Mesospheric ozone – theory and observation

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SUMMARY

The predictions of a radiative-photochemical model are compared with observations of the diurnal variation of mesospheric ozone obtained from rocket-borne experiments. Temperature observations from the SAMS instrument on the Nimbus-7 satellite are used to define the basic atmospheric state. Good agreement is found, provided that low water vapour abundances are accepted, together with slow rate coefficients for the recombination of odd hydrogen species. Sensitivity tests performed with the model show that uncertainties in the ozone calculations arise chiefly from uncertainties in water vapour concentrations, solar irradiance, $O_3$ absorption cross-sections and certain rate coefficients, and that the sensitivity of ozone to these parameters may be markedly different at different times of day, especially above 60 km. The model's representation of the ozone variation around dawn is also used to estimate the error caused by the assumption of spherical uniformity when deriving ozone concentrations from solar occultation experiments.

1. INTRODUCTION

The study of atmospheric ozone has assumed great importance in recent years because of fears that pollutants might contribute to its catalytic destruction, as summarized in WMO (1981). Factors that must be considered in a complete theory for the ozone distribution are both manifold and complex, involving detailed interrelations between photochemical, radiative and transport processes. In order to test such theories it is very advantageous to be able to isolate parts of the atmosphere where one or other of these processes is dominant. Such conditions occur in the upper stratosphere and lower mesosphere between 40 and 70 km (Frederick 1980; Prather 1981), where the photochemical lifetime of odd oxygen is less than a day, while typical time scales for transport (both advective and diffusive) between regions of significantly different ozone concentrations are greater than five days, except for occasions when the winter circulation is particularly disturbed.

The varying zenith angle of the sun through the day induces, through its effect on photodissociation rates, a diurnally forced modulation on atmospheric chemical processes. This may be reflected in minor constituent concentrations if their chemical lifetime is comparable to or less than the time scale of the disturbance, so a diurnal variation in ozone amount is to be expected above 40 km (Tuck 1977; Herman 1979; Groves and Tuck 1980; Prather 1981; Aimedieu et al. 1981). A comparison between measurements of this diurnal variation and predictions from photochemical theory therefore focuses on the faster parts of the chemistry, which are least influenced by dynamical processes.

Previous measurements of the diurnal variation of mesospheric ozone have not revealed major deficiencies in theoretical predictions (Hilsenrath 1971; Anderson et al. 1981; Wilson and Schwartz 1981), but have in most cases suffered from poor precision or inadequate vertical resolution at the heights of interest (Vaughan 1982b). An exception to this was offered by Lean (1982) with several rocket flights from Wallops Island (37°N 45°W) at different times of day. However, Lean's flights were spread over 15 days in October–November 1979, and the interpretation of his results relied on assumptions about changes in the basic state of the atmosphere (e.g. temperature and minor constituent profiles) during that time. Furthermore, in allowing for such changes, Lean used photochemical equilibrium equations based on pure oxygen chemistry (Chapman 1930), which are very sensitive to temperature (section 5(c)). In fact, however, mesospheric ozone concentrations are determined mainly by reactions with H, OH and HO$_2$ (Prather 1981), and these are much less sensitive to temperature than O + O$_3$ → 2O$_2$. A rigorous test of predicted diurnal ozone variations requires a set of ozone measurements obtained at different times on the same day and – equally importantly – a photo-
chemical model which is able to simulate as far as is possible all the atmospheric conditions pertaining to the time and place of the observations, such as temperature profiles and solar zenith angles. A suitable set of observations was published by Vaughan (1982a) and is described in section 2; this reference also included a preliminary comparison with theory. The purpose of the present paper is to describe in greater detail an attempt to simulate these observations using a numerical model which included only photochemical and radiative processes (dynamical effects being ignored in accord with the above discussion). In doing so, a number of sensitivity experiments were conducted with the model to determine how the diurnal variation of ozone is influenced by various model parameters. These are described in section 5.

2. Ozone observations

Observations of the diurnal variation of mesospheric ozone were obtained from rocket-borne experiments at South Uist (57°22'N 7°22'W) on 2 October 1979. These results have been described by Vaughan (1982a) and only essential details will be given here. Three measurements were made, at 0200 h, 0600 h (dawn) and 0930 h (all times are GMT), using narrow-bandwidth photometers (centred at 265 and 290 nm) to observe the extinction of ultraviolet light from the moon (for the first rocket) or the sun (for the other two). The first two rockets were launched with the source below the horizon (zenith angle \( \theta \approx 95^\circ \)), and gave ozone information up to 100 km. However, the third experiment (with \( \theta = 70^\circ \)) measured ozone only up to 66 km; the interpretation of the results will therefore be confined to the region 46–68 km.

The measurements provided profiles of ozone number density as a function of geometric height, and are shown in Fig. 1 with random standard error limits where these exceed 5%. Systematic uncertainties are generally less than 5%, except for nighttime values below 52 km, where signals from the moon were heavily attenuated and were

![Figure 1. Ozone number densities measured from South Uist (57°22'N 7°22'W) on 2 October 1979.](image)

- O: 0200 h, x: 0600 h, +: 0930 h (all times GMT).
- Error bars are random standard deviations, and are only shown when they exceed 5%.
contaminated by a background illumination due to airglow and scattered sunlight. This accounts for the divergence of the nighttime profile from the other two below 52 km. Above this height the lunar signals increased rapidly and errors in estimating background illumination had no significant effect on the ozone determination.

The occultation method used for the first two rockets ($\theta > 90^\circ$) effectively provided a measurement of ozone at the tangent points, where the paths from source to detector came closest to the earth's surface. (The geographical positions of these points are shown in Fig. 2.) The total amount of ozone along each ray path was derived from the observed extinction using Beer's law (Vaughan 1982b). To obtain number densities from these path totals certain assumptions had to be made about the ozone distribution. For nighttime measurement, spherical shells (1 km thick) of constant ozone number density were assumed, allowing the path total, $N(h)$, at tangent height $h$ to be written

$$N(h) = \sum_i L_i(h)n_i$$

where $n_i$ is the number density and $L_i(h)$ the path length in the $i$th shell. An exponential decay in $n$ was assumed above the highest retrieved shell. At night, ozone concentrations are expected to remain constant in the lower mesosphere and Eq. (1) is valid, but very rapid changes in concentration are expected around dawn, especially above 60 km. Substantial errors in the retrieval could therefore arise from the assumption of spherical symmetry. To allow for this, values were taken from the photochemical model described below at the ratio, $f(t)$, of the ozone concentration at time $t$ to that at 90° zenith angle. These ratios were linearly interpolated in time and height so that Eq. (1) could be rewritten in terms of the concentration profile $n_i$ at the tangent point (90° zenith angle):

$$N(h) = \sum_i L_i(h)g_i(h)n_i + \sum_i L_i(h)g'_i(h)n_i$$

where $g_i$ and $g'_i$ are the ratios in shell $i$ on the night and day side of the path respectively. A comparison between profiles retrieved using Eqs. (1) and (2) was shown by Vaughan (1982a), and is illustrated more precisely in Fig. 3. A maximum difference of 28% occurs...
at 67 km, emphasizing that the assumption of horizontal uniformity can lead to serious
errors in solar occultation measurements. The difference of 25% at 65 km is somewhat
greater than that estimated by previous workers (Llewellyn and Witt 1977; Miller and
Ryder 1973).

There are two important reasons why the use of Eq. (2) should be regarded more as a
sensitivity test than as an accurate retrieval. Firstly, no account is taken of ozone vari-
ation within the shell nearest the tangent point, leading to an overestimate of the concen-
tration at 90° zenith angle because of the sharp increase in ozone concentration on the
night side (see section 5(a)). Secondly, and more importantly, photochemical model calcu-
lations are least accurate at dawn and dusk, so the exact values of \( f(t) \) are somewhat
uncertain. Nevertheless, the assumption of spherical uniformity is clearly inappropriate
for dawn retrievals, and the comparison between dawn observations and theory will
proceed with the profiles derived from Eq. (2).

3. Temperature Observations

In order to compare theoretical calculations with ozone observations accurate coin-
cident temperature profiles were required, both because of the temperature dependence of
many of the chemical rate coefficients and because of the need to determine precisely the
heights of the pressure surfaces used in the calculations. Such temperature information
was available from three sources: a Skua rocketsonde (Almond 1969) launched shortly
after the nighttime rocket; the Stratospheric Sounding Unit (SSU) on the NOAA-6 satel-
lite (Miller et al. 1980); and the Stratospheric and Mesospheric Sounder (SAMS) on the
Nimbus-7 satellite (Drummond et al. 1980). The rocketsonde offered the best vertical
resolution of the three but could not provide the horizontal and temporal variations in
temperature needed to allow for the geographical spread of the ozone observations (Fig.
2). Temperature profiles corresponding to each observation were therefore determined
from the SAMS data, relative to the 1 mb geopotential height field as derived from the
SSU measurements (Pick and Brownscombe 1981). A comparison of the Skua profile with
the nearest available SAMS sounding revealed differences of less than 3 K at all heights,
consistent with an estimated uncertainty of \( \pm 2 \) K in the SAMS temperatures (J. J.
Barnett, personal communication).

The SAMS instrument measured radiances in the experimental area at 1522 and
2050 GMT on 1 October and 2110 GMT on 2 October, but did not cover the precise period
of the experiment. However, a comparison of near-coincident data from the three orbits
revealed no significant secular trend, and the sounding nearest to each ozone observation was taken to be representative of it (Fig. 2). The three temperature profiles are shown in Fig. 4, and show a significant difference of 6 K near 60 km between profiles corresponding to the nighttime and dawn rounds. This difference was due to a small wavenumber-2 planetary wave evident in a hemispherical analysis of the SAMS data. Near the stratosphere there is a significant diurnal variation in temperature (Reed et al. 1969; Groves and Tuck 1980) and to allow for this, version B of the photochemical model described below was used. This calculated the diurnal temperature variation explicitly, deriving the temperature profile at the time of each ozone measurement from the corresponding profile shown in Fig. 4.

![Temperature profile graph](image)

**Figure 4.** SAMS temperature profiles chosen to be representative of each ozone observation (Fig. 2). Full line: nighttime round; dashed line: morning round; dot-dash line: dawn round.

To calculate geometric heights of the model pressure surfaces, the 1 mb height as given by the SSU at each location – corresponding to midday – was taken as a starting point. Assuming a constant height at 865 mb, the model calculations described above were used to adjust the 1 mb height, by means of the hydrostatic equation, to the time of the appropriate ozone observation. The corresponding temperature profile was then integrated to obtain the heights of the model pressure surfaces. This procedure assumes that the movements of pressure surfaces at 57°N are unaffected by propagating tidal modes (Chapman and Lindzen 1970) and that they may be described, in the absence of large amplitude gravity waves, purely by means of the hydrostatic equation.

4. **The model**

The one-dimensional radiative–photochemical model used in this work was based on a single column of the two-dimensional model described by Fabian et al. (1982), but included no horizontal or vertical transport terms. The chemical continuity equations
were integrated at 24 pressure levels, separated by 0.5 in ln(pressure), with solar zenith angles corresponding to equinox at 56.8°N. The calculation of photodissociation rates was extended to zenith angles beyond 90°, allowing an explicit representation of dawn and dusk. Nevertheless, the ozone calculations were least accurate at these times because of the rapid changes in constituent concentrations and photodissociation rates (the latter being calculated at 5-minute intervals). The neglect of scattered radiation can also introduce errors of up to 25% in J(O₂) near the terminator (Zucchoni et al. 1981).

The chemical scheme used by Fabian et al. was designed to integrate the constituents (O + O₃), (N + NO), (Cl + ClO) and (H + OH + HO₂) as families, and this approach was retained in the present work below 60 km. Above 60 km a different scheme was used, with O, O₃, OH, HO₂, H, H₂O₂, H₂O, NO and NO₂ being treated independently; fewer constituents are needed at these heights because of the dominant role played by odd hydrogen in determining odd oxygen concentrations (Prather 1981).

Two sets of experiments conducted with the model are discussed, the first investigating the sensitivity of the computed ozone concentrations to different external parameters and the second aimed at obtaining a best fit to the observations. A different version of the model was used for each experiment: A for the sensitivity tests and B for the comparisons. Differences between these models are summarized in Table 1. Version B represented an attempt to include the most reliable values currently available in the literature for the model’s external parameters. Unlike the first version, wherein temperatures at each level remained constant, it incorporated a radiative scheme to determine the diurnal variation.

### Table 1. Different Versions of the Model

<table>
<thead>
<tr>
<th>Source/Model</th>
<th>Version A</th>
<th>Version B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate coefficients</td>
<td>Fabian et al. (1982)</td>
<td>JPL 81-3 (1981)</td>
</tr>
<tr>
<td>Solar spectrum</td>
<td>Ackerman (1971); Simon (1975)</td>
<td>Based on Nicolet (1981)</td>
</tr>
<tr>
<td>O₂ absorption coefficient, Herzberg bands</td>
<td>Ackerman (1971)</td>
<td>Hudson and Reed (1979)</td>
</tr>
<tr>
<td>O₂ absorption coefficient, Schumann-Runge bands</td>
<td>Ackerman (1971)</td>
<td>J(O₂) based on the parametrization of Nicolet (1980); J(H₂O) on that of Frederick and Hudson (1980a)</td>
</tr>
<tr>
<td>O₂ absorption coefficient, Lyman α</td>
<td>Parametrization of Nicolet (1981)</td>
<td>As A</td>
</tr>
<tr>
<td>Concentrations of CH₄, N₂O, H₂</td>
<td>Fabian et al. (1982)</td>
<td>As A</td>
</tr>
<tr>
<td>Concentrations of H₂O</td>
<td>4 p.p.m.v.</td>
<td>See section 6</td>
</tr>
<tr>
<td>Total chlorine (Cl + ClO + ClNO₃ + HCl)</td>
<td>1 p.p.b.v. below 60 km</td>
<td>As A</td>
</tr>
<tr>
<td>Odd nitrogen</td>
<td>NO as measured by Drummond and Jarnot (1978) up to 50 km, falling to 5 p.p.b.v. at 60 km</td>
<td>As A</td>
</tr>
<tr>
<td>Temperature profile</td>
<td>As measured by Skua sonde (section 3)</td>
<td>Derived from SAMS data, specific to each ozone observation (section 3)</td>
</tr>
</tbody>
</table>
in temperature and its effect on the chemistry. This calculated the solar heating rate in conjunction with photodissociation rates, while CO₂ cooling in the 15 μm band was calculated using a Curtis matrix (Curtis 1956; Haigh 1980) and O₃ cooling in the 9-6 μm band by the parametrization of Harwood and Pyle (1975). Temperature profiles could be initialized at any time of day, with the model calculations being constrained by removal of any secular trend to return to these values after a 24-hour integration. In this way, a reproducible diurnal variation in both temperature and constituent concentrations could be obtained after integrating for about five model days with version B – as opposed to three with the constant temperature version A (cf. Fabian et al. 1982).

A list of all the photochemical reactions used in the model is not given, since they have already been described by Fabian et al. (1982) and Vaughan (1982b). However, a list is given in Table 2 of the reactions referred to elsewhere in this text, together with the index number of the corresponding rate coefficient.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃ + hv → O(³P) + O₂</td>
<td>J(O₃)</td>
</tr>
<tr>
<td>O₃ + hv → O(¹D) + O₂</td>
<td>J(O₃)*</td>
</tr>
<tr>
<td>O₃ + hv → O + O</td>
<td>J(O₃)</td>
</tr>
<tr>
<td>H₂O + hv → H + OH</td>
<td>J(H₂O)</td>
</tr>
<tr>
<td>O + O₂ + M → O₃ + M</td>
<td>k₂</td>
</tr>
<tr>
<td>O + O₃ → 2O₂</td>
<td>k₃</td>
</tr>
<tr>
<td>O(¹D) + M → O(³P) + M</td>
<td>k₆</td>
</tr>
<tr>
<td>O(¹D) + H₂O → 2OH</td>
<td>k₇</td>
</tr>
<tr>
<td>OH + O → O₂ + H</td>
<td>k₈</td>
</tr>
<tr>
<td>H + O₂ + M → HO₂ + M</td>
<td>k₉</td>
</tr>
<tr>
<td>HO₂ + O → OH + O₂</td>
<td>k₁₀</td>
</tr>
<tr>
<td>H + O₂ → OH + O₂</td>
<td>k₁₂</td>
</tr>
<tr>
<td>OH + HO₂ → H₂O + O₂</td>
<td>k₁₃</td>
</tr>
<tr>
<td>H + HO₂ → H₂ + O₂</td>
<td>k₁₅</td>
</tr>
<tr>
<td>NO + O₃ → NO₂ + O₂</td>
<td>k₁₇</td>
</tr>
</tbody>
</table>

5. Sensitivity investigations

The aim of this work was to determine the chemical processes that have a significant influence on the diurnal variation of ozone, thereby evaluating the uncertainty in ozone calculations arising from uncertainties in data used by the model. Such a study is useful, both as a basis for simulating the observations described here and in the wider context of comparing theoretical predictions with mesospheric measurements. Sensitivities were determined in most cases by recording the change in predicted ozone amount as a function of time of day when a model parameter was changed from that used in version A to that used in version B (Table 1). A more systematic investigation, however, was conducted for changes in water vapour concentration and temperature.

Because of the contribution of ozone to the optical depth in the Hartley band, a perturbation to [O₃] at one model level altered the irradiance at levels beneath, affecting [O₃] there as well. However, optical depths in the mesosphere are small, and an investigation showed that a change of 20% in [O₃] at 50 km produced only a 3% change in [O₃] at the level immediately beneath (46 km). Thus for the part of the model under investigation, perturbations at different model levels were effectively independent of one another.

(a) Form of the diurnal variation of ozone

Calculations of the diurnal variation of mesospheric ozone are shown in Fig. 5. Similar results have been reported many times (Shimazaki and Laird 1970; Isaksen 1973; Logan et al. 1978; Herman 1979; Keneshea et al. 1979; Prather 1981) and the curves need
Figure 5. Diurnal variation of ozone calculated with model A, as fractions of the nighttime value at each level
(90° zenith angle occurred in the model at 0555 and 1805 h).
A: 1.17 mb (46 km); B: 0.710 mb (50 km); C: 0.431 mb (54 km); D: 0.261 mb (57.6 km);
E: 0.158 mb (61.4 km); F: 0.096 mb (65 km); G: 0.058 mb (68.5 km)

not be described in detail. However, an account of the processes responsible for them will
be given to facilitate understanding of the sensitivity analyses.

The equilibrium balance between O₃ and O, expressed by

\[
\frac{[O]}{[O₃]} = \frac{J(O₃) + J(O₃)^*}{k_2 [O₂][M]},
\]

(3)
causes the fraction of odd oxygen residing as O to increase rapidly with height during
daytime. Since, below 65 km, O is almost completely converted to O₃ soon after dusk the
night/day ratio in ozone concentration reflects this balance and also increases with height.
Another consequence of the increasing [O]/[O₃] ratio is that the destruction of odd
oxygen is dominated in the mesosphere by reactions involving O rather than O₃: OH
+ O → H + O₂, H + O₂ + M → HO₂ + M and HO₂ + O → OH + O₂ (Prather 1981).
Indeed, above 70 km these reactions rival O + O₂ + M → O₃ + M in their efficiency for
atomic oxygen removal, and the night/day ratio in ozone concentrations is considerably
less than the pre-dusk [O]/[O₃] ratio.

The production of HO₂ radicals below 70 km occurs predominantly by the reaction
O¹(D) + H₂O → 2OH, with an additional source from photodissociation of H₂O near
midday at the higher levels. Most of these radicals are removed during the night by the
reaction HO₂ + OH → H₂O + O₂ and the amplitude of the diurnal variation of ozone is
to a large extent governed by the time constants for the release and for the destruction of
odd hydrogen. O¹(D) concentrations fall with height above 50 km, causing the former
time constant to increase from about half an hour at 50 km to about six hours at 70 km.
This delay in the release of odd hydrogen allows ozone concentrations to increase to a
maximum in the morning. The maximum is greater in amplitude, and occurs later, at the
higher levels. Here, also, the time taken to replenish odd hydrogen depends to a large
extent on the concentration of atomic hydrogen, which exceeds those of OH and HO₂
above 65 km. Atomic hydrogen is produced and destroyed primarily by the reactions
O + OH → H + O₂ and H + O₂ + M → HO₂ + M, thus, approximately,

\[
\frac{[H]}{[OH]} = \frac{k₈[O]}{k₉[O₂][M]}.
\]

(4)
A perturbation to the chemistry which increases [O] (such as a decrease in [H₂O] and
thence \([\text{OH}]\) will therefore increase the fraction of odd hydrogen residing as \(\text{H}\), and since this species plays only a secondary role (through \(\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2\)) in the destruction of odd hydrogen below 70 km the time constant for this destruction will also increase. More odd \(\text{H}\) will therefore be present later in the day, acting to remove the excess odd oxygen. Not only does this process make the response of \([\text{O}_3]\) to a perturbation very non-linear above 65 km, but it can also cause it to have a marked diurnal variation, as the following sub-sections show.

Near the stratopause, the diurnal variation of ozone is not a function of the odd hydrogen chemistry alone, since reactions with \(\text{NO}\) and \(\text{NO}_2\), and \(\text{Cl}\) and \(\text{ClO}\), and the Chapman reaction \(\text{O} + \text{O}_3 \rightarrow 2\text{O}_2\) all contribute significantly to the odd oxygen depletion rate (Pallister and Tuck 1983). Thus, early in the morning (when the large optical depths in the Hartley band delay \(\text{HO}_x\) production) the ozone concentration is determined by a balance between production by \(J(\text{O}_2)\) and destruction by \(\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2\), \(\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2\) and \(\text{O} + \text{O}_3 \rightarrow 2\text{O}_2\). Perturbations to the \(\text{NO}_x\) and \(\text{ClO}_x\) chemistry and to temperature (which has a pronounced effect on the rate of \(\text{O}_3 + \text{O} \rightarrow 2\text{O}_2\)) are therefore most effective around dawn and dusk.

(b) Sensitivity to water vapour

Model calculations were performed with water vapour concentrations of 1, 2, 3, 5 and 6 p.p.m.v. and compared with those of the control run with 4 p.p.m.v. The effect of reducing the concentration from 4 to 3 p.p.m.v. is illustrated in Fig. 6; the concentration remains fairly constant during the day below 60 km but shows marked diurnal variation at 65 and 68 km. This occurs because of the effect of atomic hydrogen in coupling the odd hydrogen and odd oxygen chemistry, as described above. At these upper levels, the size and position of the morning maximum in \([\text{O}_3]\) (Fig. 5) depend in a complex fashion on \([\text{H}_2\text{O}]\), but lower down a simpler relation may be expected because of the shorter time constants (<2 h) involved in the creation and destruction of odd hydrogen (Prather 1981). It may readily be shown (e.g. Vaughan 1982b; Frederick 1980) that if odd hydrogen compounds alone are responsible for destroying odd oxygen, and if their only source is through \(\text{O}(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}\) then under photochemical equilibrium conditions
\[ [O_3] \propto \left( \frac{k_2 J(O_2)}{J(O_3) + J(O_3)^*} \right)^{2/3} \left( \frac{k_{13} k_6}{k_7 k_8 k_{10} J(O_3)^*} \right)^{1/3} \frac{[M]^2}{[\chi(H_2O)]^{1/3}} \] (5)

where \( \chi(H_2O) \) is the water vapour volume mixing ratio. This relation is only approximately true in the real mesosphere since odd hydrogen is released by the action of O(1D) on CH₄ and H₂ and is in any case not solely responsible for odd oxygen destruction. Nonetheless, between 50 and 60 km it was found that a relation of the type \([O_3] \propto [H_2O]^{n} \) where \( \frac{1}{4} < n < \frac{1}{2} \), gave a good fit to the model calculations for \( \chi(H_2O) \) between 2 and 6 p.p.m.v. At lower levels the dependence on \( \chi(H_2O) \) was weaker (with \( n \approx \frac{1}{3} \) at 46 km) because of the effect of \( O_3 + O \rightarrow 2O_2 \) and the other odd oxygen destruction cycles. Nevertheless, it seems that such an expression can serve as a useful guide to the sensitivity of ozone to water vapour in the lower mesosphere.

(c) Sensitivity to temperature

The sensitivity of mesospheric chemistry to temperature arises both through its effect on many of the rate coefficients and through changes in atmospheric density, the latter being particularly important for 3-body reactions such as \( O + O_2 + M \rightarrow O_3 + M \) and \( H + O_2 + M \rightarrow HO_2 + M \). The reactions between odd hydrogen compounds and odd oxygen are relatively insensitive to temperature, and if these were solely responsible for odd oxygen destruction the sensitivity of daytime ozone to temperature would follow Eq. (5), in which case a 5% increase in absolute temperature would cause a 15.2% fall in \([O_3]\). The effect of increasing the model temperature by 5% is shown in Fig. 7 and agrees reasonably well with Eq. (5) at 54 and 57 km. At night, \([O_3]\) (below 65 km) is essentially equal to the daytime sum \([O_3] + [O]\), and the decreased sensitivity to temperature of nighttime ozone follows the very small sensitivity to temperature of daytime \([O]\). This may be understood by substituting Eq. (5) into Eq. (3), and noting that the only temperature-sensitive quantity in the resulting expression for \([O]\) is the cube root of \( k_2 \). Above 60 km (Fig. 7), an increase in temperature slows the rate of \( H + O_3 + M \rightarrow HO_2 + M \), thus delaying the morning replenishment of odd hydrogen and allowing an enhancement of the ozone maximum, as explained in sub-section 5(a). Near the stratosphere, model calculations deviate markedly from the prediction of Eq. (5), indicating the

![Figure 7](image-url) Percentage change in ozone corresponding to a 5% increase in absolute temperature. Key as for Fig. 5.
contribution of the very temperature-sensitive reactions \( \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \) \((k_3 = 1.9 \times 10^{-11}\exp(-2300/T)\text{cm}^3\text{s}^{-1})\) and \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \) \((k_{17} = 9.0 \times 10^{-13}\exp(-1200/T)\text{cm}^3\text{s}^{-1})\) to the odd oxygen destruction rate. These calculations may be compared with the observations of Barnett et al. (1975) who used satellite data to derive expressions of the form \( \chi(\text{O}_3) = A \exp(B/T) \) for ozone near the stratopause. Their observed values of \( B = 1116\, \text{K} \) at 46 km and 980 K at 50 km compare favourably with the present calculations from version A of the model, which predict \( B = 1013\, \text{K} \) at 46 km and 850 K at 50 km, given that the temperature data used by Barnett et al. had a vertical resolution of 10–15 km and covered a region of the atmosphere where the temperature sensitivity is not constant with height.

A comparison was also made between ozone calculations performed with diurnally varying temperatures and those performed with constant temperatures equal to the previous midday values. Near the stratopause a temperature variation of amplitude 5 K was predicted, but because of the diminishing ozone mixing ratio this fell to 0.8 K at 68 km. The greatest difference in the ozone calculations was seen at 1800 h near the stratopause, with 3.5% more ozone in the constant temperature version. Because of the inert nature of ozone at night this excess persisted until morning, causing the daily-averaged amount of ozone to be slightly less when temperatures were allowed to vary diurnally.

(d) Sensitivity to solar irradiance and optical depth

There is a considerable spread in published values for solar irradiance (Nicolet 1981; WMO 1981) and for \( \text{O}_3 \) optical depths, particularly for \( \lambda < 200\, \text{nm} \) (Nicolet and Peetersmans 1980). Several experiments to examine the effect of such uncertainties were conducted with the model in the three wavelength regions 121–6 nm, 175–200 nm and 200–300 nm. The method used was to substitute complete sets of published data, rather than determining the relative sensitivity to selected narrow wavelength regions. However, different measurements of the solar irradiance usually disagree more in their absolute values than in the shape of the spectrum, so the method was capable of giving a useful guide to the effect of irradiance uncertainties on diurnal ozone calculations.

Lyman \( \alpha \) radiation at 121.6 nm can penetrate down to about 65 km, providing an extra source of odd hydrogen through the photodissociation of water vapour. The flux of this radiation is very sensitive to conditions on the sun, and determinations of its intensity by different groups show considerable differences (Nicolet 1981). Figure 8 shows the effect

![Figure 8](https://example.com/figure8.png)  
**Figure 8.** Percentage change in ozone at 68.5 km (level G in Fig. 5) when the flux of Lyman \( \alpha \) radiation was increased from \( 3 \times 10^{11} \) to \( 7 \times 10^{11} \) photons \( \text{cm}^{-2}\text{s}^{-1} \).
on the model ozone calculations of increasing the Lyman $\alpha$ flux from $3 \times 10^{11}$ to $7 \times 10^{11}$ photons cm$^{-2}$s$^{-1}$ (the range expected between quiet sunspot and very disturbed sunspot conditions). The optical depth at 121.6 nm is large below 70 km, causing the effect to be concentrated around midday and to diminish rapidly with decreasing height (the maximum perturbation to [O$_3$] being 6% at 65 km and 0.4% at 61 km).

Optical depths are also large in the Schumann–Runge bands of molecular oxygen between 175 and 200 nm, where once again published solar irradiances are not in close agreement. The values used in version A of the model - taken from Ackerman (1971) - are greater than those currently accepted, being about 20% higher between 185 and 200 nm than the measurements at solar maximum by Mount et al. (1980). The effect of replacing them in the model with the solar minimum values of Brueckner et al. (1976) - a reduction of about 40% - is shown in Fig. 9 for 65 km and in Table 3 for night and 1300 h at the

![Graph showing percentage change in ozone over time](image)

**Figure 9.** Percentage change in ozone at 65 km (level F in Fig. 5) on replacing the original model values with:

A: Brueckner et al.’s (1976) solar irradiance values 175–200 nm;
B: Nicolet and Peetemans’s (1980) parametrization for the contribution to $J(O_3)$ from the Schumann–Runge bands;
C: Frederick and Hudson’s (1980a) parametrization for the contribution to $J(H_2O)$ from the Schumann–Runge bands.

other levels. For these calculations $J(O_3)$ was derived by using the mean O$_3$ absorption cross-sections given by Ackerman (1971). Recent investigations (Kockarts 1976; Nicolet and Peetemans 1980; Frederick and Hudson 1980a and b) have shown that significant errors may arise when using Beer’s law in the Schumann–Runge bands, and have supplied parametrized transmission models. Accordingly, experiments were conducted with the original calculations of $J(O_3)$ and $J(H_2O)$ replaced by the parametrizations of Nicolet and Peetemans and Frederick and Hudson respectively. The results of these experiments are also included in Fig. 9 and Table 3. In order to assess the uncertainty in the ozone calculations from such perturbation studies, consideration must be given to the accuracy with which the input data are known. Frederick and Hudson demonstrated that uncertainties in the transmissions (arising primarily from inaccuracies in the line strengths and predissociation widths) have a much more marked effect on calculations of $J(H_2O)$ than on $J(O_3)$, and estimated an uncertainty of $\pm 30\%$ in the latter, of which 20% arises from uncertainties in solar irradiance. Their estimate of the uncertainty in $J(H_2O)$, however, was nearer 50% at optical depths corresponding to 65 km in this study. This is commensurate with the difference in $J(H_2O)$ between the two calculations (the original values being the smaller). Thus the ozone perturbations shown in Fig. 9 and Table 3 are a reflection of the uncertainty in [O$_3$] calculations arising from this source. The original
values of $J(O_2)$, however, were nearly twice those given by Nicolet and Peetmans’ parametrization, and since the uncertainty in $J(O_2)$ is estimated to be 30% the uncertainty in $[O_3]$ from this source should only be about a third of the values shown in Fig. 9 and Table 3.

<table>
<thead>
<tr>
<th>Height (km)</th>
<th>Experiment 1</th>
<th></th>
<th>Experiment 2</th>
<th></th>
<th>Experiment 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>night 1300 h</td>
<td></td>
<td>night 1300 h</td>
<td></td>
<td>night 1300 h</td>
</tr>
<tr>
<td>46.4</td>
<td>-2.8 -3.6</td>
<td></td>
<td>-8.7 -10.5</td>
<td></td>
<td>-0.1 -0.2</td>
</tr>
<tr>
<td>50.2</td>
<td>-2.6 -3.0</td>
<td></td>
<td>-8.2 -12.9</td>
<td></td>
<td>-0.2 -0.6</td>
</tr>
<tr>
<td>54.0</td>
<td>-2.2 -6.3</td>
<td></td>
<td>-7.1 -15.2</td>
<td></td>
<td>-0.3 -1.0</td>
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<td>57.6</td>
<td>-1.6 -7.6</td>
<td></td>
<td>-6.0 -17.1</td>
<td></td>
<td>-0.5 -2.1</td>
</tr>
<tr>
<td>61.4</td>
<td>-1.0 -8.6</td>
<td></td>
<td>-5.0 -18.4</td>
<td></td>
<td>-1.2 -4.9</td>
</tr>
<tr>
<td>65.2</td>
<td>+1.8 -9.2</td>
<td></td>
<td>-2.2 -20.0</td>
<td></td>
<td>-4.7 -8.6</td>
</tr>
<tr>
<td>68.5</td>
<td>+6.0 -10.6</td>
<td></td>
<td>+2.0 -24.0</td>
<td></td>
<td>-7.2 -14.4</td>
</tr>
</tbody>
</table>

Experiment 1: Ackerman’s (1971) irradiance values 175–200 nm replaced by those of Brueckner et al. (1976)

Experiment 2: $J(O_2)$ calculated from Nicolet and Peetmans’ (1980) parametrization

Experiment 3: $J(HO_2)$ calculated from Frederick and Hudson’s (1980a) parametrization

Radiation in the Hartley band between 200 and 300 nm contributes to both $J(O_2)$ and $J(O_3)$, with changes in one tending to offset changes in the other in their effect on ozone. Version A of the model contained irradiiances in this band taken from Simon (1975) below 230 nm and from Ackerman (1971) at longer wavelengths. These were replaced in a perturbation experiment with the values recommended by Nicolet (1981) — amounting to a reduction in intensity of about 17% between 200 and 230 nm, 60% between 230 and 260 nm and 16% between 260 and 300 nm. The resulting changes in $[O_3]$ are shown in Fig. 10; they peak around midday because the largest perturbations

![Percentage change in ozone](image)

Figure 10. Percentage change in ozone when the solar irradiance values recommended by Nicolet (1981) were used from 200 to 300 nm. Key as in Fig. 3.
coincided with the greatest optical depths. Since the solar irradiance in this band is known to about 10-15% (WMO 1981), the values shown in Fig. 10 overestimate the uncertainty in [O$_3$] arising from this source by up to a factor of two. Nevertheless, calculations of the diurnal variation of [O$_3$] – particularly above 60 km – cannot be considered insensitive to uncertainties in Hartley band irradiance.

(e) Sensitivity to certain rate coefficients

The sensitivity of [O$_3$] to the various rate coefficients was investigated for the most part by replacing values in version A of the model with those recommended in JPL 81-3. Although the model contained 45 photochemical reactions (Fabian et al. 1982) the great majority of these were found to have very little influence on mesospheric ozone concentrations, and the present discussion will be confined to reactions involving only the odd oxygen and odd hydrogen species. Of these reactions, the one that most directly influenced [O$_3$] was O + O$_2$ + M → O$_3$ + M, being the only source for ozone in the model. A sensitivity experiment was conducted with $k_2$, changed from 1.05 × 10$^{-34}$ exp(510/T) to 6.2 × 10$^{-34}$(300/T)$^2$ cm$^6$ s$^{-1}$ – an increase of between 6 and 10.5% – which yielded the ozone perturbations summarized in Table 4. These varied diurnally in much the same way as in Fig. 7 – not unreasonably since the decrease in $k_2$ is the most influential chemical consequence of an increase in temperature. The uncertainty quoted for $k_2$ in JPL 81-3 is about 25% so the uncertainties in the ozone calculations are 3–4 times the values shown in Table 4.

<table>
<thead>
<tr>
<th>Height (km)</th>
<th>Night</th>
<th>0600 h</th>
<th>0930 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.4</td>
<td>6.7</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>50.2</td>
<td>6.6</td>
<td>6.8</td>
<td>7.8</td>
</tr>
<tr>
<td>54.0</td>
<td>5.7</td>
<td>6.4</td>
<td>7.1</td>
</tr>
<tr>
<td>57.6</td>
<td>3.7</td>
<td>6.8</td>
<td>6.6</td>
</tr>
<tr>
<td>61.4</td>
<td>1.6</td>
<td>8.2</td>
<td>5.9</td>
</tr>
<tr>
<td>65.2</td>
<td>0.7</td>
<td>8.3</td>
<td>3.8</td>
</tr>
<tr>
<td>68.5</td>
<td>1.9</td>
<td>8.4</td>
<td>4.9</td>
</tr>
</tbody>
</table>

The recombination of odd hydrogen proceeds through the reactions HO$_2$ + OH → H$_2$O + O$_2$ and H + HO$_2$ → H$_2$ + O$_2$, neither of whose rate coefficients is accurately known. For the former, low pressure studies (e.g. Chang and Kaufman 1978; Keyser 1981) have reported values between 2 × 10$^{-11}$ and 6.5 × 10$^{-11}$ cm$^3$ s$^{-1}$ while studies at atmospheric pressure (e.g. Hochandel et al. 1980; de More 1979) suggest a value in excess of 1.0 × 10$^{-10}$ cm$^3$ s$^{-1}$. Experiments conducted by Burrows et al. (1981) revealed a range of values between 4 × 10$^{-11}$ and 10 × 10$^{-11}$ cm$^3$ s$^{-1}$ obtained under different conditions, but the authors were not able to elucidate the source of the variation. Recent compilations of rate coefficients (e.g. WMO 1981) have suggested a value near 8 × 10$^{-11}$ cm$^3$ s$^{-1}$ for $k_{13}$, together with a factor of 2 uncertainty, and a sensitivity experiment was conducted with the original model value of 5.1 × 10$^{-11}$ increased to 1.0 × 10$^{-10}$ cm$^3$ s$^{-1}$. The resulting perturbations in [O$_3$] are shown in Fig. 11; during daytime below 60 km they are near 20%, as would be expected from equilibrium considerations (Eq. (5)). However, even at these levels a pronounced diurnal variation in the perturbation is evident, which becomes very pronounced indeed near 68 km where the fast odd hydrogen depletion rate allows far more odd oxygen to persist after dusk.

The reaction H + HO$_2$ → H$_2$ + O$_2$ plays a similar role to HO$_2$ + OH → H$_2$O + O$_2$, becoming increasingly important above 65 km where [H] ≫ [OH] and [HO$_2$]. H and HO$_2$ are also thought to react in two other ways, yielding OH + OH or H$_2$O + O, and
the only measurements of the branching ratio so far reported have been those of Hack et al. (1978) and Sridharan et al. (1982). Hack et al. proposed a rate coefficient of $1.4 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ for $\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$, but with an uncertainty estimated by Hampson (1980) to be a factor of 2.5. Sridharan et al. suggested a smaller value, in the range $3.3 - 2.9 \times 10^{-12} \text{cm}^3 \text{s}^{-1}$. Version A of the model did not contain this reaction, and a calculation including Hack et al.'s value for the rate coefficient produced ozone increases similar in shape to Fig. 11 but amounting to less than 3% below 60 km, 7% at 61 km, 19% at 65 km and 55% at 68 km (nighttime values). The present poor understanding of odd hydrogen recombination reactions is a very significant constraint on the accuracy of mesospheric ozone calculations.

Below 60 km, the response of $[\text{O}_3]$ to changes in $k_8$, $k_9$, $k_{10}$ and $k_{17}$ followed the prediction of Eq. (5)—it was largely insensitive to the reactions involving H and varied as the inverse cube root of $(k_8 k_{10})$. Of these two, the less accurately known is $k_{10}$, with reported values between $3.5 \times 10^{-11}$ (Hack et al. 1979) and $6.1 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ (Keyser 1982) at 298 K, corresponding to an uncertainty of $\sim 30\%$ in $[\text{O}_3]$. Above 60 km, atomic hydrogen influences odd oxygen concentrations as explained in sub-section 5(a), and changes to $k_9$ and $k_{17}$ were seen to have significant effects on $[\text{O}_3]$ around midday. However, the uncertainty in $[\text{O}_3]$ arising from this source is not nearly as great at these heights as that from the odd hydrogen recombination reactions discussed above.

(f) Sensitivity to odd nitrogen and odd chlorine

Version A of the model contained about 15 p.p.b.v. of $\text{NO}_x$ ($\text{NO} + \text{NO}_2$) near the stratopause, in good agreement with the observations of this quantity summarized in WMO (1981). The total chlorine concentration, however, was about one third of the average value quoted by the same source (although not falling outside the wide spread of observations of chlorine compounds). An assessment of the sensitivity of $[\text{O}_3]$ to these minor constituent concentrations was obtained by successively halving the amount of $\text{NO}_x$ and $\text{ClO}_x$ in the model—giving a good indication of the influence of the former but rather underestimating that of the latter.

As expected, no significant changes in $[\text{O}_3]$ ensued at 54 km and above, where odd hydrogen compounds are completely dominant. At 46 and 50 km, the perturbation to
[O₃] was greatest in the early morning – corresponding to the time when odd hydrogen compounds are least effective in destroying odd oxygen. With [NO₂] halved, [O₃] increased by 7% at 46 km and 2% at 50 km (the corresponding increases in mid-afternoon were 4% and 1%). Halving ClO₂ produced a 3% ozone increase at 46 km and a 1% increase at 50 km, the time of greatest effect being somewhat later than for NOₓ because of the time needed to release Cl and ClO from their chlorine nitrate reservoir (NO is immediately available at dawn from the photolysis of NO₂). A more lengthy discussion of the effect of chlorine compounds on the diurnal variation of upper stratospheric ozone may be found in Pallister and Tuck (1983).

(g) Uncertainties in model predictions of ozone concentration

The results of this section show that uncertainties in the ozone calculations were dominated by uncertainties in the water vapour profile and the rate coefficients $k_2$, $k_{13}$, $k_{15}$ and $k_{10}$. Below 60 km, where the effects of independent perturbations may be combined linearly, uncertainty in the calculations can be estimated as a factor of two. Above 60 km, however, such an approach is not valid, and uncertainty in the calculations increases (as well as varying with time of day). For this reason, comparison of theory with observations is best conducted by attempting to choose a set of model parameters which allows an acceptable fit with the observations.

6. COMPARISON OF THEORY WITH OBSERVATION

It is clear from the results presented in the previous section that the uncertainty in model input parameters allows a large number of degrees of freedom when attempting to match model predictions to observed ozone profiles. One cannot therefore state that the observations are compatible solely with one particular model configuration. Nevertheless, in order to show that current theory is not in conflict with observations it is sufficient to demonstrate that one set of physically acceptable model parameters can be found which allows an adequate match to the observations. Such was the aim of the work described in this section, and attention was therefore focussed on those parameters which cause the greatest uncertainty in ozone calculations: the water vapour profile and the rate coefficients $k_2$, $k_{13}$ and $k_{15}$.

The first step in this exercise was to calculate, by the method of section 3, the geometric heights of the model pressure surfaces corresponding to each observation, thus allowing a direct comparison between predicted and observed ozone number densities. It is worth emphasizing at this point that the small scale height (4 km) of mesospheric ozone allows little tolerance in the positioning of pressure surfaces, making accurate coincident temperature profiles, such as were derived from the SAMS and SSU instruments, absolutely essential for this kind of comparison. The ozone number densities corresponding to each model level are shown in Table 5, where the dawn values are those retrieved using non-uniform paths as described in section 2.

<table>
<thead>
<tr>
<th>Model pressure level (mb)</th>
<th>Approximate geometric height (km)</th>
<th>Ozone number density ($10^{19}$ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>night</td>
<td>dawn</td>
</tr>
<tr>
<td>1.17</td>
<td>46.5</td>
<td>126 ($±5$)</td>
</tr>
<tr>
<td>0.710</td>
<td>50.3</td>
<td>59.6 ($±1.2$)</td>
</tr>
<tr>
<td>0.431</td>
<td>53.9</td>
<td>28.3 ($±1.4$)</td>
</tr>
<tr>
<td>0.261</td>
<td>57.6</td>
<td>14.1 ($±0.6$)</td>
</tr>
<tr>
<td>0.158</td>
<td>61.3</td>
<td>7.2 ($±0.4$)</td>
</tr>
<tr>
<td>0.096</td>
<td>64.8</td>
<td>4.9 ($±0.4$)</td>
</tr>
<tr>
<td>0.0583</td>
<td>68.2</td>
<td>2.78 ($±0.13$)</td>
</tr>
</tbody>
</table>

Note: Errors quoted are 1σ random uncertainty limits.
These ozone concentrations were initially compared with the predictions of model version B containing 4 p.p.m.v. of water vapour at all levels. Several discrepancies were noted, the most important being that the predicted concentrations were too low and the night/day ratios too high above 60 km. The results of the sensitivity analysis were then used to adjust the model parameters until a satisfactory agreement with observations was attained. This required the following changes to be made simultaneously:

(i) a water vapour profile consisting of 5 p.p.m.v. at 46 km, 3 p.p.m.v. at 65 km, 2 p.p.m.v. at 54, 57-5 and 61-3 km, 3 p.p.m.v. at 65 km and 2 p.p.m.v. at 68 km;
(ii) an increase in the temperature coefficient, \( n \), of \( k_2 \) from 2-0 to 2-5 (\( k_2 = 6.2 \times 10^{-34} (300/T)^2 \text{cm}^6 \text{s}^{-1} \));
(iii) a reduction in \( k_{13} \) from \( 5.1 \times 10^{-11} \) to \( 4.0 \times 10^{-11} \text{cm}^3 \text{s}^{-1} \);
(iv) setting \( k_{15} \) to a value of \( 5 \times 10^{-12} \text{cm}^3 \text{s}^{-1} \).

The residual differences between model and measurements are summarized in Table 6; the model run in each case used the temperature profile relevant to that observation (section 3). Bearing in mind the uncertainty in the observations, the agreement is very good, with a discrepancy of less than 5% between the model and the 1σ error limit of the observations in nearly every case. The agreement is worst where the observations are most prone to systematic error – at the bottom of the nighttime profile and near 68 km on the dawn profile (Fig. 3).

A purely photochemical model such as that used here cannot hope to represent all the physical processes affecting mesospheric ozone, nor can it allow for such dynamically controlled factors as horizontal inhomogeneities in the water vapour distribution. In view of these limitations there is little value in endeavouring to remove the residual differences of Table 6 by fine-tuning the model, and the results of this section may be accepted as a demonstration that a set of model parameters can be chosen which allows agreement with the observations. Whether these parameters are physically acceptable, thus permitting the conclusion to be drawn that photochemical theory and experiment are in agreement, will be discussed in the following section.

### TABLE 6: Deviation of Calculated Values from Observations

<table>
<thead>
<tr>
<th>Height (approx) (km)</th>
<th>Percentage deviation at night</th>
<th>Percentage deviation at dawn</th>
<th>Percentage deviation at 0930h</th>
</tr>
</thead>
<tbody>
<tr>
<td>46-5</td>
<td>-10.0</td>
<td>-1.5</td>
<td>5.0</td>
</tr>
<tr>
<td>50.3</td>
<td>-10.0</td>
<td>-1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>53.9</td>
<td>-0.7</td>
<td>0.8</td>
<td>4.8</td>
</tr>
<tr>
<td>57.6</td>
<td>-3.0</td>
<td>-3.8</td>
<td>2.1</td>
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<tr>
<td>61.3</td>
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<td>-4.1</td>
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<tr>
<td>64.8</td>
<td>-1.2</td>
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<td>-3.1</td>
</tr>
<tr>
<td>68.2</td>
<td>5.0</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

7. Implications of Match Between Theory and Observation

The greatest obstacle in the way of a precise simulation of mesospheric photochemistry is the sparse and often contradictory information on water vapour concentrations. No measurements of this quantity were made in conjunction with the present experiment, and a decision on whether to accept the profile deduced above had to rely on published data. These may be divided into two broad categories: the first showing near-constant mixing ratios between 50 and 70 km in the range 1-3–7-0 p.p.m.v. (Rogers et al. 1977; Allen et al. 1981; Deguchi and Muhleman 1982; Drummond and Mutlow 1981); the second showing a very moist layer in excess of 10 p.p.m.v. at 65 km (Radford et al. 1977; Thacker et al. 1981; Gibbins et al. 1982). There is no known chemical source for \( \text{H}_2\text{O} \) in the mid-
mesosphere (indeed, this part of the atmosphere is a sink for it), and H₂O concentrations should therefore be determined by vertical transport from the stratosphere, where its mixing ratio is believed to be less than 10 p.p.m.v. (WMO 1981) – lending theoretical support to the first category. All the observations in the second category have been obtained by the same technique – ground-based measurements of atmospheric emission at 22.2 GHz. Both Thacker et al. and Gibbins et al. report considerable variability in their measurements, with some 'anomalous profiles' consistent with a uniformly dry mesosphere, and signal fluctuations corresponding to variations in water vapour mixing ratio by factors of 2 or 3 over a period of a few hours. This would suggest large horizontal as well as vertical gradients in the water vapour mixing ratio, and conflicts with the observations of Deguchi and Muhleman (1982) who also observed the 22.2 GHz line, but as an absorption feature in sunlight rather than in emission.

There is no doubt that the present ozone observations could not be simulated by a model containing a water vapour profile of the second category. The profile used in section 6 was also on the dry side of the observations falling into the first category, which generally cluster around 4–5 p.p.m.v. However, it did not lie outside the generous error limits ascribed to these observations, and could not therefore be considered incompatible with them. More importantly, the climatology of mesospheric water vapour is completely unknown at present, and it is possible that observations like those of Allen et al. (1981) obtained over California in summer are not representative of autumn conditions further north. In this respect it is worth noting that the lowest mixing ratios (1.3–5.5 p.p.m.v.) reported in the first category were obtained by Rogers et al. (1977) from Point Barrow, Alaska, in March.

The water vapour profile used in the model simulation showed a fall in the mixing ratio near the stratopause, from 5 p.p.m.v. at 46 km to 2 p.p.m.v. at 54 km. An unambiguous choice was not possible at 46 km, since the ozone concentration there is sensitive to the presence of odd nitrogen and odd chlorine species, neither of which were measured as part of this experiment. In addition, the poor vertical resolution (about 10 km) of the SAMS profiles would tend to cause an underestimate of the stratopause temperature (as was evident on comparison with the Skua profile), thus causing an excessive amount of water vapour to be required to simulate the ozone observations. The probability remains, however, that a gradient in water vapour mixing ratio was present near the stratopause.

To postulate a reason for such a gradient the mechanism governing the water distribution must be considered.

Water vapour is destroyed in the upper mesosphere both by direct photodissociation at the Lyman α wavelength and by recombination of its dissociation products through reaction 15. Below 70 km, however, its photochemical lifetime is greater than one year (Allen et al. 1981) and its distribution is governed by transport processes, predominantly vertical turbulent transfer. The efficiency of this transfer is greatly enhanced by the breaking of gravity waves, which is believed to occur in the mesosphere. Indeed, Lindzen (1981) has considered the propagation of gravity waves and concludes that their level of breaking lies near 70 km in summer but descends to 50 km in winter. On considering also that gravity waves are believed to originate from non-linear processes in tropospheric frontal systems (Kersley and Rees 1982), which are themselves more prevalent and more energetic in winter, the possibility emerges of a rapid increase in vertical turbulent transfer near the winter stratopause. Thus water vapour reaching the lower mesosphere could rapidly be transported to the photochemical sink region above 70 km. Under such conditions, a fall in the water vapour mixing ratio near the stratopause would not be unreasonable, and the model profile cannot be rejected on this count. The profile also shows a small increase in water vapour at 65 km, but because of the greater uncertainty surrounding both theory and observations at this height and above, particular significance should not be attached to this feature.

Because of the uncertainties in the other model parameters the profile derived here cannot be considered a definitive description of mesospheric water vapour. Indeed, recent
work has suggested that the value of $k_{10}$ used in the model should be doubled (Keyser 1982) and that the O$_2$ absorption cross-sections in the Herzberg continuum were too high (Frederick and Mentall 1982). Both these changes would require even less water vapour in the model in order to obtain agreement with the ozone observations.

The only way in which agreement could be obtained with significantly higher water vapour contents than were deduced here would be to increase the rate coefficients for odd hydrogen recombination, those used in the model simulation being near the lower limit currently recommended (WMO 1981; Hampson 1980). However, the diurnal variation of ozone above 60 km is so sensitive to these rate coefficients (Fig. 11) that it is difficult to see how the observations could be simulated with the higher values reported for $k_{13}$, given that the night/day ratio in [O$_3$] (0200 h/0930 h) is relatively insensitive to the water vapour concentration at these altitudes (Fig. 6). Indeed, satisfactory agreement with observation also demanded that the temperature dependence of $k_2$ be increased to its upper limit. It is fair to conclude, then, that the present model simulation requires values of $k_{13}$ which are in accord with laboratory determinations obtained at low pressures. Similar conclusions regarding $k_{15}$ cannot be drawn since this reaction only becomes influential above 65 km, where no daytime observations were obtained and poor agreement was found between the model and dawn observations. Nevertheless, a very fast rate coefficient for this reaction would increase the night/day ozone ratio at 65 km and make it much more difficult to reconcile theory with observation. It is worth noting also that the value of $5 \times 10^{-12}$ cm$^3$ s$^{-1}$ used here for $k_{15}$ is in excellent agreement with the recent laboratory measurement of Sridharan et al. (1982).

8. Conclusions

The present study has shown that a relatively simple photochemical model is capable of reproducing observations of the diurnal variation of mesospheric ozone. In doing so, low values for both the water vapour mixing ratio and the rate coefficients $k_{13}$ and $k_{15}$ were found to be necessary. In neither case, however, could the values used be considered to lie outside the range of current recommendations, and it can therefore be stated that, within these limitations, theory and observation could be brought into agreement.

Sensitivity studies emphasized that accurate photochemical calculations cannot be made with the data currently available on mesospheric chemistry, especially above 60 km where the longer chemical time constants introduce complex variations in constituent concentrations. In order to conduct a more stringent test of theory more accurate values for the rate coefficients governing odd hydrogen recombination must be obtained, as well as accurate water vapour profiles, preferably obtained coincidentally with ozone and temperature observations. Indeed, coincident temperature information such as is available from the present generation of satellite instruments must form an essential element of any attempt to match photochemical theory with observations of minor constituents.

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