

where, 's' and 'a' subscripts denote symmetric and asymmetric case respectively.

Now, ZPE = $\frac{1}{2}$ ($v_1 + v_2 + v_3$) (where v's are vibrational frequencies of the ozone molecule expressed in cm⁻¹ unit). Using the vibrational frequencies from Hathorn and Marcus (2001), the calculated Δ ZPE values are,

$$(\Delta ZPE)_a = -22.0 \text{ cm}^{-1}$$

 $(\Delta ZPE)_s = -36.2 \text{ cm}^{-1}$

The ¹⁸O-enrichment in ozone (i.e. the relative difference in absorption rate) can be written as, $(\sigma_{48} - \sigma_{50})/\sigma_{48} \times 1000$ (‰), where σ_{48} and σ_{50} at a given wave number (v/c) are the absorption cross- sections of ⁴⁸O₃ and ⁵⁰O₃ respectively. σ_{48} and σ_{50} are related by the equation,

$$\sigma_{50} \left(\nu/c + \Delta ZPE \right) = \sigma_{48} \left(\nu/c \right)$$

For ozone dissociation at 253.7 nm:

Using the ozone absorption cross-section data (DeMore et al., 1997) given below, a

function of the fo	orm: $\sigma = a \exp\left(-0.5\left\{\frac{(\nu/c) - 1}{b}\right\}\right)$	$\left \frac{x_o}{x_o}\right ^2$ was fitted.
	$v/c (cm^{-1})$	σ (× 10 ⁻²⁰ cm ²) of ⁴⁸ O ₂

v/c (cm ⁻)	$\sigma (\times 10^{-5} \text{ cm}^{-}) \text{ of } {}^{10}\text{O}_3$	
41779.98	797	_
41279.98	900	
40779.94	1000	
40279.88	1080	
39779.86	1130	
39279.86	1150	
38779.90	1120	
38279.85	1060	
37779.78	965	
37279.79	834	
36779.76	692	

The corresponding fit-parameters for ⁴⁸O₃ are given below:

Parameters	Values	
а	1147.9544	
b	2684.8433	
X _o	39386.9557	

Using these parameters, σ_{48} and σ_{50} at 253.7 nm (= 39416.63 cm⁻¹) was calculated and we

obtain:	$(\Delta \sigma)_{a} = \sigma_{48} - \sigma_{50} \approx -0.065 \times 10^{-20} \text{ cm}^{2}$
therefore,	$(\delta^{18}O)_a = (\Delta\sigma)_a / \sigma_{48} \times 1000 \approx -0.056$ ‰.
Similarly,	$(\Delta\sigma)_s = \sigma_{48} - \sigma_{50} \approx -0.067 \times 10^{-20} \text{ cm}^2$
and,	$(\delta^{18}O)_{s} = (\Delta\sigma)_{s} / \sigma_{48} \times 1000 \approx -0.058 $ %.

Appendix

finally,
$$(\delta^{18}O)_{total} = 1/3 \ (\delta^{18}O)_s + 2/3 \ (\delta^{18}O)_a \approx -0.06 \ \%$$

Therefore the left-over ozone will be depleted by 0.06 ‰.

For ozone dissociation at 520:

The absorption cross-section data around 520 nm are the following:

$v/c (cm^{-1})$	σ (× 10 ⁻²³ cm ²) of ⁴⁸ O ₃
19442.39	162.3
19337.50	173.9
19233.73	182.6
19131.07	191.3
19080.33	205.8
19029.50	217.4

A function of the form: $\sigma = a \times (v/c)^3 + b \times (v/c)^2 + c \times (v/c) + d$ is fitted to the above data set and obtained the following parameters:

Parameters	Values
a	$-1.32367975047 \times 10^{-6}$
b	$7.65896904133 \times 10^{-2}$
с	- $1.47725859141 \times 10^3$
d	$9.49838314502 \times 10^{6}$

Using these parameters, σ_{48} and σ_{50} at 520 nm (= 19230.77 cm⁻¹) was calculated and we

obtain:	$(\Delta \sigma)_a = \sigma_{48} - \sigma_{50} \approx -1.90 \times 10^{-23} \text{ cm}^2$
therefore,	$(\delta^{18}O)_a = (\Delta\sigma)_a / \sigma_{48} \times 1000 \approx -1.90 / 181.9 = -10.45 $ %.
Similarly,	$(\Delta \sigma)_{\rm s} = \sigma_{48} - \sigma_{50} \approx -3.28 \times 10^{-23} {\rm cm}^2$
and,	$(\delta^{18}O)_s = (\Delta\sigma)_s / \sigma_{48} \times 1000 \approx -3.28 / 181.9 \times 1000 = -18.05 $ %.
finally,	$(\delta^{18}\text{O})_{\text{total}} = 1/3 \ (\delta^{18}\text{O})_{\text{s}} + 2/3 \ (\delta^{18}\text{O})_{\text{a}} \approx -13.0 \ \%$

Therefore, during photo-dissociation of ozone at 520 nm, the left-over ozone will be depleted by 13.0 ‰.

For ozone dissociation at 630 nm:

$v/c (cm^{-1})$	σ (× 10 ⁻²³ cm ²) of ⁴⁸ O ₃
16048.53	385.5
15976.99	373.9
15906.09	359.4
15836.07	342
15766.4	330.4
15731.68	315.9

The absorption cross-section data around 630 nm are the following:

A function of the form:

$$\sigma = a \times (v/c)^{5} + b \times (v/c)^{4} + c \times (v/c)^{3} + d \times (v/c)^{2} + e \times (v/c) + f$$

is fitted to the above data set and obtained the following parameters:

Parameters	Values
a	$3.24118687744 \times 10^{-10}$
b	- $2.57631099424 \times 10^{-5}$
с	$8.19118920805 \times 10^{-1}$
d	- $1.30214725893 \times 10^4$
e	$1.03499373478 \times 10^8$
f	- $3.29055995954 \times 10^{11}$

Using these parameters, σ_{48} and σ_{50} at 630 nm (= 15873.02 cm⁻¹) was calculated and we obtain: ($\Delta \sigma$)_a = $\sigma_{48} - \sigma_{50} \approx 5.36 \times 10^{-23} \text{ cm}^2$ therefore, ($\delta^{18}\text{O}$)_a = ($\Delta \sigma$)_a / $\sigma_{48} \times 1000 \approx 5.36$ / 359.2 = 14.9 ‰. Similarly, ($\Delta \sigma$)_s = $\sigma_{48} - \sigma_{50} \approx 8.33 \times 10^{-23} \text{ cm}^2$ and, ($\delta^{18}\text{O}$)_s = ($\Delta \sigma$)_s / $\sigma_{48} \times 1000 \approx 8.33$ / 359.2 × 1000 = 23.18 ‰.

finally,
$$(\delta^{18}O)_{\text{total}} = 1/3 \ (\delta^{18}O)_{\text{s}} + 2/3 \ (\delta^{18}O)_{\text{a}} \approx 17.7 \ \%$$

Therefore, during photo-dissociation of ozone at 630 nm, the left-over ozone will be enriched by 17.7 ‰.

PAPER PUBLISHED/ SUBMITTED

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- 1. Bhattacharya, S.K., S. Chakraborty, J. Savarino, and M.H. Thiemens, Low Pressure Dependency of the Isotopic Enrichment in Ozone: Stratospheric Implications, *J. Geophys. Res.*, 2002 (in press).
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ABSTRACTS

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