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# Oxygen isotopic anomaly in surface induced ozone dissociation

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#### Abstract

The products of ozone dissociation occurring on glass surface are enriched in heavy oxygen isotopes (<sup>17</sup>O and <sup>18</sup>O) in a mass independent ( $\Delta \delta^{17}O/\Delta \delta^{18}O = 1.0$ ) fashion. Such behavior is in contrast to the case of thermal dissociation where fractionation is mass dependent ( $\Delta \delta^{17}O/\Delta \delta^{18}O = 0.5$ ). Even photo-dissociation by visible light is a mass dependent process. The mass independent fractionation in surface dissociation can probably be explained by assuming that the dissociation takes place via a short-lived complex involving the ozone molecule and an active surface site. The anomalous isotopic fractionation in surface dissociation can be useful to decipher the mechanism of surface reaction in some cases.

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## 1. Introduction

Large mass independent enrichment of heavy oxygen isotopes (<sup>17</sup>O and <sup>18</sup>O) has been observed in stratospheric ozone [1] and also in laboratory ozone formed by photolysis of molecular oxygen [2,3]. During oxygen photolysis, ozone is formed continuously from the oxygen reservoir; as the concentration builds up its dissociation by the incoming photons and other processes becomes important. The final enrichment is, therefore, intimately related to both formation of ozone and its dissociation and in addressing the issue of isotopic enrichment in ozone, it is important to characterize the different dissociation channels. The relevant dissociation pathways of ozone are:

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(i) photo-dissociation, (ii) thermal dissociation, and (iii) dissociation through surface interaction.

Earlier studies dealing with photo-dissociation of ozone by UV and visible light [4,5] showed *slight deviation* from mass dependence in the case of UV dissociation. The UV dissociation of ozone takes place through following reactions,

$$O_3 + hv \rightarrow O(^1D) + O_2(a^1\Delta_g)$$
 (R1)

$$O_3 + hv \rightarrow O(^3P) + O_2(a^3\Sigma_g) \tag{R2}$$

$$O(^{1}D) + O_{3} \rightarrow 2O_{2} \tag{R3}$$

$$O(^{1}D) + O_{3} \rightarrow 2O(^{3}P) + O_{2}$$
(R4)

Among photo-dissociation channels (R1) and (R2), below 310 nm, about 90% dissociation is through (R1), but the relative quantum yield of these two channels changes with wavelength [6]. We have recently established that products of

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reaction (R1) are fractionated in a mass independent fashion with a slope  $(\Delta \delta^{17} O)/\Delta \delta^{18} O)$  value of unity [7]. In contrast, reactions (R3) and (R4) are like any normal chemical reactions and yield mass dependently fractionated lighter oxygen. A combination of these four reactions in UV photolysis of ozone produces the deviation from the mass dependency mentioned above.

Wen and Thiemens [5,8] and Kim and Yang [9] studied thermal dissociation of ozone in gas phase and showed that below 90 °C, thermally dissociated ozone yields isotopically light oxygen fractionated in a mass dependent fashion. Above 90 °C, however, the fractionation pattern flips and the product oxygen becomes heavier in a mass independent fashion. It would be of interest to know if surface dissociation plays a role in this peculiar flip-over since at higher temperature the chemi-sorption of ozone at the chamber surface and its dissociation are expected to be enhanced. In many laboratory experiments surface dissociation of ozone can be important. For example, it was observed that the anomalous isotopic enrichment in the oxygen formed by ozone photo-dissociation is substantially less than that for ozone formation from oxygen [4,5,8], though the source of the anomalous fractionation for both the cases can be traced to the formation of an activated complex involving vibrationally excited ozone molecule. The smaller enrichment in the dissociation process is presumably due to interference by surface effects operating in the low-pressure dissociation experiments. Again, to explain the increase in enrichment with temperature during thermal dissociation it was proposed that increased rate coefficient at higher temperature results in more effective gas phase reaction. This implies a reduced role of surface interaction of ozone molecules and higher net enrichment at higher temperature. The need to test these propositions provided the motivation for our present study.

Another goal is to understand the mechanism of dissociative reactions on surfaces followed by chemical adsorption, which are still modeled by empirical concepts without adequate microscopic picture of the underlying processes [10]. Isotopic fingerprints of the products can sometimes provide valuable insight. For example, Winter [11] showed through isotopic methods that oxygen adsorbed on metal oxide surfaces undergoes exchange with lattice oxygen. Since ozone is highly reactive, its dissociation on glass surface provides an easy set up for such studies.

#### 2. Experimental details

Ozone was produced by UV photolysis of oxygen (99.99% purity) at a pressure of 180 torr in a 5-1 spherical Pyrex chamber with a MgF<sub>2</sub> side window (1 mm thick and 2.5 cm diameter) and a cylindrical cold trap at the bottom. A resonance krypton lamp (116.5 and 123.6 nm) operated inside an Evenson cavity excited by a 120 W, 2450 MHz microwave generator (Opthos Instruments) was used as the UV source. Oxygen was photolysed for 180 min in each case. The product ozone was condensed at the bottom of the trap with  $LN_2$ and the remaining oxygen was pumped away. The ozone was transferred to a small volume ( $\sim 10 \text{ cc}$ ) and subsequently passed through a long spiral where surface dissociation took place. Two spirals of pyrex and quartz (made from 2 m long and 8 mm inner diameter tube) were used. The spiral as well as the manifold was kept opaque by wrapping with aluminum foil. The other end of the spiral was connected to another chamber ( $\sim 10$  cc) kept at LN<sub>2</sub> to collect the residual ozone. Sufficient time was given to condense the residual ozone in the second chamber and the unfrozen fraction (oxygen produced from the breakdown of ozone by surface collision) was collected in a sample bottle with molecular sieve at LN<sub>2</sub> temperature. It was estimated that about 15% of ozone was removed in the first pass. To get different fractions of product oxygen, ozone was passed through the spiral several times and the residual ozone and product oxygen were collected each time. As the number of passes increased, the percentage breakdown of ozone decreased significantly. The residual ozone was finally collected in a sample bottle (volume = 1cc) with molecular sieve at  $LN_2$  temperature. Ozone was converted to oxygen by repeated freezing and heating of the molecular sieve. In two cases, ozone was kept within the spiral for about 8 h and the left-over ozone and product oxygen

was collected as mentioned above. Based on the validity of mass balance we assumed negligible loss of ozone on glass surface or any poisoning due to repeated use.

Oxygen isotopic measurements were done on a triple collector mass spectrometer (model GEO 20-20 of Europa Scientific) with typical error of 0.2% and 0.1% ( $2\sigma$ ) for  $\delta^{17}$ O and  $\delta^{18}$ O, respectively. The amounts of the residual ozone (oxygen equivalent) and the product oxygen were measured by using the major beam (mass 32) calibrated previously.

## 3. Results

The isotopic composition ( $\delta^{17}$ O and  $\delta^{18}$ O) of the left-over ozone and oxygen product along with their amounts are shown in Table 1 for the pyrex and quartz spirals. The initial composition of ozone was calculated in each case by mass balance, knowing the amount and composition of the left-over ozone and product oxygen. The amount of ozone initially produced (sum of the amount of

Table 1

Results for surface dissociation of ozone induced by pyrex and quartz surfaces

left-over ozone measured as oxygen and oxygen
product) by photolysis shows large variation (from
about $23-57$ µmol) due to variation in the output
of the Kr lamp However the $\delta^{18}$ O of the initial
or the Ki lamp. However, the b o of the linthal
$104.4 \pm 2\%$ ) instifution and amount (mean
$\sim 104.4 \pm 2\%$ ) justifying our assumption about
negligible surface loss and the validity of mass
balance, i.e., the number of oxygen molecules
produced being equal to 1.5 times the number of
ozone molecules destroyed. $\Delta \delta^{17}$ O and $\Delta \delta^{18}$ O
(Table 1) denote the enrichment or depletion with
respect to the initial ozone composition. The data
show that dissociation of ozone yields isotopically
light oxygen and correspondingly enriched left-
over ozone. Dissociation increased with number of
passes through the spiral and the left-over ozone
became progressively heavier. The covariation plot
between $\Delta \delta^{17}$ O and $\Delta \delta^{18}$ O shows that when the
fractionation of the ozone reservoir is small
(<~15% with respect to the initial composition),
the slope of the best-fit line is about one. With
increase in fractionation the slope of the line de-
creases and beyond 25%, the points fall on a line

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

The amount of ozone is measured as oxygen after converting  $O_3$  to  $O_2$  (as described in the text). The initial composition of ozone was calculated from the mass balance of the two component (i) left-over ozone and (ii) product oxygen.  $\Delta \delta^{17}O$  and  $\Delta \delta^{18}O$  represent enrichment and depletion for ozone phase and oxygen phase, respectively, with respect to the initial ozone composition.

<sup>a</sup> The errors in measurements of  $\delta^{18}$ O and  $\delta^{17}$ O (estimated from some repeat measurements) are 0.1% and 0.2%, respectively. <sup>b</sup> These two entries reflect the thermal dissociation of the ozone as described in the text.

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Fig. 1. Covariation plot of  $\Delta \delta^{18}$ O and  $\Delta \delta^{17}$ O for surface induced dissociation process. The initial composition of ozone is calculated by mass balance of the two fractions (left-over ozone and product oxygen). The upper right quadrant represents the left-over ozone component (filled symbols) and the lower left quadrant the product oxygen (unfilled symbols). For small amount of fractionation, the slope is around unity. As the fractionation increases, the slope decreases. The two points (encircled squares) represent case of thermal dissociation as described in the text. The errors of the individual data points are comparable to the size of the symbols.

with slope value of about 0.75. The isotopic behavior does not change significantly with the change of the spiral material from pyrex to quartz. When ozone was kept within the spiral for long time ( $\sim$ 8 h) and allowed to dissociate at room temperature the left-over ozone as well as the product oxygen compositions fall on a line with a slope of 0.5 (Fig. 1).

In order to determine the fractionation factor  $\alpha$ , we assume a Rayleigh model for evolution of the isotope ratio, i.e.,  $R = R_0 f^{(\alpha-1)}$ , where R and  $R_0$  denote final and initial <sup>18</sup>O/<sup>16</sup>O ratio of O<sub>3</sub>, respectively, and *f* is the fraction of O<sub>3</sub> left. Writing in  $\delta$  notation and taking the natural logarithm:

$$\Delta = \ln(1 + 0.001 * \delta) - \ln(1 + 0.001 * \delta_0)$$
  
= (\alpha - 1) \ln(f),

where  $\delta_0$  and  $\delta$  are the  $\delta^{18}$ O of initial and final ozone, respectively. Fig. 2 shows the correlation diagram between  $\Delta$  and  $\ln(f)$ . The best fit of all the data points gives the instantaneous fractionation factor for the left-over ozone as  $\alpha_{\text{left-over ozone}} =$ 

 $1.0170 \pm 0.0012$  indicating that the product oxygen is depleted by about 17% relative to the initial ozone composition.

## 4. Discussion

The dissociation of ozone yields isotopically light oxygen similar to that of the product of photo-dissociated ozone and thermally (<90 °C) dissociated ozone [5,8,9] but does not follow the conventional mass fractionation pattern (slope value of half). Instead, it gives rise to a slope value of unity in the covariation plot of  $\Delta \delta^{17}$ O and  $\Delta \delta^{18}$ O (Fig. 1) surprisingly similar to the slope observed in case of formation of ozone (see initial ozone composition in Table 1).

Why the surface dissociation of ozone produces oxygen with mass independent fractionation is a puzzling question but one can invoke a scenario using the concepts of recently proposed Gao– Marcus theory [12], which explains the mass



Fig. 2. Plot for calculating the fractionation factor for the surface dissociation process using a Rayleigh model. *X*-axis represents the fraction left in the O<sub>3</sub> pool. Data plotted in the *Y*-axis are normalized to the initial composition of ozone. As the fraction in the O<sub>3</sub> pool decreases, the delta value increases accordingly giving a fractionation factor ( $\alpha_{\text{left-over ozone}}$ ) of 1.0170 ± 0.0012. The error of each data point is comparable to the size of the symbol.

independence in case of ozone formation. Gao-Marcus theory proposes that during ozone formation by  $O + O_2$  recombination reaction a short-lived  $O_3^*$  complex is formed. Subsequent redistribution of the total energy among the rotational-vibrational modes of this excited transient molecule proceeds at some finite rate and may be incomplete during the typical life-time of this complex (non-RRKM effect). This non-statistical effect reduces the effective density of the available quantum states and consequently the unimolecular dissociation rate of the complex increases, thereby decreasing the probability of formation of a stable ozone molecule. The reduction of the density of states is more for the symmetric molecule (which has more share of lighter isotopes) than for the asymmetric molecules (since there are fewer dynamical coupling terms in the symmetric molecule). It was shown that this small non-statistical effect amplifies as a large mass independent isotope effect in stabilized ozone molecules.

For surface dissociation of ozone, the first step involves chemi-sorption of ozone molecule on the surface as happens in case of oxygen, which is slightly less reactive. We postulate that the ozone molecule forms an activated complex (Fig. 3) with a reactive atom residing on the surface [13]. This activated complex is a transient species and may



Fig. 3. Formation of an activated complex  $(O_3W)^*$  by adsorption of ozone molecule on a surface ( $\Delta E$  represents the energy of activation). The energy redistribution among all its rotational-vibrational states may be incomplete during its typical lifetime resulting in a mass independent isotopic effect in the products.

dissociate after its typical lifetime in the following way,

$$O_3 + Surface (W) \rightarrow (O_3W)^*$$
  
 $\rightarrow O(^3P) + O_2(X^1\Sigma_g^+) + W^*$ 
(R6)

The ozone complex being confined to the surface has less degrees of freedom and can only have restricted rotational and vibrational motions. This reduces the density of states and makes the activated complex short-lived. We can then consider a non-statistical Gao–Marcus model [12], which favors the asymmetric molecules for its intra-molecular energy redistribution. This reduces the dissociation rate constant of the asymmetric molecules and results in mass independent isotopic enrichment in the left-over ozone. The product oxygen is correspondingly equally depleted in <sup>17</sup>O and <sup>18</sup>O. This explanation is at present speculative and needs to be tested experimentally and theoretically.

To achieve larger fractionation, the ozone had to go through the spiral many times. For example, to get around 25% enriched ozone, the required time was nearly 6 h and some amount of thermal dissociation in this time cannot be avoided. Therefore, the higher amount of fractionation (>25%) arises due to a combination of two processes, i.e., surface interaction and gas phase dissociation. The room temperature thermal dissociation yields a mass dependent slope ( $\sim 0.5$ ) in contrast to the surface dissociation (slope  $\sim 1.0$ ) and the admixture of these two components produces a resultant slope with value less than one. This explanation is supported by the thermal dissociation data (circles in Fig. 1, representing the situation when the ozone was kept within the spiral for about 8 h at room temperature). They define a slope of around a half, which is expected in case of thermal decomposition at room temperature [8].

Recently Bhattacharya et al. [14] studied the pressure dependency of isotopic enrichment in ozone (produced from oxygen photolysis at different oxygen pressures ranging from 8 to 700 torr). They explained the observed enrichment pattern for pressure upto 15 torr by considering simultaneous formation and dissociation in gas phase. However, the enrichment pattern observed below 15 torr (equal enrichment in <sup>17</sup>O and <sup>18</sup>O with lower magnitude compared to that observed at 15 torr) did not fit with the proposed hypothesis. In that pressure range, the ozone production was less than 0.05  $\mu$ mol/min [14] and ozone decomposition by interaction with the surface was assumed to be significant. The results obtained in the present experiment provide support for this assumption.

## 5. Conclusion

The isotopic behavior of ozone during dissociation on glass surface is anomalous and displays a mass independent character. The product oxygen is isotopically lighter similar to the case of visible light photo-dissociation or thermal (<90 °C) decomposition but the depletion in <sup>17</sup>O and <sup>18</sup>O are equal resulting in a slope of unity in  $\delta^{17}O-\delta^{18}O$ plot. As the experimental time increases, the effect disappears due to the dominating effect of room temperature thermal dissociation of ozone.

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