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THE SOURCE OF STRATOSPHERIC NO AND N₂O

By: Tom G. Slanger

Prepared for:
JET PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91103

Attn: Dr. W. S. Demore

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Approved:

D. C. Lorents, Director
Chemical Physics Laboratory

G. R. Abrahamson
Vice President
Physical Sciences Division

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The photodissociation of O₃ has been investigated as part of a program to study possible sources of N₂O production in the stratosphere. Photolysis was conducted at 1576 Å to generate the excited O₂ states that we propose may react with N₂ to form N₂O. We ascertained that, at this wavelength, there is a quantum yield of two for prompt production of oxygen atoms, which is a consequence of the existence of two photodissociative channels giving comparable yields. One of these channels gives O(1D) and O₂(b²Σ₊), with a quantum yield of 0.6, whereas the other results in fragmentation of the O₃, with production of three ground state oxygen atoms. The O₂(b) is generated with vibrational excitation, and we have so far determined that there are comparable populations in levels 0-3. These observations are the first to show O₂(b) production from any photodissociative process, and they were made under conditions in which the kinetics of vibrationally excited O₂(b) can be studied. It appears that O₃ photodissociation at 1576 Å is not a good system for generating the higher electronic states of O₂; it is likely that better results will be obtained at 1930 Å.

A search was made, by vuv absorption, for N₂O production during 1576 Å O₃ photodissociation in the presence of N₂. Consistent with the fact that the relevant 4-5 eV states of O₂ are not generated, no N₂O formation was observed. This study was extended to an investigation of the interaction between highly vibrationally excited OH and N₂ as a possible N₂O source, and it was established that an upper limit of 3 x 10⁻⁴ can be set for the reaction yield. Such a yield would still correspond to a large local stratospheric source of N₂O, so it is important to attempt to improve the experiment in order to get an actual yield or to decrease the upper limit.

Earlier experiments on 2537 Å photolysis of N₂O-O₃-N₂ mixtures were repeated to confirm and investigate the apparent N₂O loss that had been noted. With an improved analytical technique, no loss was observed, so the previous results were not confirmed.

The following points can be made concerning the present status of the stratospheric N₂O production problem. Excited O₂ states other than O₂(a¹Σ⁺) are produced in O₃ photodissociation at wavelengths shorter than the Hartley band. Wavelength-dependent studies are needed to further our understanding of products and yields, and to determine whether they act as N₂O sources. The
interaction between vibrationally excited OH and nitrogen is not excluded as an N$_2$O source, although we were not able to detect N$_2$O. The question of whether the interaction between N$_2$(A$^3Σ_u^+$) and O$_2$ generates N$_2$O is still an open one, and at present depends on reaching a consensus on the rate coefficient for the N$_2$(A) pooling reaction.
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INTRODUCTION

The single most important molecule in the stratosphere is ozone, because of its multifunctional character. The absorption of radiation in the Hartley band prevents destructive 2000-3000 Å light from reaching the earth. In this absorption process, O₃ generates O(^1D), a ubiquitous intermediate in stratospheric and tropospheric chemistry. O₃ is also active as a reactant, and its reactions with H, OH, and NO are all important processes.

It is therefore interesting to find that relatively little is known about O₃ photodissociation below 2000 Å, particularly in terms of the products formed. Just as O(^1D) is a reactive photodecomposition product in the Hartley band, it is important not to neglect processes taking place at shorter wavelengths, even though in terms of solar flux, much more radiation is available above than below 2000 Å.

Although both the solar flux and the O₃ photoabsorption cross sections are high in the Hartley band, there are yet other parameters to be considered. Examples are yields of photoproducts and their subsequent histories. Although O(^1D) is a very reactive species and is produced with a yield close to unity from O₃ at 2000-3000 Å, it is an extremely inefficient reactant because it is almost entirely quenched by O₂ and N₂. Therefore, only a minute fraction is available to react with N₂O, H₂O, and CH₄ to produce the important species NO and OH. Thus, it is possible for a reactive species that is produced with a far lower yield than O(^1D) to be an important atmospheric ingredient if it is used more efficiently. Such could be the case either by low quantum yield production of a species from O₃ photoabsorption in the Hartley band, or by generation of such a species at wavelengths below 2000 Å, where the solar flux is relatively weak.

The photoproducts from O₃ in the Hartley band are¹

$$O_3 + O(^1D) + O_2(a^1Δ_g) \ \ \ \ \ \ \ Φ = 0.85-0.90$$
$$+ O(^3P) + O_2(X^3Σ_g^-) \ \ \ \ \ \ \ Φ = 0.10-0.15$$

However, because the O-O₂ bond is very weak (1.1 eV), there are many thermodynamically accessible product channels. Those that are spin-allowed are listed in Table 1 with their threshold wavelengths.
# TABLE 1

O$_3$ PHOTODISSOCIATION THRESHOLDS

<table>
<thead>
<tr>
<th>Atom</th>
<th>Molecule</th>
<th>Threshold Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O($^3P$)</td>
<td>O$_2$($^3P_g^-$)</td>
<td>11250</td>
</tr>
<tr>
<td>O($^1D$)</td>
<td>O$_2$($^1D_g$)</td>
<td>3060</td>
</tr>
<tr>
<td>O($^1D$)</td>
<td>O$_2$($^1D_g^+$)</td>
<td>2638</td>
</tr>
<tr>
<td>O($^3P$)</td>
<td>O$_2$($^3D_u$)</td>
<td>2318</td>
</tr>
<tr>
<td>O($^3P$)</td>
<td>O$_2$($^3F_u^+$)</td>
<td>2275</td>
</tr>
<tr>
<td>3 O($^3P$)</td>
<td></td>
<td>1997</td>
</tr>
<tr>
<td>O($^1S$)</td>
<td>O$_2$($^1D_g$)</td>
<td>1981</td>
</tr>
<tr>
<td>O($^1S$)</td>
<td>O$_2$($^1D_g^+$)</td>
<td>1794</td>
</tr>
<tr>
<td>O($^1D$)</td>
<td>O$_2$($^1S_u^-$)</td>
<td>1741</td>
</tr>
<tr>
<td>O($^3P$)</td>
<td>O$_2$($^3S_u^-$)</td>
<td>1717</td>
</tr>
</tbody>
</table>
We have previously investigated the yield of \( \text{O}(1\S) \) below 2000 Å and have found it to be below 0.5%, at least down to 1400 Å. Thus, it is the possibility of generating excited \( \text{O}_2 \) states that raises interesting questions about the details of \( \text{O}_3 \) photodissociation below 2000 Å.

To date, there has been no demonstration of photoproduction of \( \text{O}_2 \) states from \( \text{O}_3 \) other than the ground state and \( \text{O}_2(a^1\Delta_g) \). In fact there is no known photodissociative process that generates these higher states \( (b^1\Sigma_g^+, c^1\Sigma_u^-, A^3\Delta_u, A^3\Pi_u^+) \) from any molecule, although recombinant of oxygen atoms both in the laboratory and in the airglow is a well-known source.

Our interest in investigating \( \text{O}_3 \) photodissociation has to do with the possibility that a highly excited \( \text{O}_2 \) molecule could in principle react with the dominant atmospheric molecule, \( \text{N}_2 \), to generate \( \text{N}_2\text{O} \),

\[
\text{O}_2^* + \text{N}_2 \rightarrow \text{N}_2\text{O} + \text{O}(3\Pi) \quad \Delta H = 3.4 \text{ eV} \tag{2}
\]

The candidate \( \text{O}_2 \) states are \( A^3\Delta_u \) and \( A^3\Pi_u^+ \) at 4.25 and 4.35 eV, respectively. The \( c^1\Sigma_u^- \) state is excluded because of the spin requirements of Reaction (1).

Current models of the troposphere and stratosphere assume that \( \text{N}_2\text{O} \) is generated by biogenic soil processes, rises through the atmosphere, and is destroyed by photodissociation and reaction with \( \text{O}(1\D) \). However, Zipf and Prasad have suggested several ways of generating \( \text{N}_2\text{O} \) in situ. The first idea was that \( \text{N}_2(A^3\Pi_u^+) \) is produced in the upper stratosphere by \( \text{N}_2 \) absorption of solar radiation at ~2000 Å and that this \( \text{N}_2 \) state reacts rapidly with \( \text{O}_2 \) to produce \( \text{N}_2\text{O} \). It is certain that \( \text{N}_2(A) \) is removed exclusively by \( \text{O}_2 \), but it is less clear whether the reaction product is \( \text{N}_2\text{O} \). Zipf claims that the reaction efficiency is 60%, Iannuzzi et al. find it to be less than 2%, and our measurements on the first year of this contract indicated an upper limit of 8%. However, our value depends on the figure adopted for the \( \text{N}_2(A) + \text{N}_2(A) \) pooling reaction rate coefficient; if it is as fast as Zipf claims, our efficiency becomes compatible with his, whereas if it lies closer to the value measured at SRI several years ago, then we have agreement with Iannuzzi et al. Thus, the final answer on this reaction scheme awaits more experimentation.
More recently, Zipf\textsuperscript{10} observed that interaction between OH(A\textsuperscript{2}Σ\textsuperscript{+}) and N\textsubscript{2} appears to generate N\textsubscript{2}O. The OH(A) can be produced in the stratosphere by solar pumping of ground state OH, which is a much more efficient process than pumping of N\textsubscript{2}, but is offset by the rapid radiation of OH(A), and the low density of OH. In a private communication,\textsuperscript{10} Zipf also discussed generation of N\textsubscript{2}O from interaction of highly vibrationally excited OH with N\textsubscript{2}, the OH(vib) being produced in the stratosphere at v=9 by the reaction between H atoms and O\textsubscript{3}. From H and O\textsubscript{3} atmospheric models, one may calculate the OH(v=9) production rate and determine that even a small efficiency for its reaction with N\textsubscript{2} to produce N\textsubscript{2}O would perturb current source models. In the present study, we have evaluated N\textsubscript{2}O production both for interaction of N\textsubscript{2} with the products of ozone photodissociation at 1576 Å and for the OH(v=9)-N\textsubscript{2} interaction.

The overall approach to the study has been two-fold: to investigate O\textsubscript{3} photodissociation below 2000 Å and to determine whether N\textsubscript{2}O is produced by any of the mechanisms discussed above. A secondary goal has been to follow up some results reported in the first year of the present contract,\textsuperscript{8} which had indicated that photodissociation of an N\textsubscript{2}O-O\textsubscript{3}-N\textsubscript{2} mixture at 2537 Å leads to the partial destruction of N\textsubscript{2}O. These results are difficult to understand on the basis of our knowledge of the O\textsubscript{3} photoproducts, the high quenching efficiency of O\textsuperscript{(1)D} by N\textsubscript{2}, and the transparency of N\textsubscript{2}O at 2537 Å.
EXPERIMENTAL METHODS

The major part of this study has been performed with the use of a Lumonics Model 861T-3 F2 laser as a photodissociation source. With this instrument, which delivers 10 mJ pulses of 1576 Å radiation at a repetition rate of up to 100 Hz, we have been able to obtain adequate signal levels in the more difficult experiments, which involved signal averaging for as many as 2 x 10^4 shots.

For the measurements of product yields from O_3, experiments were performed in a flowing system, with a Pyrex reaction cell. At right angles to the incoming laser beam, a photomultiplier (EMI 9558) was mounted, and in the orthogonal direction, radiation entered a 0.3-m McPherson 218 monochromator, at the exit of which was mounted a solar-blind phototube (EMR 542-08-18). Measurements of O_2 emissions were made with the EMI tube; there was insufficient radiation to detect, except for the O_2(b-X) 0-0 band, after passage through the monochromator. A series of 100 Å wide interference filters were used to measure the radiation, between 7600 and 7900 Å.

For detection of oxygen atoms, an oxygen lamp was mounted on the system, orthogonal to both the laser beam and the monochromator axis. This microwave-powered lamp was run with a flow of 1% O_2 in helium and was a source of 1302-1306 Å resonance radiation. The resonantly scattered light from this lamp was a measure of oxygen atoms and was detected after passage through the monochromator by the solar-blind tube.

All the transient data were processed and recorded with a Nuclear Data ND-100 signal averager, generally using the smallest channel width, 10 µs.

For the experiments involving N_2O generation, concentrations of products were determined by vuv absorption, using either an H_2 discharge lamp or a high pressure argon lamp. Initially, analyses were performed by developing a set of absorption spectra for the various system components, N_2O, O_3, O_2, and H_2O, then trying to reconstruct an experimental spectrum by summing these individual spectra, with computer assistance. This procedure was reasonably successful, but it was never possible to eliminate the spurious signals inherent in such a procedure to the point where the required sensitivity could be attained.
When we ascertained that the system components could be separated by trapping at low temperature, it became obvious that this was the preferable procedure. At the pressures used, neither O₂ nor O₃ condenses at 77 K, whereas N₂O does, although it does not condense at 196 K, where H₂O is completely trapped. Thus, it was a simple matter to separate N₂O from the other gases and measure it alone, a much more straightforward and accurate procedure than the one we had originally tried.

The O₃ was prepared in an ozone generator and held in a molecular sieve trap at 196 K. Once a day the slowly evolving oxygen was pumped off, and during a run the O₃ (swept into the system by a helium flow) was O₂-free, as demonstrated by lack of O₂ bands in the absorption spectrum and by the temporal behavior of the O₂(b-X) emission, which was very sensitive to the presence of O₂.

The H₂O used in the experiments was added by bubbling He through water, but the outgassing rate was so high that adding H₂O was unnecessary. The problem was to remove the water, which was accomplished with the above-mentioned trap.

For the studies at 2537 Å, a mercury discharge lamp was used, the output of which was on the order of 10¹⁷ quanta s⁻¹, capable of destroying O₃. The 40-cm-long reaction vessel used in this experiment was water-jacketed, both to keep the walls cool to prevent heterogeneous reactions, and to prevent any 1849 Å radiation from entering the cell.

Pressures were measured with a Baratron gauge, and the small concentrations of O₂ and N₂O that were used were added as 1% or 10% mixtures in helium. O₃ pressures were determined in various ways: by 2537 Å absorption, by 1216 Å absorption, and by the decay rates of O(¹D) and O₂(b), for which O₃ quenching rate coefficients are known.
ACCOMPLISHMENTS

O₃ Photodissociation at 1576 Å

Two types of measurements were made in this first detailed study of vuv O₃ photodissociation: determination of the identity and yield of the initial atomic oxygen fragments and determination of the yield of O₂(b¹Σ⁺). Although this O₂ state will not react with N₂ to generate N₂O, its investigation is essential for understanding the photodissociation dynamics. Obviously, if it is produced with a quantum yield of unity, a search for higher excited O₂ states becomes less interesting.

The oxygen atom yields from O₃ are measured absolutely by comparison with the yields from O₂, where at 1576 Å the sole process generates O(1D) + O(3P). The atoms are measured as O(3P) by 1304 Å resonance fluorescence; thus to get a total yield, O(1D) must be quenched to O(3P). This is accomplished by N₂ addition. Figure 1 shows the resonance fluorescence signals obtained from photodissociation of O₂ and O₃. The 2 torr N₂ quenches O(1D) within 0.5 µs, much less than the 10 µs/channel averaging time, so the jump in signal when the laser is fired represents total oxygen atoms produced. The signal ratio, I(O₂)/I(O₃), is given by

\[ \frac{I(O_2)}{I(O_3)} = \frac{[O_2]}{[O_3]} \times \frac{\sigma(O_2)}{\sigma(O_3)} \times \Phi(O_2) \times \Phi(O_3) \times f \]  

or

\[ 2I(O_3) \times [O_2] = \frac{\sigma(O_2)}{\sigma(O_3)} \times [O_3] \times \Phi(O_3) \times \Phi(O_2) \times f \]  

where \( \sigma(O_2)/\sigma(O_3) \) is the ratio of photoabsorption cross sections at 1576 Å, and \( \Phi \) is the atom yield. The correction term, \( f \), is used because at the probe wavelength of 1304 Å the O₃ absorbs some radiation, thereby decreasing the atom detection efficiency, an effect not occurring with O₂. At 11.8 mtorr O₃, \( f = 1.12 \) for the geometry used.

The O₂ pressure was measured directly, and the O₂ cross section of 6.3 × 10⁻¹⁸ cm² at 1576 Å was obtained by interpolation from the data of Ogawa and Ogawa. The cross-section ratio was determined by measuring the attenuation of wall-scattered 1576 Å light through the monochromator, with the O₃ pressure being measured by 2537 Å absorption. A value of \( [\sigma(O_2)/\sigma(O_3)]_{1576} = 4.3 \) was found, just the figure reported by Tanaka et al. Substituting into...
FIGURE 1 

$O(3P)$ YIELD FROM 1576 Å PHOTODISSOCIATION OF $O_2$ AND $O_3$

$[He] = 17$ torr, $[N_2] = 3$ torr, 3500 laser shots
equation (3), we find that \( \Phi(0_3) = 2.0 \pm 0.1 \), i.e. each \( 0_3 \) photodissociation process results in production of two prompt oxygen atoms.

More information is available if the \( N_2 \) is left out because then \( 0(1D) \) does not appear immediately as \( 0(3P) \), and the slower production then gives differentiation between prompt \( 0(3P) \) and slow \( 0(3P) \) from \( 0(1D) \) relaxation, enabling us to evaluate the \( 0(1D)/0(3P) \) ratio. With a total \( 0(1D) + 0(3P) \) yield of 2.0, this ratio then gives absolute yields for each state.

Figures 2 and 3 show the results of this determination. The initial jump represents prompt \( 0(3P) \), as before, and Figure 2 shows that for \( 0_2 \) photodissociation, the magnitude of the subsequent rise is approximately the same, indicating that equal amounts of \( 0(1D) \) and \( 0(3P) \) are produced. In the \( 0_3 \) data of Figure 3, however, the slower rise is considerably smaller than the initial jump, showing that the \( 0(3P) \) yield is larger than that of \( 0(1D) \).

Amito et al.\(^{16}\) have shown that when \( 0(1D) \) interacts with \( 0_3 \), one \( 0(3P) \) is produced for every \( 0(1D) \) consumed, but it seems unlikely that the process is

\[
0(1D) + 0_3 \rightarrow 0(3P) + 0_3
\]

Instead, we believe that two other channels are involved:

\[
\begin{align*}
0(1D) + 0_3 & \rightarrow 0_2 + 0_2 + 0_2 & \Phi_1 \\
& \quad + 20(3P) + 0_2 & \Phi_2
\end{align*}
\]

where \( \Phi_1 = \Phi_2 \). This results in an effective unity quantum yield for \( 0(3P) \) production. However, we find that the total \( 0(3P) \) yield from \( 0_3 \) is slightly decreased by the presence of \( N_2 \), indicating that \( \Phi_2 \) is slightly larger than \( \Phi \). At the \( 0_3 \) pressure used in Figure 3, the \( 0(1D) + 0(3P) \) conversion requires 40 \( \mu s \), consistent with the data.

The ratio of prompt \( 0(3P) \) to \( 0(3P) \) produced from \( 0(1D) \) is approximately 70:30 from Figure 3 which we adjust to 75:25 on the basis of the above discussion. Because the total \( 0(3P) \) yield is two, we conclude that the yield for prompt \( 0(3P) \) is 1.5 and that the yield for \( 0(1D) \) is 0.5. Since it is obviously not possible to have a photodissociative process in \( 0_3 \) that yields
two atoms, such a yield can be explained only by a process that generates three atoms, i.e., complete fragmentation of $O_3$. If this takes place, then the yield for that process is 0.5, making the total $O_3$ photodestruction yield unity and making explicable the observation that the atom quantum yield is two. Thus, the data are explained by hypothesizing two channels, occurring with similar probabilities,

$$O_3 + O(3P) + O(3P) + O(3P) \quad \Phi = 0.5 \quad (8)$$

$$\rightarrow O(1D) + O_2(\text{singlet}) \quad \Phi = 0.5 \quad (9)$$

Interestingly, this interpretation leaves no room for any other processes; in particular, no excited triplet $O_2$ can be formed. However, the fragmentation process is best thought of in two steps in which a highly excited triplet $O_2$ molecule is produced, which then dissociates or predissociates.

The identity of the excited singlet $O_2$ is very important for understanding the overall mechanism, and the candidates are $a^1\Delta_g$, $b^1\Sigma_g^+$, and $c^1\Sigma_u^-$. We were not able to look for the emission from $a^1\Delta_g$ in the ir, and emission from the $c^1\Sigma_u^-$ state is difficult to detect because of its long radiative lifetime, estimated to be about 30 s, and its expected rapid quenching by $O_3$. However, the $b^1\Sigma_g^+$ state is simple to detect, by $b-X$ emission in the near ir, and we were able to show that it is the principal partner of $O(1D)$.

Figure 4 shows a trace of the signal detected at 7700 A (the b-X 1-1 band position) from $O_3$, characterized by the fact that the emission begins promptly during the laser pulse, which is consistent with $O_2(b)$ being a primary fragment. To be certain that there is no ultra-fast collisional process giving the apparent instantaneous production in Figure 4, we added a small amount of $O_2$ to the cell, which has the effect of generating $O(1D)$. This $O(1D)$ can then react with $O_2$ to give $O_2(b)$ by energy transfer,

$$O(1D) + O_2 + O(3P) + O_2(b). \quad (10)$$
FIGURE 2  PROMPT AND SLOW O(3P) YIELDS FROM 1576 Å O₂ PHOTODISSOCIATION

\[ [O_2] = 10 \text{ mtorr}, [\text{He}] = 30 \text{ torr}, 2000 \text{ laser shots} \]
FIGURE 3  PROMPT AND SLOW O($^3P$) YIELDS FROM 1576 Å O$_2$ PHOTODISSOCIATION

[O$_2$] = 3 mtorr, [He] = 18 torr, 2000 laser shots
FIGURE 4  \( \text{O}_2 \) (b-X) 1-1 BAND EMISSION (7700 Å) FROM 1576 Å O\(_3\) PHOTODISSOCIATION

\([\text{O}_3]\) = 3 mtorr, [He] = 18 torr, 10,000 laser shots(normalized intensity scale).
The rate at which the signal from this reaction builds up is determined by the \( O(1D) \) removal rate, which is governed not by \( O_2 \) but by \( O_3 \). Because the rate coefficient\(^{15} \) for the \( n(1D) - O_3 \) interaction is \( 2.4 \times 10^{-10} \) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), close to collision frequency, a demonstration that the buildup can be discerned will substantiate that the data of Figure 4 indicate that \( O_2(b) \) production from \( O_3 \) is a primary process.

Figures 5 and 6 show two traces of \( O_2(b) \) temporal behavior. Figure 5 shows the effect of adding 4 mtorr of \( O_2 \) to the 3 mtorr \( O_3 \) used for the run in Figure 4. It is clear that there is now a buildup of signal, and we can therefore be certain that the instantaneous appearance of \( O_2(b) \) in Figure 4 is truly a primary process. This is also a demonstration that the \( O_2(b-X) \) emission in Figure 4 is not a consequence of a small amount of impurity \( O_2 \) in the \( O_3 \). Figure 6 shows the temporal behavior of \( O_2(b) \) produced from \( O_2 \) alone; the buildup is slower in the absence of \( O_3 \), as \( O(1D) \) is removed more slowly by \( O_2 \) than by \( O_3 \).\(^{15} \)

Comparing the \( O_2(b-X) \) signal in Figure 4 with that in the \( O_2-O_3 \) experiment of Figure 5 makes it possible to calculate the quantum yield for \( O_2(b,v=1) \) production from \( O_3 \), since it is known that the yield from \( O_2 \) is 0.3. To perform this calculation, we need to know what fraction of the \( O(1D) \) is quenched by \( O_2 \) (0.18 from the known rate coefficients\(^{15} \)), the 1576 A cross section ratio for \( O_2 \) and \( O_3 \) (4.3), and the ratio of signals from \( O_3 \) in Figure 4 and from \( O_2-O_3 \) in Figure 5. These are \( \tau = 0 \) signals, which requires a short extrapolation for the \( O_2-O_3 \) case; the ratio \( I(O_2+O_3)/I(O_3) \) is 4.2. With these figures, we determine that the yield for production of \( O_2(b^1Pg^+) \) in the \( v=1 \) level from 1576 A \( O_3 \) photodissociation is 0.09.

We have used a series of filters to measure the emissions from \( O_3 \), sampling at the positions not only of the 1-1 b-X band but also of the 0-0, 2-2, and 3-3 bands. We find that in each case there is no buildup of emission intensity, indicating primary production, and that the intensities are comparable. Figures 7 and 8 show \( O_2(b-X) \) 2-2 band results at 7800 A. By determination of filter factors, phototube sensitivities, and using published Franck-Condon factors, we have determined absolute nascent populations of each level. These are presented in Table 2, and show roughly comparable values for each level with a slow increase with increasing level. Given that the \( O(1D) \) yield is 0.5, we should not exceed this value for the \( O_2(b) \) quantum yield;
FIGURE 5  $\text{O}_2$ (b-$X$) 1-1 BAND EMISSION (7700 Å) FROM 1676 Å PHOTODISSOCIATION OF $\text{O}_2 + \text{O}_3$

FIGURE 6  \( \text{O}_2 \) (b-X) 1-1 BAND EMISSION (7700 Å) FROM 1576 Å PHOTODISSOCIATION OF \( \text{O}_2 \\
[\text{O}_2] = 4 \text{ mtorr}, [\text{He}] = 10 \text{ torr}, 2000 \text{ laser shots} \)
FIGURE 7  $O_2$ (b-X) 2-2 BAND EMISSION (7800 Å) FROM 1576 Å $O_3$ PHOTODISSOCIATION
$[O_3] = 3$ mtorr, $[He] = 18$ torr, 10,000 laser shots (normalized intensity scale).
FIGURE 8  O$_2$ (b-X) 2-2 BAND EMISSION (7800 Å) FROM 1576 Å PHOTODISSOCIATION OF O$_2$ + O$_3$

Table 2

<table>
<thead>
<tr>
<th>Level</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>1</td>
<td>0.09</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
</tr>
</tbody>
</table>
the sum of the values in Table 2 is 0.47.

A frustrating conclusion of these experiments is that, although we have been able to perform a self-consistent analysis of the O\textsubscript{3} photodissociation products, we find ourselves unable to answer the initial question: Do O\textsubscript{2} excited states, formed from O\textsubscript{3} photodissociation, react with N\textsubscript{2} to produce N\textsubscript{2}O? This uncertainty arises because we have accounted for all the products, but find that at 1576 Å none of the relevant O\textsubscript{2} states (those between 4 and 5 eV), are formed. This is perhaps to forceful a statement, since 10% yields could be hidden in the data, but from the indirect evidence of O(\textsuperscript{3}P), O(\textsuperscript{1}D), and O\textsubscript{2}(b) yields, there is little room for O\textsubscript{2}(A,A',c) production. However, the three-atom fragmentation process is likely to have a much lower yield at longer wavelengths (its threshold is 1997 Å), so that measurements at the ArF laser wavelength, 1930 Å, which is in any case more relevant to stratospheric photoabsorption, may show substantial yields of the O\textsubscript{2} triplet excited states.

These studies constitute the first report of the photolytic production of any electronically excited O\textsubscript{2} state other than O\textsubscript{2}(\textsuperscript{1}A\textsubscript{g})\textsuperscript{+}. Furthermore, previously reported laboratory emission studies of vibrationally excited O\textsubscript{2}(b) above v=1 have been limited to spectroscopic observations\textsuperscript{16,17} because they were performed under conditions (CO-O\textsubscript{2} explosions, for example) where kinetic studies were not possible.

The direction of further work on this system is self-evident. Although the emissions that we observe are sufficiently characterizable by their kinetic behavior (buildup and decay times), it is important to produce an actual spectrum. This task is not trivial because the rapid quenching by O\textsubscript{3} and the long radiative lifetime of O\textsubscript{2}(b), 12 s, mean that a very small fraction of the molecules radiate. At 3 mtorr O\textsubscript{3}, this fraction is less than 10\textsuperscript{-6}.

It would be interesting to learn more about the fragmentation in which three atoms are produced. This would need to be a time-of-flight experiment, and given that one could discriminate against detection of O(\textsuperscript{1}D), the ground state atoms would show two-thirds having the same velocity and one-third having a different velocity. However, before embarking on such a program, we should extract the maximum amount of information from optical experiments.
One of the most important issues is to study the photodissociation process as a function of wavelength. This is a far easier task with a laser source than with conventional vuv light sources, at least for $O_2(b)$ detection, but we anticipate that, if the experiments are repeated with an ArF laser at 1930 Å, the results may be very revealing. Although the $O_3$ photoabsorption cross section is smaller by a factor of three at this wavelength than at 1576 Å, the available laser intensity is at least ten times greater, so that to obtain the same signal levels, we ought to be able to work with less $O_3$ (and thus limit quenching). As mentioned above, it may be possible to access higher $O_2$ states at 1930 Å because with 1.5 eV less energy available for dissociation, the three fragment process may be suppressed, with the excited triplet molecule surviving. Even if we cannot get information on the excited molecular species in the absence of laser excitation, measurements of $O(3P)$ yields should be possible at different vuv source wavelengths: 1470, 1236, and 1216 Å. Such data will at least be a guide to unravelling the processes that occur.

$N_2O$ Loss in $N_2O-O_3-N_2$ 2537 Å Irradiation

In the measurements made last year, in which $N_2O$ loss was observed in 2537 Å radiation of $O_3-N_2O-N_2$ mixtures, analysis was complicated by the need to take reaction mixture samples to another laboratory to be analyzed by electron capture gas chromatography. We were concerned about undesirable handling of the samples as well as the possibility that $O_3$ might react further at some point, making the results spurious. Thus, the present study was designed around analysis of the reaction mixtures in situ, by vuv absorption, with the species to be measured being $O_3$, $N_2O$, $O_2$, and $H_2O$. The last was included because we suspected that there might be both outgassing and water driven off the walls during photolysis.

The experiment to test the earlier conclusion, that $N_2O$ was destroyed by 2537 Å irradiation of an $N_2O-O_3-N_2$ mixture, was performed in a straightforward manner. The 40-cm-long absorption cell, containing 100 mtorr $O_3$, 20 mtorr $N_2O$, and 250 torr $N_2$, was irradiated with a mercury discharge lamp for 15 minutes, during which time the $O_3$ reached an equilibrium value of roughly 15 mtorr. However, this $O_3$ loss does not represent photon input because $O_3$ is reformed rapidly by recombination of the $O + O_2$ products. We estimate that,
with the geometry used, the photon absorption rate into the system was well above $10^{17} \, \text{s}^{-1}$, for a total of more than $10^{20}$ photons absorbed during a

Figure 9 shows two $\text{N}_2\text{O}$ absorption spectra, taken before and after 2537 Å irradiation. Because we wish to look only at the $\text{N}_2\text{O}$ optical depth, each of these spectra has had a blank spectrum (containing no $\text{N}_2\text{O}$) subtracted from it. For the irradiated sample, this had the effect of generating the same amount of $\text{O}_2$ as was made when $\text{N}_2\text{O}$ was present, so the absorption bands of neither $\text{O}_2$ nor $\text{O}_3$ appear in the final spectrum. There are some differences in the two spectra, particularly at long wavelengths where the system becomes optically thick due to $\text{O}_2$ generation, resulting in inaccuracy in taking differences in optical depth. However, the basic conclusion is that, within reasonable error limits, there is no loss of $\text{N}_2\text{O}$ during 2537 Å irradiation. If anything, the spectrum taken after irradiation contains slightly more $\text{N}_2\text{O}$ than the one taken before, but the difference is probably not significant.

Figure 10 shows the same sort of data taken with argon substituted for nitrogen. Again, there is little difference between the two spectra, with slightly more $\text{N}_2\text{O}$ being indicated after irradiation. Because in this case $\text{N}_2\text{O}$ generation is not possible, we conclude that these differences represent the precision of the analysis system. It therefore appears that, when $\text{N}_2\text{O}$ is measured in situ under these conditions, there is no evidence for its photodestruction and that the earlier conclusions are not confirmed.

$\text{N}_2\text{O}$ Production in $\text{O}_3-\text{N}_2$ Photolysis at 1576 Å

After completion of this phase of the work, we returned to the initial problem, which was to ascertain whether the high-lying states of $\text{O}_2$ could produce $\text{N}_2\text{O}$ upon reaction with $\text{N}_2$. It was presumed that $\text{O}_3$ photodissociation at 1576 Å would provide a good source of these states, although it is evident from Table 1 that the thresholds lie at much longer wavelengths. As described earlier, it now appears that the $\text{O}_3$ photoproducts do not include the relevant $\text{O}_2$ states, although that is not yet a rigorous conclusion.

We had noticed that $\text{H}_2\text{O}$ was generated by outgassing in the closed reaction cell used in the 2537 Å experiments, but because it does not absorb at that wavelength, we did not feel that its presence was an issue. This is Figure 9
FIGURE 9  EFFECT OF 15 MINUTE 2537 Å IRRADIATION OF N₂O-O₃-N₂ MIXTURE ON [N₂O]

Light Line – Before irradiation
Dark Line – After irradiation
FIGURE 10 EFFECT OF 15 MINUTE 2537 Å IRRADIATION OF N₂O-O₃-Ar MIXTURE ON [N₂O]

[N₂O]₀ = 20 mtorr, [O₃]₀ = 100 mtorr, [Ar] = 250 torr
Light Line - Before Irradiation
Dark Line - After Irradiation
not true at 1576 Å, however, so in setting up the laser experiment, we equipped the smaller cell with a trap, above the laser beam path, which effectively removed H₂O at dry ice temperatures and, when operated with liquid nitrogen, removed N₂O as well. With water removed, we could conduct the desired study, which consisted of photolyzing O₂-N₂ mixtures, the necessary O₃ rapidly being produced from O-O₂ recombination. In the presence of H₂O, an entirely different study became possible, discussed below, in which we could explore the question of the interaction of OH(v=9) with N₂.

The fact that we have an approximate material balance of states, i.e. that the photodecomposition products are basically accounted for, does not mean that N₂O cannot be produced. Even a 1% yield of an O₂ state that could react efficiently with N₂ could result in considerable N₂O generation. Thus, the experiment was performed with the intention of setting the N₂O detectability limit as low as possible. Figure 11 shows an absorption spectrum of N₂O at a pressure of 6 mtorr. This spectrum was produced by putting O₃, O₂, H₂O, N₂O, and N₂ into the cell, trapping the N₂O and H₂O with liquid N₂, pumping out the O₃, O₂, and N₂, warming the trap to room temperature, then trapping at 196 K with dry ice-acetone. This procedure has the effect of (1) calibrating the absorption peak and showing that it has the magnitude expected, (2) showing that such a procedure results in full recovery of the N₂O added, and (3) determining if there are any interfering absorptions.

The peak absorption cross section¹⁸ in the N₂O 1285 Å band is 2470 cm⁻¹ atm⁻¹. For the 14-cm absorption path, an optical depth of 0.27 is therefore expected, and this is close to the value shown in Figure 11. The only additional features seen are the two strong O₂ bands at 1205 and 1243 Å; presumably there is some occlusion of O₂ in the condensing vapor, but it does not interfere with N₂O detection. The amount of O₂ corresponds to a few mtorr.

Figure 12 shows the results of the same procedure conducted with 2-hour irradiation of an O₃-O₂-N₂ mixture to search for evidence of N₂O production. The trap was kept at 77 K to remove any outgassing N₂O and to remove any N₂O as it was formed. The only discernible features are weak O₂ bands. There is no 1285 Å N₂O band, and a reasonable limit of detectability corresponds to an optical depth of 0.02 and a pressure of 0.4 mtorr, or 10¹³ N₂O molecules/cm³.
FIGURE 11  \( \text{N}_2\text{O} \) ABSORPTION SPECTRUM

\[ [\text{N}_2\text{O}] = 6 \text{ mtorr} \]
FIGURE 12  ABSORPTION IN N₂O 1285 Å BAND REGION AFTER 120 MINUTES 1576 Å IRRADIATION OF O₂-N₂ MIXTURE

\( [O_2] = 250 \) mtorr, \( [N_2] = 250 \) torr
To ascertain the significance of this limit, we may calculate the number of O₃ molecules that have been dissociated during the 2-hour irradiation period. We find experimentally that the O₃/O₂ ratio at equilibrium is ~0.15. The photoabsorption cross section ratio favors O₂ by a factor of 4. Half of the incoming 1576 Å photons are absorbed, so we conclude that 2% of the laser photons dissociate O₃. The total laser photon flux is 5 x 10²⁰ hr⁻¹; thus, 2 x 10¹⁹ O₃ molecules are dissociated during the 2-hour experiment, resulting in <10¹⁶ N₂O molecules produced (the cell volume is one liter).

If N₂, the preponderant mixture component by three orders of magnitude, is the principal deactivator of the relevant excited O₂ state, we conclude that less than 0.1% of the O₂⁺N₂ deactivating collisions lead to N₂O production, if the O₂ state in question is produced with a unity quantum yield. We already know that the second issue is moot: the quantum yields of the c, A, or A' states of O₂ are produced, if at all, with yields far less than unity from O₃ at 1576 Å. On the first issue, it is probable, from what is known about O₂(A) and O₂(c) deactivation,¹⁹ that a 3 to 4 order-of-magnitude excess of N₂ over O₂ and O₃ will assure that a large fraction of O₂⁺ quenching is by N₂. For example, O₂(A) quenching by N₂ has a rate coefficient²⁰ on the order of 10⁻¹⁴ cm³ molec⁻¹ s⁻¹, so that even if that for O₃ were 10⁴ times faster, half the quenching would still be due to N₂⁺. In most cases, the O₂ and N₂ rate coefficients are likely to be similar, certainly not differing by as much as the 10³ pressure ratio of the experiment.

If we say that the yield of the high O₂ states does not exceed 10%, it is reasonable to conclude that the yield of N₂O from O₂⁺N₂ is less than 1%. However, this is not a useful conclusion because O₃ photodissociation at 1576 Å is evidently not a good way of accessing these states. It remains to be seen whether dissociation at longer wavelengths, which is in any case more aeronomically interesting, will generate these states of O₂. Judgement on the question of N₂O production from O₂⁺N₂ will have to be held in abeyance until such a time.

N₂O Production from OH(v=9) + N₂

Stronger conclusions can be drawn about the OH(v=9)-N₂ interaction. We
find ourselves able to study this reaction because H$_2$O photodissociation at 1576 Å generates H atoms with a quantum yield close to unity.\textsuperscript{21} The fate of these atoms in an O$_3$-O$_2$-H$_2$O-N$_2$ mixture will be to react with O$_3$, producing OH($v=9$) almost exclusively. Although the relative rates of OH($v=9$) quenching by the four components are a matter in some dispute,\textsuperscript{22,23} it is expected that N$_2$ will in fact be the dominant quencher, being in excess of the other components by at least $10^3$. At the pressure conditions used, 15% of the photons are absorbed by H$_2$O, and half of the total laser output is absorbed in the cell. At a flux of $5 \times 10^{20}$ photons hr$^{-1}$, the H atom production rate is $4 \times 10^{19}$ hr$^{-1}$, which is equal to the production rate of OH($v=9$). If this is entirely quenched by N$_2$ to produce N$_2$O, the final N$_2$O concentration would be 1.3 torr.

Figure 13 shows the results of an experiment similar to that described above, except that H$_2$O was one of the added components and it was not trapped during irradiation. We again seen no evidence for N$_2$O, with the limit corresponding to an optical depth of 0.02, or 0.4 mtorr. We are thus able to set an upper limit of $3 \times 10^{-4}$ on the yield of N$_2$O from the interaction between OH($v=9$) and N$_2$, and this time there is no ambiguity about the production rate of the N$_2$ collision partner.

The thermodynamics of this system has been investigated from the point of view of the reverse reaction

$$N_2O + H + OH + N_2$$

which is known to have an activation energy of 15 kcal/mole.\textsuperscript{24} The exothermicity of the forward reaction, with OH($v=9$), is 12.6 kcal/mole, thus falling slightly short of the required energy. This is not a significant issue when considering a reaction that must in any case have a low yield. However, it is not clear how efficiently vibrational energy can be used in surmounting the barrier; sometimes there is equivalence of vibrational and translational energy, and other times vibrational energy is relatively inefficient. For low yield processes it is best to rely on experimental determinations on the system in question.

To show how our results impact atmospheric processes, we have calculated the production rate of OH($v=9$) as a function of altitude, determined from an H
FIGURE 13 ABSORPTION IN N₂ O 1285 Å BAND REGION AFTER 60 MINUTES IR RADIATION OF O₂-H₂ O-N₂ MIXTURE

\[ [O_2] = 250 \text{ mtorr}, [H_2 O] = 65 \text{ mtorr}, [N_2] = 250 \text{ torr} \]
and \( \text{O}_3 \) model given by Nicolet\textsuperscript{25} and using as an interaction rate coefficient\textsuperscript{26} the value of \( 2.9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \). At the top of the stratosphere, at 50 km, the \( \text{N}_2 \) density is \( 3 \times 10^{16} \text{ cm}^{-3} \), and if we take the \( \text{OH}(v=9) + \text{N}_2 \) rate coefficient to be \( 5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \), as given by Streit and Johnston\textsuperscript{27}, then all \( \text{OH}(v=9) \) quenching is by \( \text{N}_2 \). For our limiting efficiency factor, the \( \text{N}_2\text{O} \) production rate is then \( 1 \times 10^{3} \text{ cm}^{-3} \text{ s}^{-1} \) at that altitude. To put this figure into perspective, we can use the analysis performed by Zipf and Prasad\textsuperscript{6} on the \( \text{N}_2(A^3\Pi_u^+) + \text{O}_2 \) reaction as a source of \( \text{N}_2\text{O} \), in which they found that a production rate of \( 100 \text{ cm}^{-3} \text{ s}^{-1} \) at 50 km was of nonnegligible proportions compared with known sources. Thus, a source that is ten times stronger would severely perturb existing models, and since our value is only a limit, it is evident that an order-of-magnitude decrease in the experimental sensitivity for \( \text{N}_2\text{O} \) is needed before the \( \text{OH}(v=9)-\text{N}_2 \) reaction can be ruled out as an \( \text{N}_2\text{O} \) source. Zipf\textsuperscript{10} in fact claims to have evidence that some \( \text{N}_2\text{O} \) is produced by this reaction, but the efficiency is not yet available. As an experimental problem, an order-of-magnitude increase in sensitivity should not be difficult to achieve because we can increase photolysis times, increase the \( \text{H}_2\text{O}/\text{O}_2 \) ratio, and reconfigure the cell so that analysis can be performed at a higher \( \text{N}_2\text{O} \) optical depth than is generated during irradiation.
PRESENT STATUS OF N₂O SOURCE PROBLEM

This study has demonstrated that there are still a variety of questions to be addressed before the possibility of finding in situ stratospheric N₂O sources is clarified. We have shown that at wavelengths shorter than the Hartley band, an O₂ state higher than O₂(a) is in fact produced, and it is important to continue this line of investigation, as there is reason to believe that even more energetic states will be found at wavelengths around 1900 Å. Whether they can interact with N₂ to make N₂O can only be determined experimentally. The issue of whether vibrationally excited OH can react with N₂ to form N₂O is still open, since even our limiting yield of 3 x 10⁻⁴, if an actual figure, would severely perturb present models. Progress in this area will also involve obtaining improved rate coefficient data on quenching of OH (v=9). The question of the N₂O yield from the N₂(A) + O₂ reaction is still not definitively settled, and at present revolves around the question of the N₂(A) energy pooling rate.
REFERENCES


