Derivation of Photochemical Information Near 1 mbar From Ozone and Temperature Data

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An analysis procedure has been developed for derivation of information about the photochemical behavior of ozone near 1 mbar by explicitly accounting for the dynamical transport terms in the continuity equation for perturbations from the zonal mean. The procedure is shown to be valid using data from a numerical transport model and is then applied to LIMS ozone and temperature data, using geostrophic winds to estimate the transport terms. The data study is restricted to March at 2, 1 and 0.7 mbar. Because the temperature deviations are dynamically produced, large temperature deviations are associated with significant ozone transport terms. The anticorrelation between the deviations of ozone and temperature disappears when the transport terms are small. The derived photochemical information is compared to photochemical theory. Although there is overall agreement in the magnitude as well as the latitude, altitude, and time dependencies, discrepancies are suggested which may be related to the long-standing failure of photochemical models to calculate ozone accurately near 1 mbar. The theory suggests that the addition of Cl_x to the stratosphere will affect the relationship of ozone and temperature at 2 and 1 mbar. Comparison of the photochemical information derived from future ozone and temperature measurements with the results of the present analysis should provide a critical test of the photochemical scheme thought to describe the behavior of odd chlorine in the stratosphere.

1. INTRODUCTION

Remote sensing by satellite of ozone and temperature fields provides a large body of data which should be useful for testing the schemes which are thought to describe the photochemical behavior of ozone in the stratosphere. Because of the temperature dependence of the loss processes for odd oxygen in the stratosphere, ozone and temperature deviations are expected to have a correlation coefficient close to -1 when the deviations are in photochemical equilibrium. Previous studies which have considered the relationship of ozone and temperature fields and the interpretation of the observed temperature dependence in terms of photochemical loss processes include *Barnett et al.* [1975], *Krueger et al.* [1980], *Solomon et al.*, [1983], and *Chandra* [1985, 1986]. However, as discussed by *Rood and Douglass* [1985] and demonstrated in the work by *Douglass et al.* [1985] (hereafter referred to as DRS), the appearance of a -1 correlation coefficient does not guarantee that the ozone and temperature perturbation fields are in photochemical equilibrium.

The evolution of the ozone perturbation field is approximated by

$$\frac{\partial \gamma'}{\partial t} \simeq -(\bar{u} + u')\frac{\partial \gamma'}{\partial x} - v'\left(\frac{\partial \bar{\gamma}}{\partial y} + \frac{\partial \gamma'}{\partial y}\right) - w'\frac{\partial \bar{\gamma}}{\partial z} - \Gamma\gamma' - \theta T'$$

(1)

where γ is the ozone mixing ratio; t is the time; u, v, and w are the zonal, meridional, and vertical winds in the x, y, and z directions, respectively; T is the temperature, an overbar indicates the zonal mean, and a prime indicates deviations from the zonal mean. Terms $\bar{v}\partial\gamma'/\partial y$, $\bar{w}\partial\gamma'/\partial z$, and $w'\partial\gamma'/\partial z$ were found to be small and are neglected. The parameters Γ and θ may be derived as given by *Stolarski and Douglass* [1985] and

represent the relaxation for odd oxygen perturbations and the response to temperature perturbations, respectively. In DRS it was shown that at 2 mbar, 40°N–60°N, during the winter, the dynamic terms in (1) are of the same order of magnitude as the photochemical terms throughout the winter and that the appearance of a -1 correlation coefficient between ozone and temperature deviations occurs not when the photochemical terms dominate the dynamic terms, but when the sum of the dynamic terms is small due to cancellation. It was also shown that the tests of photochemical theory that can be derived from the data during winter at 2 mbar are at best weak. Although the overall consistency of the dynamical and photochemical terms is determined, there are substantial errors associated with the calculation of the dynamical terms, and it is not possible to derive quantitative information about the photochemical relationship between ozone and temperature from the winter data.

The primary objective of this work is to extract information about the actual photochemical behavior of stratospheric ozone from data by examining the interaction between the dynamic and photochemical terms in (1). A procedure was developed to derive the ratio of the photochemical parameters, θ/Γ, by specifically accounting for the dynamic contributions. The procedure is initially applied to model data to illustrate its validity and then to LIMS ozone and temperature data, using geostrophic winds derived from geopotential height fields. Errors in calculation of the dynamic terms in (1) limit the applicability of the method to situations in which the photochemical terms are the largest, the geostrophic winds are good approximations to the actual winds, and the planetary wave activity is sufficient to produce amplitudes of γ' and T' which are substantially above the noise level. This study will consider March 1979, because during this time these conditions are met for middle latitudes at 2, 1, and 0.7 mbar. The method is shown to fail when the dynamical terms in (1) reach their minimum values, because then the measured ozone and temperature deviations are too small to derive meaningful values of either the correlation coefficient or the ratio θ/Γ from the data.

The second objective is to test the photochemical schemes from which the theoretical parameters are derived by deter-

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TABLE 1. The Relative Contributions to the Theoretical Parameters Γ_τ and θ_τ of Odd Oxygen, Odd Nitrogen, Odd Chlorine, and Odd Hydrogen Loss Processes for Odd Oxygen, and the Sensitivity of the Ratio θ_τ/Γ_τ to Changes in Species Concentrations

	p, mbar	Γ_i/Γ_τ, %	θ_i/θ_τ, %	$\dfrac{[\Delta(\theta/\Gamma)/(\theta/\Gamma)]}{(\Delta\gamma_i/\gamma_i)}$
O_x	2	21	43	1.19
	1	28	51	1.08
	0.7	24	43	1.03
Cl_x	2	35	8	−0.28
	1	20	$\simeq 0$	−0.18
	0.7	11	$\simeq 0$	−0.14
NO_x	2	29	35	0.14
	1	8	9	0.02
	0.7	3	4	0.03
HO_x	2	15	14	$\simeq 0$
	1	44	41	−0.02
	0.07	61	54	0.06

The value $i = O_x$, Cl_x, NO_x, and H_2O for HO_x.

mining the consistency of the derived ratios with theoretical values. The values of the ratio θ/Γ derived from data, both neglecting and including transport terms, are compared to each other and to the values derived from photochemical theory. The notation that distinguishes these variously derived ratios is presented in the text and summarized in the notation list at the end of this work. Latitude, altitude, and time dependences of the ratios will be estimated and compared. The discrepancies between theory and measurement will be interpreted by considering the theoretical altitude, latitude, and mean ozone and temperature field dependences of the separate odd oxygen loss processes.

2. DATA SOURCES

The ozone, temperature, and geopotential height fields used in this study are mapped LIMS data [*Gille and Russell*, 1984], which were obtained through the National Space Science Data Center at Goddard Space Flight Center. Data are mapped on constant pressure surfaces from 100 mbar up to 0.5 mbar; latitudinal coverage of the data set is from 64°S to 84°N at 4° intervals. Longitudinal structure is calculated from a Fourier expansion at each latitude and pressure, using up to four wave numbers each for the ascending node and descending node data. Discussions of the quality of the LIMS ozone and temperature data are given by *Remsberg et al.* [1984] and *Gille et al.* [1984].

For this work the data from March 1979 at three levels (2, 1, and 0.7 mbar) and the middle latitudes 40°N–60°N are considered. These levels are chosen because the photochemical terms are not dominated by the dynamic terms in (1), because the amplitudes of ozone and temperature deviations from the zonal mean are not small, and because the ozone concentration is a good approximation to the total odd oxygen. At levels below 2 mbar the photochemical effects for ozone are too small relative to dynamic effects to be able to gain information about the photochemical parameters by evaluating the dynamic terms and the day-to-day changes in the ozone perturbation. Above 0.7 mbar interpretation of the results is complicated by the increasing importance of O atoms to total odd oxygen. At 0.7 mbar, total odd oxygen is calculated from the measured ozone, assuming photochemical equilibrium between production of O by photodissociation of O_3 and recombination of O with O_2 to form ozone. The maximum contribution of O to total odd oxygen in this study is 9%.

3. PARAMETERIZATION

Theoretical values of the parameters θ and Γ are required both for model calculations and for comparison with the ratio θ/Γ derived from the data. The theoretical values used here are subscripted by τ and are calculated following *Stolarski and Douglass* [1985]. The theoretical parameters may be written as sums of contributions due to the separate odd oxygen loss processes, i.e., $\Gamma_\tau = \Gamma_O + \Gamma_N + \Gamma_{Cl} + \Gamma_H$, $\theta_\tau = \theta_O + \theta_N + \theta_{Cl} + \theta_H$, where subscripts O, N, Cl, and H refer to odd oxygen, odd nitrogen, odd chlorine, and odd hydrogen loss processes. The calculation requires chemical kinetic data to evaluate reaction rates, solar flux and cross-section data to evaluate dissociation rates, and ozone, water vapor, odd nitrogen, odd chlorine, and temperature distributions.

The reaction rate and dissociation rate data are taken from evaluation 7 of the NASA Panel for Data Evaluation [*DeMore et al.*, 1985]. Within the uncertainties given for reaction rate data, the ratio θ_τ/Γ_τ is relatively insensitive to changes in reaction rates, although the values of Γ_τ and θ_τ are affected individually. The ratio is less sensitive to changes in the constant factor of a reaction rate than to changes in the temperature dependence. For example, the values of Γ_τ and θ_τ calculated using the upper limits of the constant factor for the reactions $O + O_3$ and $O + O_2 + M$ differ by as much as 7% from the baseline values, but the ratios differ by at most 3%. The values of Γ_τ and θ_τ calculated using the upper limits of the temperature dependence for these reactions differ by as much as 35% from the baseline values, but the ratios differ by only 12%. These differences are nearly independent of pressure.

In contrast, the ratio θ_τ/Γ_τ is sensitive to the species distributions for odd oxygen and chlorine adopted for the calculation. This sensitivity is observed because although both Γ_τ and θ_τ are affected in the same sense by a change in species distribution, the relative contributions of each species to the sum differ. Sensitivities to changes in all trace species are compared in Table 1. At all three pressures, odd oxygen loss due to recombination of O and O_3 makes a larger contribution to θ_τ than to Γ_τ, therefore increasing odd oxygen produces a larger theoretical value of θ_τ/Γ_τ. At all pressures, odd oxygen loss due to reaction with chlorine species makes a smaller contribution to θ_τ than to Γ_τ, and increases in chlorine species lead to a decrease in the theoretical ratio. Since reactions with odd nitrogen species and odd hydrogen species contribute nearly equally to θ_τ and Γ_τ, the theoretical ratio is relatively insensitive to the assumed odd nitrogen and H_2O distributions.

The ozone and temperature distributions from which the parameters are calculated are zonal mean values of LIMS measurements. Because the parameters are sensitive to the fraction of the total loss that is due to each of the loss processes, the distributions for the other trace gases, which are derived from one-dimensional model calculations, are constrained to reflect the relative magnitudes and the altitude and latitude dependences of the much more detailed data-based calculations reported by *Jackman et al.* [1986]. The ratio θ_τ/Γ_τ calculated from these species distributions should have the proper relative contribution to the temperature response and to the odd oxygen lifetime from each of the loss processes.

Between 2 and 0.7 mbar, both of the parameters Γ_τ and θ_τ decrease with latitude because the dissociation rates decrease. Both parameters increase with altitude as a result of an increase in dissociation rates; however, the percent increase in θ_τ is smaller than the corresponding increase in Γ_τ, reflecting a change in the mix of species controlling odd oxygen loss to-

TABLE 2. Expressions for the Daily Theoretical Values of the Photochemical Parameters

Latitude	p, mbar	Γ_r, 10^{-5} s^{-1}	θ_r, 10^{-6} ppmv s^{-1}	θ_r/Γ_r, 10^{-2} ppmv K^{-1}	$[\theta_r/\Gamma_r]$, 10^{-2} ppmv K^{-1}
40°	2	1.8 + 0.039t	1.5 + 0.027t	8.0 − 0.028t	7.6
	1	5.3 + 0.057t	2.4 + 0.017t	4.5 − 0.012t	4.3
	0.7	8.1 + 0.055t	2.7 + 0.019t	3.4 + 0.001t	3.4
60°	2	0.81 + 0.036t	0.78 + 0.030t	9.5 − 0.024t	9.2
	1	2.6 + 0.12t	1.5 + 0.041t	5.6 − 0.041t	5.0
	0.7	4.7 + 0.15t	2.0 + 0.040t	4.1 − 0.024t	3.7

The value t is the number of days from March 1. The monthly mean value of the ratio is indicated by square brackets.

wards dominance by nearly temperature independent odd hydrogen reactions.

Because the theoretical ratio θ_r/Γ_r will be compared to values derived from data and because an estimate of the photochemical relaxation is necessary to determine the effect of dynamic forcing in (1), it is important to consider sources of variability in both θ_r/Γ_r and Γ_r. Possible sources of time and latitude dependence include changes in solar insolation, in the mean temperature field, and in the mean constituent fields. Changes in the mean constituent fields on the time scale of 1 month which affect NO_x, Cl_x, and HO_x species have little effect on the parameters. Calculations indicate that although both Γ_r and θ_r are dependent on zenith angle and temperature, the ratio θ_r/Γ_r is nearly independent of changes in these quantities at middle latitudes, 2–0.7 mbar, during March. Dependence on the odd oxygen mixing ratio has been shown to be significant for Γ_r, θ_r, and θ_r/Γ_r (Table 1); this must be considered because changes in the mean ozone during March are substantial, as much as −0.04 parts per million by volume (ppmv)/day (−1%/day) at 1 mbar, 60°N. The expressions for daily values of Γ_r, θ_r, and θ_r/Γ_r are calculated assuming linear changes in the ozone mixing ratio and temperature over the month and are given along with the monthly mean value, indicated by square brackets, in Table 2.

It is useful to relate the ratio θ_r/Γ_r considered in this work to the temperature coefficients considered in previous studies [e.g., Barnett et al., 1975; Krueger et al., 1980; Natarajan et al., 1986]. These have sought a relationship between ozone and temperature of the form

$$\gamma = A\ e^{B/T} \quad (2)$$

The values of A and B are derived from daily values of zonal mean ozone and temperature. If photochemical equilibrium is assumed, this type of analysis is equivalent to calculating the ratio θ/Γ from the data as can be seen by a Taylor series expansion of (2). Assuming that the mean values are related by $\bar{\gamma} = A\ e^{B/\bar{T}}$, B is related to the ratio θ/Γ by

$$\frac{\theta}{\Gamma} = A\ e^{B/\bar{T}}\frac{B}{\bar{T}^2} = \frac{\bar{\gamma}}{\bar{T}^2}\ B$$

Chandra [1985, 1986] has also examined the relationship between zonal mean ozone and temperature, focusing on changes in $\bar{\gamma}$ and $\bar{T}$ of time scales between 5 and 35 days.

There are three advantages of the formulation used in the current work. First, the advective terms in the perturbation continuity equation are not assumed to be small; rather, the possible dynamical influence on γ' is evaluated directly through (1). Second, the ratio θ/Γ can be interpreted in terms

of the catalytic cycles contributing to ozone loss at a given latitude and pressure more directly than the coefficient B defined above. Third, because the calculation of the theoretical parameters used here is based on measurements of ozone and other trace species, the dependence of ozone loss on the odd oxygen concentration is represented as accurately as possible. In contrast, parameters taken from a self-consistent calculation [e.g., Natarajan et al., 1986], which produces upper stratospheric ozone values that are lower than observations, do not have the correct dependence on temperature because the importance of the highly temperature dependent $O + O_3$ loss process is underestimated.

4. MODEL DESCRIPTION

There are two primary reasons for the use of numerical experiments of ozone transport in this study: first, to test the analysis technique in an environment where the winds and chemistry are known exactly, and second, to aid in the interpretation of the results obtained in the data analysis.

The dynamical model is the same as described by Schneider and Geller [1985]. Briefly, it is a global primitive equation model that extends from 10–100 km. The model was originally devised to perform mechanistic studies of stratospheric warmings.

The experiment used here simulated a wave 1 warming. Dissipative processes are modeled by Newtonian cooling and Rayleigh friction. The model is initialized with the same wind profile used by Holton [1976], and a wave 1 perturbation is forced at the lower boundary. The wave grows and decelerates the mean flow, with easterlies appearing in the stratosphere between days 20 and 25.

Transport is calculated using the square root scheme [Schneider, 1984]. The ozone is initialized with LIMS monthly average February 1979 zonal mean data. The chemical source and sink terms are parameterized as in (1) and the chemical parameters are averaged February values. The ozone transport is characterized by strong poleward transport during the warming, particularly in the middle and lower stratosphere.

Although the data and the parameters used in the model do not correspond to the time period focused upon in the data analysis, the amplitudes of the disturbances in the model results and in the data are shown to be similar (see Figures 1 and 3). Because the terms in (1) are calculated more accurately from model results than from data, the photochemical terms do not have to be larger than the dynamic terms for the technique to work. The single most important aspect of the model results is that the chemistry is exactly specified by the parameters, and it is therefore possible to isolate dynamical and chemical influences on the model ozone distribution with confidence.
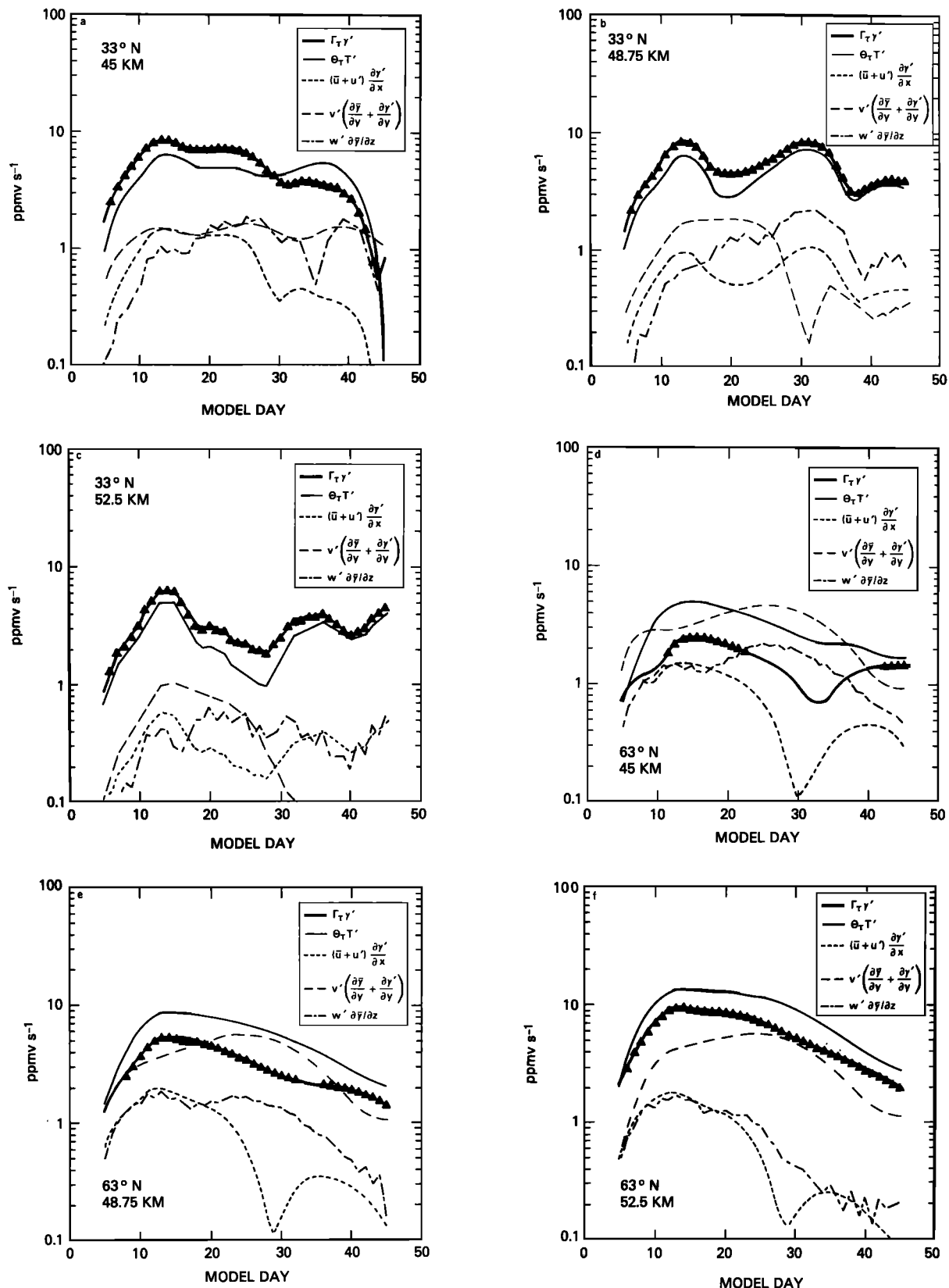
Fig. 1. Model results are used to evaluate the strengths (equation (3)) of the photochemical and dynamic terms in equation (1). The days for which the correlation coefficient between γ' and T' is -0.9 or less are indicated by triangles. (a) Results at 45 km, 33°N. Although the photochemical terms are generally the largest, the strengths of the dynamic terms do not indicate that they are negligible compared to the photochemical terms. (b) Results at 48.75 km, 33°N. As in Figure 1a the dynamic terms are not negligible compared to the photochemical terms. (c) Results at 52.5 km, 33°N. Although the photochemical terms are clearly the largest, the dynamic effects are not negligible during the middle of the model calculation. (d) Results at 45 km, 63°N. The dynamic terms are clearly important throughout the time period. (e) Results at 48.75 km, 63°N. The meridional advection term is comparable to the photochemical terms throughout the time period. (f) Results at 52.5 km, 63°N. The meridional advection is not negligible compared to the photochemical terms throughout the time period.