

Extraordinary isotopic fractionation in ozone photolysis

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[1] Analysis of experimental ozone absorption spectra reveals that ultraviolet photolysis within the structured Huggins band yields extraordinary wavelength-dependent isotopic fractionation, oscillating between complete enrichment and complete depletion for changes of less than 2 nm in the excitation wavelength. Visible photolysis yields wavelength-dependent fractionation that varies from -300% to $+300\%$. Photochemical modeling demonstrates photolysis contributes fractionation up to $+45\%$ to the heavy ozone anomaly in the middle stratosphere with measurable ^{17}O and ^{18}O isotopologue-dependent variations as a function of altitude despite the fact that the extraordinary photolysis-induced isotopic fractionation effect is dampened in the atmosphere due to the integration over all excitation wavelengths. **Citation:** Miller, C. E., R. M. Onorato, M.-C. Liang, and Y. L. Yung (2005), Extraordinary isotopic fractionation in ozone photolysis, *Geophys. Res. Lett.*, *32*, L14814, doi:10.1029/2005GL023160.

1. Introduction

[2] The unusual enrichment of heavy ozone isotopologues in the stratosphere, the heavy ozone anomaly (HOA), poses an intriguing problem [Irion *et al.*, 1996; Johnson *et al.*, 2000; Mauersberger *et al.*, 2003; Meier and Notholt, 1996] and has caused considerable debate [Anderson and Kaye, 1987; Cicerone and McCrumb, 1980; Gao and Marcus, 2001; Gellene, 1996; Heidenreich and Thiemens, 1983; Houston *et al.*, 1996; Kaye, 1986; Kaye and Strobel, 1983; Thiemens, 1999] since it is intrinsically linked to the fundamental photochemical processes of the Chapman mechanism [Chapman, 1930]



Cicerone and McCrumb [1980] hypothesized that the preferential photodissociation of $^{16}\text{O}^{18}\text{O}$ in (R1) could lead to the observed enrichment of heavy ozone in the strato-

sphere. Kaye and Stroebel [1983] demonstrated that the isotopic exchange of O atoms with O_2 was sufficiently fast under atmospheric conditions to negate this mechanism. Subsequent efforts to explain the heavy ozone anomaly have emphasized fractionation mechanisms based on the ozone formation reaction (R2) [Mauersberger *et al.*, 2003]. Ozone destruction has not been considered as the source of the observed fractionation; however, stratospheric ozone concentrations are in photochemical steady-state during daylight hours due to the rapid (R2)–(R3) cycle, suggesting that any isotopic dependence in ozone photolysis rates, (R3), will impart its signature on the heavy ozone anomaly with a weighting comparable to the signature imparted by ozone formation, (R2).

[3] Yung and Miller [1997] introduced the photo-induced isotopic fractionation effect (PHIFE) to explain the unusual $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\delta^{15}\text{N}$ enrichment of stratospheric N_2O . The theory successfully reproduced the sign and magnitude of each of the observed atmospheric fractionations as well as predicting the preferential enrichment of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ over $^{15}\text{N}^{14}\text{N}^{16}\text{O}$. That work demonstrated that the small wavelength dependent changes in the UV absorption cross sections caused by isotopic substitution lead to measurable effects in the fractionation of different isotopologues in atmospheric systems for which photodissociation is a principal loss mechanism. Photodissociation also plays a central role in determining the concentration of stratospheric ozone and, not coincidentally, stratospheric ozone exhibits unusual enrichment of its heavy isotopologues. These facts, combined with the interesting dynamics of ozone photochemistry, suggested that PHIFE might help explain the heavy ozone anomaly.

[4] Our analysis of experimental ozone absorption spectra reveals that photolysis at all wavelengths, especially within the structured Huggins band, yields extraordinary wavelength-dependent isotopic fractionation. In this paper experimental absorption cross sections are used to assess the wavelength dependent PHIFE for $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ (888). Absorption cross sections and wavelength dependent PHIFE for the singly substituted isotopologues $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ (668), $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ (686), $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ (667), and $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ (676) are approximated using the semianalytic Born-Oppenheimer approximation method of Liang *et al.* [2004]. The total photodissociation rates are calculated and used to calculate altitude-dependent fractionation.

2. Methods

[5] The physics underlying PHIFE have been described in detail previously [Liang *et al.*, 2004; Miller and Yung, 2000; Yung and Miller, 1997]. The fundamental concept is that isotopic substitution causes observable changes in the absorption cross section, the dissociation rate, and/or quantum yields of the substituted isotopologue, thereby inducing

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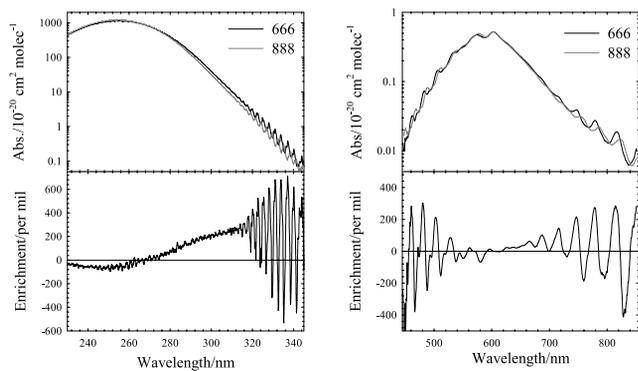


Figure 1. (top) Experimental $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ absorption spectra and (bottom) wavelength dependent $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ photo-induced isotopic fractionation functions. Extraordinary fractionation is observed in regions of the absorption spectra exhibiting resolved vibronic structure. Experimental spectra from *Parisse et al.* [1996] and *Anderson and Mauersberger* [1995].

isotopic fractionation. Assuming that photolysis represents an irretrievable loss mechanism, the fractionation δ , given in units of per mil (‰), may be expressed as

$$\delta = \delta_0 + \varepsilon \text{Ln}(f) \quad (1)$$

where f is the fraction of the sample remaining after the loss mechanism has been applied and δ_0 is the initial fractionation. Since $0 \leq f \leq 1$ which leads to $\text{Ln}(f) < 0$ for all cases, it is convenient to define the wavelength dependent enrichment factor $-\varepsilon(\lambda)$ as

$$-\varepsilon(\lambda) = -\left(\frac{\sigma'(\lambda)}{\sigma(\lambda)} - 1\right) \quad (2)$$

where $\sigma(\lambda)$ and $\sigma'(\lambda)$ are the absorption cross sections of the parent and substituted isotopologues, respectively. Values of $-\varepsilon(\lambda) > 0$ indicate enrichment of the substituted isotopologue while values of $-\varepsilon(\lambda) < 0$ indicate depletion. The total photo-induced enrichment factor may be expressed as

$$-\varepsilon = -\left(\frac{J'}{J} - 1\right) = -\left(\frac{\int I(\lambda)\sigma'(\lambda)d\lambda}{\int I(\lambda)\sigma(\lambda)d\lambda} - 1\right) \quad (3)$$

where J and J' are the total photodissociation rates of the parent and substituted isotopologues, respectively, and $I(\lambda)$ is the wavelength dependent solar flux.

[6] The 888 PHIFE is evaluated from the experimental absorption cross sections of 666 and 888 reported by *Parisse et al.* [1996] and *Anderson and Mauersberger* [1995]. Figure 1 shows the absorption cross sections and wavelength dependent enrichment function, $-\varepsilon(\lambda)$, for 888. The enrichment function shows two distinct fractionation regimes in the UV, correlating with the well-known Hartley and Huggins bands of the ozone UV absorption spectrum.

3. Results and Analysis

[7] The strong continuum absorption of the Hartley band (230–310 nm) produces an enrichment function that varies

smoothly with wavelength. This results from the blue shift of the 888 absorption spectrum relative to the 666 spectrum, as seen in Figure 1. The 888 spectrum also exhibits a somewhat larger maximum and a narrower overall contour than the 666 spectrum. These features lead to an enrichment function that predicts depletion of 888 for photodissociation with $\lambda < 270$ nm with a maximum depletion of $\sim 80\%$ predicted at 250 nm. The 888 enrichment function increases uniformly for $\lambda > 270$ nm, reaching a maximum predicted enrichment of 250‰ at 310 nm.

[8] In contrast, the vibronic structure of the Huggins band (310–350 nm) produces an enrichment function that oscillates dramatically as a function of wavelength. Isotopic substitution shifts the vibronic bands of the 888 spectrum such that the maxima occur close to the minima separating vibronic bands of the 666 spectrum. The resulting fractionation function rapidly oscillates between extreme enrichment and extreme depletion. For example, the 888 fractionation swings from -530% at 335.3 nm to $+710\%$ at 337.1 nm. Our calculations predict similar behavior for the singly substituted isotopologues 667, 676, 668 and 686, but with even smaller wavelength differences between extrema.

[9] Ozone absorption in the visible region (450–850 nm) is dominated by the Chappuis band, shown in the right hand panel of Figure 1. This band is characterized by a continuum with weak vibronic structure superimposed on it at shorter wavelengths. Vibronic structure due to the Wulf bands is observed at longer wavelengths. The function $-\varepsilon(\lambda)$ exhibits both enrichments and depletions, consistent with the vibronic structure, but the fractionation varies only from -300% to $+300\%$ and the wavelength dependence is much weaker than in the Huggins band, consistent with the diffuse nature of the vibronic structure and the dominance of the continuum absorption. For example, the enrichment function decreases from $+100\%$ at 528.8 nm to -67% at 537.5 nm. There is essentially no fractionation near the Chappuis band absorption maximum.

[10] The Huggins band absorption spectra and wavelength dependent PHIFE also exhibit a significant temperature dependence, as shown by the 295 K and 228 K plots in Figure 2. The absorption maxima sharpen and the minima

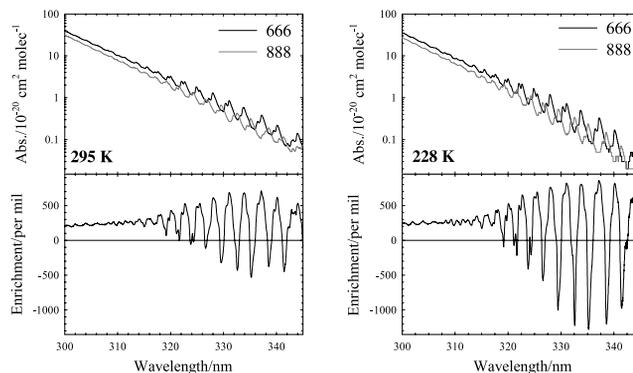


Figure 2. Same as Figure 1 for 295 K and 228 K conditions. At low temperatures the reduced hot band absorption between vibronic features in the Huggins band accentuates the extraordinary photo-induced isotopic fractionation. Experimental spectra from *Parisse et al.* [1996].

deepen at the lower temperature due to reduced contributions from thermally excited hot band absorptions. The resulting fractionation functions exhibit both enrichments and depletions that exceed 1000‰. These values should not be interpreted quantitatively since they result from conditions outside the approximation of equation (1). Nonetheless, the analysis suggests that at stratospheric temperatures specific wavelengths exist for which photolysis leads to total enrichment or total depletion of the 888 isotopologue. PHIFE calculations indicate that this is a general result for all ozone isotopologues with the main difference being the wavelengths at which the enrichments and depletions occur.

[11] Photo-induced isotopic fractionations of 668, 686, 667, and 676 were evaluated using the semianalytic Born-Oppenheimer approximation method of *Liang et al.* [2004] and experimental absorption cross sections [*Anderson and Mauersberger, 1995; Parisse et al., 1996*] and Δ ZPE values [*Flaud and Bacis, 1998*]. The enrichment functions for the singly substituted isotopologues are qualitatively similar to the 888 enrichment function, exhibiting smoothly varying and highly oscillatory regions depending on whether the associated absorption is predominantly continuum or vibronic structure.

[12] The relative magnitudes of the enrichment functions for the singly substituted isotopologues follow a distinct pattern. The enrichments of the ¹⁸O isotopologues 686 and 668 are nearly a factor of 2 greater than the enrichments of the corresponding ¹⁷O isotopologues 676 and 667, clearly a mass dependent effect. The enrichments of the symmetric (*C_{2v}*) isotopologue 686 are predicted to be a factor of 2 larger than the enrichments of the asymmetrically substituted (*C_s*) isotopologues 668. The same relationship holds true for the 676 and 667 isotopologues. The predicted increase in the enrichment function is not a direct result of higher molecular symmetry, but rather a mechanical consequence of increased atomic mass at the central site and associated reductions in the vibrational frequencies and zero point energy. Interestingly, Gao and Marcus noted that the mechanical effect of changing the zero point energy was the primary factor governing large mass-dependent isotope effects in their RRKM treatment of ozone formation rates [*Gao and Marcus, 2001*].

[13] Atmospheric PHIFE for the singly substituted isotopologues have been predicted by integrating equation (3) within the one-dimensional Caltech/JPL KINETICS photochemical model [*Gladstone et al., 1996*], assuming isotope-dependent formation and photolysis rates and unit quantum yield for photolysis over the entire wavelength range (M. C. Liang et al., Isotopic composition of stratospheric ozone, submitted to *Journal of Geophysical Research*, 2005, hereinafter referred to as Liang et al., submitted manuscript, 2005). The results are presented in Figure 3. Not only do vestiges of the extraordinary photolysis-induced isotopic fractionations persist under atmospheric conditions, but PHIFE is predicted to contribute up to +45‰ to the heavy ozone anomaly. Additionally, ozone PHIFE exhibit clearly defined altitude and isotopologue dependencies. The total PHIFE for each isotopologue increases by a factor of 3 as the altitude decreases from 50 km to 35 km. This reflects the increasing importance of longer UV wavelength photolysis at lower altitudes and the concomitant increase in $-\epsilon$ at longer wavelengths. The fractionation decreases below

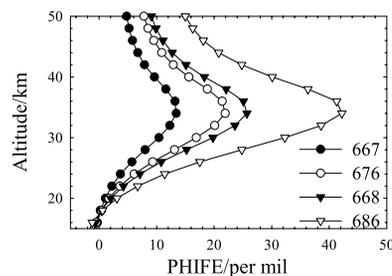


Figure 3. Altitude dependent PHIFE calculated for ¹⁶O¹⁶O¹⁷O (667), ¹⁶O¹⁷O¹⁶O (676), ¹⁶O¹⁶O¹⁸O (668), and ¹⁶O¹⁸O¹⁶O (686).

35 km for all isotopologues as Chappuis band photolysis becomes increasingly important. In fact, photolysis via the Chappuis band dilutes the extraordinary UV PHIFE signature at all altitudes. Below 20 km and into the troposphere, there is little enrichment, perhaps even slight depletion, of the heavier isotopologues.

[14] The isotopologue dependent PHIFE results follow the general trends from *in situ* and remote sensing data [*Irion et al., 1996; Johnson et al., 2000; Mauersberger et al., 2003; Meier and Notholt, 1996*]. PHIFE predicts 12–45‰ enrichments in ⁴⁹O₃ and ⁵⁰O₃ in the 30–40 km altitude range with ⁵⁰O₃ enrichment about two times larger than the ⁴⁹O₃ enrichment. The photolysis-induced enrichment profiles are consistent with remote sensing data, and account up to 50% of the total observed enrichment [*Irion et al., 1996; Johnson et al., 2000; Mauersberger et al., 2003; Meier and Notholt, 1996*]. We note that the PHIFE model predicts larger enrichments in the symmetric 686 and 676 isotopologues while the atmospheric measurements show preferential enrichment of the asymmetric 668 and 667 isotopologues [*Irion et al., 1996; Johnson et al., 2000; Meier and Notholt, 1996*]. This suggests that a quantitative analysis of the relative contributions of formation, (R2), and photolysis, (R3), to the heavy ozone anomaly must be performed within a modeling framework that accurately accounts for isotopic dependence in both processes. A comprehensive analysis of the temperature, pressure, and isotope effects in the photochemical modeling will be presented elsewhere (Liang et al., submitted manuscript, 2005).

[15] Recently, *Chakraborty and Bhattacharya* [2003] presented experimental results for the effect of UV and visible photolysis on ozone fractionation. They found that photodissociation of ozone produces isotopically light oxygen, enriching the heavy isotopologues in the leftover ozone pool. The heavy ozone enrichments determined by *Chakraborty and Bhattacharya* [2003] are similar in magnitude to the enrichments presented in Figure 3 rather than the extraordinary fractionations depicted in Figures 1 and 2. This could be due to the fact that the excitation wavelengths used (184.5 + 253.6 nm, 520 ± 2 nm, or 630 ± 4 nm) did not photolyze ozone at wavelengths with maximum sensitivity to PHIFE or that the experiments were carried out in a static cell, allowing for secondary photochemistry and wall reactions, rather than under collisionless conditions. Our analysis suggests that both UV and visible PHIFE would be better tested with the selection of more appropriate excita-

tion wavelengths. The convenient UV laser wavelengths 248.5, 266, and 308 nm are predicted to produce $\delta(888) = -75, 0$ and $+250\%$, respectively. The results for singly substituted isotopologues will be of similar magnitude and sign. Excitation via the visible laser wavelengths 514.8 and 532 nm are predicted to produce $\delta(888) = -55$ and $+50\%$, respectively. Examples of the extraordinary fractionations possible with small changes in the excitation wavelength in the Huggins band were given above. We note that the magnitude and variation of wavelength specific PHIFE are comparable to or larger than the fractionations observed in the isotope-dependent variants of the O + O₂ recombination reaction [Gao and Marcus, 2001; Gellene, 1996; Mauersberger et al., 1999; Mauersberger et al., 2003].

[16] In summary, our analysis of experimental ¹⁶O¹⁶O¹⁶O and ¹⁸O¹⁸O¹⁸O absorption spectra has shown that UV photolysis will lead to extraordinary wavelength- and temperature-dependent isotopic fractionation in the remaining ozone. This assessment employs the same photolysis-induced isotopic fractionation concept that correctly accounted for the isotopologue-dependent fractionation of stratospheric N₂O [Liang et al., 2004], although the ozone fractionation functions exhibit significantly larger magnitude and variation due to the presence of well-defined vibronic structure. We predict that the photolysis-induced isotopic fractionation for singly substituted isotopologues is a function of the mass and chemical position of the substituted oxygen atom(s), and that substitution at the central oxygen atom site produces twice the enrichment as substitution at one of the terminal oxygen atom positions. Photochemical modeling indicates that Chappuis band photolysis dilutes extraordinary fractionation in the atmosphere, but that altitude- and isotopologue-dependent photolysis-induced enrichments persist. These effects are large and should be measurable in the atmosphere and the laboratory. We continue to investigate the mechanism by which ozone isotopologue-dependent photolysis contributes to the heavy ozone anomaly and how ozone photochemistry transfers heavy oxygen enrichment to other atmospheric trace gases [Thiemens, 1999].

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