Investigation of mass independent isotopic fractionation in photochemical reactions

A thesis submitted to

Gujarat University

for the degree of Doctor of Philosophy in Physics

By

Sasadhar Mahata



Planetary and Geosciences Division PHYSICAL RESEARCH LABORATORY, AHMEDABAD - 380 009, INDIA

January, 2009

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.

> Sasadhar Mahata (Author)

Certified by :

Prof. S. K. Bhattacharya

(Thesis Supervisor) Planetary and Geosciences Division, Physical Research Laboratory, Navrangpura, Ahmedabad, INDIA

To My Parents

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Acknowledgements

I owe a great deal to my mentor Professor S. K. Bhattacharya for his example and his invaluable guidance throughout the course of this work. His leadership, companionship and friendship have played a major role not only to shape my scientific thinking but also to flourish in every aspect of life as a whole. It is through his guidance that I have learnt how to be a good scientist. His extraordinary skill in doing experiment and exceptional way of thinking has put a big impression on me. It has been my good fortune to work with him. I also thank him for critically going through the manuscript and for making important suggestions towards its improvements.

I am greatly indebted to Prof. R. Ramesh for his constructive criticism and advice that helped me to think more critically. Special thanks to Prof. J. N. Goswami, Prof. S. Krishnaswami, Prof. S. V. S. Murty, Prof. M. M. Sarin and Prof. A. K. Singhvi for the encouragement and stimulating discussions I had with them on many occasions.

I gratefully acknowledge many fruitful discussions with Dr. Bhas Bapat, Dr. K. P. Subramanian, Dr. D. Banerjee, Dr. J. R. Trivedy and Dr. Dilip Angom. I sincerely thank them. I greatly acknowledge the help provided at some stage or the other by Dr. Sunil Singh, Dr. J. S. Ray, Dr. Navin Juyal, Dr. M. G. Yadav, Dr. R. D. Deshpande, Mr. Som Sharma, Mr. Ravi Bhusan, Mr. Anil Shukla, Dr. Dibendu Chakraborty, Dr. Vinai Rai, Dr. Kuljeet Kaur Marhas and Mr. N. B. Vaghela.

I thank Prof. S. D. Rindani, Prof. Utpal Sarkar, Dr. P. Sharma and other members of the Academic Committee both present and past for critically reviewing the progress of my work and giving valuable suggestions at various stages of my research in this laboratory. Special thanks are due to Mr. R. A. Jani (Janiji) and Mr. D. K. Rao (Raoji) for their support, encouragement and assistance throughout the years. I thank Mr. Pranav R. Adhyaru and Mr. G. D. Panchal for helping me in maintaining the electronics units. This work would almost never have been possible but for the excellent glass blowing support provided by Mr. K. K. Sivasankaran during the early days and Mr. Bankim Pandya at the later stage of my research.

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

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

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

I wish to express my sincere gratitude to my senior Dr. S. Chakraborty for his encouragement and many fruitful discussions. My sincere thanks to my immediate senior Dr. (Mrs) Antra for keeping VG mass spectrometer alive and the valuable discussion with her.

I take this opportunity to thank all of my batchmate Uma, Sanat, Satya, Shreyas, Sumanta, Subimal, Parimal and Shilpy for their company and discussion in many occasions. Special thanks to Shreyas for many discussions ranging from science to human philosophy. I am pleasantly obliged to Amzad for his careful and patient reading of the text and making useful suggestions. Thanks can never be enough to express my feelings to him. Special thanks to Ashutoshbhai for helping me in drawing the figures. Mahalingam's help in correcting english is greatly appreciated. The company with my immediate junior batch, Rajesh, Ramkrishna, Sontosh, Salman, Rohit, Akhilesh, and Ritesh have been a rewarding experience to me. Many discussions with Waliur Rahaman, Suratna are always acknowledged.

I am thankful to all PRL friends who helped me in various ways. To name a few Alok, Gyan, Ashwani, Sumanta, Kripa, Arvind, Lokesh, Nabin, Vineet, Tyagi, Rabiul, Suman, Bhaswar, Jayati and many more. Company with Seniors like Sontoshji, Koushikda, Utpalda and Suranjanadi are really rewarding.

I am really grateful to my parents for their support and sacrifice throughout the years.

The missing of several names in the list, does not in the least mean that many more helping hands were not extended to me in accomplishing this task. To them, my apology and assurance that they are very much in my mind. It matters.

Sasadhar

Abstract

Unusual enrichment of heavy oxygen isotopes in ozone formed in gas phase by UV dissociation or Tesla discharge of oxygen is known for quite some time. The unusual nature lies in the high isotopic enrichment values as well as almost equal enrichment in the two heavy isotopes ¹⁷O and ¹⁸O or the so called Mass Independent Fractionation (MIF). Symmetry of the triangular ozone molecule is thought to play a major role in this process. It seems that the formation of ozone isotopomer with the heavy isotope at the terminal position (asymmetric form of ozone) is more probable compared to the formation of ozone isotopomer with the heavy isotope at the terminal position at CALTECH showed that analysis of photochemistry of ozone formation under the RRKM paradigm of unimolecular dissociation subject to the symmetry constraint leads one to expect the observed MIF.

Apart from the MIF associated with ozone formation there is also fractionation involved in ozone dissociation which can be anomalous. Over the last few years several other cases of molecular dissociation have been discovered which are associated with unusual fractionation. CO_2 molecule in particular is a prospective candidate which can be easily dissociated by ultraviolet light to form CO and O atoms with the latter eventually forming O_2 molecules. If there is isotopic anomaly in the product CO and O_2 gases it would be of great interest since CO_2 is an abundant gas in Mars and Earth as well as in many astrophysical objects and the anomaly may get transferred to molecules with which they can interact. Photodissociation of CO_2 is expected to occur due to incident flux of energetic photons or particles in such settings. For example, in a study of Martian meteorites Farquhar et al. [1998] found anomalous excess of ¹⁷O in carbonates which was ascribed to photochemical processes occurring on the Martian surface.

Oxygen isotopic composition of O₂ and CO produced by CO₂ photolysis at 185 nm studied by Bhattacharya et al. [2000] showed a large enrichment ($\sim 100 \%$) in ¹⁷O but essentially no enrichment in ¹⁸O. This was a very surprising result since in normal cases of dissociation one expects a small depletion in heavy isotopes rather than enrichment. Moreover, the fractionation should have been mass dependent i.e., depletion in ¹⁷O should have been half the depletion in 18 O. The CO₂ dissociation at 185 nm is a spin forbidden process since the dissociation involves a singlet to triplet transition due to the presence of spin orbit coupling which can cause the change in spin. However, the spin-orbit coupling of electrons cannot be different for different isotopes. Bhattacharya et al. discussed this issue in detail and concluded that the anomalous enrichment of ¹⁷O in the product gases can be ascribed to the nuclear spin of ${}^{17}O(5/2)$ which can add extra coupling to enhance dissociation of ¹⁷O isotopic species. This intriguing finding has not been confirmed by further work. The carbon isotope ratio in the CO product is an additional candidate for such confirmation since ${}^{13}C$ also has a nuclear spin (1/2). We have extended this earlier research by investigating oxygen isotope ratios in both the products (CO and O₂) and carbon isotope ratio in CO. CO₂ was photolyzed by UV from a low pressure resonance Hg UV lamp producing 184.9 and 254 nm photons. Among the two, only 184.9 nm photons have sufficient energy to dissociate CO₂. After photolysis, CO₂ was frozen and the noncondensable products CO and O₂ were separated from each other by GC techniques and analyzed by Isotope Ratio Mass Spectrometer.

This work confirmed the finding of Bhattacharya et al. The δ^{17} O values of CO and O₂ show unusual enrichment without any significant enrichment in ¹⁸O. To claim that the data indeed show any enrichment in ¹⁷O and evaluate it quantitatively we need to compare the observed δ -values with the values expected based on standard model of isotopic fractionation in photodissociation (Yung and Miller, 1997). Using the available photoabsorption cross section and the zero point energy shift model of Yung and Miller we obtained the absorption coefficients of the isotopic variants of CO₂ molecule. These were incorporated in a chemical simulation model (KINTECUS) to compute the expected composition of the photoproducts CO and O₂.

When we compare the observed δ -values with that predicted by the model we indeed see high level of enrichment in ¹⁷O. The enrichment in ¹⁷O (expressed as $\Delta(\delta^{17}O)$ relative

to the model prediction) varies from 89 to 95 ‰ for O_2 and 75 to 99 ‰ for CO. In contrast, the values of $\Delta(\delta^{18}O)$ are smaller, varying from 16 to 21 ‰ for O_2 and from 7 to 14 ‰ for CO.

Interestingly, $\Delta(\delta^{13}C)$ (relative to the expected value based on the model) in the product CO is also high with ¹³C enrichment varying from 36 to 38 ‰ . It is intriguing to note that the isotopologues with odd neutron numbers (¹⁷O and ¹³C) and associated nuclear spins experience higher rates of dissociation. A connection between dissociation and nuclear spin is therefore strongly suggested. In contrast to the case of Hg lamp photons at 184.9 nm energy, dissociation by higher energy Kr lamp photons (123.6 nm and 116 nm) shows no anomalous isotopic enhancement implying that the fractionation in CO₂ photodissociation depends on the photon energy.

We conclude that the isotopic enhancement in case of Hg lamp photons is probably due to a hyperfine interaction between nuclear and electron spins causing enhanced dissociation of isotopologues of CO_2 containing ¹⁷O and ¹³C. The ¹⁷O enhancement is higher than that of ¹³C by a factor of about 2.3 which can be easily explained by the known magnetic moment ratio of ¹⁷O and ¹³C due to differing nuclear spins.

It is now clear that the isotopic fractionations associated with photo- induced dissociation of CO_2 molecules are highly anomalous and the nature of the anomaly depends critically on the photon energy. Our results provide unique experimental evidence of anomalous mass independent isotopic fractionation in photodissociation of molecules caused by presence of nuclear spin. These results demonstrate a genre of isotopic anomaly different from the symmetry driven isotope anomaly in ozone resulting in a line of slope 1 in the ¹⁷O - ¹⁸O covariation plot.

The nuclear spin hypothesis can probably be used in understanding an enigma in stratospheric CO₂. Stratospheric CO₂ is found to be anomalously enriched in heavy oxygen isotopes and the slope relating the ¹⁷O and ¹⁸O enrichments is found to be about 1.7 which is radically different from that of the stratospheric ozone presumed to be the origin of the enrichment. It is clear that neither the enrichment of ¹⁷O in CO₂ nor the slope can be explained by simple mixing of ozone with CO₂. To resolve this issue we note that in the O(¹D)-CO₂ exchange there is spin violation since the process involves a singlet triplet transition. Based on our study we propose that the O(¹D)-CO₂ exchange rate is faster for ¹⁷O due to its nuclear spin than that of ¹⁸O. This would mean a higher enrichment of ¹⁷O.

resulting in a ¹⁷O-¹⁸O enrichment slope greater than one. It is possible that such anomaly can be seen in any molecular process associated with spin violation.

These results have potential implications in studies of the planetary atmospheres. The photodissociation products having unique isotopic signatures can be used as tracers to study the evolution of the Martian atmosphere. The anomalous signature seen in the energy window which leads to the ¹⁷O selectivity nearly matches with the solar UV availability at an altitude of about 30 km in Earth's atmosphere. Therefore it is reasonable to expect that the atmospheric CO at this height will have excess ¹⁷O due to contribution from the CO₂ photodissociation which could be used as tracer for stratosphere-troposphere exchange.

CHAPTER 1

Introduction

The pioneering studies of Urey [1947] established the basic principles of equilibrium statistical thermodynamics applied to isotope exchange reactions and showed that minor variations in chemical and physical properties of isotopes of light elements (like H, C, N and O) can lead to measurable variations in isotopic ratios in many natural systems. Ever since this paper was published there have been many applications of these ideas in both pure and applied sciences. In basic science the use of isotope ratio variations helps to understand many facets of molecular structure, quantum effects and chemical kinetics. In biological science, isotope properties are widely used to understand the growth and morphology of plants and animals while in geosciences isotope properties are useful in studying paleo-temperature variations, biogenesis and origin and evolution of the planetary atmospheres and solar system. The isotope chemistry field is dominated by experimental studies barring a few outstanding theoretical analysis. In atmospheric science, the importance of isotope ratio measurements is considered as next to concentration and flux analysis since the information obtained by this technique is not possible to get by other techniques so easily. Very often this technique provides a unique way to understand some anomalous phenomena occurring in nature and to discover their causes. Stable isotope ratio measurements have been successfully employed as diagnostic probe for a wide range of processes. In particular, its use as tracer in atmospheric science to better understand the atmospheric chemistry at molecular level has yielded significant insight in issues like global warming or pollution source identification. However, the subject of

photochemistry dealing with interaction of photons with molecules has not been explored adequately in the past through isotopic studies. The present study focuses on stable isotope ratio variations in photochemical reactions. Understanding the isotope effects arising out of photochemical interactions of molecules in the laboratory and atmosphere poses interesting challenges. These challenges bear on characterizing the phenomena itself and also on understanding the new chemical physics responsible for the phenomenon. This thesis deals with the issue of isotope anomaly associated with photodissociation of carbon dioxide molecules.

1.1 Some definitions and concepts

In this section terminologies and basic definitions used in the present study are given in brief. We use the word *abundance* of a stable isotope in a given sample to mean the proportion in which it is present. This can be expressed as a fraction or percentage. For example, oxygen has three stable isotopes ¹⁶O, ¹⁷O, ¹⁸O and their abundances are 99.763%, 0.0375% and 0.1995% respectively, they can also be written as 0.99763, 0.000375 and 0.001995 if expressed as fraction of the total. The term isotope ratio for the heavy isotope ¹⁸O is defined as,

$${}^{18}\mathrm{R} = \frac{[{}^{18}\mathrm{O}]}{[{}^{16}\mathrm{O}]} = 0.0019997 \tag{1.1}$$

It is expressed in the above form because in general (for mass number less than 50), the abundance of the heavy isotope is lees than that of the corresponding light isotope.

The above ratios are usually very small numbers. However, these ratios can vary from one material to another depending on the processes involved in their formation. These variations bring the concept of isotopic fractionation. In any physico-chemical process isotopes do not participate at the same rate due to differences in chemical and physical properties of the isotopes. The phenomenon of modification of isotope ratio during a process is called isotopic fractionation which distributes the isotopes in two phases in slightly different way. The above partitioning of isotopes between two phases A and B can be written mathematically in terms of isotope ratios in individual phases (R_A and R_B) to define a fractionation factor (α):

$$\alpha = \frac{R_A}{R_B} \tag{1.2}$$

This factor is usually close to one, sometimes slightly less and sometimes slightly more than one depending on the system and the phenomenon considered. To avoid dealing with such small numbers and for the sake of comparison δ notation is introduced which is defined as:

$$\delta = \left(\frac{\mathrm{R}}{\mathrm{R}_{\mathrm{s}}} - 1\right) \times 10^3 \tag{1.3}$$

where R and R_s denote a particular isotope ratio (say ¹⁸O/¹⁶O) in a given sample and a standard accepted by all workers. "delta" provides a very convenient way of expressing small relative differences between the sample and the standard and is directly measured by a suitable mass spectrometer. If δ is positive we call the sample as enriched in heavy isotope and if it is negative we call it as depleted with respect to the standard. For convenience, the standard CO₂ or O₂ gases used for measurement are laboratory reference gases calibrated with respect to the accepted international standard. For oxygen isotopes the standard is known as SMOW (an abbreviation for Standard Mean Ocean Water) a water standard derived from ocean. For carbon (as well as oxygen in some cases) a standard known as PDB (made from Belemnite fossil from the Pee Dee Formation in USA) is used. If the sample δ value is measured relative to the laboratory standard gas, to express it relative to the international standard, following relationship is useful:

$$\delta_B^A = \delta_C^A + \delta_B^C + 10^{-3} \delta_C^A \delta_B^C \tag{1.4}$$

where A=sample, B=international standard and C= laboratory standard. In recent times SMOW and PDB have been replaced by equivalents V-SMOW and VPDB (where V stands for Vienna since they were made in IAEA, Vienna).

1.2 Background and theory

The basic classical theory behind isotope fractionation is presented in this section. The motivation behind the thesis is described at the end.

1.2.1 Isotope effects

Isotope effects addressed in this study strictly refer to the stable isotope effect. Since the difference in neutron number has only minor effect on the electronic structure, isotope change should have no large effect on the chemistry of the element. Variations in

the thermodynamic and other physical properties due to isotopic compositional changes are small but modern mass spectrometric techniques and other spectroscopy methods can determine such small isotope effect. There are two kinds of isotope effect:

1. Kinetic isotope effect: The kinetic isotope effect can be described using classical thermodynamic theory which states that mean energy of a particle of mass m is equal to the mean thermal energy of the system on per particle basis:

$$\frac{3}{2}KT = \frac{1}{2}mv^2$$
 (1.5)

Therefore, for a given temperature all isotopic species will have the same kinetic energy which leads to different translational velocity as isotopes have different masses. Examples of this kind are diffusion of gases, evaporation etc. Another example is the dissociation of molecules where breaking up of bond is involved. It is easier to break the molecules that contain the lighter isotopes as they are endowed with higher intrinsic energy since their vibrational frequencies are higher. As a consequence lighter isotopes will be preferentially incorporated in the products whereas heavier isotopes will become enriched in the leftover [Bigeleisen, 1965].

2. Equilibrium isotope effect: This type of isotope effect cannot be described using classical theory as it contributes nothing towards the difference at equilibrium. Therefore, quantum theory is necessary for explaining such effect. The equilibrium isotope fractionation is due to the translational, rotational and vibrational motion of molecules which are dependent on mass. Following the principle of minimization of Gibbs Free Energy for a system in equilibrium isotopes are distributed in certain fashion among the reactants and products. Among the three types of energies vibrational energy is the most important in determining the equilibrium fractionation. Quantification of the equilibrium fractionation is done by calculating the equilibrium constant of the exchange reaction which requires the knowledge of partition function of the reacting molecular components. Equilibrium thermodynamics of multiply substituted isotopologue of molecular gases can be found in many classic review articles [Urey, 1947; Richet et al., 1977; Wang et al., 2004; Thorstenson and Parkhurst, 2004].

1.2.2 Mass dependent isotope fractionation

The isotope effects mentioned above have a common feature - they all depend on mass of the isotopes involved. The exact mass dependency is determined by the process involved. For example, isotope exchange between two isotopically substituted species results primarily due to the difference in Zero Point Energy (ZPE) of the isotopomers. The vibrational frequencies for two isotopically substituted species v_1 and v_2 differ by a factor,

$$\frac{v_1}{v_2} = \sqrt{\frac{\mu_1}{\mu_2}}$$
(1.6)

which leads to a mass dependence in fractionation. For three isotope system like oxygen the mass dependent rule can be expressed in δ -notation as:

$$\delta^{17} \mathcal{O} = \beta \delta^{18} \mathcal{O} \tag{1.7}$$

where β is slightly more than half (ranging from 0.51 to 0.53 depending upon the particular process involved) [Young et al., 2002; Miller, 2002]. Reported oxygen isotope ratios of many oxygen bearing species are shown in the three isotope correlation diagram (Figure 1.1) which shows that ${}^{17}\text{O}/{}^{16}\text{O}$ and ${}^{18}\text{O}/{}^{16}\text{O}$ ratios of all oxygen bearing terrestrial samples follow closely a line of slope half with small systematic variation depending on the actual fractionation process involved. In all the above fractionation processes molecules involved are in electronic ground state and therefore the process can be described using ground state ZPE which essentially depends on mass. The mass fractionation laws for kinetic as well as equilibrium processes derived mathematically can be found in several publications [Matsuhisa et al., 1978; Young et al., 2002]. The mass dependent rule can be visualized in a very simple manner. For example, in case of three isotope system like oxygen among the three isotopes ¹⁶O, ¹⁷O and ¹⁸O the mass difference of ¹⁸O from ¹⁶O is 2 unit whereas mass difference between ¹⁷O and ¹⁶O is one unit. Since for small changes in isotope ratio the change is a linear function of mass difference the change in ratio ${}^{18}\text{O}/{}^{16}\text{O}$ should be two times that of the ratio ${}^{17}\text{O}/{}^{16}\text{O}$. As mentioned above, in case of equilibrium isotope exchange reactions, the fractionation laws are derived by calculating the equilibrium constant in terms of partition function ratios which depend on temperature. Therefore, the distribution of stable isotopes between different reservoirs at equilibrium can be used as a precise thermometer. This has important implication in Earth Sciences to reconstruct the climate history of the Earth. For example, the δ^{18} O values of carbonate shells in the ocean

depend on the equilibrium temperature of carbonate precipitation. Therefore, if the water isotopic composition can be inferred the carbonate delta value can be used to estimate the temperature of the ancient oceans.



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

1.2.3 Mass independent isotope fractionation

The processes described above refer to mass dependent cases of isotopic fractionation. There are, however, exceptions to the above simple mass dependent law. For example, in case of ozone formation by electrical discharge the degree of fractionation for ¹⁷O is not half of that of ¹⁸O [Thiemens and Heidenreich, 1983]. Instead, it was found that $\delta^{17}O$ is nearly equal to $\delta^{18}O$. This effect is now known as non-mass-dependent fractionation (NOMAD) or Mass Independent Isotopic Fractionation (MIF) or simply anomalous fractionation. In general, isotopic anomaly refers to abundance variation in isotopes of a given element which does not obey normal rules of fractionation and Mass Independent Isotopic Fractionation (MIF) is a particular case of such anomalies. This anomalous behavior results from inherent molecular property and hence gives valuable information about atomic and

molecular processes occurring in nature. Anomalous isotope effect may arise from changes in chemical or nuclear properties upon isotopic substitution (such as nuclear spin, size or shape). These isotopic changes are accompanied by shifts in electronic spectra as well as vibrational and rotational energy levels [Bigelesisen, 1996]

Mass independent anomaly is reported normally in terms of $\Delta^{17}O$ which is defined as:

$$\Delta^{17} O = \delta^{17} O - \beta \delta^{18} O.$$
 (1.8)

For small $\Delta^{17}O$ values the above definition can often lead to a conclusion of anomaly which is not a "true anomaly" since the so called anomaly can be due to a change in beta value applicable to that particular process. A discussion on this topic can be found in Assonov and Brenninkmeijer [2005] and Miller [2002]. It is convenient to express the above relation in normalized form which is more general.

$$(\delta^{17}O/1000 + 1) = (\delta^{18}O/1000 + 1)^{\beta}$$
(1.9)

$$\ln(\delta^{17}O/1000 + 1) = \beta \ln(\delta^{18}O/1000 + 1)$$
(1.10)

Currently, more sophisticated definitions are in use and a comparative study of various representations can be found in literature [Assonov and Brenninkmeijer, 2005].

1.2.4 Example of MIF in Solar system, Earth and Planetary atmosphere

Deviations from mass dependent rule have been observed in many extra terrestrial materials. Anomalous isotope effects were first detected in so called high temperature Ca-Al inclusions (CAI) in Allende meteorite Clayton et al. [1973]. They found that the three isotope correlation slope of oxygen isotopes in CAI is one rather than 0.5. They suggested that since normal isotope effect can only produce fractionations with $\delta^{17}O - \delta^{18}O$ slope of 0.5, the CAI data must reflect intervention of nuclear processes. It was also suggested that the progenitor of the observed isotope anomaly could be monoisotopic ¹⁶O which is produced by explosive carbon or helium burning. The nuclear origin explanation for CAI data was challenged by the discovery of equal heavy isotope enrichment in ozone produced by electrical discharge in oxygen by Thiemens and Heidenreich [1983] mentioned before. The striking similarity between the two raises the possibility that the meteoritic oxygen isotope anomaly is the result of some chemical process rather than nuclear. Subsequent work on ozone confirmed the chemical nature of the effect. A great deal of work

has been done on ozone formation and dissociation since then to reveal the exact nature of the process. A molecular symmetry selective reason for the ozone isotope effect was suggested by Heidenrich and Thiemens in their subsequent work which was refined later in a comprehensive theory by Marcus group at CALTECH [Gao and Marcus, 2001a, 2001b].

Ozone isotope study was done simultaneously in earth's atmosphere. The first atmospheric measurements were done by Mauersberger in 1981 [Mauersberger, 1981] who found that stratospheric ozone is enormously enriched in 18 O ($\sim 400 \%$). In later work Mauersberger [1987] showed that the enrichment is not constant, but varies with the sampling latitude. Later on, more precise isotope measurement were performed and it was shown that δ^{17} O is about 0.7 that of δ^{18} O but can be variable to a limited extent. Mass independent effect in atmospheric ozone has been confirmed by several groups by using a variety of techniques. Krankowsky et al. [2000] performed ozone isotopic measurements by five different balloon flights during 1998-2000 up to an altitude of around 33 km. Apart from mass spectrometric measurements of stratospheric ozone samples, many workers have carried out both space and ground based spectral analysis of ozone isotopomers. Isotope ratio monitoring by ground based FTIR (Fourier Transform Infrared) spectrometer, Satellite measurements using ATMOS (Atmospheric Trace Molecule Species Experiment) etc have provided data as well as details of the isotopometric distribution of ozone in the stratosphere [Abbas et al., 1987; Goldman et al., 1989; Irion et al., 1996; Meier and Notholt, 1996; Johnson et al., 2000; Wolf et al., 2000; Krankowsky et al, 2000; Haverd et al., 2005; Mauersberger et al., 2005].

In addition to the above, the effect of pressure [Thiemens and Jackson, 1988, 1990; Gunther et al., 1997; Bhattacharya et al., 2002], temperature and third body [Gunther et al., 1997] on ozone isotope anomaly was investigated in various laboratories in great detail. Ozone database is presently very much enriched in all these aspects. Laboratory experiments on pressure dependence reveal that the enrichment decreases towards high pressure. In a follow up experiment Heidenreich and Thiemens [1986] found that for oxygen pressure below 3 torr ozone was depleted and a deviation from the 1:1 correlation of δ^{17} O and δ^{18} O was also observed. Bains-Sahota and Thiemens [1987] extended the study in lower pressure (20 mtorr < P < 62 torr) using microwave discharge flow reactor experiment. They concluded that in lower pressure the depletion is not pronounced whereas in higher pressure the enrichments for ¹⁸O and ¹⁷O are 10.1% and 8.2% respectively. A

heterogeneous ozone formation mechanism was suggested to be the cause of this change over. Mass dependent depletion has been found in the pressure range 56 to 87 atmosphere [Thiemens and Jackson, 1990]. At about 100 mbar pressure the measured enrichments are about 110 and 130 ‰ in $^{49}O_3$ and $^{50}O_3$ respectively [Mauersberger et al., 1993]. To study the temperature and pressure dependence in ozone formation process Morton et al. [1990] designed a photolysis recycling experiment. It was found that in the temperature range between 170 K and 370 K the enrichment increases with temperature.

An important conclusion has been drawn from all these careful laboratory studies. The conclusion is that the observed isotope effect is an intrinsic molecular phenomenon independent of the O₂ starting composition. Only the magnitude of enrichment is determined by the above physical quantities. Another aspect of ozone formation investigation is the determination of relative rates as a function of isotope substitution [Yang and Epstein, 1987; Mauersberger et al., 1993, 1999; Anderson et al., 1997; Janssen et al., 1999, 2001, 2002; Wolf et al., 2000; Tuzson., 2005; Janssen and Tuzson, 2006]. In all these cases enriched oxygen is used to produce ozone isotopomers. Anderson et al. [1997] quantified that the exchange reaction between oxygen atom and oxygen molecule has larger rate coefficients than the recombination reaction. This study was further extended by Janssen et al. [2001] who quantified the reaction rates for heteronuclear molecule reactions in the binary ¹⁶O-¹⁸O system by using tunable-diode infrared absorption spectroscopy together with isotope ratio mass spectrometry.

A number of systems with mass independent fractionation has been discovered besides the ozone system. Anomalous three isotope relation has been found in the atmospheric sink reaction CO+OH and this MIF promises to provide a signature of time and space integral of OH concentration to understand the chemistry of the atmosphere [Rockmann et al., 1998a, 1999; Feilberg et al., 2002]. Huff and Thiemens found MIF in CO samples collected from various locations in California [Huff and Thiemens, 1998]. Another strong candidate for MIF is the photolysis of N₂O [Yoshida and Matsuo, 1983; Johnston et al., 1995; Rahn and Wahlen, 1997; Cliff et al., 1997, 1999 ; Yoshida and Toyoda, 2000; Kaiser et al., 2002 ; Yung et al., 2004]. In addition, anomalous effect has been observed in non ozone system like SF₅+SF₅ \rightarrow S₂F₁₀ [Bains-Sahota and Thiemens, 1987]. MIF has been extensively investigated recently in the reaction O+CO \rightarrow CO₂ by Pandey and Bhattacharya [2006] which showed a level of enrichment almost similar to that of ozone. It is believed that these two

systems have exactly similar symmetry in the reaction intermediate and therefore they would have similar enrichment level if symmetry plays a dominant role in this process. A fall out of atmospheric ozone anomaly is the expectation that the ozone anomaly can be transferred to other atmospheric trace molecules. Careful measurements showed this to be true. Anomalous enrichment effect has been observed in atmospheric aerosol (particulate), nitrate [Michalski et al., 2002, 2003], sulfate [Savarino et al., 2000, 2003; Lee et al., 2001, 2002; Thiemens et al., 2001; Alexander et al., 2002; Romero and Thiemens, 2003; Baroni et al., 2007]. Lastly, the isotope exchange reaction $O(^1D)+CO_2 \rightarrow O(^3P)+CO_2$ also demonstrates a significant mass independent anomaly whose origin is still under debate [Yung et al., 1991, 1997; Wen and Thiemens, 1993; Johnston et al., 2000; Chakraborty and Bhattacharya, 2003; Boering et al., 2004; Shaheen et al., 2006; Liang et al., 2006].

1.2.5 Theoretical developments

To explain the anomalous isotope effect in ozone molecule many theoretical models were developed at various stages after the discovery of the effect [Valentini, 1987; Bates, 1990a, 1990b; Gellene, 1992, 1993, 1996; Hathorn and Marcus, 1999, 2000, 2001; Gao and Marcus., 2001a, 2001b; Robert and Camy-Peyret, 2001; Gao et al., 2002; Marcus, 2004; Robert, 2004]. The qualitative argument proposed by Heidenreich and Themenms [1986] later on emerged as a semi-empirical theory by Gao and Marcus. Heidenreich and Thiemens suggested that the effect is due to isotopically selective stabilization of O₃ formation reaction intermediate through a symmetry selective process. In a series of publications, Marcus and coworkers proposed a modified version of unimolecular theory of dissociation known as RRKM theory (after the scientists Rice, Ramsperger, Kassel, Marcus) to explain the unusual ozone isotope effect. Among the many aspects of this theory within the conventional RRKM paradigm two major mechanisms contribute to the observed isotope effect. The first one is a nonstatistical factor which arises due to the fact that the formation of symmetric and asymmetric ozone molecule occurs through substantially different pathways. The second one is associated with the competing dissociation channels of the intermediate O₃* due to difference in ZPE in ozone formation. Both the factors are consequences of the symmetry of the intermediate complex. Because of the dynamical constraints of symmetry in RRKM model, the vibrationally excited asymmetric isotopomers have lifetimes that are longer than that of the symmetric isotopomers. Thereby at low

pressure they have a better chance of being deactivated by a collision and forming a stable ozone molecule. This automatically leads to an equal fractionation of the heavy isotopes in ozone relative to that expected based on pure statistical consideration. Gao and Marcus [2001a] also proposed that the constraint due to symmetry/asymmetry in the transition complex is not restricted to ozone but can be applied to any molecule that has the possibility of forming symmetric or asymmetric isotopomers, but the magnitude of the effect would depend on the nature of the intermediate complex (e.g., its state density) and the physical conditions of the reaction (like temperature and pressure).

Janssen et al. [2001] discovered a linear correlation between the rate coefficient and the ZPE change of the exchange reactions that compete with ozone formation. This finding could be incorporated in the Gao-Marcus theory. To explain the ozone effect, a different approach was undertaken by Miklavc and Peyerimhoff [2002] with the consideration that ozone formation is the transfer of kinetic energy of the incident O atom into the vibrational energy of the O₂ collision partner. This formalism is known as Landau Teller formalism and this formalism is in good agreement with cases where rate coefficients are large. Similar approach was adopted by Charlo and Clary using an ab initio potential energy surface to calculate wave functions for scattering resonances which arise from collisions of O+O₂ [Charlo and Clary, 2000]. The above approach was further modified by Babikov et al. [2003a, 2003b] where rigorous quantum scattering calculations were carried out using the global PES developed by Schinke and coworkers [Grebenshchikov et al. 2007]. Their calculation shows that for a dissociating molecule zero point energy difference of dissociating channels is one important controlling factor to produce different relative rates. The authors carried out full quantum mechanical scattering calculations including all six dimensions to determine energies and lifetimes of resonances for ¹⁶O¹⁸O¹⁸O, ¹⁶O¹⁸O¹⁸O and ¹⁶O¹⁶O¹⁶O. They found a pronounced non statistical behavior at the threshold energy of the reaction where there are many long-lived metastable states near the threshold leading to efficient stabilization but only a few metastable states at much higher energy than the threshold energy resulting in less efficient stabilization.

In a recent article, Marcus has reviewed some theoretical aspects of mass independent oxygen isotope fractionation in selected systems from mechanistic point of view [Marcus, 2008]. It is known that the reaction CO+OH \rightarrow CO₂ +H has anomalous oxygen isotope behavior [Feilberg et al., 2005]. The symmetry effect responsible for ozone and other

molecules is absent in this system since the intermediate has no symmetry with respect to isotopes. Obviously, here the origin is different from symmetry/asymmetry restriction. In this reaction, large discrepancy exists in theory and experiment and this issue is still unresolved.

The above discussion refers mainly to cases of molecule formation but isotope effect also can occur in dissociation of molecules. Yung and Miller proposed a simple model to explain isotope effect in direct dissociation of molecules by photon absorption. They applied this theory to explain the isotopic nature of products of N₂O photodissociation [Yung and Miller, 1997]. The method is based on calculation of absorption cross section of isotopologues by shifting the absorption spectrum of heavy isotopologues relative to the normal one corresponding to their ZPE difference. However, this could not explain all the experimental features. A more sophisticated theory has been used by Johnson et al. [2001] which introduces the concept of wavefunction propagation on the PES with time. This model is known as Hermite Propagation model (HP model) and results in larger isotope effects than the ZPE model. A recent theory by Prakash et al. [2005] modified the work of Johnson et al. by including contributions of the various bending mode vibrations to the transition dipole moment. The prediction from this theory is quite close to the experimental results. The absorption cross section calculation of various isotopic molecules has been recently reviewed by Jost [2008] who introduced certain simplifying concepts for estimating the average behaviour in dissociation.

1.3 Motivation for the thesis

It is generally believed that in processes occurring in low energy environment where molecules are confined to the ground electronic state the partitioning of isotopes follow mass dependent rule. In contrast, if the fractionation occurs in high energy environment where molecules in excited states are involved there could be dramatic deviation from the mass dependent rule. It is also assumed that the exact nature of deviation depends on the energy used and the effects might be molecule specific. Therefore, isotopic study of photodissociation products of molecules using ultraviolet light of different energy offers an exciting possibility to understand fractionation associated with processes occurring in excited states of molecules. Photochemical reactions in several cases are known to be as-

sociated with MIF. As mentioned, in formation of ozone by O+O₂ reaction [Heidenreich and Thiemens, 1983] or formation of CO₂ by O+CO reaction [Bhattacharya and Thiemens, 1989a ; Bhattacharya and Thiemens, 1989b ; Pandey and Bhattacharya, 2006] one obtains large MIF. An interesting discovery has been made some time back in analysis of isotope ratios of atmospheric CO₂. It has been possible to measured accurately the oxygen isotope ratio of stratospheric CO₂ and the three isotope correlation plot of this CO₂ shows a puzzling feature. It is seen that the enrichments in ¹⁷O and ¹⁸O are related by a slope between 1.2 and 1.7 [Thiemens et al., 1991; Gamo et al., 1995; Alexender et al., 2001; Lammerzahl et al., 2002]. An attempt was made to explain the enrichment in CO₂ as due to transfer of anomaly from ozone to CO₂ through UV dissociation products of ozone. Even though this model can explain the isotope enrichment the high value of the slope could not be reproduced. It is not clear why ozone with three isotope slope less than unity (close to 0.7) can result in isotope transfer with a much higher slope. Researchers in this field feel that a different mechanism is needed to explain the high slope in CO₂. The above studies so far did not take into account any possible isotopic fractionation arising out of molecular spin and its change during the reactions. Only recently, two groups have examined the case of spin forbidden exchange reaction involved in quenching of $O(^{1}D)$ by CO_{2} [Mebel et al., 2004; Yang et al., 2005].

The surprising possibility of isotope fractionation due to nuclear spin effect was invoked in liquid phase chemical reactions. Similar to mass in chemical isotope effect, nuclear spin can play an important role in sorting of isotopes. If the reaction rate depends on symmetry restrictions imposed by change in total spin of the system (or magnetic moment) it is possible to visualize a type of fractionation in chemical reactions involving isotopes with nuclear spin and without nuclear spin. [Buchachenko et al., 1976, 1994; Sagdev et al., 1977; Turro et al., 1985a, 1985b, 1995; Buchachenko and Khudyakov, 1991a, 1991b; Buchachenko, 1995, 2000, 2001]. Sorting of isotopes based on thier nuclear spin was first observed in carbon isotope (13 C, nuclear spin 1/2) fractionation during photolysis of dibenzyl ketone which is known to occur via fragmentation of triplet molecules and generation of triplet radical pairs [Buchachenko, 1976]. They observed enrichment in 13 C to be about 100 ‰ in the left over dibenzyl ketone. Later on, nuclear spin effect of 13 C was seen on triplet sensitized photolysis of benzoyl peroxide which produces phenyl benzoate enriched in 13 C by ~60 ‰. Similar effect has also been observed in 17 O (nuclear spin

5/2) in the liquid-phase oxidation of ethylbenzene by molecular oxygen [Belyakov et al., 1978]. The left over molecular oxygen was enormously enriched in ¹⁷O (by ~120 ‰) relative to the ¹⁸O. This result was confirmed by Buchachenko et al. [1984, 1995] and Yasina and Buchachenko [1990] in chain oxidation of polymers and hydrocarbons by molecular oxygen.

In the context of the above background, we decided to study the photodissociation products of CO_2 for isotopic anomaly. CO_2 being a dominant molecule in the planetary atmospheres anomalies arising from such processes would have diverse applications. CO_2 molecule can be dissociated by UV light to form CO and O atoms with the latter eventually forming O_2 molecules. If there is isotopic anomaly in the product CO and O_2 gases it would be of great interest since CO_2 is an abundant gas in Mars and Earth as well as in many astrophysical objects and the anomaly may get transferred to molecules with which they can interact. Photodissociation of CO_2 is expected to occur significantly due to incident flux of energetic photons or particles in such settings. For example, in a study of Martian Meteorites Farquhar et al. [1998] found anomalous excess of ¹⁷O in carbonates which was ascribed to photochemical processes occurring on the Martian surface. The mechanism of production of O and CO in different energy states depends on the wavelength of the absorbed UV photons as given below [McElroy and McConnel, 1971; Lawrence, 1972; Okabe, 1978]

$$\mathrm{CO}_2 + \mathrm{h}\nu \to \mathrm{CO}(\mathrm{X}^1\Sigma) + \mathrm{O}(^3\mathrm{P}) \,(\,\mathrm{for}\,167.2 < \lambda < 227.5\,\mathrm{nm}) \tag{1.11}$$

$$CO_2 + h\nu \to CO(X^1\Sigma) + O(^1D) \text{ or } O(^3P) (\text{ for } 120.0 < \lambda < 167.2 \text{ nm})$$
 (1.12)

$$CO_2 + h\nu \to CO(X^1\Sigma) + O(^1S) \text{ or } O(^1D) (\text{ for } < 120.0 \text{ nm})$$
 (1.13)

The electronically excited oxygen atoms $O(^{1}D)$ and $O(^{1}S)$ are quenched to $O(^{3}P)$ by collisions. Subsequently, molecular oxygen is formed by recombination of $O(^{3}P)$ atoms:

$$O(^{3}P) + O(^{3}P) + M \to O_{2} + M$$
 (1.14)

Here M is the third body required to carry away the excess energy of the association process. Oxygen isotopic composition of O₂ and CO produced by CO₂ photolysis at 185±5 nm was first studied by Bhattacharya et al. who discovered a large enrichment (~100 %) in ¹⁷O but essentially no enrichment in ¹⁸O. This was a very surprising result since, as explained before, in normal cases of dissociation one expects a small depletion in the heavy

isotopes rather than enrichment. Moreover, the fractionation is normally mass dependent i.e., the depletion or enrichment in ¹⁷O should have been about half that in ¹⁸O. Bhat-tacharya et al. ascribed the ¹⁷O enrichment in the product oxygen gas to an effect due to nuclear spin. Their proposition is explained below in more detail.

The CO₂ dissociation at 185±5 nm is a spin forbidden process since the spin of the CO₂ at ground state (${}^{1}\Sigma_{g}$) is zero whereas the total spin of CO+O(${}^{3}P$) is one. The dissociation involves a singlet to triplet transition, which is forbidden according to spin conservation rule. The fact that CO₂ can still dissociate at this energy is obviously due to the presence of a perturbation, which can cause the change in spin. For example, a spin orbit coupling involving outer shell electrons can be such a perturbation. However, the spin orbit coupling of electrons can not be different for different isotopes and therefore, cannot explain the anomalous enrichment in 17 O and more so without any effect on 18 O. To explain the unusual enrichment in only 17 O isotope Bhattacharya et al. proposed that the nuclear spin of 17 O (5/2) may augment the usual spin orbit coupling and result in larger dissociation rate of the 17 O containing isotopomer.

The intriguing finding of Bhattacharya et al. and their novel proposition have not been further confirmed by more extensive work. We realized that the carbon isotope ratio in the CO product is a potential candidate for such confirmation since ¹³C also has a nuclear spin. In the present work, we have extended the earlier research by investigating oxygen isotope ratios in both the products (CO and O_2) and carbon isotope ratio in CO. We also studied the temperature variation of fractionation to obtain more insight into this unusual fractionation process. The following investigations were carried out:

- Experimental analysis of oxygen isotope ratio in gases O₂ and CO produced by UV photodissociation of CO₂ at two wavelength regions (185 nm produced by a resonance Mercury (Hg) lamp and 116 and 123 nm photons obtained from a resonance Krypton (Kr) lamp). For comparison, simple dissociation induced by high energy electron impact by Tesla discharge was also studied.
- 2. Experimental analysis of carbon isotope ratio in the CO molecule.
- 3. Study of temperature dependence of the above isotope effects.
- 4. Calculation of expected isotopic composition of O_2 and CO gases by a Chemical

Kinetic Reaction Simulation Model based on theory of Direct Photodissociation and its comparison with the observed results.

1.4 Scope of the present thesis

The present thesis investigates extensively the phenomena of anomalous isotope effect in CO_2 photodissociation first observed by Bhattacharya et al. [2000]. The thematic division of the chapters are as follows.

The experimental techniques which have been developed to carry out the proposed study are presented in **Chapter 2**. **Chapter 3** gives an overview of the Chemical Kinetic model (named as Kintecus) used in this study. The rationale and procedure for use of this model to interpret the laboratory results are described in detail. The major results obtained in the present study are presented in **Chapter 4**. **Chapter 5** deals with the temperature effect on the photolysis products. Implications of these laboratory results towards understanding some isotope anomalies observed in nature along with the discussion of major conclusions and the future scope are presented in **Chapter 6**.

CHAPTER 2

Experimental Technique

This chapter describes the experimental techniques used in the present study. In this study the earlier CO measurement protocol was extended to make it simple and reliable. A technique developed for separating CO and O_2 is discussed in detail. This procedure can be especially useful in measuring isotopes of CO having mass independent character.

2.1 Isotope Ratio Mass Spectrometry (IRMS)

In the present work the relative abundances of isotopes and their small variations were determined by mass spectrometric methods using two mass spectrometers VG 903 (upgraded) and GEO 20-20. Both the mass spectrometers are dual inlet, gas source, triple collector type machine. A broad introduction to the techniques of mass spectrometry is given below.

2.1.1 Principle

Basically, a mass spectrometer is an instrument which produces, accelerates, deflects and detects ions from a given sample so as to measure its isotopic composition. The basic components of a gas source mass spectrometer are (Figure 2.1):

1. An inlet system: As the mass spectrometer operates in high vacuum special arrangements are needed for sample inlet. Normally, gases are introduced into the source of the mass spectrometer through a long metal capillary (~1 m length) that has a crimp at its end. These crimps are also used to balance the currents of sample and reference gases. To avoid molecular flow which causes large isotope fractionation, the length and the internal diameter of the capillary (typically 10^{-4} m) are chosen such that a viscous flow is maintained. A cluster of four solenoid controlled changeover valves allows for rapid switching between sample and reference gases. The gases are fed from adjustable bellows to adjust the inlet pressure. For micro-quantities of gas, sample is cryo-trapped in a cold finger (less than a ml volume including associated valves) to obtain necessary pressure/ current. Using the cold finger, it is possible to measure less than about a μ mol gas. In VG-903, an indigenously made cold finger with molecular sieve was used to measure non-condensable gases like O₂ and CO. In this machine ~4 μ mol gas is required to get appreciable ion current. To account for any fractionation across capillaries routine zero enrichment procedure was carried out using the same gas on the sample and reference side.

2. The ion source: Gas molecules enter the ion source of the mass spectrometer from the inlet system where a fraction of them is ionized by electron bombardment whereby outermost electrons of the molecules are knocked off producing positively charged ions. The sensitivity of the mass spectrometer depends on the efficiency of the ionization process which in turn is dependent on various parameters like ionization cross section, concentration and energy of the electrons and concentration of the molecules. The number of molecules needed to get one ion is typically within 1500-2000 in the mass spectrometers used in this study. Electrons are emitted from a heated (2000°C) filament (thoria coated for high emission) the heating being done by passing about 4 amp current from an emission regulatory circuit. Before entering the ionization region, electrons are accelerated by a potential difference to an energy of about 75 eV. A magnetic field of about 500 Gauss intensity is applied to increase the path length and consequent ionization. The electrons are collected by a plate called trap located at the end of the ion box. The number of electrons reaching this plate is called the trap current. The trap current is controlled by an emission regulatory circuit. Normally it is fixed at a few hundred μ amp the exact value being dependent on the gas analyzed. The produced ions are extracted from the ion box perpendicular to the electron beam by applying a repeller potential. The potential gradient across the ionization region is such that it minimizes the energy loss and ion-molecular reactions. After emerging from the ion box, ions are accelerated by a high voltage. They pass through various exit slits kept at various potentials in a collimated manner and enter into the analyzer section.

- 3. The mass analyzer: The collimated beam passes through a strong magnetic field kept perpendicular to the flight direction generated either by a permanent magnet (VG-903) or electromagnet (GEO 20-20). The magnetic field deflects the ions in a circular trajectory according to ratio of charge to mass. The magnetic field normally employed is of the order of a Tesla. Light ions are deflected more strongly than heavy ones of the same charge causing a physical separation between ions of different isotopologues of the molecule. Focussing of ion beam of same mass is done by double focusing technique where the magnet is placed at an offset by about 26.5° from the normal entry so that both x and y focusing can be achieved.
- 4. The ion collector assembly: Faraday cups are placed along the focal plane of the mass spectrometer for detection of ions. As the relation between mass and radius of curvature is not linear, positions of adjacent peaks change with mass. Therefore, each set of isotopes needs its own Faraday cup assembly. Due to the high incident energy of the ions the surface of the detector is sputtered and secondary electrons and ions are ejected. These must be suppressed to prevent a false measurement of the ion current. Therefore, Faraday cups are thin, deep boxes with graphite surfaces and an electric field at the entrance is used to force the secondary electrons back into the cup. The ions picked up by the collector give rise to electric currents that pass through operational amplifier (with ultra low input bias current) and high (10^9 to) $10^{12}\Omega$) resistors to ground. The intensities of the voltage produced are proportional to the quantities of ions being collected. The output voltages are then converted to trains of short pulses by voltage to frequency converter and the repetition rate is linearly proportional to the input voltage. Signals are converted to frequencies at a rate of 2000 Hz/V. Multiple collectors are often used in modern mass spectrometry and various type of softwares are available for dealing with varieties of operations employed.



Figure 2.1: Schematic diagram of a mass spectrometer

2.1.2 Equation for mass spectrometry

When moving charge species (ions) experience a magnetic field, they are deflected. The magnitude of the deflection is governed by the momentum of the ion and is described by the equation 2.1 and 2.2. First, the kinetic energy (k) of the ion is equal to the energy gained through acceleration from the ion source.

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

Second, the centrifugal force on the ion as its path is deflected by a magnetic field is equal to the force exerted on the charge by the field.

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

where, q= charge of the molecule, V= electric field, v= velocity of the charged particle and B= magnetic field

If the field and the ion velocity are orthogonal to each other the path followed by the

ions are circular and the radius of the circular path is given by,

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

As evident from the above formula, the ions with same $\frac{m}{q}$ follow the same radial path. Therefore, for same q, ions of different masses follow different radial paths and get separated in the magnetic field. The Faraday cups are so located that each one collects ions of a particular mass when focussing conditions are satisfied.

2.2 Measurement of O_2

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

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

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

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

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

where,

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

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

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

Table 2.1: The oxygen isotopic composition of two samples of tank BOC-O₂ first measured in VG-903 in PRL, Ahmedabad and later in MAT 251 in UCSD, San Diego. The isotopic compositions are expressed with respect to V-SMOW. The results from the two laboratories agree within 0.05 ‰ for ¹⁸O and 0.5 ‰ for ¹⁷O.

Sample	PRL data		UCSD data		Difference (PRL-UCSD)	
	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$	$\Delta \delta^{18} O$	$\Delta \delta^{17} O$
	‰	‰	‰	‰	‰	‰
A-BOC- O_2	24.2	12.7	24.3	12.2	-0.1	+0.5
$B-BOC-O_2$	24.1	12.6	24.1	12.1	0.0	+0.5

Oxygen isotope ratios were measured by the VG903 triple collector mass spectrometer. A tank of oxygen gas supplied by BOC company was used as running standard which was calibrated relative to the international standard SMOW. To confirm our calibration and measurement accuracy an inter laboratory comparison was performed by getting a few samples analyzed in PRL and in the Stable Isotope Laboratory of the University of California, San Diego, USA and the values are presented in Table 2.1. The uncertainties in PRL measurement of oxygen isotope ratios in δ^{18} O and δ^{17} O are estimated to be 0.05 ‰ and 0.2 ‰ respectively.

2.3 Measurement of CO

The major CO isotopomers are

$${}^{28}\text{CO} = {}^{12}\text{C}{}^{16}\text{O}$$

 ${}^{29}\text{CO} = {}^{13}\text{C}{}^{16}\text{O} + {}^{12}\text{C}{}^{17}\text{O}$
 ${}^{30}\text{CO} = {}^{12}\text{C}{}^{18}\text{O} + {}^{13}\text{C}{}^{17}\text{O}$

The isotope ratios of a CO gas sample are defined as ${}^{13}R={}^{13}C/{}^{12}C,{}^{17}R={}^{17}O/{}^{16}O$ and ${}^{18}R={}^{18}O/{}^{16}O$ and in a similar way for a CO gas standard they are ${}^{13}R_s,{}^{17}R_s$ and ${}^{18}R_s$ respectively. Therefore we have

$${}^{29}R = \frac{[{}^{13}C^{16}O] + [{}^{12}C^{17}O]}{[{}^{12}C^{16}O]}$$
(2.8)

and

$${}^{30}R = \frac{[{}^{12}C^{18}O] + [{}^{13}C^{17}O]}{[{}^{12}C^{16}O]}$$
(2.9)

In terms of delta notation, the above two equations can be written as,

$$\delta^{29} \text{CO} = \left(\frac{1}{1+2z}\right) \delta^{13} \text{C} + \left(\frac{z}{1+z}\right) \delta^{17} \text{O}$$
(2.10)

$$\delta^{30} \text{CO} \approx \delta^{18} \text{O} \tag{2.11}$$

where $z = {}^{17}R_s / {}^{13}R_s$

To calculate ¹³C/¹²C, ¹⁷O/¹⁶O and ¹⁸O/¹⁶O of a CO sample the above two equations are not sufficient as three quantities cannot be determined from two raw mass spectrometric numbers δ^{29} CO and δ^{30} CO. To address this problem we developed a separate method to measure the δ^{13} C value of the CO sample (described in detail in the next section) and by putting that value in the above equation (2.10) we obtained the δ^{17} O of CO. The correction term for the δ^{18} O of CO is small (about 0.1 ‰) and can be determined after calculation of other terms. The standard used for CO measurement is a tank of CO gas supplied by the Vadilal company which was calibrated with respect to the international standard V-SMOW for oxygen isotope ratios and with respect to VPDB-CO₂ (CO₂ generated from Vienna PDB at 25°C) for carbon isotope ratio.

2.3.1 Carbon isotope ratio measurement of CO

To measure the carbon isotope ratio of the CO sample we followed the method originally developed by Stevens and Krout [1972] and subsequently modified by Brenninkmeijer [1993]. This method is now widely used for carbon isotope ratios measurement of CO [Bhattacharya et al., 2000; Rockmann et al., 1998]. In this method CO is converted to CO_2 by passing through Schutze reagent (SR) which adds one oxygen atom to CO to produce CO_2 without any isotope exchange. Schutze reagent is I_2O_5 acidified with H_2SO_4 on a silica gel support. Commercially available Schutze reagent was used by us and its performance was tested frequently by using the laboratory standard CO. Its conversion efficiency and the carbon isotope ratio of the final CO_2 for a few test cases are shown in Table 2.2. The reagent was kept in a quarter inch U tube whose sides were connected to the vacuum line through stopcocks. To prevent light exposure and consequent degradation of SR the U tube was covered by aluminium foil. The effectiveness of SR was checked by injecting pure CO gas through the column. A narrow band of brown colour appeared at the beginning due to the formation of I_2 . Each sample of formed CO_2 was cleaned from contaminants (water released from the SR and the I_2 vapour) by cryogenic means using two
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traps. In the first trap an alcohol slush (-60°C) was kept for trapping the water and in the second trap LN₂ was put for CO₂ collection. This CO₂ was purified again by alcohol slush and LN₂ to remove any remaining contaminant. Next, the newly formed CO₂ was equilibrated with CeO₂ at high temperature whereby the oxygen isotopes of the exchanged CO₂ become mass dependently fractionated; this allows us to determine the δ^{13} C value of the exchanged CO₂. Assuming that the δ^{13} C of CO₂ equals the δ^{13} C of the original CO the δ^{17} O value of the original CO can be recovered. The CeO₂ exchange was carried out in a reaction tube made of quartz (20 cm in length and 1 cm in diameter and positioned horizontally) having a small cold finger which was connected to the main vacuum line by a stopcock. Approximately 10 g of CeO₂ (preheated at \sim 1000°C in air and crushed to make grains of size 0.25-0.5 mm) was kept in the reaction tube with silica glass wool as filter plug to prevent fine grains escaping to the vacuum line. Before each CO₂ exchange, CeO₂ was preconditioned by flushing it with tank oxygen and then keeping it at 650°C under high vacuum for more than one hour to remove excess oxygen. In order to heat CeO₂ a cylindrical jacket heater was put over the reaction tube. The CO_2 gas was transferred to the cold finger attached to the reaction tube. After ensuring complete transfer, the exchange reaction of CO₂ with CeO₂ was allowed to proceed. At 700°C the exchange reaction reaches equilibrium in 30 min. After that, the CO₂ was collected back in the cold finger, transferred to the sample tube and analyzed. The above exchange converts the CO₂ oxygen isotopes to mass dependent entities without change in carbon isotope ratio as shown by Assonov and Brenninkmeijer [2001].

Mass spectrometric measurements of CO_2 after exchange with CeO_2 yield two equations,

$$\delta^{46} \mathrm{CO}_2(\mathrm{ex}) = \delta^{18} \mathrm{O}(\mathrm{ex}) \tag{2.12}$$

and

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

As the exchange is known to be mass dependent we get an additional equation,

$$\delta^{17} O(ex) = 0.512 \times \delta^{18} O(ex)$$
(2.14)

Table 2.2: Uncertainty in $\delta^{13}C$ determination of CO by SR and CeO₂ method. The isotope composition of the CO used for this control experiment are: $\delta^{18}O=28.7\%$, $\delta^{17}O=14.9\%$ relative to V-SMOW and $\delta^{13}C=-26.6\%$ relative to VPDB-CO₂. CO₂ is measured against the laboratory working standard Vadilal-CO₂ whose isotopic compositions are: $\delta^{18}O=17.4\%$, $\delta^{17}O=9.1\%$ relative to V-SMOW and $\delta^{13}C=-36.5\%$ relative to VPDB-CO₂. The last column gives difference of measured $\delta^{13}C$ value and the real value. The final row gives the Mean Absolute Difference (MAD) of the six determinations.

Sample	Initial amount	Recovered amount	$\frac{\text{After Ceo}}{\delta^{45}\text{CO}_2}$	$\frac{O_2 \text{ Exchange}}{\delta^{46} \text{CO}_2}$	(δ ¹³ C)	$\Delta(\delta^{13}C)$
	(μ mol)	(μmol)	‰	‰	‰	‰
1	8.7	8.7	9.57	-1.14	-26.6	03
2	8.5	8.4	9.77	-0.87	-26.4	0.17
3	10.1	10.0	10.0	-1.15	-26.1	0.45
4	15.0	14.9	10.0	-0.04	-26.5	0.41
5	-	-	9.83	-1.43	-26.3	0.26
6	-	-	9.7	-1.40	-26.4	0.14
MAD	-	-	-	-	-	0.24

The value of δ^{17} O calculated from the above equation is used in equation 2.13 to calculate δ^{13} C(ex). Since, there is no appreciable loss in the CO₂ amount, it is assumed that,

$$\delta^{13}C(\text{CO original}) = \delta^{13}C(\text{exch}) \tag{2.15}$$

As mentioned before, putting the value of δ^{13} C (CO original) and using the raw δ^{29} CO and δ^{30} CO, δ^{17} O value of the original CO sample can be calculated. To check the reproducibility and the inherent accuracy of the above method CO samples with known isotope compositions were run. Results listed in Table 2.2 show that the 13 C/ 12 C ratio is preserved within ±0.2 ‰ of the original CO carbon ratio.

2.4 CO₂ isotope measurements

As in this study only mass dependent CO_2 was measured, the conventional approach was adapted. The most abundant CO_2 isotopomers are: ${}^{44}CO_2 = {}^{16}O^{12}C^{16}O$ ${}^{45}CO_2 = {}^{16}O^{12}C^{17}O, {}^{17}O^{12}C^{16}O$ and ${}^{16}O^{13}C^{16}O$ ${}^{46}CO_2 = {}^{16}O^{12}C^{18}O, {}^{18}O^{12}C^{16}O, {}^{16}O^{13}C^{17}O, {}^{17}O^{13}C^{16}O$ and ${}^{17}O^{12}C^{17}O$

Mass spectrometric measurement of CO₂ gives two ratios $\frac{^{45}CO_2}{^{44}CO_2}$ and $\frac{^{46}CO_2}{^{44}CO_2}$ which can

be expressed in terms of the individual oxygen and carbon isotope ratios as follows:

$$\frac{{}^{45}\text{CO}_2}{{}^{44}\text{CO}_2} = \frac{[{}^{16}\text{O}{}^{12}\text{C}{}^{17}\text{O}] + [{}^{16}\text{O}{}^{13}\text{C}{}^{16}\text{O}]}{[{}^{16}\text{O}{}^{12}\text{C}{}^{16}\text{O}]} = \frac{2[{}^{17}\text{O}]}{[{}^{16}\text{O}]} + \frac{[{}^{13}\text{C}]}{[{}^{12}\text{C}]}$$
(2.16)

$$\frac{{}^{46}\text{CO}_2}{{}^{44}\text{CO}_2} = \frac{[{}^{16}\text{O}{}^{12}\text{C}{}^{18}\text{O}] + [{}^{16}\text{O}{}^{13}\text{C}{}^{17}\text{O}] + [{}^{17}\text{O}{}^{12}\text{C}{}^{17}\text{O}]}{[{}^{16}\text{O}{}^{12}\text{C}{}^{16}\text{O}]}$$
(2.17)

$$\approx \frac{2[^{18}O]}{[^{16}O]} \approx 2^{18}R$$
 (2.18)

Mass 45 represents mainly ¹³C-bearing isotopomer and the contribution from ¹⁷O bearing isotopomer is \sim 6.5%. Mass 46 is mainly due to ¹⁸O bearing isotopomer.

In terms of delta notation,

$$\delta^{46} \text{CO}_2 = \left[\frac{{}^{46}\text{R}}{{}^{46}\text{R}_{\text{s}}} - 1\right] \times 10^3 = \left[\frac{{}^{18}\text{R}}{{}^{18}\text{R}_{\text{s}}} - 1\right] \times 10^3 = \delta^{18}\text{O}$$
(2.19)

$$\delta^{45} \text{CO}_2 = \left[\frac{^{45}\text{R}}{^{45}\text{R}_\text{s}} - 1\right] \times 10^3 = \left[\frac{(2^{17}\text{R} + ^{13}\text{R})}{(2^{17}\text{R} + ^{13}\text{R}_\text{s})} - 1\right] \times 10^3$$
(2.20)

$$=\frac{\delta^{13}C + 2z\delta^{17}O}{1+2z}, where \ z = \frac{{}^{17}R_s}{{}^{13}R_s}$$
(2.21)

$$\delta^{17} \mathcal{O} = \left(\frac{1+2z}{2z}\right) \delta^{45} \mathcal{C} \mathcal{O}_2 - \frac{1}{2z} \delta^{13} \mathcal{C}$$
(2.22)

Solving these sets of equations along with mass dependent relation between δ^{17} O and δ^{18} O for both sample as well as reference gases the δ^{13} C value of CO₂ can be determined. For VPDB-CO₂ the value of z is 0.033888.

Measurements of carbon and oxygen isotopic compositions of CO₂ were done using a Europa GEO 20-20 mass spectrometer. The δ - values of the laboratory reference gas (Vadilal-CO₂) are calibrated to be: $\delta^{18}O=17.4 \%$, $\delta^{17}O=9.1 \%$ with respect to V-SMOW and $\delta^{13}C=-36.5 \%$ with respect to VPDB-CO₂. To check the machine precision, one aliquot of the tank Vadilal-CO₂ was taken and measured against the laboratory working standard several times [Table 2.3]. Typical error in isotopic measurement of CO₂ is estimated to be: 0.02 and 0.08 % for $\delta^{45}CO_2$ and $\delta^{46}CO_2$ respectively.

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Sample	$\delta^{46} \text{CO}_2$	$\delta^{45} \text{CO}_2$
	‰	‰
1	-0.11	-0.02
2	-0.10	-0.02
3	0.13	0.03
5	-0.15	-0.02
4	-0.16	-0.06
6	-0.15	-0.03
7	-0.17	-0.04
8	-0.10	-0.01
9	-0.08	-0.02
10	-0.10	-0.03
11	-0.10	-0.02
12	0.13	-0.04
13	-0.14	-0.03
15	-0.13	-0.03
Std (1σ)	0.08	0.02

Table 2.3: Isotopic measurement of several samples of tank Vadilal-CO₂ measured against the laboratory working standard (Vadilal-CO₂) whose isotopic compositions are: $\delta^{18}O=17.4\%$, $\delta^{17}O=9.1\%$ relative to V-SMOW and $\delta^{13}C=-36.5\%$ relative to VPDB-CO₂.

2.5 Experimental configuration

To extract and purify the gases resulting from CO_2 dissociation by UV lamps a suitable vacuum system was constructed. The schematic diagram of the system is given in Figure 2.2.

The vacuum line was made of pyrex glass with greaseless Kontes stopcocks having viton O-rings. A Pfeiffer pumping station was used for getting the high vacuum $(10^{-5}$ torr) as deemed appropriate for this work. The turbo pump was connected with the vacuum system through "T" connection with one end going to the system and the other end connected to a rotary pump through valves. This allowed us to use roughing pump in the beginning and then revert to the turbo pump. Indigenously made Pirani gauges were connected to the line to monitor the level of vacuum. On the higher side the gas pressure was measured by a calibrated Setra pressure gauge. A portion of the vacuum line was calibrated for measuring the amount of gas with the help of a MKS Baratron Gauge which is an absolute high sensitive pressure gauge with accuracy of ± 0.05 torr. A 5 litre pyrex flask with cold finger at the bottom was used as the reaction chamber for dissociat-





ing CO₂. It was connected to the vacuum line with a "Cajon" ultra-torr joint to facilitate gas transfer and cleaning. The vessel was isolated from the vacuum line by a stopcock. A 2 mm thick and 25 mm dia MgF₂ window was attached to the side of the chamber for transmitting UV light (cutoff wavelength at ~113 nm). Mercury and Krypton electrodeless low-pressure resonance UV lamps were used as source of UV photons. The Hg lamp has two main resonance lines at 184.9 and 253.7 nm in 10 nm band and the Kr lamp has lines at 123.6 and 116.5 nm. For photon generation, lamps were excited by a 200-watt, 2450 MHz microwave generator (Opthos Instruments) coupled to the lamp by cylindrical cavity. The photon flux obtained from these lamps are about 10^{15} photons per sec. The choice of MgF₂ as the window material was dictated by two reasons: its higher transmission capacity at this wavelength range and its superior resistance to corrosion by water vapour.

2.6 CO₂ photolysis experiment

For photolysis CO_2 was taken from a tank of ultra pure CO_2 gas (kindly supplied by Colin Allison of CSIRO, Melbourne, Australia) into the 5 litre chamber at a pressure of 800 torr. The isotopic compositions of tank CO₂ as given by Dr. Allison are: δ^{13} C=-6.684 % (relative to VPDB-CO₂), δ^{18} O=26.7 % and δ^{17} O=13.9 % (relative to Vienna Standard Mean Ocean Water (V-SMOW)). The CO₂ was exposed to photons coming from the Mercury (Hg) lamp for 5-8 hours. The lamp was placed flush with the MgF_2 window which matches exactly the emitting face of the lamp. Among the two lines of Hg-lamp only 184.9 nm photons have sufficient energy to dissociate CO₂. The absorption coefficient at 184.9 nm is, however, small at a value of $(4.2\pm0.3)\times10^{-3}$ atm $^{-1}$ cm $^{-1}$ [Demore and Mosesman, 1971]. The lamp is kept flush to ensure that maximum flux enters the chamber through the MgF₂ window with minimum possible air absorption. Over the path length equivalent to the chamber diameter (25 cm) only \sim 10% photons are absorbed. The product gases were oxygen and carbon monoxide with total amount ranging from 10 to 30 micromoles. After photolysis, the CO₂ was frozen by putting LN₂ at the cold finger attached to the chamber. The non condensable CO and O_2 were absorbed in a trap filled with molecular sieve (5Å, 8-10 mesh size) kept at LN₂ temperature. This section was part of a calibrated volume containing a MKS Baratron Gauge so that the amount of the gas mixture could be measured. A GC separation procedure (described below) was developed for the separation of CO and

O₂ gases from the mixture for isotope analysis.

2.7 CO and O₂ gas separation procedure

We essentially followed the method developed by Barkan and Luz [2003] for O₂ and N₂ separation. A slightly different method was used by Thiemens and Meagher [1984]. Barkan and Luz measured only O₂ but in our case we collected both CO and O₂. The present method is an improved procedure over that followed by Bhattacharya et al. [2000]. The schematic of the separation system is shown in Figure 2.2. The method uses a gas Chromatographic (GC) column through which the gas mixture passes with the help of helium carrier and allows collection of both CO and O₂ for analysis. The helium carrier gas as it comes out of the helium tank was scrubbed using a copper spiral trap filled with molecular sieve and kept at LN₂ temperature. The GC column consists of a stainless steel tube (1/8 inch, id 2 mm packed with fine molecular sieve (MS) 10Å, 13X, mess size 80-100 mesh) of total length 50 cm from which about 30 cm length (made into four spiral turns) was filled with MS. This spiral trap is connected to the glass line by quarter inch cajon ultratorr joint through reducer. The MS was filled first in the linear SS tube with quartz wool at two ends (to stop fine grains of MS flying out) and the bending was done later to make the final spiral shape. The separation was carried out in a part of the system consisting of three traps filled with MS. The traps were made of U shaped glass tube filled with MS grains of size 5^{A} (8-10 mesh) having stopcock at both ends. The gas separation procedure was as follows. The GC column was kept at -60°C. The temperature was maintained by an alcohol slush into which a Cryocool (model CC-100) cold finger was immersed along with a thermocouple monitoring the temperature. Two collection traps (#2 and #3) were placed after the GC column and kept at LN₂. The gas mixture was first transferred to the trap #1 located before the GC Column by LN₂. After complete transfer, the carrier gas flow was established at a flow rate of 20 cc/min at a pressure slightly above the atmosphere. The exit path of the helium gas was through a small water column to prevent backward air flow by diffusion. This also allowed us to continuously monitor the pressure matching for a smooth and continuous flow. The length of the waste line was about 2 m to reduce any possible air diffusion. The positions and opening of the valves were carefully adjusted to maintain a constant flow rate which was optimized for best separation. After collection

of the gas mixture the LN_2 of the collecting trap #1 was replaced by warm water and the gas mixture was allowed to enter the GC column in one short pulse. A short pulse of injection is essential for a clean separation. The O₂ came out completely from the GC column in about 12 min and was allowed to get absorbed in the trap #2 [Figure 2.3]. Thereafter, the flow path was diverted through trap #3 for CO collection. For CO release the GC column temperature was raised by replacing the -60°C slush with hot water; the CO collection takes about 15 min. The separated CO and O₂ were made to undergo freezethaw cycle several times to get rid of any trapped He. The helium scrubbing trap was reactivated at the end of each day by warming it to room temperature and purging with a stream of helium. After each experiment all molecular sieve traps were baked at 150°C and pumped for next use. To establish the accuracy of the separation procedure six control experiments were done by taking samples of known amount of tank CO and O₂. For this, the isotope ratios of aliquots of each sample were measured initially. The two gases were then mixed up in chosen proportion and separated. The Mean Absolute Difference (denoted by acronym MAD) between the two sets of values presented in Table 2.4 in case of O₂ is: 0.7 for δ^{18} O and 0.6 for δ^{17} O. For CO the differences in δ^{29} CO and δ^{30} CO values are 0.17 and 1.2 % respectively.

2.8 Reproducibility of the procedure

In order to calculate the total uncertainty of the final isotopic values, it is necessary to establish the individual errors associated with each step of the procedure. The total analytical error of the procedure (S_{total}) is determined by the formula:

$$S_{total}^{2} = S_{1}^{2} + S_{2}^{2} + S_{3}^{2}$$
(2.23)

where S₁, S₂, S₃ etc are estimates of uncertainty in individual steps.

The isotope measurement of O₂ involves only separation and the measurement of isotopes with corresponding uncertainties being denoted by S₁ and S₂ respectively. For δ^{18} O of O₂, we estimate S₁=2*0.7 (twice the Mean Absolute Difference (MAD value in Table 2.4) between the composition before and after the separation step the factor two being taken due to large spread) and S₂=0.05.

Similarly for δ^{17} O, S₁=2*0.6=1.2 and S₂=0.2 (see Table 2.5 and Table 2.4). Therefore, the uncertainties in the final oxygen isotope ratios of the oxygen gas are estimated to be,

	ore se	eparatio	ų				After	separatic	u		
2	и	Ũ	<i>а</i> О	Õ	2	Cha	nge	C	0	Chê	mge
osit	ion	Comp	osition	Compc	osition		I	Comp	osition		1
\0		0~	00	~~ ~	c	~	00	_ 0<	00	0~	00
δ^1	⁷ 0	δ^{29} CO	δ^{30} CO	$\delta^{18}O$	$\delta^{17}O$	$\Delta(\delta^{18}O)$	$\Delta(\delta^{17}O)$	δ^{29} CO	δ^{30} CO	$\Delta(\delta^{29}$ CO)	$\Delta(\delta^{30} \text{CO})$
Ϋ́	5.3	0.06	0.0	-13.0	-6.3	0.1	0.0	0.28	-2.8	0.22	-2.8
Ψ	5.4	-0.02	-0.0	-15.1	-7.4	-2.1	-1.0	0.22	-3.7	0.24	-1.6
φ	5.4	06	-0.0	-15.1	-7.3	-2.0	-0.9	0.32	0.20	0.38	0.3
Ŷ	5.4	0.06	0.0	-12.6	-7.7	0.5	-1.5	0.08	0.4	0.02	0.4
φ	5.2	0.25	0.8	-15.2	-7.1	-2.1	-0.9	0.24	0.0	-0.01	-0.8
Ŷ	5.2	0.11	0.1	-14.8	-8.0	-1.6	-1.8	0.15	-0.9	0.04	-0.9
φ	5.4	0.25	0.8	-13.0	-6.9	0.1	-0.5	0.8	-1.3	-0.01	-2.1
φ	5.4	0.12	0.1	-13.1	-6.0	0.0	0.4	0.1	-1.9	0.04	-1.9
φ	5.2			-13.4	-6.5	-0.3	-0.3				
Ψ	5.2			-13.1	-6.0	0.0	0.2				
Ψ	5.2			-13.5	-6.9	-0.1	-0.7				
φ	5.2			-13.1	-7.1	-0.2	-0.9				
Ŷ	5.2			-13.2	-6.1	-0.5	0.1				
Ŷ	5.2			-13.3	-6.4	-0.4	-0.2				
φ	5.2			-13.2	-6.3	-0.3	-0.1				
Υ	5.2			-14.2	-6.5	-1.1	-0.3				
	.	1	1	MAD ^c		0.7	0.6	1	ı	0.17	1.2

Table 2.4: Typical change in δ - values caused by separation procedure for O_2 and CO

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Figure 2.3: Schematic chromatogram showing separation of O_2 and CO from a mixture. Helium flow rate is ~20 cc/min. As seen, the oxygen comes out faster followed by CO after about 12 minutes as monitored by a pirani gauge. The separation was checked by Mass spectrometric analysis.

For δ^{18} O $S_{total} = \sqrt{((1.4)^2 + (0.05)^2)} = 1.4.$

And for δ^{17} O $S_{total} = \sqrt{((1.2)^2 + (0.2)^2)} = 1.2$

Uncertainty in the isotopic values of CO is the sum of the individual uncertainties from (1) separation from the mixture (2) conversion of CO to CO₂ (3) equilibration of CO₂ with CeO₂ (4) analysis by the mass spectrometer both for CO δ^{29} CO and δ^{30} CO and the final CO₂ measurement.

We estimate $S_1=2*1.2$ (the estimate of uncertainty from oxygen separation being two times the MAD value from Table 2.4) and $S_2=0.1$ (uncertainty of mass spectrometric analysis of oxygen) for δ^{18} O of CO.

Therefore total uncertainty in δ^{18} O of CO,

$$S_{total} = \sqrt{((2.4)^2 + (0.1)^2)} = 2.4 \%$$

The uncertainty in δ^{17} O of CO has to include the uncertainty (S₁) in determination of

 δ^{13} C and mass spectrometric analysis (S₂). The uncertainty in δ^{13} C measurement includes the step for conversion of CO to CO₂ and CO₂- CeO₂ equilibration. The data reported in Table 2.2 shows that the uncertainty in arriving at the actual value is 0.24 ‰. The uncertainty in determining δ^{17} O of CO is to be obtained from the equation 2.13 cast in the form:

$$\delta^{17}O = A \times \delta^{29}CO - B \times \delta^{13}C \tag{2.24}$$

where A=30.98 and B=29.05. Therefore,

$$S_{total}^{2} = A^{2} \times (S_{1}^{2}) + B^{2} \times (S_{2}^{2})$$
(2.25)

So S_{total} = 7.3 ‰ since S_1 = 0.08 (Table 2.6) and S_2 = 0.24 (Table 2.2).

It is clear from above that mass spectrometric analysis contributes only a small part in the total error the major part coming from the gas separation procedure and estimating δ^{17} O from two separate analysis. The error in δ^{17} O of CO should, however, be lower than the above estimate since the errors in δ^{29} CO and δ^{13} C are not entirely un-correlated. As seen in Table 2.7 the uncertainty in actual determination is closer to 2*2.3=4.6 ‰.

Table 2.5: The isotopic composition of gas samples taken from tank BOC-O₂ was measured several times against the laboratory working standard (a 5 litre chamber filled with BOC-O₂) ($\delta^{18}O=24.6\%$, $\delta^{17}O=12.5\%$ relative to V-SMOW). These data show that the VG-903 mass spectrometer can measure $\delta^{18}O$ and $\delta^{17}O$ of oxygen gas with a precision of 0.05 ‰ and 0.2 ‰ respectively.

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

Table 2.6: Isotopic measurement of several samples of tank Vadilal-CO measured against the laboratory working standard (Vadilal-CO) whose isotopic compositions are: $\delta^{18}O=28.7 \ \%$, $\delta^{17}O=14.9 \ \%$ relative to V-SMOW and $\delta^{13}C=-26.6 \ \%$ relative to VPDB-CO₂.

Sample	δ^{29} CO	δ^{30} CO
	‰	‰
1	-0.13	-0.28
2	-0.17	0.06
3	-0.15	-0.02
4	-0.04	-0.02
5	-0.01	0.07
6	-0.07	0.15
7	-0.02	-0.09
8	0.01	0.04
9	-0.02	0.09
10	-0.18	-0.08
Std (1σ)	0.08	0.11

control experiment are: δ^{18} O=28.7‰, laboratory standard Vadilal-CO. CO ₂ is	$\beta^{17}O=9.1$ % relative to V-SMOW and	r real value. The final row gives the Mean	
of CO. The isotope composition of the CO used for this 5.6 % relative to VPDB-CO ₂ measured against the same	<i>Jadilal-CO</i> ² whose isotopic compositions are: δ^{18} O=17.4 %	e columns give absolute difference of measure value and th	15.
Table 2.7: Reproducibility of $\delta^{17}O$ determination $\delta^{17}O=14.9$ %. relative to V-SMOW and $\delta^{13}C=-26$	neasured against the laboratory working standard V	5^{13} C=-36.5 % relative to VPDB-CO ₂ . The last three	Absolute Difference (MAD) of the six determination

	$\Delta(\delta^{18}O)$	%00	0.82	0.72	0.21	0.01	0.06	0.47	0.38
Change	$\Delta(\delta^{17}\mathrm{O})$	00/	1.57	3.01	2.89	1.26	2.64	2.48	2.3
	$\Delta(\delta^{13}C)$	%00	0.43	0.12	1.42	0.09	0.01	0.05	0.35
	$(\delta^{18}O)$	%00	27.9	28.0	28.9	28.7	28.8	28.2	
0	$(\delta^{17}O)$	%00	13.4	17.9	12.0	16.2	12.3	12.4	
	$(\delta^{13}C)$	%00	-26.1	-26.4	-25.1	-26.6	-26.6	-26.6	1
)2Exchange	$\delta^{46} CO_2$	%0	-1.14	-1.15	-1.14	-1.43	-1.43	-1.45	1
After CeC	$\delta^{45} \text{CO}_2$	00/	9.97	9.67	10.93	9.46	9.53	9.52	1
surement	δ^{30} CO	%00	-0.80	-0.70	0.21	-0.01	-0.06	-0.46	ı
CO mea	δ^{29} CO	%0	0.38	0.22	1.32	-0.04	-0.09	-0.13	1
	Sample			7	С	4	IJ	9	MAD

CHAPTER 3

An overview of chemical reaction model KINTECUS

Kintecus is a commercially available software originally developed by James C. Ianni, Vast Technologies Developement, USA (www.kintecus.com). We made use of this model to simulate the experimental conditions and obtain expected isotopic composition of the products to interpret our laboratory results. All known kinetic schemes which are possibly occurring in our experiment are put as input parameters in this simulation. After describing the basic features of the model, its use in CO_2 dissociation case is discussed in detail.

3.1 Basic features of the model

The word KINETICUS originated from a Latin word which means "Energized Movement". Molecules or atoms move before they react and hence the name KINETICUS modified to KINTECUS. It is now written in FORTRAN77 with FORTRAN95 and some C⁺⁺ for accessing in Windows registry. It is used to model a set of reactions occurring in chemical and atmospheric processes. Kintecus program can deal with as large as 12,000 chemical reactions in a relatively short time period. One can fit or optimize values of rate constants, initial concentrations, third body enhancement, energy of activation, starting temperature etc. against an experimental dataset. An important feature is its interface with excel which the user can modify according to the requirement. To do this one should have a knowledge in Macros program and Visual basic code [Ianni, 2003].

3.2 Description of the files

Kintecus uses three input spreadsheet files namely:

- reaction spreadsheet
- species description spreadsheet
- parameter description spreadsheet

It generates the species spreadsheet file using the reaction spreadsheet and then using species spreadsheet, reaction spread sheet along with the the parameter spread sheet, it calculates the concentration of the selected species. The concentration of the species is displayed only if it has changed significantly from its past values.

3.2.1 Species spreadsheet

The fields in the species spreadsheet are Species, Residence time, Initial Concentration and Display Output, External concentration etc. The Species field holds the name of a species that will show up in a chemical reaction. The Initial Concentration field holds the starting concentration of each species in the reaction. The Display Output field can hold either a Yes or No. If coded yes, the respective species concentration will be stored in the default output file "CONC.TXT".

3.2.2 Parameter spreadsheet

The model parameters are described in this sheet. A number of fields are available for use. By editing the parameter spreadsheet one can enter the time of the simulation, temperature, concentration etc. Simulation length has five fields: DAYS, HOURS, MIN-UTES, SECOND, and PICOSECONDS. These fields control the length of the simulation. This allows one to set the total time of the simulation during a run from yearly events to femtosecond experiments. Temperature is entered in Kelvin. The unit field allows one to use different concentration unit. Normally, moles/cm³ is used. The unit should be chosen in such a fashion that the number should appear close to unity to minimize error.

The Percent (%) field is used to limit the size of the output concentration file without causing distortion. Kintecus will output the concentration of the species only when one or

more displayed species has changed more than given percent value. A value of 0% will output all values.

The Starting Integration Time, Maximum Integration Time and Accuracy fields determine how fast Kintecus can integrate the model and the error in the final concentration. Accuracy determines how far out in the decimal place the concentration is computed. Therefore, a value of 1.0E-9 will keep the first nine digits of the integrated concentration accurately computed. The Starting Integration Time (in seconds) determines the starting time step to integrate the model. After the first integration, this will change according to the set value of accuracy. After the run one can plot the output values given by the model by clicking on one of the buttons located on the Control worksheet.

3.3 Validity of the model: Ozone simulation

The validity of the KINTECUS model in prediction of isotopomer fractionation has been established earlier [Pandey and Bhattacharya, 2006]. In particular, the process of ozone dissociation was simulated successfully. This process was experimentally studied earlier by many workers including our group and could be conveniently used as a test case [Bhattacharya and Thiemens, 1988; Wen and Thiemens, 1991; Liang et al., 2006; Cole and Boering, 2006]. In the dissociation experiments at PRL ozone was made in a 70 cc volume by tesla discharge in oxygen. After freezing the formed ozone by LN₂ the left over O₂ was pumped away. Next, the frozen O₃ was brought into gas phase. A visible light lamp was turned on for a few minutes causing photolytic decomposition of ozone. After photolysis, product oxygen was separated from the left over ozone and its isotopic composition and amount were measured. The left over ozone was also collected on a molecular sieve and its amount and isotopic composition were measured after converting it to oxygen by heating the molecular sieve. The isotopic composition and amount of the initial ozone was determined from the mass balance. The ozone dissociation rate depends on the photon flux at a given λ which is not known a priori. Therefore, the rate was determined by adjusting the yield of O₂. The kinetic scheme controlling ozone production and dissociation was written and it was shown that the model prediction agrees well with the laboratory results [see Pandey and Bhattacharya, 2006]

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Isotopologue	mass (in u)	Fractional Abundance	Abundance in (%)	
OCO	44	0.984	98.4	
ODO	45	0.01093	1.093	
PCO	45	0.00074	0.074	
QCO	46	0.004052	0.4052	
PDO	46	0.00000826	0.000826	
PCP	47	0.000000160	0.0000140	
QDO	47	0.000045	0.0045	
QCP	47	0.0000015	0.000153	
PDP	47	0.0000000156	0.00000156	
QCQ	48	0.000000417	0.0000417	
QDP	48	0.00000017	0.0000017	
QDQ	49	0.00000046	0.0000046	

Table 3.1: Abundances of CSIRO CO_2 isotopologues (${}^{13}R=11104 \times 10^{-6}$, ${}^{17}R=378 \times 10^{-6}$, ${}^{18}R$ $=2058 \times 10^{-6}$).

Calculation of initial concentration of isotopologues of CO₂ 3.4

For convenience, the following notations are used: $O=^{16}O$, $P=^{17}O$, $Q=^{18}O$, $C=^{12}C$, and $D=^{13}C$.

The initial concentrations of the isotopomers as applicable to CSIRO CO₂ gas (used for our experiments) are calculated from the initial total CO₂ concentrations, known ¹³R, ¹⁷R and ¹⁸R for this gas (kindly supplied by Colin Allison) and simple trinomial probability distribution law [see Table 3.1].

The various isotope ratios for sample gases (CO₂, CO and O₂) are given by,

$${}^{18}R_{CO_2} = \frac{[COQ] + [DOQ]}{2 \times [COO] + 2 \times [DOO] + [COQ] + [COP] + [DOP] + [DOQ]}$$
(3.1)

$${}^{17}R_{CO_2} = \frac{[COP] + [DOP]}{2 \times [COO] + 2 \times [DOO] + [COQ] + [COP] + [DOP] + [DOQ]}$$
(3.2)
$${}^{13}R_{CO_2} = \frac{[DOO] + [DOQ] + [DOP]}{[COO] + [COO] + [COP]}$$
(3.3)

$$_{O_2} = \frac{[DOO] + [DOQ] + [DOP]}{[COO] + [COQ] + [COP]}$$
(3.3)

$${}^{18}R_{CO} = \frac{[CQ] + [DQ]}{[CO] + [DO]}$$
(3.4)

$${}^{17}R_{CO} = \frac{[CP] + [DP]}{[CO] + [DO]}$$
(3.5)

An overview of chemical reaction model KINTECUS

$${}^{13}R_{CO} = \frac{[DO] + [DP] + [DQ]}{[CO] + [CP] + [CQ]}$$
(3.6)

$${}^{18}R_{O_2} = \frac{[OQ]}{2 \times [OO] + [OP] + [OQ]}$$
(3.7)

$${}^{17}R_{O_2} = \frac{[OP]}{2 \times [OO] + [OP] + [OQ]}$$
(3.8)

In terms of delta (relative to tank CO₂) the above quantities can be expressed as,

$$\delta^{18} R_{O_2} = \left(\frac{{}^{18} R_{O_2}}{{}^{18} R_{CO_2}} - 1\right) \times 10^{-3} \tag{3.9}$$

$$\delta^{17} R_{O_2} = \left(\frac{{}^{17} R_{O_2}}{{}^{17} R_{CO_2}} - 1\right) \times 10^{-3} \tag{3.10}$$

$$\delta^{18} R_{CO} = \left(\frac{{}^{18} R_{CO}}{{}^{18} R_{CO_2}} - 1\right) \times 10^{-3} \tag{3.11}$$

$$\delta^{17} R_{CO} = \left(\frac{{}^{17} R_{CO}}{{}^{17} R_{CO_2}} - 1\right) \times 10^{-3} \tag{3.12}$$

$$\delta^{13} R_{CO} = \left(\frac{{}^{13} R_{CO}}{{}^{13} R_{CO_2}} - 1\right) \times 10^{-3} \tag{3.13}$$

3.5 KINTECUS model to simulate CO₂ dissociation by Hg lamp photons

The KINTECUS model described above was used to calculate the expected isotopic composition of the products of CO_2 photodissociation. This model is normally used for a chemical system of molecular species. We modified it to apply in the present case where reactions and exchanges occur among isotopomers of the molecules (i.e., isotopic species of molecules). To do this, we assume that CO_2 dissociates by the UV photons to produce CO and O-atomic species in a simple and direct way. The molecules first get excited to a higher electronic energy state and then follow an exponentially decaying potential energy path (Herzberg, Vol-I, page 389). Subsequently, the O-atoms recombine to make oxygen molecules. We also assume that by a reasonable choice of the rate constants of the reactions involving various isotopomers and isotopologues in the model one can have an estimate of the expected isotopic composition of the formed CO and O_2 . This is important since an expected composition provides a reference level to compare the observed results and determine whether there is an anomaly or not. If there is significant level of anomaly we

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need an explanation regarding its possible origin which can be very different from the model assumptions depending upon the level of the anomaly.

The model is used by incorporating all the basic combination/ recombination reactions as well as isotopic exchange reactions involving isotopes and isotopomers of O, O₂, O₃, CO, and CO₂. These reactions are summarized in Table 3.2 along with the adopted rate coefficients. To simplify the calculations multiply substituted species having very small abundances (less than 10 ppm of the major one) were not included. Since the photon flux was not known a priori and it is possible that the UV flux was variable from one sample to another, the rate coefficient of CO₂ dissociation was adjusted in each case to match the CO yield (considering only the major isotopomer $^{12}C^{16}O$) for the corresponding photolysis time. This procedure is valid since CO is a primary product and does not undergo further dissociation.

The rate coefficients for the various isotopologues of CO_2 were adjusted in the light of the general discussion given in **Chapter 4** which explains the basic reason behind the phenomenon of photo-induced isotopic fractionation [Miller and Yung, 2000 ; Liang et al., 2004]. The absorption of photon by a CO_2 molecule takes it from a singlet ground state to a singlet excited state. Subsequently, it can dissociate into CO and O but during the dissociative breakdown there is a change of total spin from S=0 to S=1. However, the issue of spin violation has so far been not considered in any model. For the model we are constrained to assume that the molecule is on a simple dissociative curve and falls apart during the asymmetric stretch mode of vibration with O atom and CO molecule as partners. Since the photodissociation rate is proportional to the absorption cross section the ratio of the absorption cross section of the isotopically substituted species and the normal species should define the relative rate of dissociation and fractionation. The fractionation is calculated using the formula (based on the concept of blue shift):

$$\frac{\sigma'(E)}{\sigma(E)} - 1 = F = \frac{(slope) \times \Delta ZPE}{\sigma(E)}$$
(3.14)

where,

$$slope = \frac{d\sigma}{dE} = \frac{\Delta\sigma}{\Delta E}$$

Note that d is different from Δ - one is a differential and the other is a small but of finite quantity and is used to approximate the differential.

 σ = Absorption cross section of normal CO₂ at the chosen wavelength λ

Table 3.2: List of various gas phase reactions along with the rate coefficients used in the KINTECUS model for simulation of photolysis of CO_2 by Hg lamp photons at $T=25^{\circ}C$. The reaction constants have units of cm^3 molecules⁻¹sec⁻¹ for two body and cm^3 molecules⁻²sec⁻¹ for three body reactions. O, P, Q, C, D denotes ¹⁶O, ¹⁷O, ¹⁸O, ¹²C, ¹³C respectively.

	Reactions	Rate Coefficient
	R1(CO ₂ Photolysis)	
R(1a)	COO+h <i>v</i> →CO+O	$k_1 = 5.12 \times 10^{-9}$
R(1b)	$COQ+h\nu \rightarrow CQ+O$	$k_2 = 0.5 \times k_1 \times 0.979 \times (1 + a)$
R(1c)	$COQ+h\nu \rightarrow CO+Q$	$k_3 = 0.5 \times k_1 \times 0.979 \times (1 - a)$
R(1d)	$COP+h\nu \rightarrow CO+P$	k_4 =0.5× k_1 ×0.989×(1 - a/2)
R(1e)	$COP+h\nu \rightarrow CP+O$	$k_5 = 0.5 \times k_1 \times 0.989 \times (1 + a/2)$
R(1f)	DOO+ $h\nu \rightarrow DO+O$	$k_6 = k_1 \times 0.971$
R(1g)	$DOP+h\nu \rightarrow DO+P$	$k_7 = 0.5 \times k_1 \times 0.964 \times (1 - a/2)$
R(1h)	$DOP+h\nu \rightarrow DP+O$	$k_8 = 0.5 \times k_1 \times 0.964 \times (1 + a/2)$
R(1i)	$DOQ+h\nu \rightarrow DO+Q$	$k_9 = 0.5 \times k_1 \times 0.954 \times (1-a)$
R(1j)	$DOQ+h\nu \rightarrow DQ+O$	k_{10} =0.5× k_1 ×0.954×(1 + a)
	R2(Isotopic exchange of O	atom with CO)
R(2a)	Q+CO→O+CQ	k_{11} =8.30×10 ⁻¹⁶
R(2b)	O+CQ→Q+CO	k_{12} =7.50×10 ⁻¹⁶
R(2c)	$Q+DO \rightarrow O+DQ$	k_{13} =8.30×10 ⁻¹⁶
R(2d)	O+DQ→Q+DO	k_{14} =6.90×10 ⁻¹⁶
R(2e)	$P+CO \rightarrow O+CP$	k_{15} =8.30×10 ⁻¹⁶
R(2f)	O+CP→P+CO	k_{16} =7.90×10 ⁻¹⁶
R(2g)	P+DO→O+DP	k_{17} =8.30×10 ⁻¹⁶
R(2h)	O+DP→P+DO	k_{18} =7.30×10 ⁻¹⁶
	R3(O-O recombination)	
R(3a)	O+O+A→OO+A	k_{19} =2.7×10 ⁻³³
R(3b)	O+Q+A→OQ+A	$k_{20} = k_{19} \times 0.972$
R(3c)	$O+P+A \rightarrow OP+A$	k_{21} = k_{19} ×0.985
	R(Isotopic exchange with	O atom with Oxygen)
R(4a)	Q+OO→O+OQ	k_{22} =2.90×10 ⁻¹²
R(4b)	O+OQ→Q+OO	k_{23} =1.34×10 ⁻¹²
R(4c)	P+OO→O+OP	k_{24} =2.90×10 ⁻¹²
R(4d)	O+OP→P+OO	k_{25} =1.39×10 ⁻¹²

 σ' = Absorption cross section of the isotopomer of CO₂ at the same λ

 Δ ZPE= ZPE shift of the minor species relative to the major species without considering the bending mode since the bending mode does not contribute to the dissociation (The derivation of the above formula is given in the appendix)

To estimate the absorption cross section in case of CO₂ isotopologues we calculated the blue shift of each by taking the values of ZPE from Wang et al. [2004] [Table 3.3]. In order to calculate fractionation (expressed by F in the formula given above) one should know both the absorption cross section of the heavy isotopologues as well as the cross section of the normal isotopologue. However, the absorption cross section is normally available only for the major isotopes. Therefore the concept of blue shift is used to estimate the cross section for the minor species. Using this concept F can be expressed in terms of the slope of the available absorption cross section curve in the zone of interest. To calculate the F for our case, the absorption cross section curve given by Parkinson et al. [2003] is used. The nature of the cross section-energy curve is shown in Figure 3.1 [Parkinson et al., 2003]. The slope calculation is done by fitting a straight line through the points in the plot of cross section versus energy curve over the range $54083\pm200 \text{ cm}^{-1}$. Since the maximum ZPE seems adequate. The slope of this line is 0.00019 and this value is taken for calculating the value of F in equation 3.14.

Since the bending mode does not contribute to the dissociation the Δ ZPE value is calculated by excluding the bending mode vibration [Hanisco and Kummel, 1993]. The F values for all isotopologues in the two wavelength regimes corresponding to the Hg lamp emission and Kr lamp emission are shown in Table 3.4 (as a fraction as well as in term of permil (‰) fractionation). These values are used in the KINTECUS model. While calculating fractionation one has to keep in mind the sign of the Δ ZPE as well as the slope of the absorption cross section with energy (positive for 184.9 nm and negative for 123.6 nm).

One additional factor in rate coefficient variation was introduced following the idea proposed by Jost [2008]. For an asymmetric isotopologue there are two channels of dissociation. A factor of 0.5 in the rate for each channel is normally introduced in case of two equivalent channels. However, it is possible that one channel is favored relative to the other due to difference in ZPE of the two products [Figure 3.2] and this difference has to be accounted for. Unfortunately there is no previous isotopic study on CO_2 dissocia-



Figure 3.1: A portion of the experimental CO_2 absorption cross section data taken from Parkinson et al. [2003] corresponding to the Hg lamp photon energy. The slope of the best fit line is used in the ZPE factor calculation [see text for details].

tion pathways to guide us in deciding this channel propensity factor. We, therefore, used the available experimental data on the N₂O photolysis [Rahn and Wahlen, 1997] to infer relative reaction rates of two non-equivalent channels like, for example, $OCQ \rightarrow O+CQ$ and $OCQ \rightarrow Q+CO$. This assumption is probably justified since N₂O has a linear structure similar to that of CO₂. We adopted a value of 14 ‰ favouring the formation of CQ over that of CO. This value is slightly higher than the theoretical value (6 to 7 ‰) predicted by Mebel et al. [2004] for $O(^1D) + CO_2$ isotope exchange reaction. According to Jost [2008] the channel propensity difference is significant near the threshold and should vanish at energies well above the threshold especially near the maximum of the cross section. Since Hg lamp photons are near the threshold of dissociation we are rather justified in taking a higher value. A parameter a is introduced to account for the channel propensity factor such that (1+a)/(1-a) = 1.014. As explained above, one channel is faster relative to the other but together they add up to a given value. This is introduced in the calculation by the factors are

taken to be (1+a/2) and (1-a/2) which ensures the mass dependence.

Table 3.3: Harmonic vibrational frequencies and Zero Point Energies (ZPE) (in cm^{-1}) for several CO₂ isotopologues [from Wang et al., 2004]. ZPE= $1/2\sum_i g_i \omega_i$ and (ZPE)' denotes ZPE excluding the bending mode ω_2 .

Isotopologue	ω_1	ω_2	ω_3	ZPE	Δ (ZPE)	(ZPE)'	Δ (ZPE)/
OCO	1348.479	670.315	2387.185	2525.394	0	1867.832	0
OCQ	1309.544	665.205	2369.462	2492.277	33.117	1839.503	28.329
OCP	1328.175	667.609	2377.682	2507.955	17.439	1852.925	14.904
ODO	1348.479	648.452	2309.472	2472.905	52.489	1828.976	38.857
ODP	1328.154	645.600	2309.472	2455.240	70.190	818.813	49.019
ODQ	1309.467	645.976	2301.041	2439.355	86.039	1805.259	62.574

The exchange rate coefficients for the relevant reactions were obtained from earlier compilations [Johnston et al., 2000; Pandey and Bhattacharya, 2006]. The isotope exchange rate coefficients for O atom with CO and their isotopic variants (SetR2) were taken from Pandey and Bhattacharya [2006]. k_{13} , k_{15} and k_{17} denoting rates for ^{13}CO are assumed to be same as k_{11} (for ¹²CO) since the carbon isotope has no role in oxygen isotope exchange [Jaffe and Klein, 1966]. The O atom recombination rate coefficient in presence of third body (k₁₉) was taken from Pejakovic [2008]. Rates of recombination of heavy oxygen isotopes were reduced by respective collisional frequency factors (0.985 and 0.972 for ¹⁷O and ¹⁸O respectively). The O atom produced undergoes a fast isotope exchange reaction with O₂ and CO. For isotope exchange reaction between Q and OO, the forward exchange rate $k_{22}=2.9\times10^{-12}$ cm³ molecules⁻¹sec⁻¹ was taken from Anderson et al. [1885]. Using the equilibrium constant k_{eq} for this reaction as 1.94 $\times \exp(32/T)$ [Kaye and Strobel, 1983] the backward exchange rate (at T=300K) was obtained from the relation: $k_{23}=k_{22}/k_{eq}$ =1.34×10⁻¹² cm³ molecules⁻¹sec⁻¹. Similarly, for the exchange reaction of P and OO (k_{eq} =1.97× exp(16.6/T)) the backward rate was obtained as 1.39×10^{-12} cm³ molecules⁻¹sec⁻¹. Under the above assumptions and rate coefficients the KINTECUS model was run to simulate each individual experiment and the abundance of each isotopomer was obtained. These abundances were combined to define δ^{13} C, δ^{17} O and δ^{18} O (always relative to the starting gas CSIRO CO₂) of the two products CO and O₂. These delta values define the expected composition which are then compared with the experimental data to get an estimate of the net depletion or enrichment in the heavy isotope ratios. The model results are displayed in Table 3.6. It is observed that there is no significant effect of changing



Figure 3.2: In dissociation of NO₂ the propensity of one channel relative to other (${}^{16}O{}^{14}N{}^{18}O \rightarrow {}^{16}O{}^{+14}N{}^{18}O$: ch I or ${}^{18}O{}^{+14}N{}^{16}O$: ch II) is depicted pictorially. This propensity change is due to differing zero point energy of the two channels indicated by ZPE_{1418} and ZPE_{1416} and their difference, ΔZPE . D_{01} and D_{02} denote dissociation energy for the two channels (following Babikov et al. [2003b]).

experimental conditions on the final predicted δ -values from one experiment to another. Obviously, the rate coefficients are the primary determinants in the predictions.

Table 3.6 shows that for the Hg lamp case the predicted δ^{18} O value of the O₂ phase is -33.2 ‰ while the same for the CO phase is -8.9 ‰. The CO phase is enriched by about 24.3 ‰ relative to the O₂ phase due to the isotope exchange that takes place between the product O atom and the CO molecule after the initial CO₂ dissociation step. As seen from reaction set R2 in Table 3.2 the forward exchange rate whereby CQ is formed is much faster (rate $\approx 8.3 \times 10^{-16}$) compared to the rate of formation of CO by exchange (rate $\approx 7.5 \times 10^{-16}$). The rate ratio is about 1.1 which means that at equilibrium the CO phase would be enriched by about 100 ‰ relative to the O₂ phase. However, since this step competes with the O₂

Isotopologue			Yung-Mil	ler model	
		Hg la	Hg lamp		amp
	Δ (ZPE)/	F(in ‰)	fraction	F(in ‰)	fraction
OCO	0	0	1	0	1
OCQ	28.329	-21.2	0.979	11.2	0.011
OCP	14.904	-11.2	0.989	5.9	0.006
ODO	38.857	-29.1	0.971	15.3	0.015
ODP	49.019	-36.7	0.963	19.4	0.019
ODQ	62.574	-46.9	0.953	24.7	0.025

Table 3.4: Factors expressing rate coefficient variation of major isotopic species of CO_2 due to isotope dependence of CO_2 photodissociation calculated from Yung and Miller [1997] model.

formation step the full value of the equilibrium enrichment is not achieved and only about 24.3 ‰ is obtained for δ^{18} O under the given kinetic conditions. For δ^{17} O the enrichment of CO phase is about half of that for δ^{18} O (~ 12.7 ‰) as expected for a mass dependent kinetic scheme.

3.6 KINTECUS model to simulate CO₂ dissociation by Kr lamp photons

We also used the model simulation in case of photolysis by Kr lamp photons. In this case some more reactions are to be added to the set R1 since the product oxygen atoms produced by the higher energy Kr lamp photons are mainly in the ¹D state and are thus capable of exchange reactions with CO₂ through formation of a reaction intermediate CO₃* [Katakis and Taube, 1962; Chakraborty and Bhattacharya, 2003]. Relevant rate coefficients for these reactions are shown in Table 3.5. The fractionation factor in CO₂ dissociation by Kr lamp photons is calculated using the same formula as Hg lamp case. In this case the slope calculation is done by fitting a straight line through the points in the plot of cross section versus energy curve over the range 80906 ± 200 cm⁻¹. The slope of this line is - 0.005227. The 116.5 nm line is smaller (by a factor of 4) in intensity compared to 123.6 nm and is not considered for calculation. The rate of formation of CO₃* (k₂₆) intermediate due to reaction of O(¹D) with CO₂ is taken from Demore and Dede [1970]. Reaction rates of other intermediate channels of this set (R5) are multiplied with respective collisional frequency factors. The intermediate CO₃* can dissociate into two channels, CO₂ +

 $O(^{3}P)$ (dominant component) and $CO_{2} + O(^{1}D)$ (minor component) [Perri et al., 2003]. For simplicity, only the dominant component is considered here. The dissociation rate (k_{36}) is taken from Demore and Dede [1970]. As the intermediate complex CO_3^* has a reasonably long life time [Baulch and Brekenridge, 1966] one could argue that the complex can randomize its energy among all available vibrational/ rotational modes before dissociating to CO_2 and $O(^{3}P)$. This would imply that in the complex CO_3^{*} all oxygen atoms are equivalent to one another irrespective of isotopic nature and each has an equal chance of being emitted as the product oxygen atom. However, Mebel et al. [2004] argued that during emission the lighter atomic isotope would be preferred due to a ZPE effect and the probability of ¹⁶O emission would be greater than the statistical probability of 2/3 in case of [C¹⁶O¹⁶O¹⁸O]* type molecule. They determined the ejection rate of O-atom from COOQ* and showed that the rate of ¹⁶O being ejected is 2.014 (relative to rate of Q emission) when the CO_3^* forms by CO_2^+O collision at an energy of 4.2 kcal/mol. Using this information, k_{37} and k_{38} of the dissociation channels of COOQ* was multiplied by (2/3+b) and (1/3-b) respectively and the value of b is calculated from (2/3+b)/(1/3-b)= 2.014 as b= 0.001548. Similarly in case of COOP*, the rates were multiplied by (2/3+c) and (1/3-c) respectively and the value of c is estimated to be 0.00078 (half that of b using the usual mass dependent rule). The rate coefficients for the various isotopologues of CO_2 were adjusted following the procedure described in Hg lamp case keeping in mind that the blue shift effect reverses in case of Kr lamp since the relevant energy is beyond the peak of the absorption spectrum (Figure 3.3). The factors are given in Table 3.4. The rate constants for ozone formation reaction (R8) are mostly taken from Janssen et al. [2001]. In reactions k_{50} and k_{51} , an O atom collides with heteronuclear oxygen molecule OQ and leads to the formation of OOQ. The relative reaction probability for these reactions are for k_{50} is $1.45 \times k_{49}$ and for k_{51} it is $1.08 \times k_{49}$. The corresponding relative rate coefficients were obtained by dividing these numbers by two which is needed to account for the numbers of product channels. For reactions k_{54} and k_{55} , we used the argument of Janssen et al. [2001] relating change in zero point energy of the corresponding exchange reaction (O+OP⇔ P+OO) with the relative reaction probability and used the same linear relation given by them. This relation is k=[0.013× ΔZPE +1.2]× k₄₉. In R(8f), the zero point energy change is 11.7 cm⁻¹ which corresponds to $k_{54} = 1.32 \times k_{49}$. As the exchange reaction in R(8g) involves no change in zero point energy, $k_{55} = 1.04 \times k_{49}$ was obtained by comparing it with k_{51} and assuming

mass dependence. An additional factor of 0.5 is applied to account for the symmetry number for obtaining each rate coefficient. The reaction set R9 describes a secondary channel of ozone dissociation by its collision with O atom. O and O₃ collision rate (k_{58}) is taken from DeMore [1997]. Other rates were calculated by correcting for frequency factors obtained from relative reduced masses of the colliding pairs. In the reactions k_{59} to k_{64} , a simple two-body collision is considered, where Q and P atoms collide with O₃ at rates of 0.957 and 0.978 times that of O and O₃. Similarly OOQ and OOP collide with O atom at rates of 0.995 and 0.997 times that of O and O₃ collision. The reaction coefficients k_{65} to k_{80} are taken from Pandey and Bhattacharya [2006] who used most of the reaction rate coefficients given in the earlier studies [Atkinson, 1996; DeMore, 1997]. The rate coefficient of the ozone destruction by NO₂. The dissociation rate of O-Q and O-P bond was reduced by a factor of 0.972 and 0.988 (relative to O-O bond) respectively [Wen and Thiemens, 1991]. Note the factor 0.5 for rate constants in reactions involving two product channels.

For the case of Kr lamp the predicted δ^{18} O value for the CO phase is higher at a value of 18.7 ‰ while the same for the O₂ phase is -8.9 ‰. In this case the enrichment is 27.6 ‰ which is slightly larger than the Hg lamp case. It is easy to see why this is so. In the case of dissociation by Kr lamp the heavy isotopes are enriched in the products since the blue shift effect is opposite to that in case of Hg lamp. The CO phase is enriched by about 15 ‰ relative to the starting CO₂ reservoir in the very first step of dissociation. But unlike the Hg lamp case the O atom formed is in ¹D state and undergoes exchange with bath gas CO₂ at a rapid rate which forms the O atom at the ground state. The ground state O-atom can exchange with CO but the effect would be small. This results in a CO phase δ^{18} O value of about 18.7 ‰ . The enrichment of CO relative to the O₂ phase is 27.6 ‰ in δ^{18} O and 14.6 ‰ in δ^{17} O. The two relative enrichments again follow a mass dependence rule as expected. The small deviation from strict mass dependance is due to minor interference form ozone formation.

	Reactions	Rate coefficient
	$R1(CO_2 Photolysis)$	
R(1a)	$COO+h\nu \rightarrow CO+O(^{1}D)$	$k_1 = 2.12 \times 10^{-8}$
R(1b)	$COQ+h\nu \rightarrow CQ+O(^{1}D)$	$k_2 = 0.5 \times k_1 \times 1.011 \times (1 + a)$
R(1c)	$COQ+h\nu \rightarrow CO+Q(^{1}D)$	$k_3 = 0.5 \times k_1 \times 1.011 \times (1-a)$
R(1d)	$COP+h\nu \rightarrow CO+P(^{1}D)$	k_4 =0.5× k_1 ×1.006×(1 - a/2)
R(1e)	$COP+h\nu \rightarrow CP+O(^{1}D)$	$k_5 = 0.5 \times k_1 \times 1.006 \times (1 + a/2)$
R(1f)	DOO+ $h\nu \rightarrow DO+O(^{1}D)$	$k_6 = k_1 \times 1.015$
R(1g)	DOP+h $\nu \rightarrow$ DO+P(¹ D)	$k_7 = 0.5 \times k_1 \times 1.019 \times (1 - a/2)$
R(1h)	DOP+ $h\nu \rightarrow DP+O(^{1}D)$	$k_8 = 0.5 \times k_1 \times 1.019 \times (1 + a/2)$
R(1i)	$DOQ+h\nu \rightarrow DO+Q(^{1}D)$	$k_9 = 0.5 \times k_1 \times 1.025 \times (1-a)$
R(1j)	$DOQ+h\nu \rightarrow DQ+O(^{1}D)$	k_{10} =0.5× k_1 ×1.025×(1 + a)
	R2(Isotopic exchange of O	atom with CO)
R(2a)	Q+CO→O+CQ	k_{11} =8.30×10 ⁻¹⁶
R(2b)	O+CQ→Q+CO	k_{12} =7.50×10 ⁻¹⁶
R(2c)	$Q+DO \rightarrow O+DQ$	k_{13} =8.30×10 ⁻¹⁶
R(2d)	O+DQ→Q+DO	k_{14} =6.90×10 ⁻¹⁶
R(2e)	P+CO→O+CP	k_{15} =8.30×10 ⁻¹⁶
R(2f)	O+CP→P+CO	k_{16} =7.90×10 ⁻¹⁶
R(2g)	P+DO→O+DP	k_{17} =8.30×10 ⁻¹⁶
R(2h)	O+DP→P+DO	k_{18} =7.30×10 ⁻¹⁶
	R3(O-O recombination)	
R(3a)	O+O+A→OO+A	k_{19} =2.7×10 ⁻³³
R(3b)	O+Q+A→OQ+A	$k_{20} = k_{19} \times 0.972$
R(3c)	$O+P+A \rightarrow OP+A$	k_{21} = k_{19} ×0.985
	R4(Isotopic exchange with	O atom with Oxygen)
R(4a)	Q+OO→O+OQ	k_{22} =2.90×10 ⁻¹²
R(4b)	$O+OQ \rightarrow Q+OO$	k_{23} =1.34×10 ⁻¹²
R(4c)	$P+OO \rightarrow O+OP$	k_{24} =2.90×10 ⁻¹²
R(4d)	O+OP→P+OO	k_{25} =1.39×10 ⁻¹²

Table 3.5: List of various gas phase reactions along with the rate constants used in the KINTECUS model for simulation of photolysis of CO_2 by Kr lamp photons [a=0.00705] at T=25°C.

	Reactions	Rate coefficient				
R5 (Formation of COOO*)						
R(5a)	O(¹ D)+COO→COOO*	k_{26} =1.1×10 ⁻¹⁰				
R(5b)	$Q(^{1}D)+COO \rightarrow COOQ^{*}$	k_{27} =0.958× k_{26}				
R(5c)	$O(^{1}D)+COQ\rightarrow COOQ^{*}$	k_{28} =0.994× k_{26}				
R(5d)	$P(^{1}D)+COO \rightarrow COOP^{*}$	k_{29} =0.978× k_{26}				
R(5e)	$O(^{1}D)+COP \rightarrow COOP^{*}$	k_{30} =0.997× k_{26}				
R(5f)	$O(^{1}D)+DOO \rightarrow DOOO^{*}$	k_{31} =0.997× k_{26}				
R(5g)	$O(^{1}D)+DOQ \rightarrow DOOQ^{*}$	k_{32} =0.994× k_{26}				
R(5h)	$Q(^{1}D)+DOO \rightarrow DOOQ^{*}$	k_{33} =0.958× k_{26}				
R(5i)	$O(^{1}D)+DOP \rightarrow DOOP^{*}$	k_{34} =0.997× k_{26}				
R(5j)	$P(^{1}D)+DOO \rightarrow DOOP^{*}$	k_{35} =0.978× k_{26}				
	R6 (COOO* dissociation: triplet channel)					
R(6a)	COOO*→COO+O	k_{36} =1.0×10 ⁸				
R(6b)	COOQ*→COQ+O	$k_{37}=(\frac{2}{3}+b)\times k_{36}$				
R(6c)	$COOQ^* \rightarrow COO+Q$	$k_{38} = (\frac{1}{3} - b) \times k_{36}$				
R(6d)	$COOP^* \rightarrow COP + O$	$k_{39} = (\frac{2}{3} + c) \times k_{36}$				
R(6e)	$COOP^* \rightarrow COO+P$	$k_{40} = (\frac{1}{3} - c) \times k_{36}$				
R(6f)	DOOO*→DOO+O	$k_{41} = k_{36}$				
R(6g)	$DOOQ^* \rightarrow DOQ+O$	$k_{42}=(\frac{2}{3}+b)\times k_{36}$				
R(6i)	$DOOQ^* \rightarrow DOO+Q$	$k_{43}=(\frac{1}{3}-b)\times k_{36}$				
R(6j)	DOOP*→DOP+O	$k_{44}=(\frac{2}{3}+c)\times k_{36}$				
R(6k)	$DOOP^* \rightarrow DOO+P$	$k_{45} = (\frac{1}{3} - c) \times k_{36}$				
	R7 (O(¹ D) Quenching)					
R(7a)	$O(^{1}D)+OO \rightarrow O+OO$	k_{46} =8×10 ⁻¹²				
R(7b)	$Q(^{1}D)$ +OO \rightarrow Q+OO	k_{47} =0.962× k_{46}				
R(7c)	$P(^{1}D)+OO \rightarrow P+OO$	k_{48} =0.980× k_{47}				
	R8 (Ozone formation)					
R(8a)	O+OO+M→OOO+M	k_{49} =6.0×10 ⁻³⁴				
R(8b)	$O+OQ+M \rightarrow OOQ+M$	k_{50} =0.5×1.45× k_{49}				
R(8c)	$O+OQ+M \rightarrow OQO+M$	k_{51} =0.5×1.08× k_{49}				
R(8d)	$Q+OO+M \rightarrow OOQ+M$	k_{52} =0.92× k_{49}				
R(8e)	$Q+OO+M \rightarrow OQO+M$	k_{53} =0.006× k_{49}				
R(8f)	$O+OP+M \rightarrow OOP+M$	k_{54} =0.5×1.36× k_{49}				
R(8g)	O+OP+M→OPO+M	k_{55} =0.5×1.06× k_{49}				
R(8h)	$P+OO+M \rightarrow OOP+M$	k_{56} =0.98× k_{49}				
R(8i)	$P+OO+M \rightarrow OPO+M$	k_{57} =0.006× k_{49}				

	Reactions	Rate coefficient
	R9 (ozone decomposition)	
R(9a)	OOO+O→OO+OO	k_{58} =8.0×10 ⁻¹⁵
R(9b)	OOO+Q→OO+OQ	k_{59} =0.957× k_{58}
R(9c)	OOQ+O→OO+OQ	k_{60} =0.995× k_{58}
R(9d)	OQO+O→OQ+OO	k_{61} =0.995× k_{58}
R(9e)	OOO+P→OO+OP	k_{62} =0.978× k_{58}
R(9f)	OOP+O→OO+OP	k_{63} =0.997× k_{58}
R(9c)	OPO+O→OP+OO	k_{64} =0.997× k_{58}
R(9g)	$OOO+O(^{1}D)\rightarrow OO+O+O$	k_{65} =0.5×1.2×10 ⁻¹⁰
R(9h)	OOO+O(¹ D)→OO+OO	$k_{66} = k_{65}$
R(9i)	$OOO+Q(^{1}D)\rightarrow OO+O+Q$	k_{67} =0.957× k_{65}
R(9j)	$OOO+Q(^{1}D)\rightarrow OO+OQ$	$k_{68} = k_{67}$
R(9k)	$OOQ+O(^{1}D)\rightarrow OO+Q+O$	k_{69} =0.5×0.995* k_{65}
R(91)	$OOQ+O(^{1}D)\rightarrow OQ+O+O$	$k_{70} = k_{69}$
R(9m)	$OOQ+O(^{1}D)\rightarrow OO+OQ$	k_{71} =0.995× k_{65}
R(9n)	$OQO+O(^{1}D)\rightarrow OQ+O+O$	k_{72} =0.995× k_{65}
R(90)	OQO+O(¹ D)→OQ+OO	$k_{73} = k_{72}$
R(9p)	$OOO+P(^{1}D)\rightarrow OO+O+P$	k_{74} =0.978× k_{65}
R(9q)	$OOO+P(^{1}D)\rightarrow OO+OP$	$k_{75} = k_{74}$
R(9r)	$OOP+O(^{1}D)\rightarrow OO+O+P$	k_{76} =0.997× k_{65}
R(9s)	$OOP+O(^{1}D)\rightarrow OP+O+O$	$k_{77} = k_{76}$
R(9t)	$OOP+O(^{1}D)\rightarrow OO+OP$	k_{78} =0.997× k_{65}
R(9u)	$OPO+O(^{1}D)\rightarrow OP+O+O$	k_{79} =0.997× k_{65}
R(9v)	OPO+O(¹ D)→OP+OO	$k_{80} = k_{79}$
R(9w(a))	OOO+A→O+OO+A	k_{81} =1.2×10 ⁻¹³
R(9w(b))	OOQ+A→O+OQ+A	$k_{82}=0.5 \times k_{81}$
R(9w(c))	OOQ+A→Q+OO+A	k_{83} =0.5×0.972× k_{81}
R(9w(d))	OQO+A→O+OQ+A	k_{84} =0.5×0.972× k_{81}
R(9w(e))	OOP+A→O+OP+A	$k_{85}=0.5 \times k_{81}$
R(9w(f))	$OOP+A \rightarrow P+OO+A$	k_{86} =0.5×0.988× k_{81}
R(9w(g))	OPO+A→O+OP+A	k_{87} =0.988× k_{81}



Figure 3.3: Experimental CO_2 absorption cross section curve (thick line) shown along with the position of the photon wavelengths for the Hg lamp and the Kr lamp. Thin line is a schematic curve showing the blue shift effect for the heavier isotopic species (like ${}^{16}O{}^{12}C{}^{18}O$). Cross section of the H species is lower compared to the L species for the Hg lamp photons but reverse is true for the Kr lamp photons. The 116.5 nm line is smaller (by a factor of 4) in intensity compared to 123.6 nm and is not considered for calculation.

Table 3.6: Delta values predicted by the KINTECUS model for CO_2 photolysis by Hg lamp photons and k	٢r
lamp photons. The isotopic ratios are expressed in ∞ deviation from the tank CO ₂ (CSIRO tank) for bot	th
O_2 and CO samples. Values given in the final row indicate enrichment of CO relative to O_2 .	

Hg lamp photon						Kr lamp photon				
Sample	O ₂		СО		O_2		СО			
No	‰		%0		%0		%			
	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$	δ^{13} C	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$	δ^{13} C
SM-1	-33.2	-17.4	-8.9	-4.7	-29.1	-8.9	-5.1	18.7	9.5	15.3
Enrichment			24.3	12.7				27.7	14.6	

CHAPTER 4

Anomalous enrichment of heavy isotopes of oxygen and carbon in photodissociation of CO₂

 CO_2 molecule can be dissociated by UV light having wavelength smaller than 227 nm [Okabe, 1978] to form CO and O_2 . Oxygen isotopic composition of these O_2 and CO was first studied by Bhattacharaya et al. [2000] who discovered a surprisingly large enrichment (~100 ‰) of ¹⁷O in 184.9 nm photolysis. This was explained by invoking the effect of nuclear spin. They proposed that during the dissociation of CO_2 by 184.9 nm photon a spin forbidden singlet-triplet transition takes place and nuclear spin can play a role in this process by adding an extra term in the spin orbit coupling. The carbon isotope ratio in the CO product is another potential candidate to see the spin effect. However, the ¹³C/¹²C ratio in CO gas was not analyzed by them. In the present work, we have investigated the carbon isotope ratio in CO along with the oxygen isotope ratios in both CO and O_2 . We also investigated the temperature variation of fractionation to obtain more insight in this unusual process.

4.1 Photodissociation of isotopic molecules

Before discussing the results of our experiment we need to discuss some basic aspects of the process of photodissociation of molecules and their isotopic variants. When a molecule absorbs light in the UV or visible region it undergoes an electronic transition which may lead to fragmentation of the excited but still-bound molecule; this phenomenon is known as photodissociation [Schinke, 1993]. The absorbed energy is transferred to the internal energy of the molecule. If this energy exceeds the binding energy of the weakest bond and by internal energy transfer processes concentrates there the molecule will break apart. Photodissociation can be classified as direct or indirect (or predissociation). In case of direct dissociation, the molecule dissociates immediately (in a time comparable to the typical vibrational period of the molecule $\sim 10^{-13}$ sec) while executing an asymmetric stretch mode of vibration and coming to the extreme stretched point. In contrast, in case of indirect dissociation a potential barrier hinders direct fragmentation of the excited complex and the wavepacket spends a finite lifetime in the local potential energy well before dissociating [Schinke, 1993]. A direct dissociation in spectroscopy is characterized by a structureless absorption spectrum. In case of isotopologue dissociation (like ¹⁶O¹⁶O, ¹⁶O¹⁷O and ¹⁶O¹⁸O for oxygen molecule) the Reflection Principle predicts that the difference in rate of absorption should result in a mass dependent rule; the isotope ratio change for ${}^{17}O/{}^{16}O$ would be nearly half that of ¹⁸O/¹⁶O. The reflection Principle was mentioned in chapter 3 while deriving the rate coefficients of isotopomer dissociation but a fuller description is given below. Generally, in case of direct dissociation one expects a depletion of heavy isotopes in the product, i.e., the dissociation is controlled by a kinetic isotopic effect [Kaye, 1987] which discriminates against the heavy isotopes. In the direct process, rates of photodissociation of the isotopomers are not very different, however, substantial differences may be observed for the same in indirect mechanism due to sensitivities in the coupling matrix elements to small shift in the vibrational energy levels [Kirby and Dishoeck, 1988].

The characterization of photodissociation of molecules is done by calculating the absorption cross section of the molecule. Pack [1976] presented a theory of direct photodissociation which predicts vibrational structure in the dissociative upper electronic states. More detailed theoretical calculations of absorption cross section of molecules were carried out by several groups [Heller, 1976; Lee, 1982; Lee et al., 1983; Schinke, 1993; Prakash and Markus, 2005]. The R-matrix method developed by Light and Walker [Light and Walker, 1976] for calculating the Frank-Condon factors for the photodissociation of triatomic molecules was used to explain the nature of CO₂ dissociation [Kulander and Light, 1980]. This theory proved that the asymmetric motion of a molecule resulting in dissociation is weakly coupled and therefore vibrational resonances could exist in the dissociation continuum [Kulander and Light, 1980]. The calculation of absorption cross section of molecules has been reviewed recently by Jost [2008] by compiling and comparing the available absorption cross section of a few molecules with the model predictions. The isotopic fractionation induced by photon molecular interactions was explained most simply by Zero Point Energy (ZPE) shift theory which is based on the use of reflection principle in direct dissociation [Yung and Miller, 1997; Miller and Yung, 2000; Blake et al., 2003; Liang et al., 2004]. The basic features of the reflection principle are described below.

The Reflection Principle relates the energy dependence of the absorption cross section as well as the final state distribution of the products with the initial coordinate distribution of the parent molecule in the electronic ground state. According to Born-Oppenheimer approximation, both the position and momentum of the nuclei are conserved during photoexcitation. Accordingly, the ground state probability density function (probability variation with internuclear distance) is first mapped onto the upper state potential surface and then this mapping is projected onto the energy axis since energy is related to the relevant internuclear distance [Figure 4.1]. The essence of Reflection Principle is transformation of space coordinate to energy coordinate. The energy width of the spectrum is proportional to the width of the initial coordinate distribution and to the steepness of the excited state potential energy surface. As the steepness increases the spectrum gets broader and its magnitude decreases. In practice, the steepness varies with internuclear distance and usually rises considerably over short distances. This disturbs the symmetry in reflection resulting in an amplification of the spectrum in the blue side at the expense of the red side.

Apart from dissociation from a continuum or unbound state as applicable in case of direct photodissociation, dissociation is also possible from bound states. In spectroscopy this dissociation is termed as predissociation. This is basically due to the overlapping of some bound state molecular energy levels (namely electronic, vibrational and rotational) by a dissociative continuum. Predissociation can happen in many ways. In case I, two electronic states overlap among which only one is dissociative. It is also possible to have vibrational predissociation. In this case, the bound levels of the excited electronic state are coupled to the vibrational continuum of a third state of different symmetry (case II) [for detailed discussion see Herzberg, Vol-1, 1950].

The isotopic fractionation in case of direct photolysis can be modeled in a simple way using the classical view of photodissociation. Yung and Miller [1997] were the first to do so in case of photon induced dissociation of isotope fractionation of nitrous oxide. They postulated that the upper and lower potential energy surfaces are invariant for isotope substitution but the energy levels are shifted. Therefore, the absorption coefficient of the minor isotopologue can be obtained by shifting the whole absorption spectrum of the major isotopologue by an amount equal to the difference in zero point energy of the minor isotopologue. This would result in different absorption rates of the two at a given energy of the incident photon. Photodissociation model based on the Reflection Principle was found suitable to explain the laboratory results for N₂O molecule [Liang et al., 2004]. However, isotopic substitution not only changes the zero point energy of a given isotopologue but also modifies the shape of the corresponding vibrational wavefunction. As a result, the absorption cross section changes significantly more than the prediction of the above simple model especially away from the peak of the spectrum.

Figure 4.1 is a schematic (adapted from Liang et al., 2004) to explain the blue shift effect arising from the change in ZPE of isotopomers and the wave function. As can be seen, the cross section curve for the heavy species H is shifted towards higher energy relative to the lighter species L. This results in relatively higher cross section for H over L in the part of the spectrum beyond the peak and contrarywise in the part before the peak. The Hg lamp line is located in the rising part and the Kr lamp line is located in the falling part of the absorption cross section. The quantitative features of the absorption cross section are very different in these two wings (Figure 3.3). The cross section of the H species is lower (by a factor of ~ 1.3) compared to L species for the Hg lamp photons but reverse is true for the Kr lamp photons (higher by a factor ~ 1.1). We have used these ideas to model the expected isotopic composition in CO₂ photodissociation in case of Hg lamp photons and Kr lamp photons as discussed in **Chapter 3**.

4.2 Results

4.2.1 CO₂ photolysis by Hg lamp photons

Before discussing the results we should mention about some initial steps adopted in implementation of the experiment. In order to judge the validity of our analytical procedure and gain confidence in the accuracy of the measured numbers we analyzed eleven oxygen samples in the Laboratory of Glaciology, Geophysics and Enviroment (LGGE), Grenoble, France (courtesy Dr. Joel Savarino). We made CO and O₂ gas samples by CO₂ dissociation



Figure 4.1: Schematic diagram of the direct photodissociation process illustrating the Born-Oppenheimer approximation and the Reflection Principle (dashed lines). L and H refer to the standard and isotopically substituted species respectively. Ψ_0 , V_g , and V_e denote the vibrationally averaged ground state wavefunction, ground state electronic potential, and dissociating electronic potential respectively [adapted from Liang et al., 2004].

in PRL and sent them to LGGE where only O₂ was analyzed by Continuous Flow mass spectrometry using a MAT 250 mass spectrometer. The data from this exercise are given in Table 4.1 and shown in Figure 4.2. For comparison, data from another set of O₂ samples made by the same way and analyzed in PRL are also shown in Figure 4.2. The two sets are slightly different from each other; the mean of the PRL set is δ^{18} O=-14.8 ‰; δ^{17} O=74.6 ‰ and that of the LGGE set is δ^{18} O=-16.0 ‰, δ^{17} O=67.1 ‰. The average difference for δ^{18} O is 1.2 ‰ and for δ^{17} O it is 7.6 ‰. The observed discrepancy can be ascribed to the difference in experimental methods followed in the two laboratories. In PRL the two gases were separated by a modified GC method whereas in LGGE a Continuous Flow method was adopted. Thus, small mass dependent fractionation may have crept in during separation whose magnitude was different in the two laboratories. In addition, the mass spectrometer reference gases were different and they were not intercalibrated. Notwithstanding these issues, the difference is quite small in case of δ^{18} O. The difference is slightly larger in case of δ^{17} O due to the fact that ¹⁷O analysis involves measurement of an ion beam which is
				Oxy	/gen
Sample	O_2 amount	Exposure	Pressure		
No	μ mol	time	Torr	$\delta^{18} \mathrm{O}$	$\delta^{17} O$
		(min)		‰	‰
LGGE-1	16.3	130	937	-14.8	69.0
LGGE-2	23.8	150	937	-18.5	75.3
LGGE-3	18.8	158	937	-15.5	66.6
LGGE-4	24.4	170	937	-13.0	64.1
LGGE-5	18.3	150	937	-17.6	64.9
LGGE-6	17.4	140	937	-19.2	63.2
LGGE-7	25.3	200	937	-15.0	62.6
LGGE-8	15.6	160	937	-12.1	73.4
LGGE-9	16.3	150	937	-19.5	65.5
LGGE-10	20.3	200	937	-14.6	65.9
LGGE-11	20.7	180	937	-15.7	67.2
Mean of	LGGE set			-16.0	67.1
Mean of	PRL set			-14.8	74.6

Table 4.1: Isotopic composition of dissociation products of CO_2 in case of Hg lamp photons (relative to tank CO_2). These measurements were done at LGGE, France to check if the range of values are similar to those obtained in PRL experiments.

about five times smaller and is, therefore, more sensitive to possible contamination and interference. However, the large ¹⁷O enrichment in the products (about 80 ‰) is validated by the data obtained in both the laboratories and in view of the natural spread in the data, an uncertainty of 7 to 8 ‰ in δ^{17} O has no significant impact on our final conclusions.

The amount of CO and O₂ depends directly on the time of UV exposure. The CO₂ pressure was kept constant at 780 torr in all the experiments since the pressure has only a minor role in dissociation. The O₂ to CO ratio varied from 0.47 to 0.52 with a mean (and standard deviation) of 0.50 ± 0.02 . Since CO and O₂ are derived exclusively from the dissociation of CO₂ molecule, ideally, the ratio should be equal to 0.5 if there is no loss. However, experimental uncertainty in measurement of two gases after separation by GC associated with some surface loss of O atoms may cause the O₂/CO ratio differ slightly from the ideal value.

In what follows, the δ - values are expressed relative to the CSIRO tank CO₂ since this CO₂ is the starting reservoir whose dissociation products are of interest in the present study and the main issue is the level of fractionation of the product gases relative to the



Figure 4.2: A comparative study of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios of oxygen produced by photodissociation of CO₂ using Hg lamp photons (184.9 nm) carried out at PRL and LGGE. The LGGE measurements are somewhat depleted relative to those obtained in PRL. The mean difference in ¹⁸O is small being about 1.2 ‰ and that in ¹⁷O it is about 7.6 ‰. The difference could be due to some unknown mass dependent fractionation during gas separation (see text).

parent CO₂.

The isotopic ratios of oxygen and carbon in CO and O₂ obtained in several dissociation experiments and measured in PRL are presented in Table 4.2 and shown in Figure 4.3. In the O₂ phase the δ^{18} O varies from -12.1 ‰ to -17.6 ‰ (Mean=-14.8 ‰) and δ^{17} O varies from 71.6 to 78.2 ‰ (Mean=74.6 ‰) whereas in the CO phase δ^{18} O varies from -1.7 ‰ to 5.3 ‰ (Mean=1.5 ‰) and δ^{17} O varies from 70.6 to 94.3 ‰ (Mean=80.4 ‰). The δ^{13} C in CO varies from 6.6 to 8.6 ‰ (Mean=7.7 ‰). The surprising result is that δ^{17} O is highly enriched in contrast to δ^{18} O where the fractionation is nominal. To look at it in another way, the δ^{17} O- δ^{18} O covariation plot is shown in Figure 4.4 for O₂ and Figure 4.5 for CO. It is clear that there is no correlation between these two ratios; this is a unusual result since in normal physical/ chemical process we expect a strong correlation between the two. This particular feature forces us to conclude that the process of dissociation affects ¹⁷O/¹⁶O ratio in a totally different way than it does the ratio ¹⁸O/¹⁶O. As we will see later, this

finding lends strong support to the nuclear spin hypothesis (in CO₂ photodissociation by the Hg lamp photons) which affects only ¹⁷O but not ¹⁸O thus resulting in unusually high value of δ^{17} O and absence of any correlation between ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios.



Figure 4.3: ¹⁷O/¹⁶O and ¹⁸O/¹⁶O covariation diagram for the products of photodissociation of CO₂ carried out using Resonance line Hg lamp photons (184.9 nm). Both CO and O₂ are anomalously enriched in ¹⁷O [left side y-axis] denoted by Δ^{17} O; CO is also enriched in ¹³C [right side y- axis] denoted by Δ^{13} C. Model results are also given for estimation of enrichment of observed values over the classical prediction.

The δ^{17} O- δ^{18} O covariation plot of O₂ and CO when put together in a single figure (Figure 4.6) show that the group of CO points are isotopically heavier than the group of O₂ points. This is consistent with the expected variation since CO₂ dissociates into a molecular product CO and an atomic product O and the heavy isotopes would be enriched in CO due to the ZPE effect. The normal rule in chemical changes dictates that the heavy isotope is preferentially incorporated in the molecule where it is more strongly bonded. However,

		0	\mathbf{b}_2		CO ^a		J	O_2		CO^{b}		
Sample ^c	Exposure Tr		c17 0		c170		د ₁ ^x)	c170	618) (18)	c17)	داع د	5
No	lime	$\int_{\Omega} \nabla \nabla \rho$	ρ_{τ}, ρ	$\bigcap_{o_T} \varrho$	0, , θ	$\rho^{\tau \rho}$	$O_{OT}Q$	ρ^{+}	$\bigcap_{n \in I} Q$	$\rho_{\tau\tau}$	∂_{τ}	Slope
	Min	%0	%00	%00	%0	%00	%00	%o	%00	%o	%0	
SM-1	405	10.1	93.0	32.1	104.8	0.9	-16.1	78.0	5.3	89.7	7.6	0.55
SM-2	600	8.9	88.2	28.2	105.5	-0.1	-17.4	73.3	1.4	90.4	6.6	0.91
SM-3	600	10.9	86.7	30.2	109.5	0.7	-15.4	71.8	3.4	94.3	7.4	1.20
SM-4	480	10.8	89.8	31.0	89.0	0.8	-15.5	75.0	4.2	74.1	7.5	0.04
SM-5	400	10.6	92.8	29.8	100.0	0.7	-15.7	77.8	3.0	84.9	7.4	0.38
SM-6	600	14.3	93.2	28.5	97.1	0.2	-12.1	78.2	1.8	82.1	6.9	0.28
SM-7	660	14.1	90.06	28.4	96.5	0.6	-12.2	75.1	1.6	81.4	7.3	0.46
SM-8	600	8.6	88.4	27.7	88.2	1.8	-17.6	73.5	0.9	73.3	8.6	0.01
SM-9	600	13.7	89.0	25.7	91.8	1.8	-12.7	74.1	-1.0	76.8	8.5	0.23
SM-10	600	12.3	88.7	25.4	92.8	1.6	-14.1	73.8	-1.3	77.8	8.4	0.32
SM-11	009	11.3	86.7	25.0	88.9	0.9	-15.0	71.8	-1.7	73.9	7.6	0.16
SM-12	009	10.1	86.5	26.3	90.9	0.7	-16.1	71.6	-0.4	76.0	7.4	0.28
SM-13	009	13.6	91.4	29.0	85.4	1.6	-12.8	76.5	2.3	70.6	8.6	0.39
Mean							-14.8 ± 2	74.6 ± 2.4	1.5 ± 2.2	$80.4{\pm}7.5$	$7.7{\pm}1.0$	~ 0.40

Table 4.2: Isotopic composition of dissociation products of CO₂ carried out using Resonance line Hg lamp photons(184.9 nm): The isotopic composition of the Tank CO₂ used for dissociation is $\delta^{18}O = 26.7 \ \%$, $\delta^{17}O = 13.9 \ \%$ relative to SMOW and $\delta^{13}C = -6.7 \ \%$ relative to PDB.

22/01 ^b Column eight to twelve represent δ -values relative to tank CO_2 ^c Experiments were done at pressure 780 torr ^dSlope= $(\delta^{17}O(O_2)-\delta^{17}O(CO))/(\delta^{18}O(O_2)-\delta^{18}O(CO))$

the preferential effects on the two heavy oxygen isotopes are different for reasons that will be discussed later.



Figure 4.4: ${}^{17}O/{}^{16}O$ and ${}^{18}O/{}^{16}O$ covariation diagram for O_2 produced by photodissociation of CO_2 carried out using Resonance line Hg lamp photons (184.9 nm). The two ratios are uncorrelated due to the hyperfine interaction of ${}^{17}O$ isotope alone.

As seen above, the nature of the fractionation in ¹⁷O and ¹⁸O are not the same and ¹⁷O alone is enriched in the products. To determine the magnitude of the enrichment we need to know what should have been the expected ¹⁷O abundance based on normal rules of fractionation. As explained in Chapter 3 the expected composition can be calculated using the KINTECUS model. For comparison, the model values are shown in the Table 4.3 and 4.4. It is noted that the predicted model δ -values do not change from one experiment to another. This is not unexpected since the rate coefficient of dissociation is the main determinant for the isotope redistribution among the products. The variation in photon flux, exposure time have no significant effect on the final isotope ratios even though these experimental parameters do affect the CO₂ dissociation rate. In the model prediction δ^{17} O- δ^{18} O slope is 0.52 as expected since the rate coefficient variation and exchange processes are all mass dependent. A comparison of the model values with the experimentally obtained numbers



Figure 4.5: ${}^{17}O/{}^{16}O$ and ${}^{18}O/{}^{16}O$ covariation diagram for CO produced by photodissociation of CO₂ carried out using Resonance line Hg lamp photons (184.9 nm). The two ratios are uncorrelated due to the hyperfine interaction of ${}^{17}O$ isotope alone.

[Figure 4.3 and Table 4.3 and Table 4.4] shows that both CO and O₂ possess large enrichment in ¹⁷O (conveniently expressed as $\Delta(\delta^{17}O)$ indicating enhancement relative to the model prediction). The enrichment varies from 89 to 96 ‰ for O₂ (mean= 92.0 ‰) and 76 to 100 ‰ (mean= 85.1 ‰) for CO corresponding to the pressure/temperature regime used. For simplicity of discussion, we take 89 ‰ to be the over all mean ¹⁷O enrichment in products of CO₂ dissociation by Hg lamp photons. In contrast, the values of $\Delta(\delta^{18}O)$ are small, varying from 16 to 21 ‰ for O₂ and from 7 to 14 ‰ for CO. Interestingly, $\Delta(\delta^{13}C)$ (observed ¹³C/¹²C ratio in the sample relative to the expected value based on the model) in the product CO is also high with ¹³C enrichment varying from 36 to 38 ‰ . This type of enrichment in carbon isotope ratio is also quite unusual. It is intriguing to note that the two isotopologues with odd neutron numbers (¹⁷O and ¹³C) and associated nuclear spins experience higher rates of dissociation. The ratio between the mean enrichment in ¹⁷O and ¹³C is about 2.3. A connection between dissociation and nuclear spin, therefore, seems to be suggested by the data.

Table 4.3: Isotope ratios of O_2 (expressed relative to tank CO_2) obtained from experiment and model calculations (as discussed in the text). The values of enrichment defined as: $Enrichment(\Delta) = \delta_{expt} - \delta_{model}$ are also given.

	С) ₂	O ₂ (m	odel)	Enricl	nment
Sample						
No	$\delta^{18} O$	$\delta^{17} O$	$\delta^{18} O$	$\delta^{17} O$	$\Delta(\delta^{18}\text{O})$	$\Delta(\delta^{17}\text{O})$
	‰	‰	‰	‰	‰	‰
SM-1	-16.1	78.0	-33.2	-17.4	17.1	95.4
SM-2	-17.4	73.3	"	"	15.8	90.7
SM-3	-15.4	71.8		"	17.8	89.2
SM-4	-15.5	75.0	"	"	17.7	92.3
SM-5	-15.7	77.8	"	"	17.5	95.2
SM-6	-12.1	78.2	"	"	21.1	95.6
SM-7	-12.2	75.1	"	"	21.0	92.5
SM-8	-17.6	73.5	"	"	15.6	90.9
SM-9	-12.7	74.1	,,	"	20.5	91.5
SM-10	-14.1	73.8	,,	"	19.1	91.2
SM-11	-15.0	71.8	,,	"	18.2	89.2
SM-12	-16.1	71.6	"	"	17.1	89.0
SM-13	-12.8	76.5	"	"	20.4	93.9
Mean					$18.4{\pm}2.0$	92.0±2.3

	³ C)		7	7	5	9	5	0	4	7	9	5	7	5	7	-1.0
	$\Delta(\delta^1$	»	36.	35.	36.	36.	36.	36.	36.	37.	37.	37.	36.	36.	37.	36.8±
Enrichmen	$\Delta(\delta^{17}{ m O})$	%00	94.4	95.1	0.06	78.8	89.6	86.8	86.1	78.0	81.5	82.5	78.6	80.7	75.3	85.1 ± 7.5
	$\Delta(\delta^{18}{ m O})$	%	14.2	10.3	12.3	13.1	11.9	10.7	10.5	9.8	7.9	7.6	7.2	8.5	11.2	10.4 ± 2.2
[]	δ^{13} C	%00	-29.1													
)(Mode	δ^{17} O	%0	-4.7	:	:	:	:				:	:	:	:	:	
ŭ	δ^{18} O	%00	-8.9													
	δ^{13} C	%00	7.6	6.6	7.4	7.5	7.4	6.9	7.3	8.6	8.5	8.4	7.6	7.4	8.6	
00	δ^{17} O	%00	89.7	90.4	94.3	74.1	84.9	82.1	81.4	73.3	76.8	77.8	73.9	76.0	70.6	
	δ^{18} O	%0	5.3	1.4	3.4	4.2	3.0	1.8	1.6	0.9	-1.0	-1.3	-1.7	-0.4	2.3	
	Sample No		SM-1	SM-2	SM-3	SM-4	SM-5	SM-6	SM-7	SM-8	SM-9	SM-10	SM-11	SM-12	SM-13	Mean

Table 4.4: Isotope ratios of CO (expressed relative to tank CO₂) obtained from experiment and model calculations (as discussed in the text). The values of enrichment defined as: Enrichment(Δ) = δ_{Expt} - δ_{model} are also given.

The overall spread of the experimental data are as follows (mean \pm sd): 1.5 \pm 2.2 ‰; 80.4 \pm 7.5 ‰ for δ^{18} O and δ^{17} O of CO respectively and 7.7 \pm 1.0 ‰ for δ^{13} C of CO and -14.8 \pm 2.0 ‰ ; and 74.6 \pm 2.4 ‰ for δ^{18} O and δ^{17} O of O₂ respectively. Clearly the spread of data is beyond the experimental uncertainty (discussed in chapter 2) and points to some unaccounted factors in the experimental procedure which can introduce isotopic variations. Some of the factors can be easily identified. For example, surface effect can play a role in principle in low pressure range as revealed by some experiments [Papacosta and Corrigan, 1975]. However, in our experiments surface effect should not be significant since the experiment was done at high pressure (~1 atm). Temperature variation is another potential factor. To determine the effect of possible temperature variation we carried out a separate study and found that it has a rather large effect. This is discussed in chapter 5 in more detail. Since temperature was not controlled in the present experiments possible room temperature variation might have introduced some amount of δ - variation. Another important point relates to the gas separation step. The freezing of CO₂ at the bottom of the 5 litre photolysis chamber after the UV exposure can in principle absorb some amount of CO and O₂ resulting in variations in the isotope values of the products. Minor amount of ozone formation can also cause some variations.

The combined three isotope plot of CO and O₂ (Figure 4.6) show that the δ -values are scattered in both the phases. The scatter is more in CO compared to O₂. The three isotope slope calculated for each CO-O₂ pair is given in Table 4.2. As seen, the slope varies from 0.01 to 1.20. Even though the CO phase is enriched relative to O₂, the ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios do not obey a mass dependent rule (i.e., slope 0.5). This is of course quite expected since the ¹⁷O distribution is influenced by the nuclear spin effect whereas ¹⁸O distribution is not and obeys normal fractionation. This contrast results in a non mass dependent pattern between ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios. The large increase in ¹⁷O/¹⁶O affects the slope from one experiment to another and results in deviation from the value of 0.5. In dissociation of CO₂ molecule one obtains CO molecule and O atom. Two O atoms combine to form the O₂ molecule. It seems logical that the effect of nuclear spin on dissociation and subsequent molecule formation leads to different ¹⁷O/¹⁶O ratio enhancement in O₂ and CO. This can be understood easily from the schematic diagram shown in Figure 4.7 which shows the combined effect of ZPE and ¹⁷O enhancement due to nuclear spin effect. Apart from the above issues, there is a possibility of isotope exchange between O atom

and CO molecule. This isotope exchange leads to preferential formation of ${}^{12}C^{17}O$ over ${}^{12}C^{16}O$. The exchange also tries to erase the rate difference resulting in variation in isotope ratios in the two gases. The rates of dissociation of ${}^{16}O$ —-[${}^{12}C^{17}O$] and [${}^{16}O^{12}C$]—- ${}^{17}O$ to form ${}^{12}C^{17}O$ and ${}^{16}O^{12}C$ are also expected to be different due to the channel propensity effect in dissociation. In addition to the above, the experimental uncertainty in isotope ratio measurements is larger in case of CO as we have seen in the experimental chapter. This experimental uncertainty also affects the slope. Therefore, the final ${}^{17}O/{}^{16}O$ ratios of the products are the results of combination of all the processes described above which not only introduce the spread in the data but also result in deviation from strict mass dependence rule.



Figure 4.6: ${}^{17}O/{}^{16}O$ and ${}^{18}O/{}^{16}O$ covariation diagram for the products of photodissociation of CO₂ carried out using Resonance line Hg lamp photons (184.9 nm). CO is enriched relative to O₂ for reasons explained in the text.



Figure 4.7: Schematic diagram showing effect of nuclear spin on ${}^{17}O/{}^{16}O$ and ${}^{18}O/{}^{16}O$ ratio for the products of photodissociation of CO_2 (see the text text for details).

4.2.2 CO₂ photolysis by Kr lamp photons

Dissociation experiments were also performed using higher energy photons from a Kr lamp. This lamp is a resonance source giving two types of photons at 116 nm and 123 nm both of which can initiate the dissociation. The experimentally obtained isotopic ratios of oxygen and carbon in CO and O₂ are presented in Table 4.5. Isotope ratios are given relative to tank CO₂ after appropriate conversion. In O₂ phase δ^{18} O varies from -36.2 ‰ to -42.6 ‰ (Mean=-38.0 ‰) and δ^{17} O varies from -1.6 to 5.7 ‰ (Mean=3.0 %). In contrast, in CO phase δ^{18} O varies from 52.0 ‰ to 60.8 ‰ (Mean=57.1). The δ^{13} C in CO varies from 51.5 to 59.5 ‰ (Mean=55.8 ‰). As is clear, in this case the results are radically different from those in case of Hg lamp [Figures 4.8, 4.9]. Most importantly, the δ^{18} O values are negative and the mean δ^{17} O value is positive in O₂ phase. Surprisingly, the δ^{18} O and δ^{13} C are highly positive in the CO phase. As explained before, to decide whether there is enrichment or depletion one has to calculate the values based on the kinetic model which would have a different set of reactions as we are dealing with much higher energy photons in this case. In particular there is possibility of exchange of O-isotopes with CO₂ at this energy. The model predicted values are 18.7, 15.3 % for δ^{18} O and δ^{13} C of CO and -8.9 and -5.1 % for δ^{18} O, δ^{17} O of O₂. Therefore, in this case the O₂ phase is depleted in ¹⁸O and enriched in ¹⁷O with $\Delta(\delta^{18}O)$ varying from -25.1 to -33.7 ‰ and $\Delta(\delta^{17}O)$ varying from 3.5 to 11.1 %. In the CO phase, $\Delta(\delta^{18}\text{O})$ is positive varying from 33.4 to 42.2 ‰. Unfortunately, the ¹⁷O in CO could not be measured due to experimental problems. Interestingly, δ^{13} C in the product CO is also very high with $\Delta(\delta^{13}$ C) varying from 36.2 to $44.2\ \%$. Possible explanation for these enrichments will be discussed later.

	C	$\mathbf{)}_2$	Ŭ	0	O_2 (N	[odel)	CO(m	odel)	O ₂ (Enric	chment)	CO(Enri	chment)
Sample ^a						!				1	,	
No	$\delta^{18} \mathrm{O}$	$\delta^{17} O$	$\delta^{18}{ m O}$	δ^{13} C	$\delta^{18}{ m O}$	$\delta^{17} O$	$\delta^{18} \mathrm{O}$	δ^{13} C	$\Delta(\delta^{18}{ m O})$	$\Delta(\delta^{17}\mathrm{O})$	$\Delta(\delta^{18}\mathrm{O})$	$\Delta(\delta^{13}C)$
		%00	%00	%00	%00	%00	%00	%0	%o			
Kr-1	-41.6	-1.6	52.0	53.8	-8.9	-5.1	18.7	15.3	-32.7	3.5	33.4	38.4
Kr-2	-36.2	4.4	58.7	59.5				:	-27.3	9.5	40.0	44.2
Kr-3	-34.0	4.1	56.4	55.5				:	-25.1	9.2	37.6	40.2
Kr-4	-38.0	1.6	59.2	58.2				:	-29.1	6.7	40.5	42.9
Kr-5	-38.5	2.9	55.5	55.4				:	-29.6	8.0	36.8	40.1
Kr-6	-37.8	4.5	56.2	51.5					-28.9	9.6	37.6	36.2
Kr-7	-42.6	-0.5	59.1	54.8				:	-33.7	4.6	40.4	39.5
Kr-8	-36.3	5.7	60.8	57.4				:	-27.4	10.8	42.2	42.2
Kr-9	-37.2	6.0	55.7	55.7				:	-28.3	11.1	37.0	40.5
	-38.0	3.0							-791+77	8 1+7 7	30 0+0 05	40 7+7 4

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^{*a*}Experiments were done at 790 torr pressure



Figure 4.8: ${}^{17}O/{}^{16}O$ and ${}^{18}O/{}^{16}O$ covariation diagram for the O_2 phase produced by photodissociation of CO_2 carried out using Kr lamp photons (116.5 nm and 123.6 nm). ${}^{17}O$ is enriched and ${}^{18}O$ is depleted relative to the expected values based on the KINTECUS model.



Figure 4.9: ${}^{13}C/{}^{12}C$ and ${}^{18}O/{}^{16}O$ covariation diagram for the CO produced by photodissociation of CO₂ carried out using Kr lamp photons. Both ${}^{13}C$ and ${}^{18}O$ are enriched compared to the KINTECUS model predictions.

			C	`		\overline{CO}	
			(y_2		CO	
Sample	Exposure	Pressure					
No	time	Torr	$\delta^{18} \mathrm{O}$	$\delta^{17}\mathrm{O}$	$\delta^{18} \mathrm{O}$	$\delta^{17} O$	δ^{13} C
	(min)		‰	‰	‰	‰	‰
TD-1	60	50	-43.0	-30.4	-7.7	-46.0	-16.6
TD-2	35	90	-43.9	-34.9	-3.0	-37.4	-12.4
TD-3		90	-45.8	-36.8	-7.0	-45.5	-14.3
TD-4	-	50	-46.1	-33.7	-8.7	-39.5	-17.4
TD-5	-	90	-56.8	-42.7	-7.6	-40.9	-15.0
TD-6	120	170	-42.5	-33.7	-9.5	-47.1	-16.1
TD-7	-	50	-49.9	-40.2	-	-	-12.9
TD-8	-	95	-51.3	-41.5	-8.4	-72.5	-11.7
TD-9	-	90	-51.7	-41.2	-6.0	-93.1	-8.4

Table 4.6: Isotopic composition of dissociation products of CO_2 carried out by Tesla discharge showing depletion of heavy isotopes as expected but the mutual relation between the ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios is not mass dependent for reasons explained in the text.

4.2.3 CO₂ dissociation by Tesla discharge

In case of Tesla discharge, both the heavy isotopes of oxygen are depleted [Figure 4.10]. The δ^{18} O values vary from -43 to -57 ‰ for O₂ and -3 to -16 ‰ for CO ; the δ^{17} O values vary from -30 to -43 ‰ for O₂ and -37 to -48 ‰ for CO [Table 4.6]. The slope of the best-fit line through the O₂ points is 0.83±0.10 demonstrating a strong mass independent phenomenon. Interestingly, the ¹³C of the product CO is also depleted (varying from -11 to -17 ‰ with respect to the starting CO₂ gas). The oxygen data are in agreement with that published earlier by Heidenreich and Thiemens [1985].



Figure 4.10: ¹⁷O/¹⁶O and ¹⁸O/¹⁶O covariation diagram for the products of photodissociation of CO₂ carried out using Tesla discharge. Both CO and O₂ are depleted in ¹⁷O and ¹⁸O. The data points for the O₂ phase fall on a line with slope 0.83 ± 0.10 . ¹³C in CO phase is also depleted. δ - values are expressed relative to the isotopic ratios of starting reservoir CO₂.

4.3 Discussions

4.3.1 CO₂ photolysis by Hg lamp photons

As mentioned before, the results of the Hg lamp case suggest a connection between dissociation and nuclear spin. The reasons for this proposition are given below in detail in terms of electronic states and absorption of UV photons by CO_2 .

Although the electronic absorption spectrum of CO₂ has been known for a long time, its interpretation was not clear. There have been several attempts to calculate the electronic structure of ground states as well as excited state of CO2 and these calculations were modified from time to time as more experimental data became available [Xantheas et al., 1990; Xantheas and Ruedenber, 1994; Lu and Yan, 2000]. Spectroscopic information about the electronic excited states of CO₂ are very limited. The first experimental observation was made by Dixon in the CO flame emission band which was ascribed to a transition from ${}^{1}B_{2}$ state [Dixon, 1963]. This result was confirmed by subsequent theoretical calculations. For example, Winter et al. [1973] found four low lying states of CO₂ from their extensive configuration interaction (CI) calculations. These states are ${}^{1}A_{1}$, ${}^{3}B_{2}$, ${}^{3}A_{2}$, and ${}^{1}A_{2}$ with respect to $CO(^{1}\Sigma)$ + $O(^{3}P)$. Clyne and Thrush [1962] found from their chemiluminescent experiment that ¹A₁, ³B₂ of CO₂ are bound with respect to CO+O. The isotope-labeling experiments of Shortridge and Lin [1976] confirmed the existence of a intermediate complex which forms in the singlet state and then crosses to the triplet state before it dissociates to produce the ground state O atom. Lin and Bauer [1969] proposed the crossing of two surfaces namely ${}^{1}B_{2}$ and ${}^{3}B_{2}$ to reconcile with the experimental results. A mechanism of curve crossing through complex formation was also proposed from the same experiment. Existence of two low lying excited states of CO₂ was further confirmed by Engelbrecht and Liu [1983] through multiconfiguration self-consistent field (MCSCF) plus configuration interaction (CI) calculations. Both states were found to have C_{2v} potential minima with ${}^{3}A_{2}$ state lying above ³B₂ state. Based on similar calculations carried out by other groups [England and Ermler, 1979; Knowles et al., 1988] it is now widely accepted that two excited states of CO₂ namely ${}^{3}B_{2}$ and ${}^{1}B_{2}$ are bent and ${}^{1}B_{2}$ is above the ${}^{3}B_{2}$.

Among various energy transfer processes the curve crossing mechanism is known to be quite efficient. The transition probability is given by the Landau-Zener Formula where the variation in energy of the initial and final state is explicitly taken into account [Witting, 2005]. Basically, for a non adiabatic transition, it states that longer the interaction time, greater is the transition probability. Whenever two spin-constrained potential energy surfaces cross, non adiabatic effects become important and Landau-Zener formula expresses the factors that influence the crossing. For exact treatment of surface crossing the spin-orbit coupling term in the Hamiltonian has to be calculated. Possible reasons for the occurrence of spin forbidden transitions are summarized by Herzberg [1950] as follows: a) The selection rule that is violated may hold only to a first approximation. b) The selection rule may hold strictly for dipole radiation but not for quadrupole radiation or magnetic dipole radiation. c) The selection rule may hold only for the completely free and uninfluenced molecule and may be violated in the presence of external fields or collision with other molecules. A recent review [Harvey, 2007] deals with the kinetics of various spin forbidden reactions. According to this study the reactivity is determined by two factors. The first is the critical energy required to reach the minimum energy crossing point between the potential energy surfaces corresponding to the different spin states. The second one is surface hopping probability which depends on the spin-orbit coupling matrix element between the two electronic wavefunctions.

To bring out the possible role of nuclear spin in molecular photodissociation a general discussion of hyperfine interaction is in order. The hyperfine interaction refers to any kind of interaction between electrons and nuclei except the Coulombic interaction between their point electric charges. For the present case we are mainly concerned with the magnetic interaction between the magnetic dipole moment of the nucleus (due to its spin) and that of the surrounding electrons due to their net spin and orbital motion. Among the two types of magnetic interaction the familiar one is the direct dipolar interaction between the two magnetic moments. The position of the valence electrons plays a major role in this interaction. It can be shown that if the electron is in s-orbital, the net magnetic interaction is zero; for other orbitals it is non zero. In reality the nucleus has a finite size and the point dipole approximation is not valid. The hyperfine interaction due to overlap of nuclear and electronic wave functions is the well known Fermi contact interaction. A more detailed discussion on hyperfine interaction is given in the Appendix.

Among the three isotopes of oxygen only ¹⁷O has a nuclear spin whose magnitude is 5/2; similarly, between the two isotopes of carbon ¹³C has a nuclear spin of 1/2. The nuclear spin and dipole moments of ¹³C and ¹⁷O nucleus are listed in Table 4.7. The en-

richment of ¹⁷O and ¹³C in the photolysis products of CO₂ can be explained easily if the nuclear spin plays a role in the dissociation of CO₂ in the case of Hg lamp photons. The effect of hyperfine interaction can be envisaged as follows. It is known that the ground state of CO₂ is linear and singlet while the first excited state is bent and can be singlet as well as triplet. As discussed above, it is also known that the singlet surface crosses the triplet surface in certain geometry along an intersection seam. By absorption of 184.9 nm photons the CO₂ molecule makes a transition from the ground state to the singlet excited state (in photon absorption the spin of the molecule does not change according to Wigner-Whitmer rule [Okabe, 1978]) at a vibrational level which is above the cross-over region [Figure 4.11] by about 1.00 eV. However, the singlet state has a deep well (approximately 1.73 eV) and a direct dissociation from this state at this energy is not possible. In contrast, the triplet state has a shallow well and the cross-over zone is above the dissociation level by about 0.27 eV. Therefore, dissociation can take place if the molecule can reach near the cross-over zone by loss of energy (for example, through collisions) and then make a Landau-Zener transition from the singlet to the triplet state. Since this is a spin forbidden process it can occur only through a perturbation like spin orbit coupling which mixes these states. The strength of this coupling is not high in case of CO₂ and this is the reason why the dissociation rate is small. This spin forbidden step would compete with fluorescence. Quantum yield studies at 1849Å [Krezenski et al., 1971; Slanger et al., 1974; Slanger and Black, 1978] showed that for photon absorption by CO₂ at low energies the quantum yield is quite high at high pressure (~1 atm). As a consequence it is expected that fluorescence is not significant relative to dissociation, although the collisional deactivation must be high and could be responsible for effecting major part of the singlet triplet transition. In addition, there is spin-orbit coupling in the molecule which is independent of isotopes. Therefore, one can not find a competing process which might be isotope discriminatory in favour of ¹⁷O and ¹³C. We propose that the nuclear spins of ¹³C and ¹⁷O introduce two small extra coupling to facilitate dissociation of the corresponding isotopologues and enrich the products in these isotopes. The observed enrichment in ¹³C is lower by a factor of about 2.3 compared to 17 O. The 13 C has a high g factor (1.4) but low spin (1/2) whereas even though 17 O has 5/2 spin the g factor is low (-0.76). Taken together the enrichment ratio between 17 O and 13 C should be about 2.7 [(2.5×0.76)/(0.5×1.4)] if we consider the magnetic moment ratio alone. Interestingly, this is close to what we obtained above (2.3) when we defined the



enrichment of ¹⁷O to ¹³C by comparing the observed delta values with model predictions.

Figure 4.11: Schematic potential energy curves of the ground state and two excited states of carbon dioxide molecule involved in the photodissociation by Hg lamp photons (184.9 nm) and Kr lamp photons (123.6 nm) [following Harding et al., 1988]. The window of energy between 5.45 eV and 7.44 eV can produce the anomalous ¹⁷O enrichment during dissociative transition from ¹B₂ to ³B₂.

Despite the close agreement between the model prediction and the observed enrichment ratio providing credence to the nuclear spin interpretation it is naive to expect that a simple magnetic moment ratio can equal the enrichment ratio. For example, in taking account of the hyperfine coupling one can argue that for every CO₂ molecule with a ¹³C the dissociative transition is affected by the ¹³C nuclear spin with high efficiency since the carbon atom is located at the centre of the molecule and the overlap integral (the perturbation being given by the expression $\int f(r)S.L$) would have a high value. Being located at the edge of the CO₂ molecule a ¹⁷O spin would not have the same overlap. Moreover, in CO₂ dissociation to O+CO the ¹⁷O atom may be the emitted one or it may be part of CO. The effects could be different in the two cases. In the absence of nuclear spin effect the non-adiabatic coupling in the triplet O atom that is formed. The nuclear spin of ¹³C

Nucleus	Spin, I	g- value	Magnetic moment	Magnetic moment ratio
^{13}C	1/2	1.4046	0.7023	2.7
¹⁷ O	5/2	-0.7572	-1.8930	

Table 4.7: Nuclear spin properties

and ¹⁷O just adds extra coupling depending on their magnitude and spatial position. A lower spin of ¹³C relative to ¹⁷O would reduce its effect while the position of the ¹³C spin in the centre of the molecule relative to the ¹⁷O spin (located near the edge of the molecule) would lead to a different (probably higher) overlap integral. Admittedly these are qualitative arguments and a detailed molecular modeling is required to estimate accurately the nuclear spin effect in CO_2 photodissociation.

The ¹⁸O isotope has no spin and consequently no hyperfine effect is expected. It is also noted that between the two species CO and O_2 , CO has more enriched heavy isotopes (both ¹⁷O and ¹⁸C). This follows from normal fractionation rule which predicts that CO would be enriched relative to O atom due to zero point energy effect during dissociation and also by subsequent exchange of CO with O atom. The present results therefore provide strong support for the nuclear spin hypothesis of Bhattacharya et al. in producing enrichment of ¹⁷O and ¹³C in the products of CO₂ photodissociation at this energy.

4.3.2 CO₂ photolysis by Kr lamp photons

It was noted that fractionation in case of CO₂ photolysis by Kr lamp is of a different nature from that of Hg lamp. We speculate below about the reason behind the observed fractionation in this case. For Kr lamp the energy range lies in the dissociative continuum corresponding to products CO+O(¹D) in reaction (1.12). However, it has been shown that a small amount (about 6 %) of O(${}^{3}P$) also forms directly [Zhu and Gordon, 1990] due to transition from the ${}^{1}B_{2}$ surface to the ${}^{3}B_{2}$ surface by the same Landau-Zener process mentioned before. According to these authors, although the molecule has excess energy over the dissociation threshold it does not dissociate readily. They postulate that since the upper state is bent it is difficult to have enough concentration of energy initially in the reaction coordinate; this would allow it to survive a number of vibrations and increase the probability of curve crossing.

We also note that the photon energies in the Kr lamp emission are near the upper

threshold of the absorption cross section curve (i.e., in the falling part of the fitted continuum in Figure 3.3). As explained earlier in this chapter, it follows from the blue shift effect in isotopologue dissociation (a consequence of the Reflection Principle) that the heavy isotopic species have larger dissociative cross section in the energy range where absorption cross section decreases with energy. This must be the main reason for the enrichment of heavy isotopes ¹⁸O and ¹³C in the CO phase. However, we note that the model predictions for ¹⁸O and ¹³C of CO fall short of the experimental values by about 40 ‰ . This means that the dissociation rate of the heavy isotopologue has been underestimated by the simple blue shift formula in case of dissociation by Kr lamp photons. The factor used is ~ 1.011 (Table 3.5) which is quite low. To reproduce the experimental values this factor should be much higher, probably close to 1.068 as found by fitting the observed δ -values with the KINTECUS predictions. The high value of the fractionation factor implies contribution from other sources which have not been considered in the simple Young-Miller formula. For example, extra contribution from excited bending mode and consequent high values of TDMS can cause this increase.

For the O_2 phase the matter is more complex compared to the Hg lamp case since the oxygen atoms are mainly formed in the $O(^{1}D)$ state which allows them to exchange rapidly with the bath gas of CO_2 . The mechanism of exchange between $O(^1D)$ and CO_2 have been studied extensively in the literature in connection with atmospheric CO₂. Yung et al. [1991] were the first to propose that the enrichment in stratospheric CO_2 is due to an isotope exchange reaction between CO_2 and $O(^1D)$, the latter being produced by UV dissociation of ozone. The mechanism proposed by them is the following. The collision of $O(^{1}D)$ and CO_{2} produces a short lived collision complex CO_{3}^{*} which dissociates into $CO_2 + O({}^{3}P)$. The quenching of $O({}^{1}D)$ by CO_2 is a spin forbidden process as it involves transition from singlet to triplet state but it proceeds at a very fast rate 1.1×10^{-10} cm³s⁻¹ at 298 K. A recent study by Perri et al. [2003] showed that above isotope exchange reaction can occur via two different channels. The major channel is a electronic quenching of $O(^{1}D)$ to $O({}^{3}P)$ ($CO_{3}^{*} \rightarrow CO_{2} + O({}^{3}P)$). In the other channel exchange occurs without quenching i.e., without crossing to the triplet surface, $CO_3^* \rightarrow CO_2 + O(^1D)$. The branching ratios of these two channels are: (68%, 32%) and (84%, 14%) at the collision energy 7.7 kcal/mol and 4.4 kcal/mol respectively. The lifetime of CO_3^* complex is sufficiently high (1-10ps) so that both isotope exchange and curve crossing from singlet to triplet surface can occur [Perri et al., 2003, 2004]. It is also noticed that the oxygen isotope exchange proceeds at a nearly statistical rate i.e., the probability that a reactant oxygen atom is incorporated into the product CO_2 molecule is close to 2/3 [Baulch and Breckenridge, 1966]. This can be explained by the long lifetime of CO_3^* which allows a faster redistribution of intramolecular vibrational energy whereby the all oxygen atoms become equivalent irrespective of their isotopic nature.

To explain the anomalous oxygen isotopic composition of stratospheric CO_2 several models have been proposed [Yung et al., 1991, 1997; Barth and Zahn, 1997; Johnston et al., 2000] but none of them could reproduce the observed stratospheric slope. The model calculations for 18 O enrichment in CO₂ by Yung et al. [1991] simply reflected the 18 O enrichment in ozone. Barth and Zahn showed that stratospheric CO₂ enrichment cannot be explained by simple mixing of ozone and CO₂. They suggested a possible fractionation during the formation of the CO₃* complex that depends on the mass of the involved oxygen isotopes. Johnston et al. [2000] also drew a similar conclusion and supported an additional mass dependent fractionation in dissociation of CO_3^* complex. A recent study by Mebel et al. [2004] has argued for a conventional isotope effect in CO₃* dissociation process. They calculated the ratio of ${}^{16}O/{}^{18}O$ in the ejected oxygen based on theoretical considerations and showed that there is a small deviation from the pure statistical probability of 2/3. They also suggested the possibility of an unconventional isotope effect (non-RRKM effect) causing anomalous enrichment in ¹⁷O and ¹⁸O which could arise due to the symmetry of transient CO_3^* complex as observed in case of O_3^* . On the whole, it is still not clear if the $O(^{1}D)$ - CO_{2} exchange process is a simple transfer of the isotope anomaly from ozone to CO2 or involves some other anomalous isotope effect associated with CO3* formation/dissociation.

In connection with the present experiment our model predicts depletion in ¹⁸O by about 8.9 ‰ in case of Kr lamp whereas the observed δ -values are about -40 ‰ . In contrast, the observed δ^{17} O is close to zero. This is again an anomalous ¹⁷O enrichment (in O₂ phase) which can be explained by the nuclear spin effect arising from partial contribution of dissociation through curve crossing (from ¹B₂ to ³B₂ surface). A recent theoretical study examined the case of spin forbidden exchange reaction involved in quenching of O(¹D) by CO₂ [Yang et al., 2005]. According to this work spin forbidden quenching occurs in two different ways. One is through complex formation and the other is by a direct route i.e., without the formation of the intermediate CO_3^* complex. These authors concluded that the direct channel is more efficient which agrees with our observation.

Various features of the CO₂ dissociation products by Kr lamp photons are still not clearly understood since the PES at this energy is not known and we do not know if this could really be treated as a direct dissociation. In a multiphoton resonance-enhanced molecular beam experiment at 157 nm photodissociation of CO_2 the $O(^{3}P)$ fragments were detected [Matsumi et al., 1991]. The study by Miller et al. [1992] also confirmed the formation of $O({}^{3}P)$ at 157 nm photodissociation of CO_{2} . The above two studies differ in the value of a calculated parameter which is a measure of the anisotropy of the photofragment recoil. One possible explanation proposed by Matsumi et al. was that $O(^{1}D)$ and $O(^{3}P)$ atoms come from different initially excited electronic states of CO₂. Stolow and Lee [1993] studied the photodissociation of CO_2 by photofragment-translational spectroscopy. They also observed two channels of dissociation and their analysis confirmed the 6% $O(^{3}P)$ formation observed by Zhu and Gordon [1990]. Their study suggests that $O(^{3}P)$ channel arises from a direct transition from an excited triplet state. A small contribution of the bending mode was seen in the same study. To further complicate the matter there is also a possibility of dissociation through resonance absorption at this energy since the experimental absorption curve shows strong oscillations in this energy region [Figure 3.3] which have been ascribed to transitions from ${}^{1}\Sigma_{g} \rightarrow {}^{1}\Pi_{g}$ surface [Yoshino et al., 1996]. A resonance transition at this wavelength may easily cause large ¹³C enrichment as observed. It appears that photolysis experiments at Kr lamp photon energies have to be investigated more extensively.

It is clear from these two sets of results that isotopic fractionation in photo-induced dissociation of CO_2 molecules is highly anomalous and the nature of the anomaly depends critically on the photon energy. These results provide unique experimental evidence of anomalous mass independent isotopic fractionation caused by photo-dissociative reactions in gas phase. The well known isotopic anomaly in the case of ozone formation or dissociation is known to be dependent on the symmetry of the molecule resulting in a line of slope 1 in the ¹⁷O⁻¹⁸O covariation plot. In contrast, the photochemistry of CO_2 demonstrates another genre of anomaly whose elucidation and understanding will shed light on the process of molecular dissociation by UV photons in some instances.

4.3.3 CO₂ dissociation by Tesla discharge

In contrast to UV dissociation CO_2 fragmentation by Tesla discharge is an electron impact phenomenon. It is expected that the dissociating CO_2 molecule should be in charged condition but the actual energy states involved are not known. In a simple assessment one might argue that the heavy isotope depletion in the products is in accordance with the expectation based on Reflection Principle at energies near the rising part of the absorption curve of normal CO_2 molecule. This argument can certainly be used to explain the ¹³C depletion but not the oxygen isotope data showing depletion of heavy isotopes in nearly mass independent fashion (as evident by the slope value of 0.83 ± 0.10).

There are two possible ways to explain the oxygen isotope data. According to Valentini [1987] the mass independent depletion could be the result of a non-adiabatic collision induced isotopic fractionation. As the CO₂ is originally in the ground electronic state ${}^{1}\Sigma_{q}$ the wave function must be symmetric with respect to exchange of the O nuclei when they are isotopically identical. Therefore, half of all the allowed rotational states would be missing when both the O atoms are ¹⁶O. Valentini assumes that the initial Tesla excitation takes some of the molecules to an excited metastable state like Δ or Π state. It is apparent that non-adiabatic collisional relaxation from these states to the ground state should be isotopically selective and would be favored when the two oxygen atoms in the CO₂ molecule are isotopically different (i.e, heavier species) and all rotational states are permitted. Therefore, in a dynamic equilibrium the metastable state and the ground state would have different isotopic populations. If dissociations from these metastable states are preferred over the ground state the products (CO and O atoms) would be depleted in the two heavy isotopes in equal measure. Since the Δ and Π states have smaller bond energy than the ground state, dissociation from these states are indeed preferred. In addition, the CO phase would be slightly enriched compared to the O₂ phase due to the fast exchange between O atoms and CO molecules which enriches the CO phase.

It is also possible that once the reservoir of molecular oxygen has accumulated significantly it may become involved in the production of ozone. If ozone formation is appreciable, the left over O_2 would be depleted in the heavy isotopes as observed. Further experiments are needed to address this issue.

CHAPTER 5

Temperature dependence of isotope fractionation in CO₂ photolysis

Studies on temperature dependence of photodissociation rate of molecules and the variation in the isotopic composition of the products constitute an important area of research since they throw much light on the mechanism of the dissociation process. For example, a recent paper by von Hessberg et al. [2004] has shown that temperature variation studies in dissociation of N₂O can be best interpreted by invoking combined effect of changes in the Transition Dipole Moment Surface (TDMS) and the Boltzmann distribution. We had another motivation to study the temperature variation of CO₂ dissociation. The isotopic data presented in the earlier chapter show large scatter which seems to be more than could be accounted for by the experimental uncertainty. Since the temperature of photolysis chamber was not controlled it could have varied over the course of the day particularly between night and day. We suspected that a possible cause for the scatter could be some variation in the room temperature around the nominal value of about 25°C. The variation could easily be a few degrees from one experiment to another. With this background we investigated the temperature variation of the CO_2 dissociation products. We used only the Hg lamp photons which were of special interest in this study. There are some previous studies on the isotopic effects of photodissociation of CO₂ which are reviewed in this chapter.

5.1 Earlier studies

Absorption cross section of CO₂ has been investigated earlier at several temperatures including the room temperature (~25°C). Ogawa [1971] reported presence of numerous bands between 1750 Å and 1980 Å at 700 torr pressure using a 3-m long vacuum absorption spectrograph. The spectrum revealed fine structure in the regime $\lambda > 1650$ Å when operated with a resolution of 0.06Å. He found that the absorption coefficients of both the bands and the continuum increase towards shorter wavelengths and postulated that the origin of the continuum is the dissociation caused by ${}^{3}B_{2}$ - X ${}^{1}\Sigma_{g}$ + transition which agreed with the experiment of Lin and Bauer [1969]. Shemansky [1972] measured absorption cross section at a resolution of 4 Å in the wavelength region of 170-210 nm using 2-m spectrometer in conjunction with a multiple path absorption cell. Analysis showed that the cross section above 204 nm is entirely due to Rayleigh Scattering. More high resolution experiment with effective bandwidth 0.6Å using a 5 cm path length and very high pressure has been reported by DeMore and Patapoff [1972] which revealed negligible temperature dependence at higher wavelength region. Their results confirmed the conclusion of Shemansky that the absorption above 204 nm could be accounted for by Rayleigh Scattering. Lewis and Carver [1983] measured the absorption cross section of CO₂ at temperatures of 200, 300 and 370 K in the range of 175-197 nm (in steps of 0.5 Å) with resolution of 0.05Å. They showed that the temperature effect is small at shorter wavelengths with a minima at 1400Å and increases steadily towards higher wavelengths. Above 1900Å the cross section increases by a factor of 20 while going from 200 K to 370 K. This study is considered quite important since it pointed out the relevance of temperature dependence in models applicable to the Martian atmosphere. The Photochemical model of the stratosphere of Venus also involves the role of CO₂ photochemistry [Yung and DeMore, 1982]. The study by Parisot and Zucconi [1984] showed the profound influence of temperature variation of CO₂ dissociation rate in modeling the atmosphere of Mars and Venus. In their calculation they used an empirical formula for the temperature and wavelength dependence of the cross section based on the earlier measurements.

Yoshino et al. [1996] measured absorption cross section using a 3-m vacuum spectrometer at two temperatures (195 K and 295 K) and twelve wavelengths in the 120-175.5 nm region. Almost no temperature dependence was noticed in the peak cross sections in the wave number region 70000-80000 cm⁻¹. However, the ratio of the cross section at two temperatures ($\sigma_{195}/\sigma_{295}$) came down to 0.7 around 60,000 cm⁻¹. Two distinct bands were observed. The stronger band was below 140 nm and the weaker band was above 140 nm. Based on theoretical calculations they concluded that the stronger band is due to ${}^{1}\Pi \leftarrow {}^{1}\sigma_{g}$ transition and weaker band due to the ${}^{1}\Sigma_{u}{}^{+}$, ${}^{1}\Delta_{u} \leftarrow {}^{1}\Sigma_{g}{}^{+}$ transitions. Parkinson et al. [2003] extended the above study by increasing the wavelength range up to 200 nm. Using high resolution grating spectrometer, they reported cross section at two temperatures 195 and 295 K and demonstrated clear temperature dependence above 150 nm. Karaiskou et al. [2004] reported absorption cross section measurements of CO₂ in the UV from 200 to 206 nm at 295 and 373K.

In a flash photolysis experiment of CO_2 over 1500-2700 K at 193 nm $O(^{3}P)$ production was observed [Koshi et al., 1991]. Surprisingly, the increase of absorption coefficient was found to be very high, about 10⁸ times higher than the room temperature value. They explored the possibility that asymmetric stretching or some other degenerate vibrations are responsible for this enhancement. Two proposals were considered: formation of vibrationally excited CO_2 which decays into $CO+O(^{1}D)$ and quenching of $O(^{1}D)$ to produce $O(^{3}P)$. Second possibility is the Landau Zener transition between $^{1}B_2$ to $^{3}B_2$ to produce $CO+ O(^{3}P)$. Ultraviolet absorption spectra of CO_2 was recorded at very high temperature behind shock wave by Schultz [2002]. Similar measurements were also performed by Oehlschlaeger et al. [2004, 2005].

5.1.1 Theoretical development

The transition moment calculation by Julienne et al. [1971] explained the absorption cross section variation with temperature fairly well. They obtained the electronic wave functions and energies of the low-lying excited states and the ground state of CO_2 as a function of the bending angle. To calculate integrated absorption coefficient, average transition moment is necessary. This was calculated by using the wave functions in the ground state and in the higher vibrational state and then taking average over the appropriate Boltzmann distribution. Their calculation shows that the absorption increases quite rapidly as a result of increase in the vibrational quantum number in the ground electronic state. According to them absorption increases by about 75% when temperature is doubled.

Selwyn and Johnston [1981] measured the ultraviolet absorption cross section of N_2O

over the wavelength range 172 nm to 197 nm and the temperature range 150 to 500 K. They concluded that the temperature effect is solely due to thermal activation of the bending mode. In analyzing the data, they further commented on the absence of any rotational structure. The above absorption cross section measurement was done as a function of nitrogen isotopic substitution, $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{15}N^{15}N^{16}O$ (denoted by 446, 456, 546 and 556 abbreviations). The absorption spectra as a function of isotope substitution and temperature is considered very important for atmospheric applications. There are various atmospheric as well as laboratory measurements made on this important molecule [Johnston et al., 1995; Rahn and Wahlen, 1997; Zhang et al., 2000; von Hessberg et al., 2004]. These measurements showed the absence of heavy isotope enrichment at 185 nm. A Zero Point Energy model was proposed to explain the lack of isotopomer enrichment of N₂O at 185 nm. Although this model could not explain the experimental results in quantitative fashion it provoked many wavelength dependent fractionation measurements [Turatti et al., 2000; Kaiser et al., 2003].

Efforts are still underway to reconcile the theory with experimental results in case of N_2O . Various theories have been proposed including an ab initio quantum mechanical calculation where up to date Potential Energy Surface (PES) was used. The profound effect of TDMS variation with temperature was pointed out by Johnson et al. [2001] who could successfully explain the temperature dependence of N_2O photodissociation. They adopted a quantum-mechanical approach using the Hermite Propagator (HP) method. In this method a PES is assumed and the wave function at the excited state is propagated with time. In their model the bending angle and the NN-O distance were taken as variables while N-N interatomic distance was taken as fixed. In the final expression of the absorption cross section several factors stand out. The cross section depends on the assumed PES, the degeneracy of the bending mode, the intensity factor which depends on the TDMS, the Boltzmann population factor, partition function and an arbitrary scaling factor. The HP model marks a significant improvement over earlier theoretical studies. Although it explains some of the measurements quite well it somehow fails to explain the 546 and 556 isotopomer behavior of N_2O photodissociation.

In a later development on the experimental side Kaiser et al. [2003] reported significantly different results at 185 nm. They observed depletion of heavy isotope in contrast to previous results which showed absence of enrichment. It is to be noted that the HP model described above predicts non-zero fractionation at this energy. Blake et al. [2003] attempted to resolve this issue by modifying the Yung-Miller ZPE model. They noted that the ZPE shift of the heavy isotopomers not only affects the position of the absorption spectrum but also its width. Taking this suggestion further, Liang et al. [2004] modified their earlier theory and included all the modes of vibration. Later on, this theory was modified by Prakash et al. [2005] to get a better agreement with the experimental results. They pointed out that the implicit assumption of a 2-D nature of the bending vibration affects the normalization constant and leads to erroneous results. They presented time independent fractionation calculation on the basis that the asymmetric stretch and the doubly degenerate bending vibration are the principal Frank-Condon active modes in the photodissociation. Their calculation was based on the Reflection Principle described before using an ab-initio PES and TDMS. An attempt was also made by Liang et al. [2004] to explain the temperature effect by extending the ZPE model. They used an empirical parameter to reproduce the measured fractionation factor. Physically, it accounted for the TDMS variation and the anharmonicities in the actual bound state wave function. A significant advance has been made recently by Jost [2008] for calculating absorption cross section of CO2 and few other molecules using the available experimental cross sections corresponding to the major isotopomers. Contribution from the hot band excitation was calculated using the wave function for v = 1 and the final expression reads as

$$\frac{\sigma(E)}{E} = A(1 - \rho + 2\rho X^2)(V_e'(1 + rX))^{-1}exp[-(X^2/(1 + rX)^2)]$$
(5.1)

Where ρ is ratio of the population in v=1 to v=0 and can be approximated as $\rho = \exp[-\hbar w/kT]$ where h=Planck constant, k= Boltzmann constant, ω = vibrational frequency and T= temperature. The quantity X=(E-V_o)/(V_e'/ β) where V_e is the vertical excitation energy at the equilibrium geometry of the ground state, β is the inverse of the width of the initial wavefunction, V_e' denotes the slope of the upper PES at the ground state equilibrium geometry and V_o=V_e-ZPE. The population of v=0 is close to (1- ρ). The factor, 1- ρ +2 ρ X² can be interpreted as follows: (1- ρ) is the contribution of the population of v=0 and 2 ρ X² is the contribution from v=1. However, this is an empirical approach based on pure Reflection Principle and the issues discussed above regarding TDMS variation have not been taken into account explicitly at this stage.

5.2 Experimental details

In view of the above discussion it is clear that the temperature dependence of isotopic nature of the products of CO_2 photodissociation would be a matter of great importance. To carry out the temperature change the photolysis chamber was heated by keeping a mantle heater at the bottom of the chamber. A calibrated thermocouple was kept inside the chamber to measure the temperature. The heater was switched on before starting the UV lamp to get a reasonably stable temperature. Temperature readings were taken several times and the average value is reported. A few low temperature experiments were also performed. For low temperature experiment cold water was circulated from an external chilled water supply. Gas collection, purification and isotope measurements are as described in the experimental chapter (see **chapter 2**).

5.3 Results and discussions

The results of photodissociation rate and isotopic composition of the product gases obtained using Hg lamp photons are presented in Table 5.1 and 5.2. The chamber temperature was varied from 288 to 345 K and we assume that the gas temperature was the same as the chamber temperature. We separated product oxygen (O₂) and carbon monoxide (CO) from each other. First the isotope ratios δ^{17} O and δ^{18} O in O₂ were measured. For CO phase, however, we could not carry out the detailed procedure outline before for derivation of the δ^{13} C, δ^{17} O, and δ^{18} O of the gas. Instead, only δ^{29} and δ^{30} of CO were measured directly relative to the Vadilal Tank CO gas. Using the known composition of this tank CO gas we could convert the δ^{30} data to the δ^{18} O value relative to V-SMOW easily.

Obviously we cannot derive individual δ^{13} C and δ^{17} O values from the δ^{29} CO data as explained before. However, the change in δ^{17} O of CO with temperature [denoted by $\Delta(\delta^{17}\text{O})(\text{CO})$] can be calculated under a simple assumption. We assumed that the variation due to temperature in δ^{17} O would parallel that in δ^{18} O since these two variations are seen to be related in case of the O₂ product. CO being intimately related to the O-atom (as both are simultaneously formed in the photodissociation process in the same step) this assumption makes sense. If this is true, the variation in δ^{17} O can be estimated from the variation in δ^{18} O by using the same relation between the two as obtained in case of O₂. Therefore, we use the relation:

Table 5.1: Various experimental parameters of products of CO₂ dissociation carried out at various temperatures using Hg lamp photons (185 nm). The δ -values are expressed relative to the tank CO₂ used for dissociation. For CO gas only δ^{29} and δ^{30} values were measured relative to the tank CO. δ^{30} is very close to δ^{18} O but δ^{29} has contributions from both δ^{13} C and δ^{17} O. We estimated the increase in δ^{13} C (denoted by $\Delta(\delta^{13}C)$) by using $\Delta(\delta^{17}O)$ - $\Delta(\delta^{18}O)$ relation obtained from the O₂ data assuming similar variation in the two products gases (explained in text in more detail).

			Am	ount	Produ	ction rate		
Expt.		Exposure	CO	O_2	CO	O_2	$\frac{O_2}{CO}$	
No	(T)	time	-	-	-	-	-	
		(min)	μ mol	μ mol	-	-		
T-1	288	600	16.5	12.5	1.65	1.25	0.76	
T-2	291	360	13.9	9.2	2.32	1.53	0.66	
T-3	291	420	15.2	7.5	2.17	1.08	0.50	
T-4	296	554	19.2	10.5	2.08	1.14	0.55	
T-5	302	600	-	19.9	-	-	-	
T-6	312	360	24.9	15.0	4.15	2.50	0.60	
T-7	315	340	20.1	15.0	3.55	2.65	0.75	
T-8	317	360	27.0	16.5	4.50	2.75	0.61	
T-9	325	300	27.6	19.7	5.52	3.94	0.71	
T-10	326	420	28.3	-	4.04	-	-	
T-11	342	200	21.2	9.4	6.36	2.82	0.44	
T-12	345	240	29.2	18.2	7.30	4.55	0.62	

Table 5.2: Isotopic composition of products of CO_2 dissociation carried out at various temperatures using Hg lamp photons (185 nm). The δ -values are
expressed relative to the tank CO ₂ used for dissociation. For CO gas only δ^{20} and δ^{30} values were measured relative to the tank CO. δ^{30} is very close to
$\delta^{18}O$ but δ^{29} has contributions from both $\delta^{13}C$ and $\delta^{17}O$. We estimated the increase in $\delta^{13}C$ (denoted by $\Delta(\delta^{13}C)$) by using $\Delta(\delta^{17}O)$ - $\Delta(\delta^{18}O)$ relation
obtained from the O_2 data assuming similar variation in the two products gases (explained in text in more detail).

				Uxygen					2		
Expt.						-					
No	(T)	$\delta^{18} { m O}$	$\delta^{17} { m O}$	$\Delta(\delta^{18}{ m O})^a$	$\Delta(\delta^{17}\mathrm{O})$	$\delta^{29} { m O}$	$\delta^{18}{ m O}$	$\Delta(\delta^{18}{ m O})$	$\Delta(\delta^{17}{ m O})^b$	$\Delta(\delta^{29})$	$\Delta(\delta^{13}{ m C})^c$
		%00	%0	%0	%0	%00					
<u>1-1</u>	288	-30.8	42.9	0.0	0.0	22.8	-8.9	0.0	0.0	0.0	0.0
T-2	291	-26.8	50.9	4.0	8.0	ı	2.0	11.0	22.0	ı	ı
T-3	291	-25.0	ı	5.8		ı	1.8	10.8	ı	ı	
T-4	296	ı	ı	ı		24.9	ı	·	ı	ı	ı
T-5	302	-17.7	52.6	13.1	9.7	33.7	18.2	27.2	20.1	10.9	10.9
T-6	312	-4.3	62.6	26.6	19.7	45.2	35.3	44.2	32.8	22.4	22.8
T-7	315	-2.0	66.5	28.8	23.6	44.1	40.3	49.3	40.3	21.3	21.4
T-8	317	-0.5	63.9	30.3	21.1	49.8	44.4	50.3	37.1	27.0	27.5
T-9	325	13.3	74.7	44.1	31.8	47.7	50.3	59.2	42.7	24.9	25.1
T-10	326	6.5	70.2	37.3	27.3	48.8	44.4	53.3	39.0	26.0	26.4
T-11	342	19.5	87.5	50.3	44.6	47.9	50.9	59.8	53.0	25.1	ı
T-12	345	34.7	98.8	65.5	55.9	47.2	57.6	66.6	56.8	24.4	ı

 $^{a}\Delta(\delta^{18}\text{O})$ and $\Delta(\delta^{17}\text{O})$ denote the increase in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ relative to the value at 288K temperature. $\Delta(\delta^{17}\text{O})=A \times \Delta(\delta^{18}\text{O})$ where A=0.81 (see Figure Δ) 1.4) ^bWe assume $\Delta(\delta^{17}O)=A \times \Delta(\delta^{18}O)$ with same A value ${}^{c}\Delta(\delta^{13}C)=X \times \Delta(\delta^{29})-Y \times \Delta(\delta^{17}O)$ where X=1.066 and Y=0.034

Temperature dependence of isotope fractionation in CO₂ photolysis

$$\Delta(\delta^{17}O)(CO) = M \Delta(\delta^{17}O)(CO)$$

where $\Delta(\delta^{17}O)$ and $\Delta(\delta^{18}O)$ are changes in δ - values and M is a parameter obtained by fitting a line to the observed oxygen isotope changes in O₂, that is,

$$\Delta(\delta^{17}O)(O_2) = M \Delta(\delta^{17}O)(O_2)$$

Once the $\Delta(\delta^{17}O)(CO)$ is known for a given temperature increase corresponding $\Delta(\delta^{13})C$ of CO can be calculated using the relation between δ^{29} , $\delta^{13}C$ and $\delta^{17}O$ for CO given before which can be cast in the form of the differential:

$$\Delta(\delta^{13}C) = (\frac{A}{B})\Delta(\delta^{29}CO) - (\frac{1}{B})\Delta(\delta^{17}O)$$

Or, $\Delta(\delta^{13}C) = X \times \Delta(\delta^{29}CO) - Y \times \Delta(\delta^{17}O)$

Where $X = \frac{A}{B} = 1.066$ and $Y = \frac{1}{B} = 0.034$ and $\Delta(\delta^{29}CO) =$ measured $\delta^{29}CO$ change.

We note that the above procedure gives us only an estimate of $\Delta(\delta^{13}C)$ of CO but not the absolute value of $\delta^{13}C$ of CO. The procedure is reasonably robust since the changes in δ^{29} are mostly due to that in $\delta^{13}C$ with only minor contribution from $\delta^{17}O$. As we are mainly interested in the changes in isotope ratios due to temperature increase such a procedure is justifiable for the present purpose.

The variations in production rate of O_2 and CO are shown in Figure 5.1 and Figure 5.2 which indicates that the production rate increases rapidly with temperature and a straight line fit to the data gives average increase as 0.05 and 0.09 μ mole/hr per °K for O_2 and CO. This means about 2% increase for 1 °K increase in temperature for both the gases when referred to the value at 320 K. The total increase (Figures 5.1, 5.2) is quite large being about 26% while going from 288 to 345 K. The O_2 to CO ratio varied from 0.44 to 0.76 with a mean (and standard deviation) of 0.62±10. Ideally, the value should be equal to 0.5 always but experimental uncertainty in measurement of two gas amounts after separation does not yield this value all the time. However, the percentage increase in both are the same as expected when averaged over several data points.

Absorption cross section of CO_2 and its temperature dependence have been reported in a number of experiments [Karaiskou et al., 2004; Parkinson et al., 2003] which show increase in cross section by factor of about 3 when temperature (T) changes from 195 to 295 K. Our results are consistent with these data.



Figure 5.1: Variation in oxygen production rate with temperature in case of CO_2 photodissociation by Hglamp photons showing increase in dissociation rate with temperature. The increase is about 2% per °K rise in temperature.

Interestingly, the heavy isotope ratios in O_2 also increase with temperature [see Figure 5.3]. The increase is about 1 % per °K increase. This means that the increase in the dissociation rate of these species does not parallel the trend for the ¹⁶O species but is higher. In addition, the effect seems to be similar for ¹⁷O and ¹⁸O species. The three isotope plot diagram (normalized to room temperature datum) shows that the slope correlating the variation of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios is 0.81 ± 0.05 [Figure 5.4]. The increase of ¹⁷O/¹⁶O is about 80% of that of ¹⁸O/¹⁶O in contrary to the mass dependent rule which would predict a value of about 50%.

The ¹⁸O/¹⁶O ratio in CO also increases with temperature [Figure 5.5]. The total increase is about 67 ‰ for a temperature increase of 57 °K (i.e., about 1 ‰ per °K increase). We note that the two increases (in O₂ and CO) are similar in magnitude. This reinforces our belief that the factor responsible for isotope ratio increase is inherent in the dissociation process. The change in ¹³C/¹²C ratio in CO estimated using the procedure outlined above is plotted in Figure 5.6. Here the change is about 0.7 ‰ per °K increase. The increase



Figure 5.2: Variation in CO production rate with temperature in case of CO_2 photodissociation by Hg-lamp photons showing increase in dissociation rate with temperature. The increase is about 2% per °K rise in temperature.

seems to be somewhat less compared to the heavy oxygen isotope δ^{18} O but the number of data points are small and the dispersion is large. We conclude that for some reason all the heavy isotope ratios increase with temperature in case of CO₂ photodissociation using Hg lamp photons.


Figure 5.3: Variation in oxygen isotope ratios of O_2 as a function of temperature in case of photodissociation of CO_2 by Hg lamp photons. Both ¹⁷O and ¹⁸O isotope ratios increase with temperature and it seems that the two ratios increase similarly (as clearly shown in Figure 5.4). The increase is about 1 ‰ for one degree increase for both heavy isotopes.



Figure 5.4: Covariation of increase in ${}^{17}O/{}^{16}O$ ratio with that in ${}^{18}O/{}^{16}O$ ratio the increases being caused by increase in temperature at which CO_2 dissociation is carried out (see Figure 5.4). The increase in ${}^{17}O/{}^{16}O$ ratio is about 80% of that in ${}^{18}O/{}^{16}O$ ratio which is contrary to what is expected in a mass dependent process (about 50%). This indicates that the increase in isotope ratio with temperature is caused by a process which is not entirely due to the effect of simple change of mass.



Figure 5.5: Variation in ¹⁸O/¹⁶O ratio in CO (produced by photodissociation of CO₂ by 185 nm photons) with temperature. There is increase in the δ^{18} O value with increase in temperature- the rate of increase being about 1 ‰ per °K.



Figure 5.6: Variation in ${}^{13}C/{}^{12}C$ ratio (plotted in terms of increase in ${}^{13}C/{}^{12}C$ value over that in room temperature) in CO produced by photodissociation of CO₂ by Hg lamp photons. The increase in $\delta^{13}C$ is about 0.7 ‰ per °K increase in temperature.

5.3.1 Probable explanation for increase in heavy isotope ratio with temperature

CO₂ is a linear triatomic molecule in its electronic ground state and hence has four normal modes of vibration: the symmetric and asymmetric stretching modes and a doubly degenerate bending mode. It has many similarities with N₂O which is also a linear molecule (and isoelectronic with CO₂) and has been studied extensively for photodissociative fractionation. To explain the pattern observed in CO_2 we can use the arguments proposed for N₂O by von Hessberg et al. [2004]. Leaving aside the isotopic ratio increase for the moment, the increase in total dissociation rate with T can easily be explained in terms of hot band excitation i.e., dissociation from excited vibrational states. In the electronic ground state, vibrational excitation can occur with increase in T for all three modes of vibrations but the bending mode being of lower energy is excited more than the others [Selwyn and Johnston, 1981]. von Hessberg et al. [2004] have shown that the transition intensity increases with bending vibrational excitation, the first three states having intensity ratios of 1:3:6 in case of N_2O [Johnson et al., 2001]. Thus, the population of excited bending states has significant influence on transition intensity. They also showed that the hot bands are especially important in the low energy side of the cross section maximum. The relative population of the excited bending states is given by the familiar Boltzmann expression:

$$\frac{n_{v_i}}{\sum_i n_{v_i}} = \frac{exp[-g_i\beta\epsilon_i]}{\sum_j exp[-g_j\beta\epsilon_j]}$$

where $\beta = \frac{1}{kT}$, ϵ_i is the energy ($\epsilon = hc\bar{\nu}$) and g_k is the degeneracy of the state in question.

The change in heavy isotope ratios with temperature in case of N₂O molecule is also known to be a consequence of the changing population in the bending states with temperature [Johnson et al. 2001; Nanbu and Johnson, 2004; von Hessberg et al., 2004]. These authors have shown that the transition intensity increases with temperature since a bent molecule has larger TDM value. In this sense, a lighter isotope system (for example, ${}^{16}O^{12}C^{16}O$ relative to ${}^{16}O^{12}C^{17}O$) will have a larger cross section due to a larger amplitude of vibration and the effect will increase with temperature due to larger number of vibrational quanta. Interestingly, this isotope effect disfavouring the heavier system is offset by the Boltzmann factor. Since heavier isotope system has lower frequency of vibration it has relatively larger number in higher excited states. With increase in T this factor also increases and acts in favour of the heavier system. We do not have information on TDMS

Table 5.3: Population calculation of excited states considering only bending mode ω_2 [Frequency values (cm^{-1}) are taken from Wang et al., 2004]. Ratio means the ratio of changes in population ratio in going from 300 K to 350 K.

Species	ω_1	ω_2	ω_3	$N_{v=1}/N_{v=0}$	$N_{v=1}/N_{v=0}$	change	ratio
				At T= 300K	At T=350K		
OCQ	1309.5	665.2	2369.5	0.041	0.065	57.86	0.996
OCP	1328.2	667.6	2377.7	0.041	0.064	58.12	

calculation and its variation with T for the CO_2 molecule. But since the heavy isotope ratios increase with T we can say that the Boltzmann factor plays a more significant role than the TDMS in case of CO_2 . This is opposite to what is observed in case of N_2O .

Calculation shows that if T is increased from 300 K to 350 K the ratio of population $N_{v=1}/N_{v=0}$ increases from 4.1% to 6.4% for both ¹⁷O and ¹⁸O species. The resultant Boltzmann factor would enhance the cross section for ¹⁷O and ¹⁸O species to equal extent (0.996) [Table 5.3]. This would mean $\Delta(\delta^{17}O)$ vs $\Delta(\delta^{18}O)$ plot should have a slope of about one. Since the data plotted in Figure 5.4 shows a slightly lower slope (0.81) we must invoke a role of TDMS variation in these two cases. If the effect of TDMS variation is slightly larger for ¹⁶O¹²C¹⁷O relative to ¹⁶O¹²C¹⁸O (both being normalized to ¹⁶O¹²C¹⁶O) it is possible to imagine the slope coming down from a value of 1 to 0.8. The reason that TDMS variation would have a larger effect for ¹⁷O species is clear from the discussion of von Hessberg et al. [2004] in case of N₂O. The ¹⁷O atom lying at the end of the molecule would have a slightly larger (in negative direction) amplitude than that of ¹⁸O species and consequently would have a larger effect. Of course, the effect is negative in nature since the TDMS variation has to be normalized to that of ¹⁶O species. Therefore, TDMS change would decrease the enhancement caused by the Boltzmann factor for both ¹⁷O and ¹⁸O species but to a larger extent for ¹⁷O species. This could in principle generate the observed slope of 0.8. It is important to note that the ¹⁷O-¹⁸O variation slope has an apparent mass independence but is generated by a combination of factors operating in case of molecular photodissociation.

As carbon atom is the central atom the ${}^{13}C/{}^{12}C$ should not increase due to the bending motion. Only asymmetric vibration will be affected. Figure 5.6 shows increase in ${}^{13}C/{}^{12}C$ ratio with T. Therefore, we can conclude that TDM is getting affected by asymmetric vibration of the molecule.

We also note that while the changes in the δ -values of O₂ and CO with temperature can

be explained by assuming a similarity of CO_2 molecule with N_2O to derive absolute cross section values for the isotopic species we need PES and TDMS for the CO_2 and apply a model like that developed by Johnson group. This should also incorporate the contribution of electronic and nuclear spin in order to reproduce the data. This can be an important agenda for future research in this field.

CHAPTER 6

Implications, conclusions and future scope

6.1 Implications

CO₂ is an abundant molecule and is present not only in the troposphere but also in stratosphere and at higher altitudes in the Earth's atmosphere. In stratosphere, the average mixing ratio is found to be 350 ppmv. Typical CO₂ concentrations are 10^{15} cm⁻³ at 18 km, 10^{13} cm⁻¹ at 50 km and 10^{11} cm⁻³ at 80 km. In the lower thermosphere, from 100 to 140 km, CO₂ concentration is in the range of 10^{10} to 10^6 cm⁻³ [Trinks and Fricke, 1978]. Photodissociation of CO₂ occurs at relatively high altitudes where solar Lyman- α and the continuum radiation at the Schumann-Runge (S-R) wavelengths are present.

The importance of photolysis in the prebiotic primitive atmosphere of Earth was pointed out by Kasting et al. [1979]. From the model calculations, it was concluded that the predominant source of oxygen at all altitudes was photodissociation of CO_2 . The strong temperature dependence of CO_2 absorption cross section has profound effect on its photolysis rate. We note that the energy window which leads to ¹⁷O selectivity nearly matches with the solar UV availability at an altitude of about 30 km in Earth's atmosphere. Based on our study we predict that the atmospheric CO at this height will have excess ¹⁷O due to contribution from the CO_2 photodissociation.

The results of this study can be used in understanding some of the observed anomaly in different oxygen containing species of the Earth's atmosphere and hence would be useful in resolving some issues related to chemistry of the atmosphere. The anomalous signature

found in CO may have components of CO₂ dissociation. In the boundary of stratosphere and troposphere anomalous CO produced in higher altitudes may come down to the lower atmospheric levels. The studies by Huff and Thiemens [1998] and Rockmann et al. [1998a; 1998b] showed excess ¹⁷O in atmospheric CO. The origin of this excess is still not clear but CO₂ dissociation can be one of the reasons. Although Rockmann et al. showed that the seasonality of excess ¹⁷O could be explained by the reaction CO+OH we feel that the CO₂ photolysis component cannot be excluded. The studies of Hayes and Olivero [1970] and Trinks and Fricke [1978] showed that the primary source of CO in the Lower Thermosphere is the photodissociation of CO₂. The eddy diffusion model presented by Allen et al. [1981] showed that the CO mixing ratio is nearly constant between 22 to 45 km. Assuming photochemical equilibrium Bhattacharya et al. [2000] calculated ¹⁷O enrichment in CO to be about 6 ‰ above the mass fractionation line assuming the model parameters of Allen et al. [1981]. This signature can be used as a tracer for quantifying the transport across the mesosphere- stratosphere boundary.

Our experiment is the first demonstration of nuclear spin effect in gas phase reaction. The proposed nuclear spin effect occurring at certain wavelength range for CO₂ dissociation is a molecular phenomena where dissociation occurs through a singlet-triplet curve crossing. It is possible to imagine the occurrence of this effect in instances involving spin violation rule, for example, in case of isotope exchange reaction between CO₂ and O-atom. If the nuclear spin effect operates in this case it may easily explain the high δ^{17} O- δ^{18} O slope of stratospheric CO₂ with value as high as 1.7. Various theoretical attempts have shown that this slope can not be explained by simple mixing. Liang et al. [2006] proposed a mesospheric source of anomalous O(¹D) to explain this effect. But this proposal is still not verified. The way the nuclear spin hypothesis can work here is as follows. It is known that the exchange reaction of $O(^{1}D)$ - CO_{2} is spin forbidden and involves an intermediate complex CO₃* which dissociates to CO₂ and oxygen atom through spin orbit coupling. If the $O(^{1}D)$ is only from ozone dissociation and exchange is the only physical effect responsible for the ¹⁷O enrichment one can invoke a nuclear spin effect similar to that found in our study. One can reason that the ¹⁷O species of O(¹D) would have a relatively higher exchange rate than the ¹⁸O and ¹⁶O species and provide the excess ¹⁷O required. A recent study by Liang et al. [2008] has tried to reproduce the seasonal cycle of isotopic species by model predictions. Their calculation is based on published cross sections in various wavelength regions. According to them, the overall effect of the excess ¹⁷O through nuclear spin effect is not significant since the window where the spin effect is expected is quite narrow.

As CO_2 is the major constituent of the atmosphere of Mars and Venus and also occurs in the atmosphere of Titan, photo-dissociation rate and its temperature dependence would be very useful in atmospheric modelling of these planets. Many attempts have been made to model the Martian atmosphere [Yung et al., 1988; Atreya and Blamont, 1990]. These models assume a temperature invariant CO_2 cross section which is not strictly valid. Anber et al. [1993] pointed out that the sensitivity of the correlation of CO_2 absorption spectrum with the photochemical rate constants requires that proper temperature variation be considered. Therefore, they included in their model the temperature dependent absorption cross section to calculate the photodissociation rate coefficient.

Farquhar et al. [1998] were the first to measure three oxygen isotopes in a secondary mineral (carbonate) separated from a Martian meteorite. Their data showed a small deviation from the mass dependent line suggesting contribution from a reservoir with mass independent oxygen isotopic composition. The measured values are quite distinct from both the host silicate and martian water [Karlsson, 1992]. Farquhar et al. suggested a photochemical origin of oxygen isotope anomaly and proposed that it is derived from atmospheric isotopic exchange reaction of $O(^{1}D)$ and CO_{2} . The source of electronically excited atom was assumed to be derived from ozone photolysis. Since our study has now established that CO₂ photolysis is associated with large mass independent isotope effect in certain energy range we feel that it may help in resolving the issue of oxygen isotope anomaly discovered in the Martian Meteorites. In addition, the photodissociation products having unique isotopic signatures can be used as tracers to study the evolution of the Martian atmosphere. Since the Martian atmosphere is optically thin it is reasonable to expect that both O2 and CO possess anomalous signature. This O2 can react with geological materials over times and transfer its anomaly to the product oxides grains. The role of photochemistry in the Martian atmosphere has also been confirmed through sulfur isotope systematics from meteoritic measurement and laboratory experiments.

6.2 Conclusions

The conclusions of the present study are:

- 1. The CO₂ photodissociation differs from conventional chemical dissociation and produces an unusual isotopic composition in the products when the photons have energy near the threshold of dissociation (5.45 eV to 7.42 eV).
- 2. Unusual enrichment in ¹⁷O and ¹³C in the dissociation products takes place possibly due to the effect of nuclear spin in singlet triplet transition responsible for dissociation in case of Hg lamp photons.
- 3. The enrichment is higher for ¹⁷O (with nuclear spin 5/2) compared to ¹³C (with spin 1/2). The ratio of enrichments (2.3) is in accordance with the expected value based on the ratio of magnetic moments (since the simple spin ratio is 5 but it reduces to 2.7 by the g-factor ratio of 0.54).
- 4. The isotopic features of the dissociation products depend critically on the photon energy. The dissociation at the range of Kr lamp energy (~ 123 nm) has features expected from direct dissociation. Since this energy range is past the peak of absorption cross section all the heavy isotopes (¹³C, ¹⁷O and ¹⁸O) are enriched in the products. This agrees generally with the prediction based on the idea of Blue Shift effect but the magnitude of the observed enrichment is higher. It seems that changes in Transition Dipole Moment Surface and shape change of wave function have to be considered for proper evaluation of fractionation associated with photodissociation CO₂ at higher energy.

6.3 Future scope

The future scope of the present work are:

- 1. Our study shows that in CO₂ photodissociation there is an unusual isotope effect in the 185 nm region. In particular, the ¹⁷O is unusually enriched in the products. The results provide strong support of the nuclear spin hypothesis first proposed by Bhattacharya et al. [2000] and thereby demonstrate the existence of a new type of anomalous isotope effect associated with gas phase spin-chemistry. This finding has many important implications. For example, the origin of the peculiar oxygen isotope ratios in stratospheric CO₂ is still not clearly understood. The nuclear spin effect may provide an explanation for the observed 1.7 slope in the ¹⁷O – ¹⁸O correlation plot of this CO₂. Further work on isotope exchange of CO₂ with energetic oxygen atoms is needed to address this issue.
- 2. It would be interesting to do the CO₂ photodissociation experiment in presence of intense magnetic field since the nuclear spin should respond to such field. This will then provide another definitive test of the spin hypothesis. In the presence of strong magnetic field, the molecular spin orbit coupling would be enhanced and therefore the nuclear spin effect will be diluted. This would result in diminished enrichment of ¹⁷O in the photoproducts.
- 3. It would also be interesting to do this experiment using other broadband UV light sources with wavelengths lying between the two sources used in here.
- 4. The Tesla discharge experiment yields an anomalous slope of 0.83±0.10 suggesting a combination of mass dependent and mass independent effects. This result needs to be investigated further as it may throw light in differentiating the two types of isotope anomaly associated with photodissociation of CO₂.

A.1 Derivation of the blue shift formula given in **Chapter 3**

The ratio of cross sections of heavy to light isotopologue is written as:

$$\frac{\sigma'(E)}{\sigma(E)} = \frac{\sigma(E + \delta Z P E)}{\sigma(E)}$$

Using Tailor series expansion and neglecting higher order terms one can write as,

$$\frac{\sigma(E) + \frac{d\sigma}{dE}\Delta ZPE}{\sigma(E)} = 1 + \frac{1}{\sigma(E)}\frac{d\sigma(E)}{dE}\Delta ZPE$$
$$\frac{\sigma'(E)}{\sigma(E)} - 1 = F(\lambda) = \frac{1}{\sigma(\lambda)}\frac{d\sigma(\lambda)}{d\lambda}\Delta ZPE$$
(1.2)

where $\sigma(E)$ = Absorption cross section of normal CO₂ at an energy E and λ corresponds to the energy in unit of cm⁻¹.

 $\sigma'(E)$ = Absorption cross section of the isotopologue species of CO₂

Therefore, to calculate fractionation $F(\lambda)$ one should have knowledge about slope of the absorption cross section curve. The absorption cross section curve is taken from Parkinson et al. [2003] and re-plotted taking only the region of our experiment. Zero point energy shift is calculated using the frequency values from Wang et al. [2004] and we have excluded the bending mode since this mode does not contribute in dissociation.

A.2 Note on hyperfine interactions

Nuclei have an angular momentum $\hat{\vec{I}}$, due presumably, to the constituent nucleons and for historical reasons it is called the nuclear spin. The magnetic moment $\hat{\vec{M}}$ of a nucleus is proportional to this angular momentum and is represented by

$$\vec{\vec{M}} = gm\vec{\vec{I}} \tag{1.3}$$

where m is the nuclear magneton and g is the nuclear g factor and the nuclear g factors differ for each nucleus (see Table1).

We anticipate that the nuclear magnetic moment will interact with a magnetic field B via

$$H = -\vec{M}.\vec{B} = -\vec{M}.(\vec{B}_{ext} + \vec{B}_{orbit} + \vec{B}_{spin})$$
(1.4)

where we partition the magnetic field \vec{B} at the nucleus into an external (Zeeman) component \vec{B}_{ext} , a component due to the orbital motion of the electrons \vec{B}_{orbit} and a component due to the field associated with the electrons spin \vec{B}_{spin} . Other nuclei in the molecule also contribute to the magnetic field experienced by the nucleus of interest but we will ignore these fields for the time being.

The Zeeman term is straightforward and contributes $(-\text{gm}\vec{I}.\vec{B}_{ext})$ to the Hamiltonian. Let us consider the contribution due to a single electron as we can easily generalize the result to a many electron system. The field at the nucleus due to the orbital motion of the electron is

$$\vec{B}_{orbital}$$
=-2×10⁻⁷ $\mu_B \frac{\vec{L}}{r^3}$

and contributes

Table 1.1: Nuclear spin properties

Nucleus	Ι	g	Nucleus	Ι	g
H^1	1/2	5.585	H^2	1	0.857
C^{13}	1/2	1.405	Li^7	3/2	2.171
N^{15}	1/2	-0.567	N^{14}	1	0.403
F^{19}	1/2	5.257	O^{17}	5/2	-0.757
Si^{29}	1/2	-1.111	Na^{23}	3/2	1.478
P^{31}	1/2	2.263	S^{33}	3/2	0.429

$$2 \times 10^{-7} \text{mg} \mu_B \frac{\hat{\vec{L}}.\hat{\vec{I}}}{r^3}$$

to the Hamiltonian. The remaining term involving the electron and nuclear spins is most conveniently developed by determining the magnetic field at the electron due to the nucleus

$$-\hat{\vec{M}_e}.\vec{B}_I.$$

Classically the vector potential at a point from a magnetic dipole moment $\vec{\mu}$

$$\vec{A} = \frac{\mu_0}{4\pi} \frac{\vec{\mu} \times \vec{r}}{r^3}$$

which we write as

$$A^N_\alpha = -\frac{\mu_0}{4\pi}\varepsilon_{\alpha\beta\gamma}\mu^N_\beta T_\gamma$$

noting that

 $T_{\gamma} = -\frac{r_{\gamma}}{r^3}$

where the sense of the position vector is from the nucleus to the electron. The magnetic induction at the electron is

$$B^{N}_{\alpha} = \varepsilon_{\alpha\beta\gamma} \nabla_{\beta} A^{N}_{\gamma} = -\frac{\mu_{0}}{4\pi} \varepsilon_{\alpha\beta\gamma} \nabla_{\beta} \varepsilon_{\gamma\lambda\rho} \mu^{N}_{\alpha} T_{\rho}$$

which simplifies to

$$B^{N}_{\alpha} = -\frac{\mu_{0}}{4\pi} (\mu^{N}_{\alpha} T_{\beta\beta} - \mu^{N}_{\beta} T_{\beta\alpha})$$

where we have recognized that $\nabla_{\alpha}T_{\beta} = T_{\alpha\beta}$. Using the identity

$$T_{\beta\beta}$$
=-4 $\pi\delta(\vec{r})$

the term in the Hamiltonian due to the electron-nuclear spin interaction becomes

$$-\hat{\vec{M}}_{e}.\vec{B}_{I} = \frac{\mu_{0}}{4\pi}g_{e}\mu_{B}\mathsf{gm}(4\pi\delta(\vec{r})\hat{\vec{S}}.\hat{\vec{I}} + \hat{S}_{\beta}T_{\beta\alpha}\hat{I}_{\alpha})$$

and is known as Fermi contact and electron spin dipole interaction. Note that we can write this as

$$-\hat{\vec{M}}_{e}.\vec{B}_{I}=-\frac{\mu_{0}}{4\pi}g_{e}\mu_{B}\text{gm}\hat{S}_{\beta}\hat{I}_{\alpha}(4\pi\delta(\vec{r})\delta_{\alpha\beta}+T_{\beta\alpha})$$

If we are dealing with a (effective) one electron system the wave functions will be products of the spatial, electron and nuclear spin wave functions, and we will ultimately need to form

$$\int \Psi_e^2(\vec{r}) (4\pi\delta(\vec{r})\delta_{\alpha\beta} + T_{\beta\alpha}) d^3r$$

and there are two special cases of interest. The first is that the electron density is spherically symmetric and non-zero at the nucleus and the first term in the integral contributes

$$4\pi\delta_{\alpha\beta}\Psi_e^2(0).$$

The second term is zero unless

 $\alpha = \beta$

and each diagonal component will contribute

$$-\frac{4\pi}{3}\Psi_e^2(0)\delta_{\alpha\beta}$$

resulting in

$$-\vec{M}_{e}.\vec{B}_{I} = -(\frac{\mu_{0}}{4\pi})\frac{8\pi}{3}g_{e}\mu_{B}\text{gm}\hat{S}_{\alpha}\hat{I}_{\alpha}\Psi_{e}^{2}(0) = \frac{8\pi}{3}10^{-7}g_{e}\mu_{B}\text{gm}\hat{S}_{\alpha}\hat{I}_{\alpha}\Psi_{e}^{2}(0)$$

This is the usual form of the Fermi contact term and we used $\frac{\mu_0}{4\pi}=10^{-7}$. The second case of interest is when the electron density is zero at the nucleus and only the dipole-dipole term survives. In this instance the term in the Hamiltonian is

$$g_e \mu_B \operatorname{gm} \hat{S}_{\alpha} \hat{I}_{\alpha} T_{\beta \alpha} 10^{-7}$$

A.3 Proposed mechanism of CO₂ dissociation by 185 nm photons

 CO_2 is a linear molecule and the two oxygen atoms are at two ends with the carbon atom at the centre. We have to consider four species of CO_2 molecule. The four species are : ${}^{16}O^{12}C^{16}O$, ${}^{16}O^{12}C^{17}O$, ${}^{16}O^{12}C^{18}O$ and ${}^{16}O^{13}C^{16}O$ (considering only major isotopomers). For convenience we denote them as 626, 627, 628, and 636 where 6, 7, 8, 2 and 3 indicate ${}^{16}O$, ${}^{17}O$, ${}^{18}O$, ${}^{12}C$ and ${}^{13}C$ respectively.

As discussed before, in case of 185 nm photons the dissociation occurs when the molecule is excited to the ${}^{1}B_{2}$ state and then breaks down to one oxygen atom and a CO molecule. So

$$626 \Leftrightarrow [626]^* \Rightarrow [6-26] \Rightarrow 6+26 \tag{1.5}$$

During the second step the ¹⁶O atom flips its spin from S=0 to S=1 state while it is trying to be separated from 26 in the third step. If there is no spin flip this step cannot proceed and the excited [626]* molecule can be de-excited by fluorescence emission and come down back to the ground state.

How does the [626]* state flip its spin? It could be induced by collision or a spin-orbit coupling (involving only electrons). Major part of the flipping occurs this way. Now let us imagine that the dissociation involves one ¹⁷O atom as:

$$726 \Leftrightarrow [726]^* \Rightarrow [7-26] \Rightarrow 7+26 \tag{1.6}$$

Here also the ¹⁷O atom flips its spin by the same process. However, having a nucleus with nuclear spin 5/2 with a g- factor of 0.757 it has a magnetic moment of (0.757*5/2)=1.89 which can add hyperfine interaction to the already existing spin orbit interaction. This may increase the rate of spin flip in the third step when the above reaction takes place. Basically it means that if the ¹⁷O atom has to separate without spin flip it has to have enough energy as necessary for it to be in ¹D state. This happens in case of dissociation by higher energy photons. But with 184.9 nm photon it can do so even in ³P state if the spins rearrange by the interaction and the atom emerges at lower energy.

The 726 species can dissociate in another way:

$$726 \Leftrightarrow [726]^* \Rightarrow [72-6] \Rightarrow 72+6 \tag{1.7}$$

In which case the process has nominally higher rate compared to reaction (1.6) due to its higher (Note ZPE of 2-6 bond is higher than 7-2) zero point energy. If we have higher

ZPE the rate is higher because we need lower energy to break the bond. At the same time the process described by equation (1.7) does not have the advantage of nuclear hyperfine interaction. However, we also have to consider the possibility of exchange:

$$7 + 26 \Leftrightarrow 72 + 6 \tag{1.8}$$

Which would scramble the products from (1.6) and (1.7) with some rate. As a result, we would obtain CO species and O species elevated in ¹⁷O relative to ¹⁶O and ¹⁸O but CO would be further enriched in ¹⁷O and ¹⁸O relative to O in a nearly mass dependent fashion caused by isotope exchange process. This is what observed in our experiments.

In case of ¹³C species the competition would be between the two following processes.

$$626 \Leftrightarrow [626]^* \Rightarrow [6-26] \Rightarrow 6+26 \tag{1.9}$$

$$636 \Leftrightarrow [636]^* \Rightarrow [6-36] \Rightarrow 6+36 \tag{1.10}$$

Our results show enhanced rate for reaction (1.10) relative to (1.9). In this case also part of the contribution may come from the ZPE effect which should favour (1.9). However, the data show a relatively larger rate for (1.10) since ${}^{13}C/{}^{12}C$ ratio increases in the product CO. So the ZPE effect is nullified and the ratio increases in opposite direction. Calculations show the enhancement to be much larger than could be accounted for by ZPE effect. It is possible that during the separation step 3 the nuclear spin of ${}^{13}C$ (spin of 1/2 but a larger g-factor of 1.40 with combined effect of 0.7 relative to 1.89 in case of ${}^{17}O$) facilitates spin flip of ${}^{16}O$ atom by providing an external magnetic moment. This would result in enrichment of ${}^{13}CO$ product as observed. The enrichment ratio of ${}^{17}O$ to ${}^{13}C$ is observed to be about (85.1/36.8)=2.3 which matches the simple magnetic moment ratio. But this coincidence could be fortuitous.

The difficulty in the estimation of enrichment lies in the getting the input parameters of the model calculations since a large number of rate constants are to be assumed or estimated separately with their inherent assumptions. But there is no doubt that the overall enrichment in both ¹⁷O and ¹³C in two products (O₂ and CO) provide strong support for the nuclear spin effect on this particular type of photodissociation at a specific energy range.

A.4 Procedure for calculation of final δ -values from raw mass spectrometric numbers

Oxygen isotope ratios of O_2 are measured relative to machine standard (BOC-oxygen). In terms of δ these ratios are displayed in columns two and three (Table 1.2). Using the absolute isotope ratios of BOC- O_2 whose δ - values are know relative to V-SMOW, sample isotope ratios are expressed in ratio form which are given in columns four and five. These ratios are again expressed relative to tank CSIRO- CO_2 in the δ form given in final two columns.

As an example we illustrate one case where sample $\delta^{18}O=-14.1 \text{ }\%\text{ w.r.t. BOC-O}_2$ (first entry in Table 1.2)

Using ${}^{18}R_s = 2055 \times 10^{-6}$ for BOC-O₂ and δ definition as:

$$\delta = \left(\frac{\mathrm{R}}{\mathrm{R}_{\mathrm{s}}} - 1\right) \times 10^3 \tag{1.11}$$

we get ${}^{18}R = 2026 \times 10^{-6}$. We follow the same procedure for CSIRO-CO₂ whose $\delta^{18}O = 26.7$ w.r.t V-SMOW. For this we get ${}^{18}R = 2058 \times 10^{-6}$. Therefore, the δ -value of the sample w.r.t. CSIRO-CO₂ is -16.1.

Similar procedure is followed for final δ calculation in case of CO.

Table 1.2: Calculation to show derivation of δ -values from raw mass spectrometric data. Second and third column report δ -values relative to laboratory standard tank BOC-O₂ and last two columns give δ - values relative to tank CSIRO- CO₂.

Sample	Oxyge	n (O ₂) measured			Final O ₂		
No	$\delta^{18}O$	$\delta^{17} \mathrm{O}$	^{18}R	^{17}R	$\delta^{18}O$	$\delta^{17}O$	
	‰	%0			‰	‰	
SM-1	-14.1	79.5	0.0020256	0.0004075	-16.1	78.0	
SM-2	-15.3	74.8	0.0020230	0.0004057	-17.4	73.3	
SM-3	-13.3	73.3	0.0020270	0.0004052	-15.4	71.8	
SM-4	-13.5	76.4	0.0020267	0.0004064	-15.5	74.9	
SM-5	-13.6	79.3	0.0020265	0.0004075	-15.7	77.8	
SM-6	-10.1	79.7	0.0020338	0.0004076	-12.1	78.2	
SM-7	-10.2	76.6	0.0020336	0.0004064	-12.2	75.1	
SM-8	-15.6	75.0	0.0020225	0.0004058	-17.6	73.5	
SM-9	-10.6	75.6	0.0020327	0.0004061	-12.7	74.1	
SM-10	-12.0	75.3	0.0020298	0.0004059	-14.1	73.8	
SM-11	-12.9	73.3	0.0020279	0.0004052	-15.0	71.8	
SM-12	-14.1	73.1	0.0020255	0.0004051	-16.1	71.6	
SM-13	-10.7	78.0	0.0020325	0.0004069	-12.8	76.5	

•	$\delta^{13}C$	%00	7.6	6.6	7.4	7.5	7.4	6.9	7.3	8.6	8.5	8.4	7.6	7.4	8.6
inal CC	$\delta^{17}O$	%0	89.7	90.4	94.3	74.1	84.9	82.1	81.4	73.3	76.8	77.8	73.9	76.0	70.6
Щ	$\delta^{18}O$	%00	5.3	1.4	3.4	4.2	3.0	1.8	1.6	0.9	-1.0	-1.3	-1.7	-0.4	2.3
	18 R		0.0020696	0.0020617	0.0020657	0.0020674	0.0020650	0.0020624	0.0020621	0.0020607	0.0020568	0.0020561	0.0020554	0.0020579	0.0020636
	17 R		0.0004120	0.0004122	0.0004137	0.0004661	0.0004101	0.0004091	0.0004088	0.0004057	0.0004071	0.0004075	0.0004060	0.0004068	0.0004047
	^{13}R		0.0111892	0.1117872	0.01118756	0.1118828	0.1118742	0.0111824	0.1118604	0.01119943	0.0111990	0.0111982	0.0111899	0.0111872	0.01120028
data	$\delta^{46} { m CO}_2$		1.0	0.4	0.7	1.2	1.0	1.6	1.6	0.1	-0.1	-0.2	-0.6	-0.7	-0.6
Raw	$\delta^{45} { m CO}_2$	%00	36.2	35.2	36.0	36.1	36.0	35.9	37.1	37.0	37.0	36.9	36.2	35.9	37.1
w data	δ ³⁰ CO	%00	3.5	-0.3	1.7	2.5	1.3	0.1	-0.1	-0.8	-2.7	-3.0	-3.4	-2.2	0.6
CO ra	$\delta^{29}O$		30.2	29.3	30.2	29.6	29.9	29.3	29.6	30.6	30.7	30.6	29.7	29.5	30.5
Sample	No		SM-1	SM-2	SM-3	SM-4	SM-5	SM-6	SM-7	SM-8	SM-9	SM-10	SM-11	SM-12	SM-13

Table 1.3: Calculation to show derivation of δ -values from raw mass spectrometric data. Second and third column report δ -values relative to Vadilal tank CO and last three columns give δ - values relative to tank CSIRO- CO₂.

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List of Publications

I. Research papers or abstracts published/ communicated/in preparation

- Sasadhar Mahata and S. K. Bhattacharya, Nuclear spin induced induced isotope enrichment in CO₂ photodissociation, 12th Indian Society of Mass Spectrometry cum Workshop, 2007, Dona Paula, Goa
- S. K. Bhattacharya and S. Mahata (2006), Nuclear spin induced isotope enrichment in CO₂ photodissociation, International Symposium on Isotopomers, ISI 2006, San Diego, USA
- 3. Mahata S., and S. K. Bhattacharya (2008), Anomolous isotope enrichment of oxygen and carbon due to hyperfine interaction in photodissociation of CO₂ (To be submitted to JCP)
- Mahata S., and S. K. Bhattacharya (2008), A new method for separating CO and O₂ from the mixture for isotopic studies (in preparation)
- 5. Sasadhar Mahata and S. K. Bhattacharya (2008), Anomalous enrichment of ¹⁷O and ¹³C due to hyperfine interaction in photodissciation of CO₂, 4th International Symposium on Isotopomers, ISI 2008, Takyo, Japan