

Chapter 7

Photochemical Fractionation of N₂O: A Comparison of Theory and Laboratory Measurements

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Abstract

Using the three-isotope plot formalism given in Prakash and Marcus,¹ and in Chen and Marcus² we compare the theory with the laboratory measurements. There is good agreement between the experimental and theoretical results for the fractionation for the limited data. Plots are also given for the wavelength dependence of the ratio of the fractionations and are similarly compared with the available data. The contribution of photodissociation to the observed isotopic anomaly and the motivation for further wavelength dependent fractionation studies are discussed.

I. Introduction

Photodissociation of N_2O and the isotopic fractionation introduced by it are of considerable atmospheric interest.³ Recently we published theoretical calculations of the absorption cross section of N_2O .^{4,5} Detailed wavelength-dependent absorption cross sections of isotopologue 446 (abbreviated form for $^{14}\text{N}^{14}\text{N}^{16}\text{O}$) and wavelength-dependent fractionation factors for the isotopologues 447, 448, 456, 546, 556 all relative to 446 were published in Prakash et al.⁴ and in Chen et al.⁵ In a separate article¹ a three-isotope plot for isotopologues 446, 447, 448 was given using these calculated fractionation values. In another article² a three-isotope plot for various isotopologues, including 456, 546 and 556, was given using these calculated fractionation values. In these articles a perturbation theoretical method using reduced masses to estimate the slope for a nearly direct photodissociation process was also given, and it served to explain why the slope from the numerically calculated photochemical result agreed with the standard thermal result. In the present note we give a graphical comparison between available laboratory measurements, presently very sparse, of fractionation and of three-isotope plots with plots based on fundamental physics-based theory, with an aim of stimulating further experiments.

II. Results

In Chen et al.⁵ the time-independent multidimensional reflection principle was used to obtain the absorption cross section σ of N_2O as a function of wavelength λ . Using $\sigma(\lambda)$, the wavelength-dependent fractionation factors such as $\epsilon_{447}(\lambda)$ were

calculated from $\varepsilon_{447}(\lambda) = \sigma_{447}(\lambda) / \sigma_{446}(\lambda) - 1$. When a broadband light source is used for excitation, the wavelength-dependent light source intensity was used as the weighting factor to obtain the averaged value of the fractionation factor.⁵

In Prakash and Marcus¹ a three-isotope plot for the isotopologues 446, 447, 448 was given using the fractionation values computed in Prakash et al.⁴ In Prakash and Marcus¹ the data from the laboratory measurements of Röckmann et al.⁶ were not used for a reason given in footnote #30; namely that the error bar in the measurements of 447 and 448 could add up to increase the uncertainty in the measurement of the ratio $\varepsilon_{447} / \varepsilon_{448}$. However, the errors in the measurement of ε_{447} and ε_{448} are usually correlated, (we thank Jan Kaiser for this point) thereby reducing the error bar on the ratio $\varepsilon_{447} / \varepsilon_{448}$. In this paper we compare the laboratory measurements of Röckmann et al.⁶ with the theoretical results given in Prakash and Marcus¹ and Chen and Marcus.²

Describing the fractionation measurement made in the closed system by a Rayleigh fractionation process the relation between the fractionation ε_{447} and isotopic enrichment δ^{17} is given by:⁷

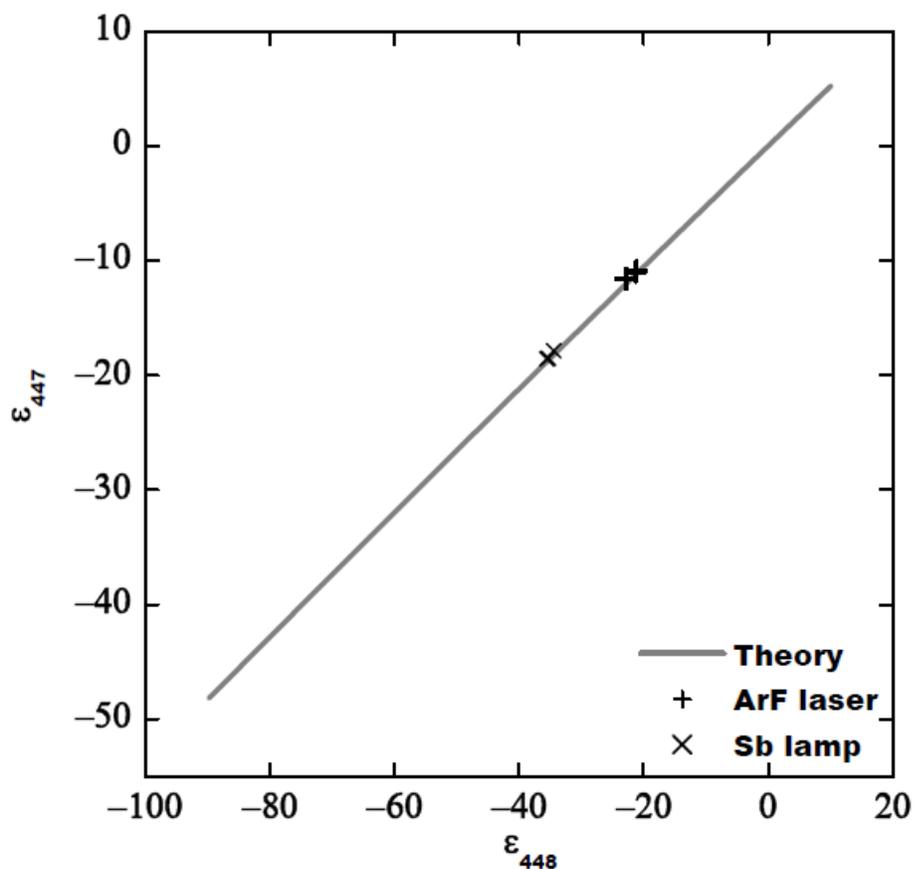
$$\varepsilon_{447} \ln y = \ln(1 + \delta^{17}) \quad (1)$$

where y is the fraction of 446 remaining. Using the values given in Table 1 of Röckmann et al.⁶ (see also Table 18 of reference 8) the fractionation factors are computed and tabulated in table 1. These values are plotted in figure 1 along with the fractionation factors calculated at 298 K in Chen et al.⁵ It can be seen that the calculations are in good agreement with the measurements.

Table 1: Experimental fractionation factors from reference 6.

Light Source	λ (nm)	Conversion (y) (%)	δ^{17a}	δ^{18a}	ϵ_{447}^a	ϵ_{448}^a
ArF laser	193.3	71.3%	3.7	7.2	-11.03	-21.21
ArF laser	193.3	51.6%	7.7	15.2	-11.56	-22.80
Sb lamp	185-225	57.6%	10.3	19.8	-18.57	-35.54
Sb lamp	185-225	59.2%	9.4	18.2	-17.83	-34.40
Sb lamp	185-225	29.1%	22.9	44.5	-18.33	-35.27

^a Unit is per mil.

Figure 1: Three isotope plot of oxygen isotopologues of N_2O in units of per mil.

In figure 1 the details of the wavelength dependence of the fractionations are not given but they are shown in figure 2. figure 2 is based on the following calculations of the individual values of fractionation factor for the wavelengths used in measurement. Corresponding to the ArF laser wavelength of 193.3 nm,⁶ the fractionation factors $(\varepsilon_{447}, \varepsilon_{448})$ obtained by calculation seen are $(-8.85, -16.78)$. They may be compared with the two sets of measured values $(-11.03, -21.21)$ and $(-11.56, -22.80)$.⁶ For the Sb source, the averaged values of the fractionation factors were calculated as described in Chen et al.⁵ The calculated values of $(\varepsilon_{447}, \varepsilon_{448})$ are $(-17.85, -33.84)$, and the measured values for three sets of measurements are $(-18.57, -35.54)$, $(-17.83, -34.40)$, and $(-18.33, -35.27)$.

A second way of showing the wavelength dependence of the fractionation is by plotting the ratios $\varepsilon_{447}(\lambda)/\varepsilon_{448}(\lambda)$ and $\ln(1+\varepsilon_{447}(\lambda))/\ln(1+\varepsilon_{448}(\lambda))$ as a function of λ , as in figure 1 of Kaiser et al.⁷ These plots comparing the experimental data from Röckmann et al.⁶ to the detailed computations of Johnson et al.⁹ and Chen et al.⁵ are shown in the present figure 2. The ratios of fractionations predicted by the two theoretical models^{5,9} are nearly similar, as seen in figure 2. It should be noted that while the comparison of the fractionations of ε_{447} and ε_{448} by taking the ratio highlights the wavelength dependence, it can lead to problems with interpretation if a ratio close to the absorption maximum (182 nm) is taken, since ε_{448} approaches zero there and is the reason for very high values of the ratio in that region. The plot of ε_{447} vs. ε_{448} has a small but finite intercept^{1,2} meaning that the zeros of ε_{447} and ε_{448} are slightly offset and so the

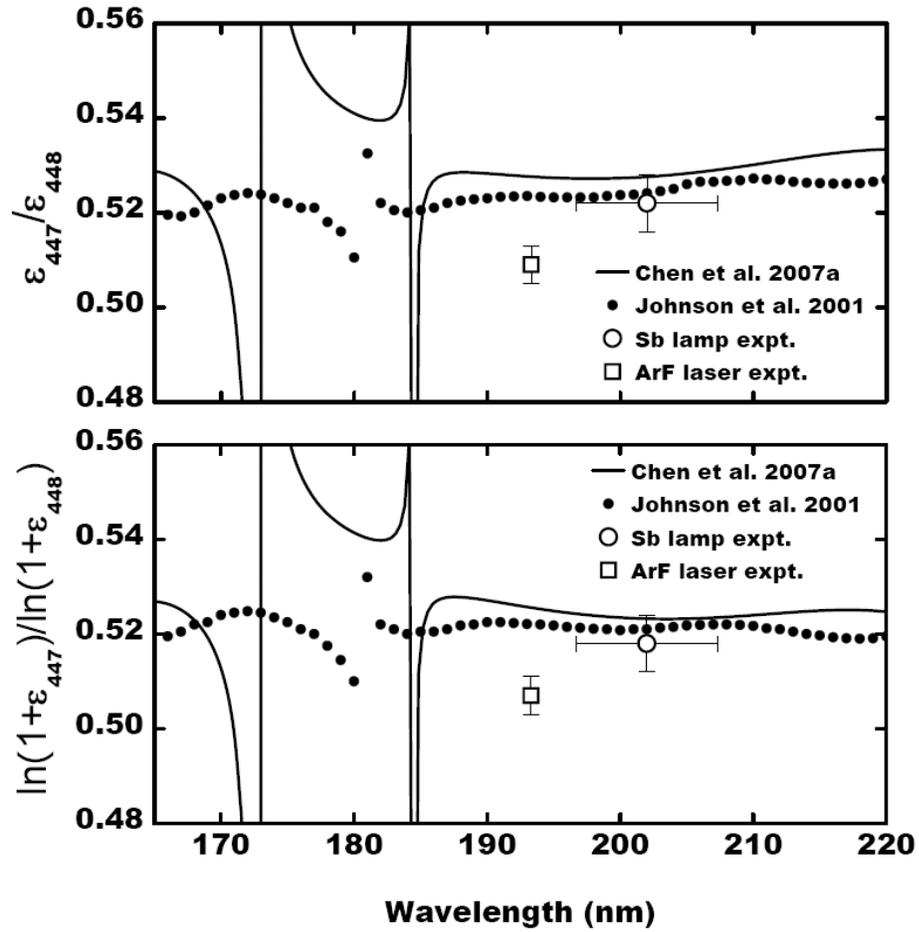


Figure 2: Wavelength dependence of isotopic fractionation ϵ_{447} relative to ϵ_{448} .

singularity in the ratio cannot be avoided by using the L'Hôpital's rule. In the former method of comparing the fractionations by making a three-isotope plot this complication is avoided, but the wavelength dependence is not explicit. These two methods—the three-isotope plot and the ratio of fractionations as a function of wavelength—thus complement each other.

III. Discussion

In the data from stratospheric samples¹⁰ an oxygen isotope anomaly Δ^{17} ($= \delta^{17} - 0.516 \delta^{18}$) ≈ 1 per mil was observed. To understand this anomaly transport models simulating the effect of various sources and sinks were used.^{7,11,12} It was shown by Kaiser et al.⁷ after pointing out some details which were overlooked by McLinden et al.¹¹ that a slope of about 0.525 in the $\ln(1+\epsilon_{447})$ vs $\ln(1+\epsilon_{448})$ plot of photolysis contributes less than 0.07 per mil to Δ^{17} .

As can be seen from the present figure 2, our calculations predict a slope of 0.525 in the log-log plot. The slope we obtained was almost independent of temperature in the range 230 K – 300 K^{1,2} although the fractionation factors themselves changed with temperature. Experimental measurements of the slope at stratospherically relevant temperatures of 220 K – 273 K¹³ are needed to verify our theoretical prediction and to give a correct definition for the calculation of the Δ^{17} in stratosphere. At present there are measurements of only the slope at room temperature.

Our calculations in figure 2 are based on the same theoretical model we used earlier and obtained an agreement with most of the available wavelength-dependent

fractionation measurements for other isotopologues better than other detailed computations in the literature.⁵ Thus the present figure 2 gives a firmer theoretical basis for the slope of 0.525 used in Kaiser et al.⁷ Incidentally the results for 447, 448 obtained by two very different theoretical approaches of Johnson et al.⁹ and Chen et al.⁵ are very similar although the results for other isotopologues were significantly different.⁴

A theoretical slope of 0.534 we obtained in conjunction with the calculations of Kaiser et al.⁷ partially confirms that the contribution of photodissociation of N₂O to Δ^{17} is insignificant. However as noted above, experimental measurement of slopes at different temperatures are needed for a more complete confirmation. Mechanisms other than photodissociation are being studied in the literature to explain the isotopic anomaly.^{14,15}

The loss of N₂O by photolysis happens throughout the stratosphere. Over such a wide range of altitudes, the intensity distribution of light ($I(\lambda)$) changes significantly (Plate 4 of reference 16). To quantify the isotopologue fractionations δ^{17} , δ^{18} at these altitudes with different $I(\lambda)$, detailed experimental measurements and theoretical predictions of the absolute values of fractionations at individual wavelengths are needed. This need for wavelength dependent fractionation is unlike the calculation of Δ^{17} . The latter depends mainly on the ratio of the two fractionations rather than on their absolute values. The presently available experimental data for 447, 448^{6,17-19} does not have such an exhaustive wavelength dependent study (e.g., cf. Figures 5 of reference 5). Detailed wavelength-dependent fractionation measurements when performed will aid transport computations, besides testing the validity of the theoretical predictions for the isotopologue fractionation factors. For example if δ^{17} , δ^{18} and Δ^{17} are to be estimated as a

function of altitude similar to the calculations of Morgan et al.,¹² these wavelength-dependent fractionation measurements of isotopologues will be very useful.

IV. Conclusion

The three-isotope plot obtained by theoretical calculation is compared with the laboratory measurements. The comparison in this plot as well as the ratio of fractionations is found to be good, for the very limited existing available experimental data. We hope that this graphical presentation, based now on fundamental physical theory, will stimulate further experiments for such comparisons.

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