

Accuracy of Some Methods for Determining Photodissociation Rates in the Modeling of Stratospheric Ozone

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ABSTRACT

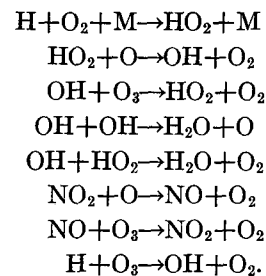
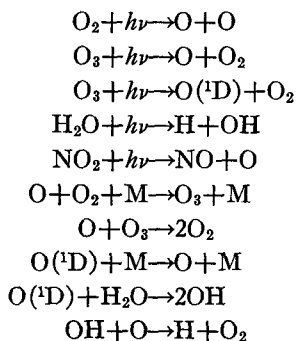
A simple model is used to estimate the accuracy of a number of methods for treating the solar zenith angle in determining photodissociation rates for the modeling of stratospheric ozone. The method of averaging the rates over the daylight hours is found to be most accurate, while various methods involving a constant solar angle are often found to be of low accuracy.

1. Introduction

In the theoretical modeling of stratospheric ozone, potentially one of the most time-consuming parts of numerical calculations is the determination of the photodissociation rates, especially those of molecular oxygen and of ozone. This is because these rates depend in a strongly nonlinear way on the solar zenith angle and upon the time-varying ozone column. In this paper we investigate the accuracy of ozone profiles calculated using some standard methods for determining the photodissociation rates, for typical stratospheric conditions.

2. Comparison of methods for calculating photodissociation rates

To indicate the accuracy of some typical methods for treating the solar angle in determining ozone distributions, we use a simple model for ozone and compare the results obtained by using some selected approximations. Consider a simple model of stratospheric ozone based on the following reactions, in which additional reactions, mass transport, and other processes affecting ozone are ignored:



For the basis of comparison we use the time average of the steady-state oscillation (time-dependent) solution for the ozone distribution, obtained by recalculating the photodissociation rates for each different solar zenith angle ϕ used. For the purposes of the comparison, that is within the constraints of the model assumptions, this result is considered to be exact. To this solution we compare the following methods:

- I. The constant distribution obtained using photodissociation coefficients time-averaged over the daylight hours.
- II. The constant distribution obtained using photodissociation coefficients time-averaged over 24 h.
- III. The constant distribution obtained using the constant solar zenith angle ϕ_a , such that $\cos\phi_a$ equals the daytime average of $\cos\phi$.
- IV. The constant distribution obtained using the constant solar zenith angle $\phi_m = \frac{1}{2}$ (solar angle at noon $+\pi/2$).
- V. The constant distribution obtained using the constant solar zenith angle at noon.

Method I corresponds to one used by, among others, Crutzen (1970, 1971); method II corresponds to one used by, among others, Johnston (1971) and

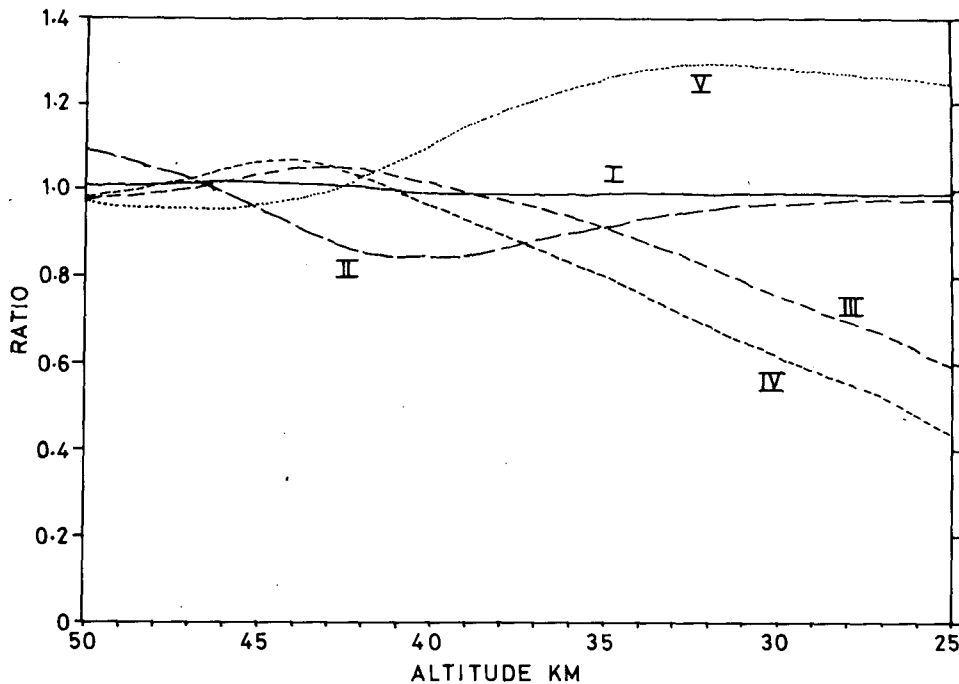


FIG. 1. Ratios of the ozone concentrations obtained using each of methods I-V to the average of the steady-state oscillation (time-dependent) solution, for conditions at 45° latitude and at the equinox.

McElroy *et al.* (1974); method III corresponds to one used by Rao (1973); and method IV to one used by Prabhakara (1963). Depending on the latitude and time of year, methods III, IV or V correspond to the use of various constant solar angles as for example by Crutzen (1972) and Nicolet (1970). Also depending on the latitude and time of year, methods III, IV or V correspond to the constant mean zenith angle used by some workers (McElroy and McConnell, 1971; Ratner and Walker, 1972) to represent conditions over all the surface of the earth.

When we say that a method "corresponds" to one used by a certain worker, this means that the essential physical assumptions and calculational procedures concerning the evaluation of the photodissociation coefficients are similar in the two cases. It does not imply that the models are related in other aspects, nor that the workers have not been sensitive to the degree of approximation involved in their methods. For example, when Nicolet in several papers (e.g., 1970, 1974) calculates ozone distributions for different constant solar angles, it is implied that the range of solutions so obtained is likely to provide upper and lower bounds for more accurate solutions. Furthermore, it should be emphasized that the results here should not be taken to imply that results obtained by workers using a method for averaging over photodissociation rates similar to one of those studied here, are necessarily as accurate or as inaccurate as suggested by the results here. For example, in many papers the absolute size of the ozone column is not the primary concern.

Details of the calculations are presented in the Appendix. Sample results are presented in Fig. 1. Plotted is the ratio of the ozone concentration obtained at different heights for methods I-V to the average concentration obtained using the time-dependent solution. We give results only for 45° latitude at the equinox. Other latitudes and other times of the year (for example 45° latitude at the winter solstice or the equator at the equinox) for the most part give results similar to the ones presented here.

Note that method I, which uses daytime-averaged rate coefficients, is the most accurate. The other methods give results, especially at lower altitudes, which are often significantly different from the steady-state oscillation solution. This should not be surprising. Two physical assumptions underlie method I: that in most of the stratosphere ozone reaches its equilibrium value on a time scale much longer than a day, and that the dominant terms in the rate of change of ozone are approximately linear in the photodissociation rate coefficients. These assumptions are fairly well satisfied. Method II is less accurate, since chemical reactions occurring during the nighttime are not greatly important in most of the stratosphere. The methods based on constant solar angles may be considered, *a priori*, to have little chance of giving accurate results. Consider for example method III based on the use of ϕ_a , such that $\cos\phi_a$ is the average of $\cos\phi$ during the day. Only if the photodissociation rates were approximately linear in $\cos\phi_a$ would this method be expected to give good results, and of course the relationship is far from linear.

The greatest shortcoming of method I is that it still requires a considerable amount of calculation, much more than methods III-V. However for lengthy problems, in which photodissociation rate coefficients must be calculated many times, the calculational effort may be much reduced by use of suitable interpolation techniques.

It may be worthwhile to mention some other possible methods. First, some workers use one of the above methods but also reduce the solar flux by one-half (e.g., McElroy and McConnell, 1971). Indeed, method II may be considered to be method I with approximately half the normal solar flux (depending on the time of year). When the present model is tested using half the normal solar flux, methods III-V give results of similar accuracy to those obtained using the full solar flux. Second, Hesstvedt (1974) used a combination of methods: above 35 km noon values of ozone are calculated using a time-dependent model (Hesstvedt, 1971), and below 35 km a constant solar angle is used to obtain an equilibrium distribution. With the model here, using the time-dependent solution above 35 km (to obtain the ozone optical thickness) and method III below 35 km, gives results below 35 km almost identical to those of method III.

3. Limitations of the results

Most of the numerous assumptions and simplifications involved in the model used here are not likely to significantly affect the results indicating the accuracy of the approximations for modeling the effect of the photodissociation rates. The two most important omissions from the simple model are other chemical reactions and transport processes.

The most important reactions omitted are ones involving odd nitrogen compounds such as NO_3 , HNO_2 and HNO_3 . The inclusion of such reactions would, on the average, probably lessen the accuracy of methods I and III-V. In particular, the inclusion of reactions leading to the formation of N_2O_5 , which can take place during nighttime, probably will improve the accuracy of method II, and certainly its accuracy relative to method I. However, it would perhaps be appropriate in most cases to use a time-dependent treatment with any model containing a set of reactions significantly more complex than the set used here, especially considering that a time-dependent treatment requires only about twice as much computational effort as methods I or II.

The effects of the inclusion of transport on the results is hard to assess precisely, but the qualitative results obtained should still hold. The dominant transport processes operate on a time scale much longer than a day, so that their main effect at any given point in the stratosphere, from the point of view of calculating the ozone concentration, is to alter the

average ozone column. We have found that any given method for treating the solar angle tends to give an ozone distribution which is systematically different from the time-dependent solution at each of the different latitudes, seasons, and the lower altitudes (or in other words at different effective ozone columns). For example, method V gives ozone concentrations higher than the time-dependent solution at all altitudes below 35-40 km. Therefore it seems safe to say that the inclusion of transport processes probably will not systematically alter the qualitative trends apparent in Fig. 1. In any case we present results only to 25 km; it is above this altitude that most of the photochemical creation of ozone occurs, and transport effects are not dominant (see, for example, Crutzen, 1972).

The absence of ozone above the top point in the model (60 km) is unrealistic, but is compensated for by increased concentrations at the uppermost points. In addition the absorbing effect of ozone at high altitudes is small compared to molecular oxygen. It might be thought that even the small amount of mesospheric ozone excluded from the model would be important because of its large diurnal variation (Dütsch, 1969; Park and London, 1974). However, the pattern of this variation is of a fairly constant ozone minimum during the day, with the only periods of rapid change being near sunrise and sunset. At these latter times the path length to the lower altitudes is the greatest, and the effect of the increase in the ozone column would be therefore only to reduce the already small rate of change of ozone near sunrise and sunset. In any case, at any high altitude most of the absorption of ultraviolet occurs within approximately one scale height above the point in question.

4. Conclusion

Whitten and Turco (1974) and Shimazaki and Ogawa (1974) note that the average concentrations of several stratospheric odd nitrogen and odd hydrogen compounds do not correspond to the concentrations computed using an average solar angle. Even though the diurnal variations in ozone directly due to the varying solar angle are not nearly so great as in the odd nitrogen and odd hydrogen compounds, we reach a similar conclusion here. Several methods for calculating the photodissociation rate coefficients in determining ozone profiles have been tested. Methods based on using time-averaged photodissociation rates give more accurate results than those based on a single solar angle.

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APPENDIX

Calculation Details

In the calculations we use the following data and method: the rate coefficients used by Blake and Lindzen (1973; see references therein); temperature and density profiles from the U. S. Standard Atmosphere (1962); solar flux and oxygen and ozone cross sections from Ackerman (1971); the constant NO_x ($=\text{NO}+\text{NO}_2$) mole fraction from Ackerman and Muller (1972), with the NO_x mole fraction increasing with height above their highest altitude to 10^{-7} at 60 km; and a constant H_2O mole fraction of 5×10^{-6} . The ozone distributions are calculated at height intervals of 1 km, from 60 to 25 km. The results are not sensitive to these aspects of the model; for example, the rate coefficients used by McConnell and McElroy (1973) give closely similar results.

Following Blake and Lindzen (1973), the following are considered to be in equilibrium: the species $\text{O}(^1\text{D})$, H and O, and the ratios $(\text{HO}_2)/(\text{OH})$ and $(\text{NO})/(\text{NO}_2)$. The equilibrium assumption for $(\text{NO})/(\text{NO}_2)$ may cause slight errors near sunrise and sunset.

To obtain the steady-state oscillation solution we use the following procedure which minimizes the number of evaluations of the photodissociation coefficients. At the highest altitude in the model the ozone optical thickness is taken to be zero. The time-dependent parameters are determined once for each time of the day used, and then a simple finite-difference representation of the time rate of change of the ozone concentration is used until a reproducible oscillation is obtained. This oscillation has an ozone concentration at each time, which is used to obtain an ozone column by simply multiplying by the height associated with the altitude. New values for the time-dependent parameters are obtained for each time at the next lower altitude by using the calculated ozone column at each time. The algorithm for the change in ozone is then used at this point until a steady oscillation is obtained. This procedure is then repeated for each succeeding point descending in altitude.

By this procedure the photodissociation rates need be calculated only once for each time of the day used and each point in altitude. About 100 time intervals are used, varying from about 100 s at sunrise and sunset to longer values at noon. For methods I and II these same divisions of the day are used, but since the ozone column does not vary in time for these methods, only half the time intervals need be used.

Accelerated convergence to the steady-state oscillation is obtained using an extrapolation technique based on the assumption that the difference between the present and the final ozone concentration at a particular time of the day drops off exponentially with the

number of days of iterations; no more than seven daily cycles are required to get convergence with a fractional accuracy of 10^{-4} to 10^{-6} .

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