EPILOGUE

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

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

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

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

It is established that the isotopic fractionations during photo-dissociation of ozone in Hartley (peak around 254 nm) and Chappuis band (peak around 600 nm) are distinctly different. The former shows a mass independent character while the latter is strictly a mass dependent process. Further investigations on Hartley band dissociation decipher the fact that pure UV dissociation is a mass independent process, which proceeds with equal enrichment in ^{17}O and ^{18}O in the left-over ozone. An explanation for this dissociation process is presented in the context of Gao-Marcus theory.

An interesting phenomenon is observed during ozone dissociation by its interaction with a surface. The origin of the mass independent character of this process is hypothesized by non-statistical breakdown of short-lived complex O_3^* (formed by adsorption of O_3 in the wall).

During the isotopic exchange between the ozone photolysis product $O(^1D)$ and CO_2, the $\delta^{17}O$ and $\delta^{18}O$ of evolved CO_2 defines a line of slope 1.7 (with initial O_3 and CO_2 compositions identical to atmospheric composition) similar to the one observed for stratospheric CO_2. The slope of the line changes with the change of initial CO_2 composition and establishes the fact that the isotopic transfer favors ^{17}O relative to ^{18}O. It is postulated that a process similar to resonant absorption affects the quenching of $O(^1D)$ such that ^{17}O containing isotopomers of CO_2 is favored during the singlet-triplet transition of the CO_3^* complex during its breakdown to O-atom and CO_2 molecule.

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

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APPENDIX

Physical Data for Ozone as found in literature:
(Determined by microwave spectroscopy)

Table A1. *Physical quantities of ozone molecule.*

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

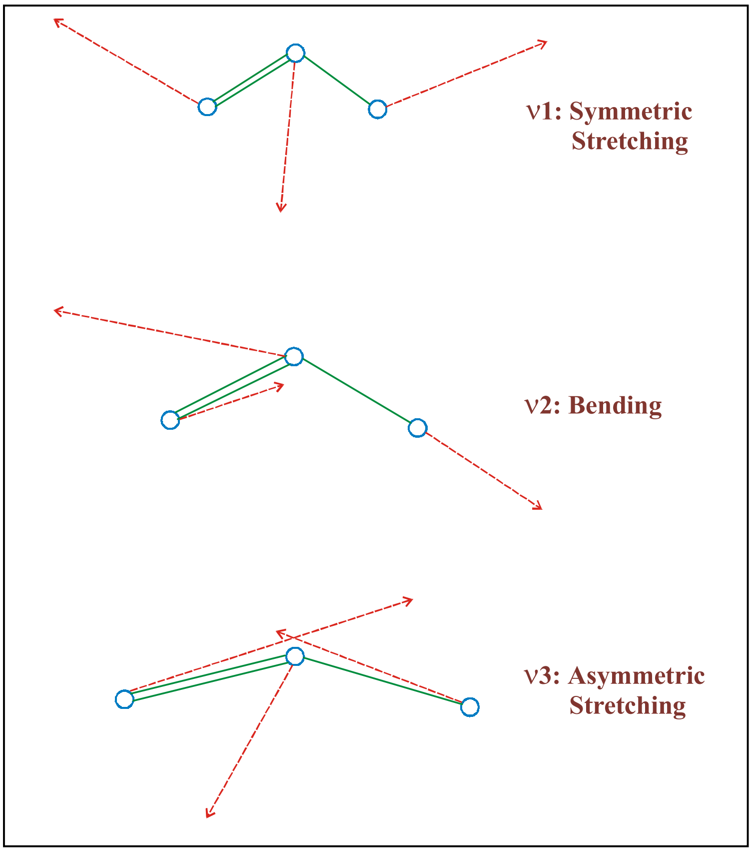

Figure A1. *A schematic representation of three types of vibration in ozone molecule.*

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

Isotopomers	Mass	Calculated (cm^{-1})			Measured (cm^{-1})		
		ν_1	ν_2	ν_3	ν_1	ν_2	ν_3
$^{16}O^{16}O^{16}O$	48	1103.9	701.3	1043.3	1103.1	700.9	1042.1
$^{17}O^{17}O^{17}O$	51	1071.0	608.3	1012.2	1070.9		1012.2
$^{18}O^{18}O^{18}O$	54	1040.8	661.2	983.7	1041.6	661.5	984.8
$^{16}O^{16}O^{17}O$	49	1095.6	692.7	1037.0	1095.7	692.4	1035.7
$^{16}O^{17}O^{16}O$	49	1088.2	697.3	1025.0	1087.8	697.1	1024.4
$^{16}O^{16}O^{18}O$	50	1088.1	685.0	1031.4	1090.4	684.6	1028.1
$^{16}O^{18}O^{16}O$	50	1074.2	693.5	1008.4	1074.3	693.3	1008.4
$^{17}O^{17}O^{16}O$	50	1079.6	688.9	1018.6			
$^{17}O^{16}O^{17}O$	50	1087.2	684.0	1030.7			
$^{17}O^{17}O^{18}O$	52	1063.3	672.5	1006.4			
$^{17}O^{18}O^{17}O$	52	1056.5	676.7	995.4			
$^{18}O^{18}O^{16}O$	52	1057.5	677.7	996.1	1060.7	677.5	993.9
$^{18}O^{16}O^{18}O$	52	1072.3	667.9	1019.4	1072.2	668.1	1019.4
$^{18}O^{18}O^{17}O$	53	1048.7	669.0	989.5			
$^{18}O^{17}O^{18}O$	53	1055.6	664.5	1000.6			
$^{16}O^{17}O^{18}O$	51	1071.9	681.3	1012.9			
$^{16}O^{18}O^{17}O$	51	1065.4	685.2	1001.9			
$^{17}O^{16}O^{18}O$	51	1079.8	676.1	1025.1			

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

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

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

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

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

Now, ZPE = ½ ($\nu_1 + \nu_2 + \nu_3$) (where ν’s are vibrational frequencies of the ozone molecule expressed in cm^{-1} unit). Using the vibrational frequencies from Hathorn and Marcus (2001), the calculated ΔZPE values are,

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

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

The ^{18}O-enrichment in ozone (i.e. the relative difference in absorption rate) can be written as, $(\sigma_{48} - \sigma_{50})/\sigma_{48} \times 1000$ (‰), where σ_{48} and σ_{50} at a given wave number (ν/c) are the absorption cross- sections of $^{48}O_3$ and $^{50}O_3$ respectively. σ_{48} and σ_{50} are related by the equation,

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

For ozone dissociation at 253.7 nm:

Using the ozone absorption cross-section data (DeMore et al., 1997) given below, a function of the form: $\sigma = a\exp\left(-0.5\left\{\frac{(\nu/c)-x_o}{b}\right\}^2\right)$ was fitted.

ν/c (cm^{-1})	σ ($\times 10^{-20}$ cm^2) of $^{48}O_3$
41779.98	797
41279.98	900
40779.94	1000
40279.88	1080
39779.86	1130
39279.86	1150
38779.90	1120
38279.85	1060
37779.78	965
37279.79	834
36779.76	692

The corresponding fit-parameters for $^{48}O_3$ are given below:

Parameters	Values
a	1147.9544
b	2684.8433
x_o	39386.9557

Using these parameters, σ_{48} and σ_{50} at 253.7 nm (≡ 39416.63 cm^{-1}) was calculated and we obtain: $(\Delta\sigma)_a = \sigma_{48} - \sigma_{50} \approx -0.065 \times 10^{-20}$ cm^2

therefore, $(\delta^{18}O)_a = (\Delta\sigma)_a/\sigma_{48} \times 1000 \approx -0.056$ ‰.

Similarly, $(\Delta\sigma)_s = \sigma_{48} - \sigma_{50} \approx -0.067 \times 10^{-20}$ cm^2

and, $(\delta^{18}O)_s = (\Delta\sigma)_s/\sigma_{48} \times 1000 \approx -0.058$ ‰.

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

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

For ozone dissociation at 520:

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

ν/c (cm^{-1})	σ ($\times 10^{-23}$ cm^2) of $^{48}O_3$
19442.39	162.3
19337.50	173.9
19233.73	182.6
19131.07	191.3
19080.33	205.8
19029.50	217.4

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

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

Using these parameters, σ_{48} and σ_{50} at 520 nm ($\equiv$ 19230.77 cm^{-1}) was calculated and we obtain: $(\Delta\sigma)_a = \sigma_{48} - \sigma_{50} \approx -1.90 \times 10^{-23}$ cm^2

therefore, $(\delta^{18}O)_a = (\Delta\sigma)_a / \sigma_{48} \times 1000 \approx -1.90 / 181.9 = -10.45$ ‰.

Similarly, $(\Delta\sigma)_s = \sigma_{48} - \sigma_{50} \approx -3.28 \times 10^{-23}$ cm^2

and, $(\delta^{18}O)_s = (\Delta\sigma)_s / \sigma_{48} \times 1000 \approx -3.28 / 181.9 \times 1000 = -18.05$ ‰.

finally, $(\delta^{18}O)_{total} = 1/3\ (\delta^{18}O)_s + 2/3\ (\delta^{18}O)_a \approx -13.0$ ‰

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

***For ozone dissociation at 630 nm*:**

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

ν/c (cm^{-1})	σ ($\times 10^{-23}$ cm^2) of $^{48}O_3$
16048.53	385.5
15976.99	373.9
15906.09	359.4
15836.07	342
15766.4	330.4
15731.68	315.9

A function of the form:

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

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

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

Using these parameters, σ_{48} and σ_{50} at 630 nm ($\equiv$ 15873.02 cm^{-1}) was calculated and we obtain: $(\Delta\sigma)_a = \sigma_{48} - \sigma_{50} \approx 5.36 \times 10^{-23}$ cm^2

therefore, $(\delta^{18}O)_a = (\Delta\sigma)_a / \sigma_{48} \times 1000 \approx 5.36 / 359.2 = 14.9$ ‰.

Similarly, $(\Delta\sigma)_s = \sigma_{48} - \sigma_{50} \approx 8.33 \times 10^{-23}$ cm^2

and, $(\delta^{18}O)_s = (\Delta\sigma)_s / \sigma_{48} \times 1000 \approx 8.33 / 359.2 \times 1000 = 23.18$ ‰.

finally, $(\delta^{18}O)_{total} = 1/3\ (\delta^{18}O)_s + 2/3\ (\delta^{18}O)_a \approx 17.7$ ‰

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

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