Planet. Space Sci., Vol. 38, No. 4, pp. 529–537, 1990
Printed in Great Britain.

0032-0633/90 $3.00+0.00
Pergamon Press plc

SME OBSERVATIONS OF $O_2(^1\Delta_g)$ NIGHTGLOW: AN ASSESSMENT OF THE CHEMICAL PRODUCTION MECHANISMS

COLIN D. HOWELL, DIANE V. MICHELANGELI, MARK ALLEN† and YUK L. YUNG
Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, U.S.A.

and

RONALD J. THOMAS
Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309, U.S.A.

(*Received* 5 *October* 1989)

Abstract—*Solar Mesosphere Explorer* (*SME*) observations of the 3 a.m. 1.27 μm nightglow at 45°N latitude, averaged over the period 10–31 July 1984, are reported. From the deduced volume emission rates, we derive the $O_2(a^1\Delta_g)$ night-time production rates for the 80–100 km altitude range. Utilizing the mean *SME*-acquired 3 p.m. ozone profile for the same latitude and time period and an updated photochemical model, we determine night-time O, O_3, H, OH, HO_2, and H_2O_2 profiles. These are used in calculating the rates of reactions which are sufficiently exothermic to produce $O_2(^1\Delta)$ or excited states of OH or HO_2, which could transfer their energy to O_2 to form $O_2(^1\Delta)$. Of these reactions, most have rates that are quite small compared with the observed night-time $O_2(^1\Delta)$ production rate. For several others, laboratory experiments have found $O_2(^1\Delta)$ yields which are insufficient for simulating the observed $O_2(^1\Delta)$. Using yields of $O_2(^1\Delta)$ based on published laboratory and observational studies, we find that the sum of two reaction sequences can approximate the *SME* measurements: (1) O+O+M and (2) H+O_3 followed by OH*+O_2.

INTRODUCTION

First identified as a phenomenon of the terrestrial atmosphere by Yntema (1909), airglow at visible and infrared wavelengths is readily observed, but the processes leading to the emission are not fully understood. In this paper, we shall examine the chemical source of the O_2 (Infrared Atmospheric System: $a^1\Delta_g \rightarrow X^3\Sigma_g^-$) nightglow at 1.27 μm.

Measurements of the 1.27 μm nightglow have been reported most recently by McDade *et al.* (1987a) and Lopez-Moreno *et al.* (1988). Both sets of airglow observations were acquired before local midnight and, consequently, contained an unknown mixture of emission resulting from night-time chemistry and from $O_2(^1\Delta)$ produced during the day by ozone photolysis in the Hartley bands (220–310 nm) (Vallance Jones and Gattinger, 1963). The *Solar Mesosphere Explorer* (*SME*) satellite measurements of the 1.27 μm emission are for a local time of ~ 3 a.m., sufficiently long after sunset to reveal the intrinsic emission produced at night by chemical reactions. The complementary *SME* daytime (~ 3 p.m.) airglow measurements, in combination with a photochemical model, allow the inference of key odd-oxygen and odd-hydrogen species profiles. Thus, the *SME* data provide a unique opportunity to explore potential mechanisms for the night-time production of $O_2(^1\Delta)$.

SME MEASUREMENTS OF NIGHT-TIME 1.27 μm EMISSION

A typical *SME* 24-h observing schedule included data acquisition during the daylight portion of five orbits and the night-time part of one orbit. The Near Infrared Spectrometer (NIRS) and the analysis of the daytime 1.27 μm radiances are described in Thomas *et al.* (1984). Interesting night-time observations are the $O_2(^1\Delta)$ emission at 1.27 μm discussed in this paper and the OH(7–5) Meinel band emission analyzed by Le Texier *et al.* (1987, 1989).

The NIRS scans the limb vertically as the *SME* satellite spins. A telescope defines a field-of-view on the limb, 3.3 km high and 33 km wide. The observed limb radiance profile can be compared directly to a model calculation, or inverted to yield a volume emis-

† Also, Earth and Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, U.S.A.

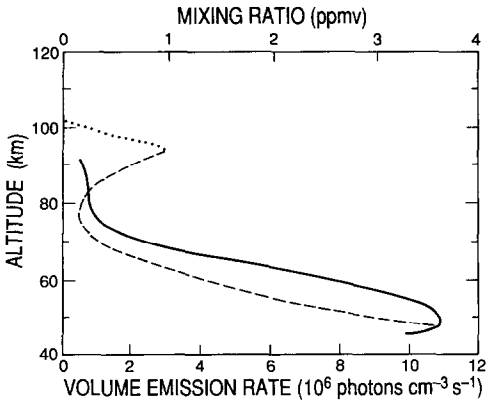

FIG. 1. *SME* DAYTIME (~ 3 p.m.) 1.27 μm VOLUME EMISSION RATES (SOLID LINE) AND THE DERIVED O_3 PROFILE (DASHED LINE) FOR 45°N LATITUDE.
The unit for the ozone mixing ratio is parts per million by volume. The limb radiances, from which these results were derived, are averages of all data in the period 10–31 July 1984. The extrapolation of the ozone profile to higher altitudes, as discussed in the text, is indicated by the dotted portion of the curve.

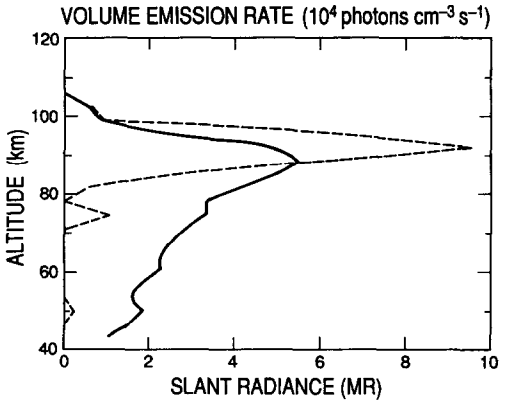

FIG. 2. *SME* NIGHT-TIME (~ 3 a.m.) 1.27 μm LIMB RADIANCES (SOLID LINE) AND THE RETRIEVED VOLUME EMISSION RATES (DASHED LINE) FOR 45°N LATITUDE, 10–31 JULY 1984.

sion rate profile. Since the instrument sensitivity was optimized for the daytime measurements, the signal-to-noise ratio at night is low. In a single scan set (six adjacent scans taken in 1 min), the noise is about 1 MR (1 MR = 10^{12} photons cm^{-2} s^{-1}), compared with a peak signal of 5 MR. When 32 scan sets have been averaged together, the noise is reduced to about 0.2 MR. Since the spectrometer is detector-noise limited, the noise is constant with altitude and independent of signal.

Another source of error arises from the manner in which the altitude of each observation was determined. For the daylight portions of an orbit, the altitude is derived using the Rayleigh scattering profiles acquired with the *SME* ultraviolet spectrometer and has an uncertainty of 1 km. The altitude scale for the night-time measurements was determined from spacecraft attitude and has an uncertainty of several kilometers. The uncertainty in assignment of altitude will tend to smear the averaged nightglow profile, decreasing the altitude resolution to ~ 5 km.

For the purposes of this paper, we averaged together the available *SME* NIRS radiance data near 45°N latitude for the period 10–31 July 1984. We display, in Fig. 1, the daytime (~ 3 p.m.) 1.27 μm volume emission rates. Above 80 km, the O_3 concentration is directly proportional to the emission rate, while below 70 km it is the O_3 mixing ratio that is directly proportional to the emission rate because collisional quenching of $O_2(^1\Delta)$ becomes important.

The daytime O_3 profile retrieved from the volume emission rates is shown in Fig. 1 and will be utilized later in this paper to infer night-time profiles of key chemical species. In Fig. 2, we display the averaged night-time (~ 3 a.m.) 1.27 μm limb radiances and the volume emission rates derived from these data. The volume emission rate peaks near 92 km and is ~ 10^5 photons cm^{-3} s^{-1}. This is 20% of the daytime value at the same altitude (cf. Fig. 1). Above the altitude of peak emission, the uncertainty in the retrieved volume emission rate is ~ 25%; below the peak the uncertainty is $\pm 2 \times 10^4$ photons cm^{-3} s^{-1}. The objective of the rest of this paper is the identification of the chemical sources of the night-time $O_2(^1\Delta)$ 1.27 μm emission.

POTENTIAL NIGHT-TIME CHEMICAL SOURCES OF $O_2(^1\Delta)$

The daytime 1.27 μm volume emission rate is five times larger than the night-time value near the night-time peak at 92 km. Although the radiative lifetime of $O_2(^1\Delta)$ is long (1.06 h; Badger *et al.*, 1965), at 3 a.m. (~ 6.5 h after sunset at the mesopause) the remnant dayglow is < 0.2% of the 3 p.m. value and only ~ 1% of the 92 km nightglow. Since photolysis of O_3 is the dominant source of daytime $O_2(^1\Delta)$ and O_3 abundances near 90 km are relatively constant during the daylight period (see Allen *et al.*, 1984), we have assumed that the observed 3 p.m. volume emission rates are constant until sunset. Near 80 km the remnant dayglow is a larger fraction of the 3 a.m. nightglow, but it is only 3% of the nightglow and therefore still unimportant. Consequently, we assume that all of the observed nightglow is the result of chemical

reactions occurring near 3 a.m. at the altitudes of the observed emission.

The lowest ro-vibrational level in the $O_2(a^1\Delta_g)$ state is 0.98 eV above the ground ro-vibrational level of the $O_2(X^3\Sigma_g^-)$ state. A number of the chemical reactions involving hydrogen- and oxygen-containing species that are likely to occur near the night-time mesopause have O_2 as a product and are exothermic by more than 1 eV. Utilizing the gas phase enthalpy data in DeMore *et al.* (1987), we have identified these reactions, which energetically could produce $O_2(^1\Delta)$ or higher excited states of O_2 [which through subsequent collision with O_2 generate $O_2(^1\Delta)$]:

$$O+O+M \rightarrow O_2+M \quad (1)$$

$$O+O_2+O_2 \rightarrow O_3+O_2 \quad (2)$$

$$O+O_3 \rightarrow 2O_2 \quad (3)$$

$$O+HO_2 \rightarrow OH+O_2 \quad (4)$$

$$H+O_3 \rightarrow OH+O_2 \quad (5)$$

$$H+HO_2 \rightarrow H_2+O_2 \quad (6)$$

$$OH+O_3 \rightarrow HO_2+O_2 \quad (7)$$

$$OH+HO_2 \rightarrow H_2O+O_2 \quad (8)$$

$$HO_2+O_3 \rightarrow OH+2O_2 \quad (9)$$

$$HO_2+HO_2 \rightarrow H_2O_2+O_2 \quad (10)$$

$$HO_2+HO_2+M \rightarrow H_2O_2+O_2+M. \quad (11)$$

In many of the above reactions, product species other than O_2 could be in an excited state with more than 1 eV of energy and through subsequent collisions transfer energy to form $O_2(^1\Delta)$. The $O_2(^1\Delta)$ may be created in the reaction between atomic O and product OH* ($v \geqslant 1$):

$$O+OH^* \rightarrow O_2+H. \quad (12)$$

In addition, product OH* in vibrational levels $v \geqslant 3$ or electronically-excited product HO_2^* may be quenched by collisions with the ambient O_2 by a mechanism resulting in the formation of $O_2(^1\Delta)$. Product OH* is energetically possible in reactions (4), (5), and (9) and in

$$H+HO_2 \rightarrow 2OH. \quad (13)$$

Product HO_2^* is energetically possible in reaction (7) and in

$$H+O_2+M \rightarrow HO_2+M \quad (14)$$

$$OH+H_2O_2 \rightarrow H_2O+HO_2. \quad (15)$$

To evaluate the possible contributions of reactions (1)–(15) to the observed 1.27 μm emission, we need to estimate their reaction rates at 3 a.m. This in turn requires knowledge of the relevant species abundances at the epoch and location of the *SME* observations. In the next section we discuss our derivation of the 3 a.m. O, O_3, H, OH, HO_2, and H_2O_2 profiles.

CALCULATION OF NIGHT-TIME PROFILES OF KEY OXYGEN- AND HYDROGEN-CONTAINING SPECIES

The Caltech/JPL one-dimensional time-dependent photochemical model (described in Allen *et al.*, 1981, 1984; update: preprint, 1989) was used, along with the mean daytime ($\sim$ 15:00 L.T.) O_3 profile corresponding to the nightglow measurements being analyzed, to calculate the concentrations of the important oxygen- and hydrogen-containing species in the lower thermosphere ($\gtrsim$ 80 km). The atmospheric parameters of temperature and pressure were taken from values in Houghton (1977) for June at 40°N latitude. The altitude scale, in nearly 2 km intervals between 50 and 105 km, was calculated assuming hydrostatic equilibrium. We ran the photochemical model through several diurnal cycles (with the radiation field varying as appropriate for a spherical atmosphere) until species abundances separated by 24 h agreed to within a few percent. This standard model yields 3 p.m. O_3 abundances significantly smaller than the *SME* measured distribution below 80 km, with the reverse result at higher altitudes. This is discussed in detail by Clancy *et al.* (1987). To improve the model simulation of the *SME* profile, we reduced the prescribed eddy diffusion profile (see discussion in Strobel *et al.*, 1987); increased O_2 photocross-sections by 40%, decreased O_3 photocross-sections by 10%, increased the reaction rate constant for $OH+HO_2$ to the upper limits defined by the uncertainties reported by Keyser (1988) (see discussion in Clancy *et al.*, 1987 and Froidevaux *et al.*, 1989); and set the lower boundary condition (50 km) for H_2O to 6 ppmv. An improvement in the model fit to observations resulted between 50 and 80 km, but above 80 km the calculated values are still higher than the *SME* data. We feel, however, that above 80 km the relative diurnal variation of species abundances and the profiles of hydrogen-containing species as computed by the modified model are reasonable for the epoch of the *SME* observations. Therefore, the 3 a.m. abundances of H, OH, HO_2, and H_2O_2 were taken directly from the output of the modified photochemical model. These profiles are displayed in Fig. 3a. At 90 km, where atomic H is long-lived, the calculated atomic H concentration is in good agreement with the measurements of Sharp and Kita (1987).

Since the *SME* O_3 profile above 80 km is not repro-

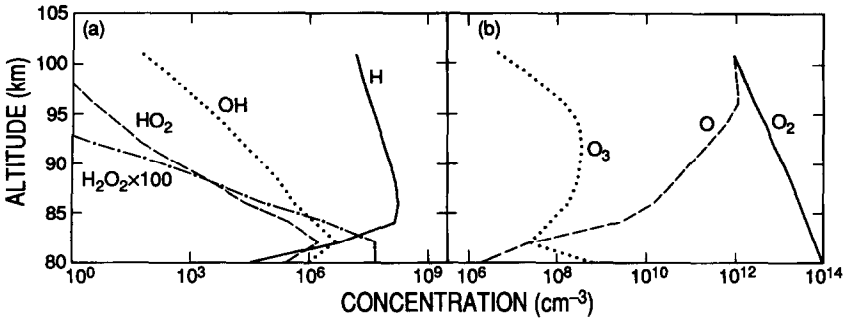

FIG. 3. SPECIES CONCENTRATIONS DEDUCED FOR 3 a.m. AS DESCRIBED IN THE TEXT: (a) H, OH, HO_2, AND H_2O_2, (b) O, O_2, AND O_3.

duced in the model calculations, we work directly from the O_3 observations to determine the appropriate night-time atomic O and O_3 distributions; because the nightglow extends over the range 80–100 km (Fig. 2) and the retrieved daytime O_3 profile extends only up to $\sim$ 93 km (Fig. 1), we extrapolated the daytime density profile to 100 km using the variation with altitude calculated by the modified model (the extrapolation is displayed in Fig. 1 in units of mixing ratio). The daytime atomic O profile was derived from the daytime *SME* O_3 by utilizing the daylight steady-state relationship between atomic O and O_3 (Allen *et al.*, 1984),

$$[O] = \frac{(J_{O_3} + k_5[H])[O_3]}{(k_2[O_2] + k_{N_2}[N_2])[O_2]}, \qquad (16)$$

where J_{O_3} is the O_3 photodissociation rate constant and k_{N_2} is the O_3 recombination rate constant for N_2 as a third body. The square brackets indicate volume densities. To obtain the 3 a.m. atomic O profile, we scaled the 3 p.m. atomic O abundances calculated from (16) by the 3 a.m./3 p.m. atomic O abundance ratio computed by the modified photochemical model. In turn, from these atomic O values, the night-time O_3 distribution was calculated from the night-time version of the photochemical steady-state expression of equation (1) in Allen *et al.* (1984):

$$[O_3] = \frac{[O][O_2](k_2[O_2] + k_{N_2}[N_2])}{k_3[O] + k_5[H]}. \qquad (17)$$

The 3 a.m. atomic O and O_3 concentrations, along with the assumed O_2 profile, are shown in Fig. 3b. The atomic O profile is similar to the summer midlatitude profile from *Aladdin* 74 (Trinks *et al.*, 1978), the differences being within the range of natural fluctuations of the atmosphere. As discussed in Allen (1986), the above simple steady-state photochemical relationships between atomic O and O_3 do not reproduce observed $[O]/[O_3]$ values in the lower thermosphere. However the discrepancy is most severe above 100 km. Moreover, our use of the photochemical relationship twice, starting with 3 p.m. O_3 and ending with 3 a.m. O_3, should minimize the error in the 3 a.m. O_3 profile due to possible uncertainties in thermospheric odd-oxygen chemistry. The approach outlined in this section for deriving the night-time species abundances, necessary for later calculations of the potential chemical sources of late night $O_2(^1\Delta)$, attempts to extract as much information as possible from the available 3 p.m. *SME* O_3 measurements.

SIMULATION OF NIGHT-TIME $O_2(^1\Delta)$ PRODUCTION

The decay of $O_2(^1\Delta)$ is the result of (1) the spontaneous emission of a 1.27 μm photon, with a rate constant k_r ($= 2.58 \times 10^{-4}$ s^{-1}) or (2) quenching upon collision with O_2, with a rate constant k_c [$= 2.22 \times 10^{-18} (T/300)^{0.78}$ cm^3 s^{-1}] (see Thomas *et al.*, 1984, and references therein). Quenching by collision with N_2 is negligible. The total $O_2(^1\Delta)$ loss rate L at 3 a.m. can be deduced from the observed volume emission rate V ($= k_r[O_2(^1\Delta)]$) through the expression

$$L = \left(1 + \frac{k_c[O_2]}{k_r}\right) V. \qquad (18)$$

Since the remnant of the daytime $O_2(^1\Delta)$ is negligible, we shall assume that the $O_2(^1\Delta)$ abundance is in steady-state and the total $O_2(^1\Delta)$ production rate P is equal to L.

Upon comparing the altitude-varying values of P which we have derived from the volume emission rate and the rates of reactions potentially producing $O_2(^1\Delta)$ directly or indirectly, we find that many of these reactions cannot make significant contributions to the observed nightglow (reactions rates $\lesssim$ 10% of P at the corresponding altitude), even when a 100%

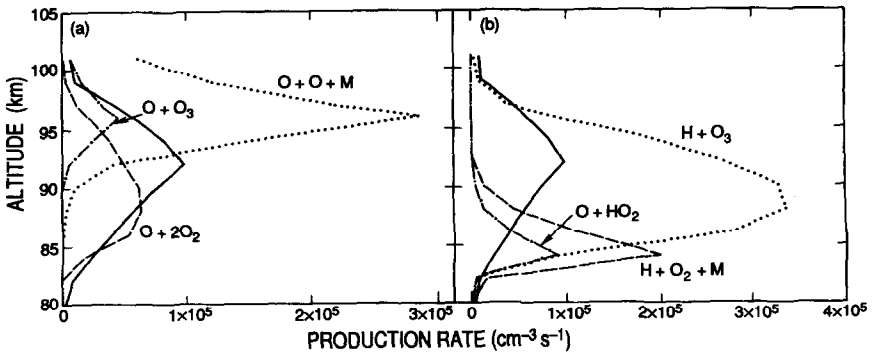

FIG. 4. CALCULATED RATES OF REACTIONS POTENTIALLY YIELDING $O_2(^1\Delta)$ EITHER DIRECTLY OR INDIRECTLY COMPARED WITH THE COMPUTED PRODUCTION RATE OF $O_2(^1\Delta)$ (SOLID LINE).
Calculations are for 3 a.m. (a) $O+O+M$, $O+2O_2$ and $O+O_3$. (b) $H+O_2+M$, $H+O_3$, and $O+HO_2$.

yield of $O_2(^1\Delta)$ is assumed. Reactions (6)–(11), (13), and (15) are in this category and will not be considered further. The potential importance of reactions (1)–(5) and (14) for producing the nightglow is illustrated in Fig. 4 in which rates of these reactions are compared with our calculated $O_2(^1\Delta)$ production profile (P). We note from this figure that the rates of (4) and (14) peak near 84 km and therefore could only effectively contribute to the nightglow in its low altitude tail; as such, these two reactions are not useful candidates for the major portion of the $O_2(^1\Delta)$ production rate. One interesting possibility that our analysis precludes is the resonance quenching of HO_2^* by O_2 to be an important source of $O_2(^1\Delta)$.

Of the remaining reactions, several can make significant contributions to the $O_2(^1\Delta)$ production rate only if their efficiency for forming $O_2(^1\Delta)$, directly or indirectly, is nearly 100%. Unfortunately, laboratory investigations of $O_2(^1\Delta)$ yields are non-existent or incomplete for many reactions. For example, no relevant laboratory data exist for (2). However, since a product of (2) is O_3, the excess energy is expected to reside initially in O_3. Pumping of $O_2(^1\Delta)$ during the collisional quenching of excited O_3 is not thought to be highly efficient (Leu, private communication, 1988). On the other hand, some useful laboratory measurements exist for (3) and (5). Washida *et al.* (1980) find upper limits for the yield of $O_2(^1\Delta)$ in the reactions of $O+O_3$ (3), and $H+O_3$ (5), to be 6 and 0.1%, respectively, at room temperature. It therefore seems that (2), (3), and (5) can be eliminated as direct sources of $O_2(^1\Delta)$. Laboratory experiments, however, cannot preclude the possibilities of these reactions yielding $O_2(^1\Delta)$ through indirect mechanisms under atmospheric conditions, which were not simulated in the experiments.

However, (5) is the primary atmospheric source of OH*, yielding OH* in excited vibrational levels $v = 4$–9 (most recent laboratory results reported in Ohoyama *et al.*, 1985). The airglow from OH* was first reported by Meinel (1950). Reaction (12) with the plentiful atomic O might then be an effective source of the 1.27 μm nightglow. We estimate an upper limit to (12) by first calculating an upper limit to the concentration profile of OH*. Assuming OH* is in steady-state and (5) has unit efficiency for produced OH* (see for example, McDade *et al.*, 1987b), we equate the reaction rate for (5), R_5, to the collisional quenching rate for OH* ($v = 1$), with a rate constant k_{19},

$$\mathrm{OH}^*(v=1)+\mathrm{M} \rightarrow \mathrm{OH}+\mathrm{M}, \tag{19}$$

yielding

$$[\mathrm{OH}^*] = \frac{R_5}{k_{19}[\mathrm{M}]}. \tag{20}$$

In this approximation, radiative and collisional processes result in rapid redistribution to the lowest excited vibrational level, from where collisional deexcitation predominates over radiative decay (see "collisional cascade model" in McDade and Llewellyn, 1987), so that the only loss of OH* ($v \geq 1$) is by reaction (19). The resulting vertical profile of OH* densities is used in calculating the rate of (12). Adopting the values $k_{12} = 4\times10^{-11}$ cm^3 s^{-1} and $k_{19} = 8\times10^{-13}$ cm^3 s^{-1} (Llewellyn and Solheim, 1978; Llewellyn *et al.*, 1978), we find that the production of $O_2(^1\Delta)$ by (12) is equal to our calculated values of P above $\sim$ 95 km if the yield for $O_2(^1\Delta)$ is $\sim$ 22%. Reaction (12) has been suggested as a significant source of $O_2(^1\Delta)$ in several previous investigations of airglow observations, most recently, by

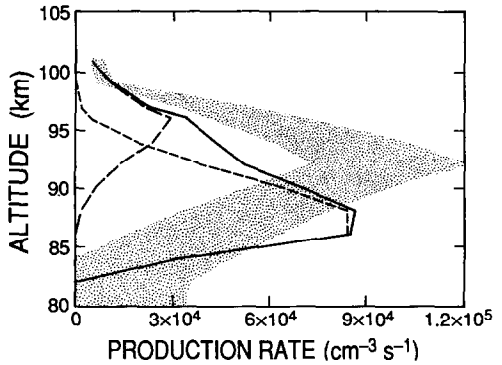

FIG. 5. THE PRODUCTION RATE OF $O_2(^1\Delta)$ DEDUCED FROM *SME* 1.27 μm NIGHTGLOW MEASUREMENTS (SHADED AREA DEFINED BY UNCERTAINTIES IN P) COMPARED WITH THE RATE FOR REACTION (1) MULTIPLIED BY $f_1(z)$ (LONG DASHED LINE) AND THE RATE FOR REACTION (5) MULTIPLIED BY $f_5(z)$ (SHORT DASHED LINE) (SEE TEXT FOR DISCUSSION OF EFFICIENCY FACTORS).
The sum of these two components, the total model production rate of $O_2(^1\Delta)$, is indicated with a solid line.

Lopez-Moreno *et al.* (1988). The $O_2(^1\Delta)$ yields in these other works were comparable to or greater than our value. However, in their recently published paper, Lunt *et al.* (1988) conclude that the yield of $O_2(^1\Delta)$ in (12) is only 2.5%, thus apparently also eliminating this channel as an important source of the nightglow measured by the *SME*.

An efficient source of $O_2(^1\Delta)$ in the laboratory is (1), the recombination of atomic O. Ali *et al.* (1986) report that the direct yield of $O_2(^1\Delta)$ is 7%, while the total yield, including indirect channels involving quenching of higher excited states of O_2, is as much as 75%. They find that the indirect yield is due to the presence of O_2, but is suppressed by atomic O. Following equation (9) of Ali *et al.* (1986), we multiply the altitude-varying rate of (1) by an efficiency factor f_1, which varies with altitude as a result of the change with altitude of the atomic O to O_2 abundance ratio:

$$f_1(z) = 0.07 + \frac{0.7}{\frac{50[O]}{[O_2]} + 1}. \qquad (21)$$

As shown in Fig. 5, the rate of $O_2(^1\Delta)$ formation thus calculated $[= f_1(z)R_1(z)]$ is comparable to the $O_2(^1\Delta)$ production rate deduced from observations above $\sim$ 97 km. Above 97 km, $f_1(z)$ is < 0.1, whereas near the peak of P near 92 km $f_1(z)$ is $\sim$ 0.6. Therefore, the rapid falloff with decreasing altitude in the production of $O_2(^1\Delta)$ due to (1) is directly the result of the rapid decrease with decreasing altitude of the atomic O abundance (see Fig. 3b). Our conclusion that the yield of $O_2(^1\Delta)$ in (1) is relatively small at the altitudes where (1) can contribute to $O_2(^1\Delta)$ formation is in disagreement with the analysis by McDade *et al.* (1987a) of their observation which suggests $O_2(^1\Delta)$ yields $\geqslant 50\%$ and the analysis by Lopez-Moreno *et al.* (1988) of their own observations which suggests a yield of 75%. On the other hand, Bates (1988) deduces from available measurements an effective yield of only 28%. Clearly, the necessary yield for $O_2(^1\Delta)$ production derived from model analyses of 1.27 μm measurements will vary depending on the accuracy of the atomic O profile observed simultaneously or deduced in a variety of ways. How close the temperature profile utilized in the calculations is to the actual temperatures, which often have not been measured simultaneously with the acquisition of the airglow data, will also affect the derived yield. Since Lopez-Moreno *et al.* (1988) do not know precisely the contribution to their 1.27 μm nightglow measurements from the dayglow remnant, any underestimate of the magnitude of this remnant will require an increase in the necessary $O_2(^1\Delta)$ yield in (1) to reproduce the observed nightglow.

We are still missing the source of $O_2(^1\Delta)$ production at and below the peak at 92 km. McDade and Llewellyn (1987) (also, McDade *et al.*, 1987b) conclude that the vibrational population of the observed OH* nightglow could be modeled equally well either assuming that collisional quenching of $OH^*(v)$ leads to population of OH* ($v' < v$) ("collisional cascade model") or assuming that collisional processes result in a net loss of OH* ("sudden death model"). We have shown above that the first possibility does not result in a rate of $O_2(^1\Delta)$ production via (12) that is sufficient to reproduce P. We now consider whether the second possibility of McDade and Llewellyn (1987), the "sudden death" assumption, may lead to a large rate of $O_2(^1\Delta)$ formation. The reaction

$$OH^*(v = 3\text{–}9) + O_2 \rightarrow O_2(^1\Delta) + OH \qquad (22)$$

is exothermic. The possibility of (22) being a source of $O_2(^1\Delta)$ in the upper atmosphere has been discussed by Han *et al.* (1973), Thomas *et al.* (1984), and Wayne (1984). Finlayson-Pitts and Kleindienst (1981) found that the rate constant for quenching of OH* ($v = 9$) by O_2 is 20 times larger than the rate constant for quenching by N_2. They suggest that the enhanced effectiveness of O_2 relative to N_2 might be understood as being the result of resonant energy transfer; according to these authors, $O_2(b^1\Sigma)$ could be the product, although they have no information as to which excited states of O_2 are the products. In the laboratory experiments of Lunt *et al.* (1988), (22) is not a significant source of the measured $O_2(^1\Delta)$ compared with other

reactions that were occurring simultaneously. However, their experimental conditions were not chosen to simulate thermospheric conditions and species abundances, so we do not believe that a definitive experimental test of (22) has yet been published. Interestingly, Llewellyn and Solheim (1978) found a correlation between their measurements of OH* and $O_2(^1\Delta)$ emission, as would be expected if (22) were to be the main contributor to $O_2(^1\Delta)$.

The rate-controlling step in the $O_2(^1\Delta)$ formation mechanism consisting of (5) followed by (22) is the reaction rate for (5), R_5. The altitude-dependent yield of $O_2(^1\Delta)$ for this overall sequence, f_5, reflects the competition between

$$OH^*(v \geqslant 3) + O_2 \rightarrow \text{all products other than OH}^* \tag{23}$$

and

$$OH^*(v \geqslant 3) \rightarrow OH^*(v < 3) + h\nu. \tag{24}$$

Consequently,

$$f_5 = \frac{f_{22}k_{23}[O_2]}{A_{24} + k_{23}[O_2]}, \tag{25}$$

where $k_{22} = f_{22}k_{23}$ and A_{24} is the radiative transition probability for OH* emission. From their analysis using the "sudden death model", McDade and Llewellyn (1987) derive a value for k_{23}/A_{24} of $\sim 5 \times 10^{-14}$ cm^3 for $v = 7$–9 and smaller values for $v < 7$. We have assumed here that atomic O is not an effective quencher of OH* compared with O_2 since $[O]/[O_2]$ is $\gtrsim 1$ only $\geqslant 100$ km and this ratio decreases rapidly with decreasing altitude (~ 0.01 at 90 km).

Since (5) yields OH* in the higher vibrational levels, we adopt the value for k_{23}/A_{24} appropriate for these levels and find that the profile of f_5R_5 that best matches P occurs when half of the quenching of OH* by O_2 yields $O_2(^1\Delta)$ ($f_{22} \sim 0.5$). These results are shown in Fig. 5. The total profile is similar to the observed emission, but the peak model production of $O_2(^1\Delta)$ is ~ 5 km below the apparent peak production level. Near 95 km, the model production rate is $\sim 30\%$ smaller than the range in values inferred from *SME* observations. Near 86 km, the model results are $\sim 30\%$ larger than the inferred values. As discussed earlier, the model results are quite sensitive to the species profiles shown in Fig. 3. Differences between the calculated and actual values of the important atmospheric species, such as atomic H, could easily be of the order of 30%, thus explaining the discrepancy between the model and inferred $O_2(^1\Delta)$ production rates. The reader should note that, in reaction (22), reduction of OH* by three vibrational levels is energetically sufficient to excite $O_2(^1\Delta)$ and still leave OH* in a highly vibrationally-excited state. This scenario is not explored in McDade and Llewellyn (1987) and would result in slightly different calculated production rates for $O_2(^1\Delta)$.

CONCLUSIONS

The *SME* observations of the 1.27 μm nightglow provide a unique opportunity to study the late night chemical sources of $O_2(a^1\Delta_g)$. Acquired at a local time of 3:00, more than 6 h after sunset, these data are relatively free of residual 1.27 μm dayglow. We have deduced from the nightglow measurements the mean vertical distribution of $O_2(^1\Delta)$ production for 45°N latitude in the period 10–31 July 1984. Of the reaction mechanisms that are sufficiently exothermic to produce $O_2(^1\Delta)$, we find that only direct and/or indirect production from O+O+M and production from the sequence $H + O_3 \rightarrow OH^* + O_2$, followed by $OH^* + O_2 \rightarrow OH + O_2(^1\Delta)$, have rates large enough to reproduce the inferred production rates. Altitude-dependent yields for $O_2(^1\Delta)$ in each mechanism were based on laboratory experiments and/or detailed analyses of airglow data. The total $O_2(^1\Delta)$ production rate thus calculated approximates the profile inferred from *SME* observations.

It is interesting to consider whether the chemical sources of $O_2(^1\Delta)$ at night could also be significant contributors to the daytime 1.27 μm emissions. Atomic O and H abundances above 80 km do not have much diurnal variation and O_3 is less abundant during the day than at night (Allen *et al.*, 1984). Thus, the key reactions we have identified remain constant or even decrease from night to day. Since the dayglow at 1.27 μm at 92 km is five times the nightglow, the chemical sources of the nightglow will contribute little to the daytime $O_2(^1\Delta)$ formation rate.

The deduced yields for $O_2(^1\Delta)$ in the reactions O+O+M and $H + O_3 \rightarrow OH^* + O_2$ [followed by $OH^* + O_2 \rightarrow OH + O_2(^1\Delta)$] are quite dependent on the key species and temperature profiles adopted in the calculations. The accuracy of these yields is a function of the degree to which these profiles appropriately represent the atmosphere for the period of the *SME* measurements. Simultaneous observations of $O_2(^1\Delta)$ and atomic O or $O_2(^1\Delta)$ and OH* have been reported in the literature. Generally, these measurements were made in the early night (before midnight). It is clear from our analysis that significant further progress in understanding the mechanisms for night-time $O_2(^1\Delta)$ production will be made upon acquiring late night (post-midnight) simultaneous

profiles of $O_2(^1\Delta)$, atomic O, O_3, atomic H, OH*, and temperature.

While we have tried to identify the specific reactions leading to the formation of $O_2(^1\Delta)$, we suggest a more general conclusion of our work is that the ultimate source of excitation is the chemical energy stored in atomic O. The upper part of the 1.27 μm nightglow layer is directly due to atomic O recombination. The lower portion of the nightglow profile is a consequence of the recombination of atomic O with O_2 to form O_3. Since O_3 is in steady-state at night, this recombination reaction is balanced by the reaction $H+O_3$, the main O_3 loss process (Allen *et al.*, 1984). In this context, the sequence $H+O_3$, followed by OH^*+O_2, is one likely means of transferring the energy of O_3 recombination to $O_2(^1\Delta)$. A similar profile of $O_2(^1\Delta)$ production would result if $O_2(^1\Delta)$ were produced directly in the process of O_3 recombination. Here also simultaneous measurements of temperature and key species (particularly, atomic O) would be needed to distinguish the specific excitation mechanism.

Finally, we note that the bulk of $O_2(^1\Delta)$ production in our calculations is due to the reaction mechanism $H+O_3$, followed by OH^*+O_2. We have previously pointed out that this mechanism is also capable of forming $O_2(b^1\Sigma)$. A comparison of night-time observations of $O_2(^1\Sigma)$ (Witt *et al.*, 1984 ; McDade *et al.*, 1986) and the *SME* measurements of $O_2(^1\Delta)$ suggests that the yield of $O_2(^1\Sigma)$ in the reaction OH^*+O_2 would need to be $\sim 5\%$. One way to test the hypothesis of whether $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ emissions are due to the same mechanism would be to monitor the correlation between them.

Acknowledgements—We gratefully acknowledge assistance received from R. T. Clancy and M. T. Leu. This work was supported by NASA grant NAGW-890 to the University of Colorado and NASA grant NAGW-413 to the California Institute of Technology. C. D. Howell was supported by a California Institute of Technology Summer Undergraduate Research Fellowship.

REFERENCES

Ali, A. A., Ogryzlo, E. A., Shen, Y. Q. and Wassell, P. T. (1986) The formation of $O_2(a^1\Delta_g)$ in homogeneous and heterogeneous atom recombination. *Can J. Chem.* **64**, 1614.

Allen, M. (1986) A new source of ozone in the terrestrial upper atmosphere? *J. geophys. Res.* **91**, 2844.

Allen, M., Lunine, J. I. and Yung, Y. L. (1984) The vertical distribution of ozone in the mesosphere and lower thermosphere. *J. geophys. Res.* **89**, 4841.

Allen, M., Yung, Y. L. and Waters, J. W. (1981) Vertical transport and photochemistry in the terrestrial mesosphere and lower thermosphere (50–120 km). *J. geophys. Res.* **86**, 3617.

Badger, R. M., Wright, A. C. and Whitlock, R. F. (1965) Absolute intensities of the discrete and continuous absorption bands of oxygen gas at 1.26 and 1.065 μ and the radiative lifetime of the $^1\Delta_g$ state of oxygen. *J. chem. Phys.* **43**, 4345.

Bates, D. R. (1988) Excitation and quenching of the oxygen bands in the nightglow. *Planet. Space Sci.* **36**, 875.

Clancy, R. T., Rusch, D. W., Thomas, R. J., Allen, M. and Eckman, R. S. (1987) Model ozone photochemistry on the basis of *Solar Mesosphere Explorer* mesospheric observations. *J. geophys. Res.* **92**, 3067.

DeMore, W. B., Molina, M. J., Sanders, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J. and Ravishankara, A. R. (1987) Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL Publ.*, JPL 87-41.

Finlayson-Pitts, B. J. and Kleindienst, T. E. (1981) The reaction of hydrogen atoms with ozone and source of vibrationally excited $OH(X^2\Pi_i)_{v=2}$ for kinetic studies. *J. chem. Phys.* **74**, 5643.

Froidevaux, L., Allen, M., Berman, S. and Daughton, A. (1989) The mean ozone profile and its temperature sensitivity in the upper stratosphere and lower mesosphere: an analysis of LIMS observations. *J. geophys. Res.* **94**, 6389.

Han, R. Y., Megill, L. R. and Wyatt, C. L. (1973) Rocket observation of the equatorial $O_2(^1\Delta_g)$ emission after sunset. *J. geophys. Res.* **78**, 6140.

Houghton, J. T. (1977) *The Physics of Atmospheres*, p. 173. Cambridge University Press, Cambridge.

Keyser, L. F. (1988) Kinetics of the reaction $OH+HO_2 \rightarrow H_2O+O_2$ from 254 to 382 K. *J. phys. Chem.* **92**, 1193.

Le Texier, H., Solomon, S. and Garcia, R. R. (1987) Seasonal variability of the Meinel bands. *Planet. Space Sci.* **35**, 977.

Le Texier, H., Solomon, S., Thomas, R. J. and Garcia, R. R. (1989) OH* (7–5) Meinel band dayglow and nightglow measured by the *SME* limb scanning Near Infrared Spectrometer: comparison of the observed seasonable variability with two-dimensional model simulations. *Ann. Geophys.* **7**, 365.

Llewellyn, E. J. and Solheim, B. H. (1978) The excitation of the infrared atmospheric oxygen bands in the nightglow. *Planet. Space Sci.* **26**, 533.

Llewellyn, E. J., Long, B. H. and Solheim, B. H. (1978) The quenching of OH* in the atmosphere. *Planet. Space Sci.* **26**, 525.

Lopez-Moreno, J. J., Rodrigo, R., Moreno, F., Lopez-Puentas, M. and Molina, A. (1988) Rocket measurements of O_2 Infrared Atmospheric System in the nightglow. *Planet. Space Sci.* **36**, 459.

Lunt, S. T., Marston, G. and Wayne, R. P. (1988) The formation of $O_2(a^1\Delta_g)$ and vibrationally excited OH in the reaction between O atoms and HO_x species. *J. chem. Soc. Faraday Trans.* 2 **84**, 899.

McDade, I. C. and Llewellyn, E. J. (1987) Kinetic parameters related to sources and sinks of vibrationally excited OH in the nightglow. *J. geophys. Res.* **92**, 7643.

McDade, I. C., Murtagh, D. P., Greer, R. G. H., Dickinson, P. H. G., Witt, G., Stegman, J., Llewellyn, E. J., Thomas, L. and Jenkins, D. B. (1986) ETON2: quenching parameters for the proposed precursors of $O_2(b^1\Sigma_g^+)$ and $O(^1S)$ in the terrestrial nightglow. *Planet. Space Sci.* **34**, 789.

McDade, I. C., Llewellyn, E. J., Greer, R. G. H. and Murtagh, D. P. (1987a) ETON6: a rocket measurement of the O_2

Infrared Atmospheric (0–0) band in the nightglow. *Planet. Space Sci.* **35**, 1541.

McDade, I. C., Llewellyn, E. J., Murtagh, D. P. and Greer, R. G. H. (1987b) ETON5: simultaneous rocket measurements of the OH Meinel $\Delta v = 2$ sequence and (8,3) band emission profiles in the nightglow. *Planet. Space Sci.* **35**, 1137.

Meinel, A. B. (1950) OH emission bands in the spectrum of the night sky, I. *Astrophys. J.* **111**, 555.

Ohoyama, H., Kasai, T., Yoshimura, Y., Kimura, H. and Kuwata, K. (1985) Initial distribution of vibration of the OH radicals produced in the $H+O_3 \rightarrow OH(X^2\Pi_{1/2,3/2})+O_2$ reaction. Chemiluminescence by a crossed beam technique. *Chem. Phys. Lett.* **118**, 263.

Sharp, W. E. and Kita, D. (1987) *In situ* measurement of atomic hydrogen in the upper mesosphere. *J. geophys. Res.* **92**, 4319.

Strobel, D. F., Summers, M. E., Bevilacqua, R. M., DeLand, M. T. and Allen, M. (1987) Vertical constituent transport in the mesosphere. *J. geophys. Res.* **92**, 6691.

Thomas, R. J., Barth, C. A., Rusch, D. W. and Sanders, R. W. (1984) Solar Mesosphere Explorer Near-Infrared Spectrometer: measurements of 1.27 μ radiances and the inference of mesospheric ozone. *J. geophys. Res.* **89**, 9569.

Trinks, H., Offermann, D., Zahn, U. von and Steinhauer, C. (1978) Neutral composition measurements between 90- and 220-km altitudes by rocket-borne mass spectrometer. *J. geophys. Res.* **83**, 2169.

Vallance Jones, A. and Gattinger, R. L. (1963) The variations and excitation mechanism of the 1.58 μm $^1\Delta_g - {}^3\Sigma_g^-$ twilight airglow band. *Planet. Space Sci.* **11**, 961.

Washida, N., Akimoto, H. and Okuda, M. (1980) Is $O_2^*(a^1\Delta_g)$ formed in the $O+O_3$, $H+O_3$, and $NO+O_3$ reactions? *Bull. chem. Soc. Japan* **53**, 3496.

Wayne, R. P. (1984) Singlet oxygen airglow. *J. Photochem.* **25**, 345.

Witt, G., Stegman, J., Murtagh, D. P., McDade, I. C., Greer, R. G. H., Dickinson, P. H. G. and Jenkins, D. B. (1984) Collisional energy transfer and the excitation of $O_2(b^1\Sigma_g^+)$ in the atmosphere. *J. Photochem.* **25**, 365.

Yntema, L. (1909) On the brightness of the sky and the total amount of starlight. *Publ. Astr. Lab. Groningen* **22**, 1.