

PHOTOLYSIS OF WET OZONE AND ITS SIGNIFICANCE TO ATMOSPHERIC HEATING OF THE OZONE LAYER*

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ABSTRACT

Results obtained at the Canadian Armament Research and Development Establishment by balloon-borne equipment measuring the infrared emission spectrum of the upper stratosphere and supporting rocket and aircraft data are used to describe chemical reactions of the upper stratosphere. Data include several features not previously observed which are, in part, attributed to emission from excited nitrogen oxides and hydroxyl radicals.

Inferences are drawn as to the composition of the upper stratosphere, and a possible role is outlined of the photochemical decomposition of wet ozone in the energy budget of the ozone layer.

INTRODUCTION

One can hardly begin to ascertain the processes controlling the stratosphere and its circulation without a knowledge of composition, input flux of energy, and the mechanisms involved. Copious observations of the behavior of total ozone and its distribution at low altitudes and relatively insignificant data on its distribution at high altitudes are available. Knowledge of the water vapor distribution is scanty and conflicting. It can be assumed that carbon dioxide is uniformly mixed in the stratosphere. One might expect methane and nitrous oxide mixing ratios to be radically changed by chemical processes in the upper stratosphere.

* Many colleagues have participated in the observations reported in this paper. Captain Letourneau was in charge of the balloon and rocket launchings. Mr. Lortie was largely responsible for instrumentation. Mr. Lowe was our principal experimenter and Dr. Cumming, Mr. Thistle, and many others have put considerable effort into the programs.

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Observations made at Quebec, Churchill (Manitoba), and Florida on infrared emission and absorption by the atmosphere appear to give relevant data which may throw light on the processes involved in controlling composition and energy balance in the atmosphere. The purpose of these investigations was to establish a framework of infrared data, assess the content of infrared active species, and investigate processes involved in the energy balance including flux divergence and photochemical behavior.

The measurements include a rocket-borne determination of the heights of the hydroxyl and sodium layers, airborne solar spectroscopy from a CF100 over Quebec and Florida, and emission spectroscopy using a series of gratings and detectors from high-altitude balloon-borne platforms in the vicinity of Quebec. The program is a continuing one and involves a family of devices in which techniques are steadily being refined. In addition to the equipment involved in the experiments conducted to date, we have constructed balloon gondolas for radiometric measurement, high-resolution solar spectroscopy, and interferometric airglow spectroscopy and have still other equipment on hand for airborne measurement of atmospheric scattering and insolation.

It is the purpose of this paper to review the experimental results of our program, introduce a number of hypotheses as to the mechanisms involved, and conjecture about their importance to atmospheric processes. The principal theme is the photochemistry of wet ozone, but this cannot be discussed adequately without bringing in the behavior of other constituents. Some of the conclusions are at variance with current concepts in the literature. It is hoped that their injection into these deliberations will encourage criticism, bringing us closer to a true interpretation of atmospheric processes.

OBSERVATIONS

Stimulated by discussions with Vallance Jones⁰ of the University of Saskatchewan, we launched a rocket to measure hydroxyl airglow at 02.59 Central Standard Time on November 17, 1958, from Churchill, Manitoba. The results¹ differed considerably from those of Heppner and Meredith² and place the peak hydroxyl emission at 85 km, in agreement with later observations³. (Fig. 1). The radiometer response peaked at 1.6 microns (μ) with 3-db points at approximately 1.5 and 1.7 μ . Hence, the 4-2 band of OH at 1.583 μ was the prime signal measured. The emission from the hydroxyl radical comes from a reaction or reactions forming part of a complex catalytic chain converting atomic oxygen and ozone to molecular oxygen.

The evidence for water vapor content in the stratosphere is conflicting. Until recently the upper atmosphere was considered dry. Data gathered from high-altitude aircraft by Moss⁴ and others gave no indication of an increasing water vapor content above the tropopause. The low water content is well illustrated in the extensive series of solar spectra we have taken. Fig. 2 is an example; absorption by water vapor is very small in comparison with carbon dioxide.

Other measurements indicate increasing humidity above the tropopause. Disregarding the contentious early measurements, three recent observations by

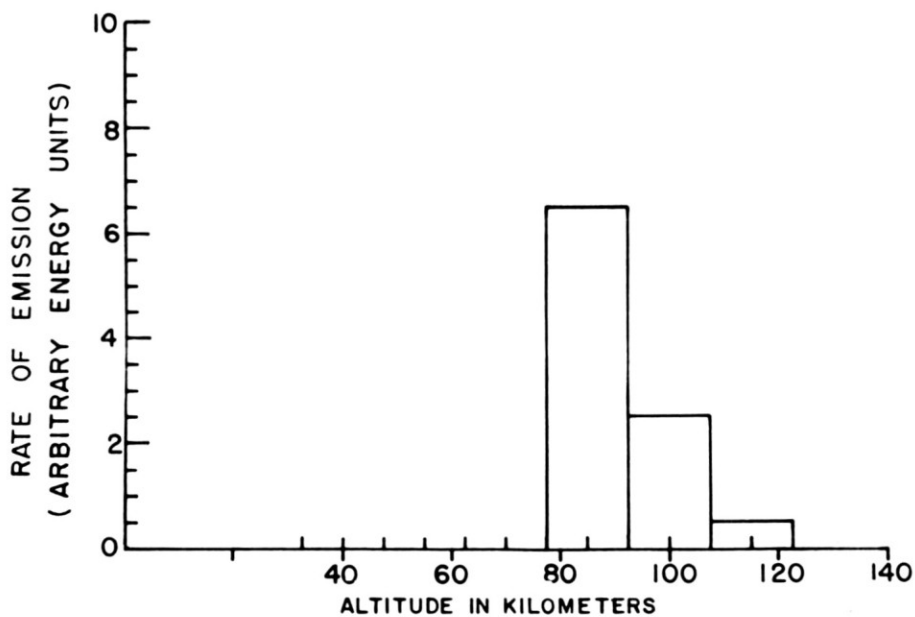


Fig. 1. Hydroxyl emission as a function of altitude (histogram).

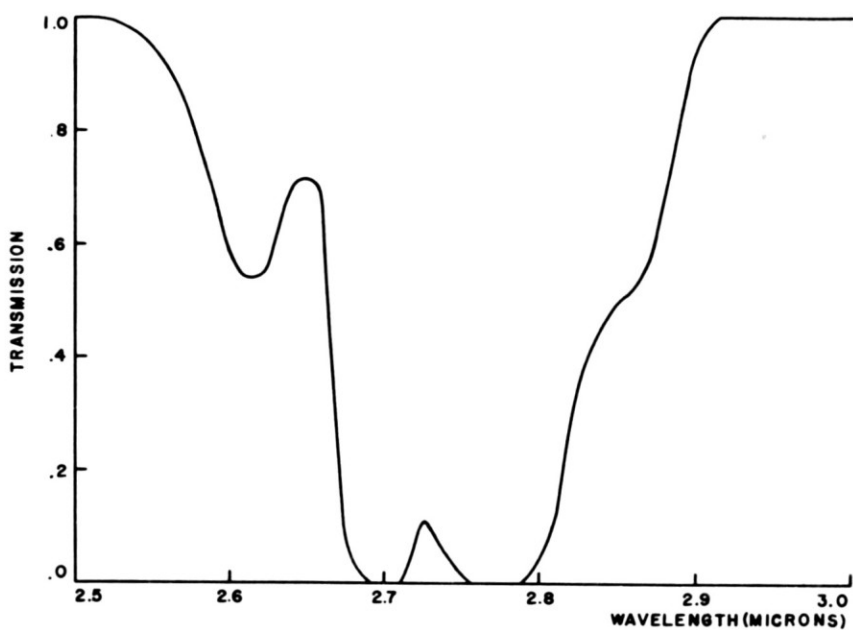


Fig. 2. High-altitude solar spectrum. (Sunset; 42,300 ft; 17.52: 26 EST; 00° - 23° .)

Strong,⁵ Murcay,⁶ and Brown⁷ are pertinent. The latter observation might be criticized on the ground that outgassing of water vapor from the balloon would greatly modify the local water-vapor concentration and since their equipment, essentially a cold trap, measures only local concentrations, their data could be in error. Though neither Murcay nor Strong employed high-resolution equipment, which may have led to slight errors in determination of water-vapor content, their instruments measured total absorption in the sun-spectrometer path and were not likely to have been affected by local water vapor. Moreover, it is difficult to see how Strong's platform, a U-2 airplane, could have produced such localized effects.

Solar spectroscopy from low altitudes (below 45,000 ft) is an unreliable method of assessing water-vapor mixing ratios at 30-km altitude, and the inference by Dobson⁸ that the 30-km mixing ratio may be lower than 10^{-5} may be in error by close to an order of magnitude.

An increasing body of evidence points to the existence of a moist upper stratosphere, but there has been no convincing mechanism proposed for its formation.

On August 14, 1959, we flew a balloon-borne grating spectrometer using a gold-doped germanium detector to measure the spectrum of airglow emission in the spectral range of 4–8 μ from an altitude of 100,000 ft. The spectra contained several surprising features. Behavior of the emission followed an obvious, perhaps trivial, course in the early stages of ascent (Fig. 3), corresponding to thermal emission principally from water vapor, methane, and nitrous oxide. At 97,000 ft the character of the spectra changed completely (Fig. 4). Nocturnal emission in the vicinity of the water vapor band showed three peaks at 5.9, 6.2,

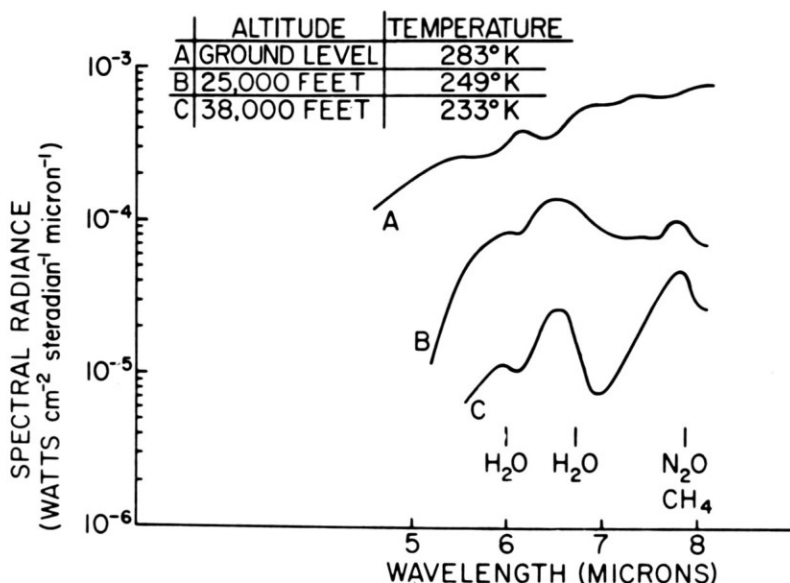


Fig. 3. Atmospheric infrared emission spectra (low altitude).

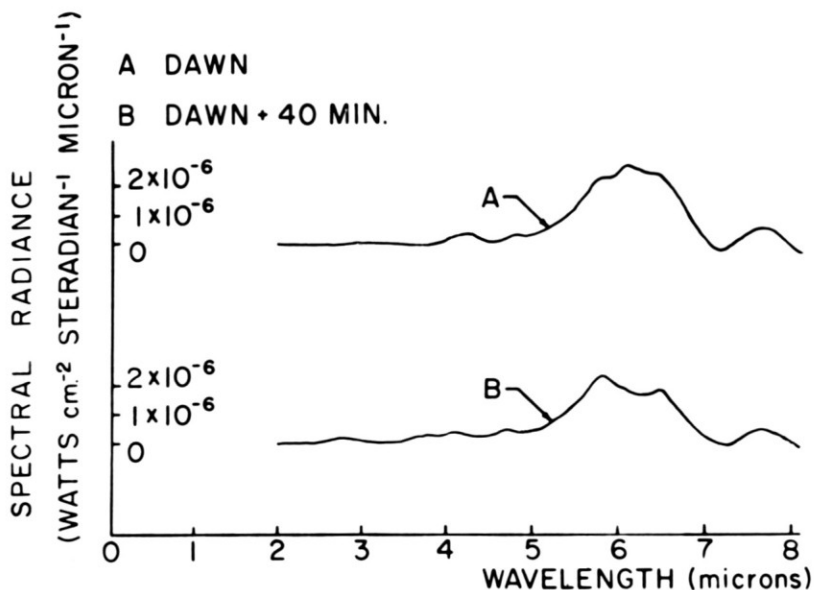


Fig. 4. Atmospheric infrared emission spectra (99,000 ft).

and 6.5μ , the central one vanishing after sunrise on the gondola. The 5.9 and 6.2μ peaks were assumed to be from a source other than water vapor, and the 6.5μ peak was assessed as water-vapor emission. From the apparent increase of 6.5μ emission with respect to 7.8μ nitrous oxide band emission when compared with lower altitudes, it was deduced that the ratio of water vapor to nitrous oxide increased with altitude above the tropopause. A later balloon experiment verified the essential features observed on August 14. More recently (September 22, 1961), we were able to fly a higher-resolution instrument. Figure 5 was obtained by averaging 20 spectra; the measured signal is seen in 5a, and the amplitude-corrected spectrum appears in 5b. The structure of the 6.6μ region supports the conclusion that it is due to thermal emission from water vapor, but on this occasion the water vapor content appeared substantially lower than the value derived from the previous measurement. The Q branch of methane at 7.66μ and the nitrous oxide emission at 7.78μ are prominent. Very little structure can be seen in the 5.9 and 6.25μ bands to permit identification. It is impossible to say how far these features are due to water vapor emission since the spectral dependence of the latter depends upon the way in which it is distributed, as well as upon the temperature. However, the apparent reduction of the 6.25μ emission after sunrise appears to preclude the possibility that it could be due to water vapor, and the 5.9μ band appears to be too intense to be solely due to water vapor. Further experiments under higher resolution are required. Emission features are strong at 4.45μ due to carbon dioxide and nitrous oxide bands, including the C_{13} isotopic band, and at 4.85μ , probably due to ozone. A weak but discernible feature exists at 5.33μ . Assuming that this is due to nitric oxide, it is probable that the 6.25μ feature is a nitrogen dioxide emission.

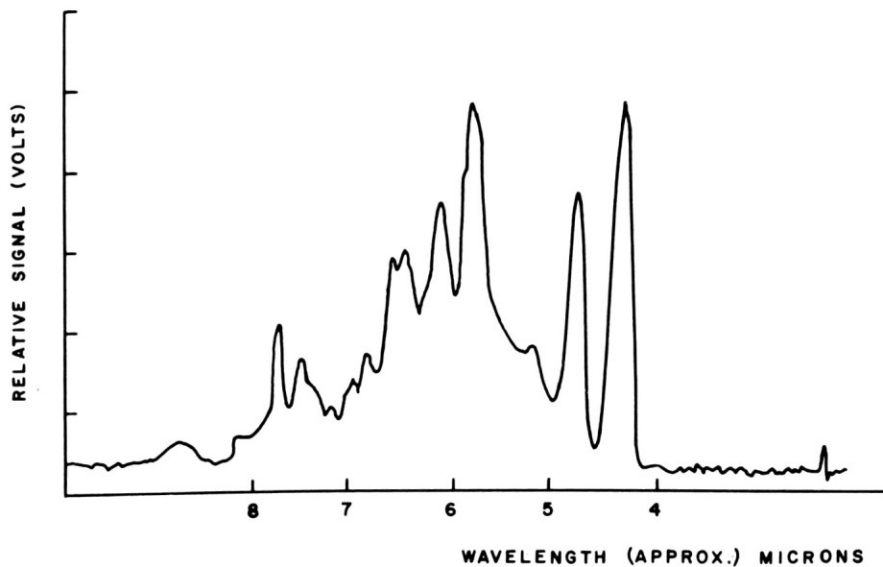


Fig. 5a. Atmospheric infrared emission spectrum (raw data).

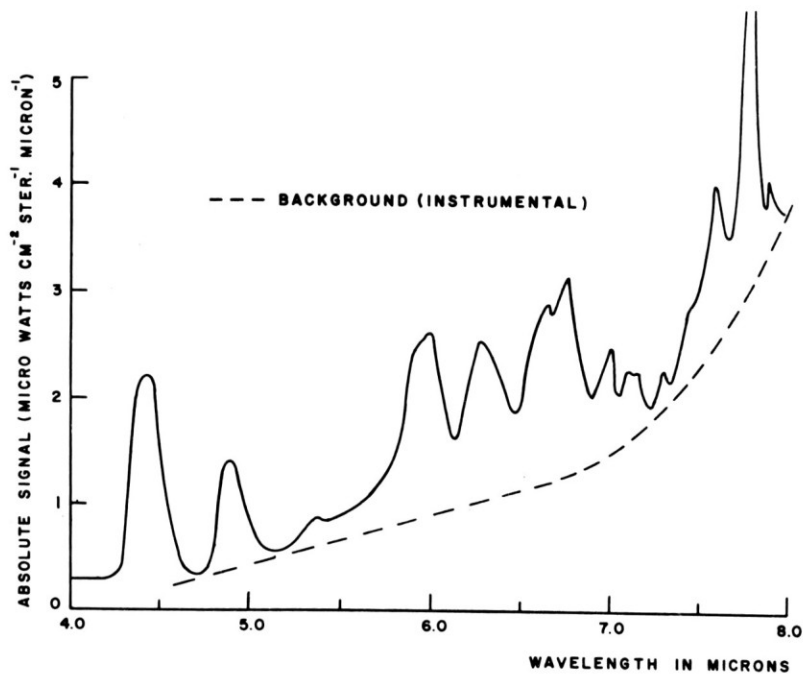


Fig. 5b. Atmospheric infrared emission spectrum (reduced). Atmospheric radiation above 30-km altitude in the 4-8 micron band.

In addition to the observation in the 4–8 μ region, we have made three measurements on airglow from 100,000 ft in the 2–4 μ spectral range. Figure 6 shows a resultant spectrum. Apart from the strong hydroxyl emission, another signal at 3.2 μ —as yet unidentified—is apparent.

Since individual spectra have a small signal to noise ratio, averaging the data is essential. A practical difficulty arises from the voluminous supply of measured data insofar as averaging the spectra without regard to possible temporal changes may cloud important features of the processes. To define the problem, models for the processes appear necessary. They form mechanisms which can be tested against experiment. Several hypotheses have been examined.

NITROGEN OXYGEN REACTIONS

One mechanism for production of the 5.3 and 6.2 μ emissions might be the transfer of vibrational energy from excited oxygen molecules. An alternative mechanism is chemiluminescent reactions similar to the hydrogen, ozone reaction.

D-layer formation has been ascribed to photo-ionization of nitric oxide by Nicolet.⁹ Inn¹⁰ has put forward an alternative suggestion. Our data appear to support Nicolet, and an extension of his scheme of reactions seems to explain the 5.33 and 6.2 μ features seen in Fig. 5.

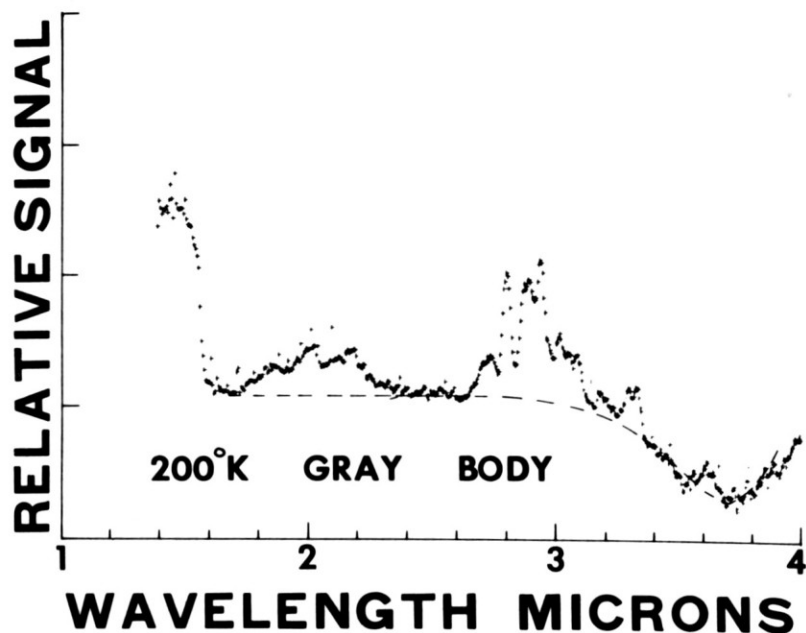
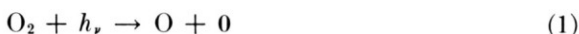


Fig. 6. High-altitude hydroxyl spectrum.

Photodissociation of oxygen molecules [Eq. (1)] leaves the products with excess energy, kinetic and electronic excitation, equal to the difference between the energy of the incoming photon and the dissociation energy of oxygen.



The subsequent collisions of hot oxygen atoms with nitrogen molecules promotes the reaction shown in Eq. (2). The first collision after formation of an oxygen atom is the only significant one since the energy of the oxygen atoms is rapidly transferred to the ambient



From shock-tube measurements at 2,000° to 3,000°K, Glick *et al.*¹¹ give the reaction rate of 3.2 as $8 \times 10^{-11} e^{-75,000/RT}$ and infer a steric hindrance factor of 0.05.

Subsequent reactions are given by 3.3 to 3.6:



Derivation of the resultant equilibrium nitrogen, nitric oxide, and ionized nitric oxide content is obviously simple. In the D layer, the only light quanta with sufficient energy to promote Eq. (3) are due to Lyman alpha. Resultant equilibrium concentrations are given by Eqs. (7), (8), and (9):

$$[\text{N}] = 3.10^{-9} e^{3,100/RT} q \quad (7)$$

$$[\text{NO}] = 4.10^{-3} e^{-3,100/RT} [\text{O}_2] \quad (8)$$

$$\text{NO}^+ = 10^{-6} e^{-1,550/RT} [[\text{O}_2] q]^{1/2} \quad (9)$$

where $[\text{O}_2]$ is oxygen concentration, and q is number of incident light quanta per unit area.

For the temperature distributions of Fig. 7 and a Lyman alpha flux of 3 ergs/sq cm/sec, the equilibrium concentrations are given in Figs. 8, 9, and 10. The concentrations above 90 km are lower than the atmospheric values since continuum radiation, important above 90 km, has been neglected.

The equilibrium nitric oxide content is lower than the experimental limits given by Jursa *et al.*¹² and by Migeotte and Neven.¹³ If one assumes that each nitric oxide molecule produced through reactions (2) and (3) is vibrationally excited and emits one photon of the fundamental band, the energy density is consistent with the experimental findings given in Fig. 5. The latter spectrum is an average of many. Not all individual spectra show the 5.3 μ emission band, and it appears possible that Eqs. (2) and (3) will be insignificant when solar illumination is absent and the ambient temperature is low. In conditions of strong X-ray and particulate bombardment, the equilibrium values of N, NO,

and NO^+ may change drastically. For example, relatively high concentrations of nitrogen atoms follow when Eq. (3) is slow.

Assuming the nitric oxide distribution of Fig. 9, and an ozone concentration of 10^{11} per cu cm, the number of nitrogen dioxide molecules produced per cm^2 column per sec is of the same order of magnitude as the number of photons per cm^2 column observed at 6.2μ (Fig. 5).

Assuming that the argument indicates the 6.2μ feature to be nitrogen dioxide, one must allow the further assumption that the nitric oxide is renewed by reaction 3.10:



and the disappearance of the 6.2μ feature after sunrise is due to daytime photodissociation of high-altitude ozone

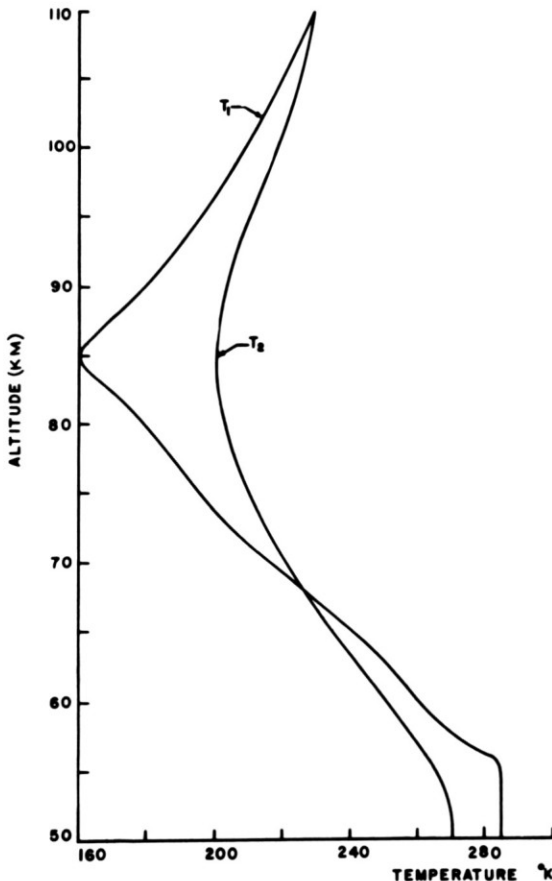


Fig. 7. Assumed temperature profiles for the mesosphere and mesopause.

This brief comment hardly does justice to the immense problems of the nitrogen, oxygen system. It is considered here not only for its intrinsic value but for several significant points affecting wet ozone and the microstructure of the atmosphere's energy balance.

Further study of the 6.2μ feature may throw light on the behavior of high-altitude ozone. Observation of the 5.33μ feature may lead to an understanding of the method of formation of the D layer and may have a direct bearing on high-altitude photodissociation of water vapor. The hypothesis advanced earlier was based essentially on the suggestion of Nicolet that the low absorption coefficient of oxygen for Lyman alpha radiation permitted the latter to penetrate to the upper stratosphere. However, water vapor has a high absorption coefficient for Lyman alpha and, under conditions where the water vapor mixing ratio is high, can substantially change the equilibrium concentrations given in Figs. 8, 9, and 10.

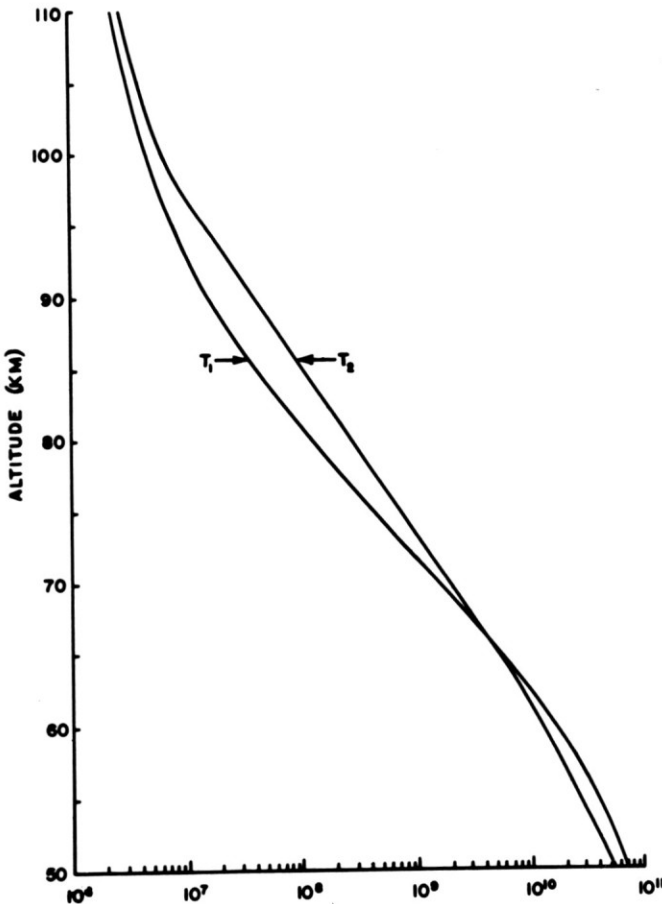


Fig. 8. Equilibrium nitric oxide concentrations below the E layer.

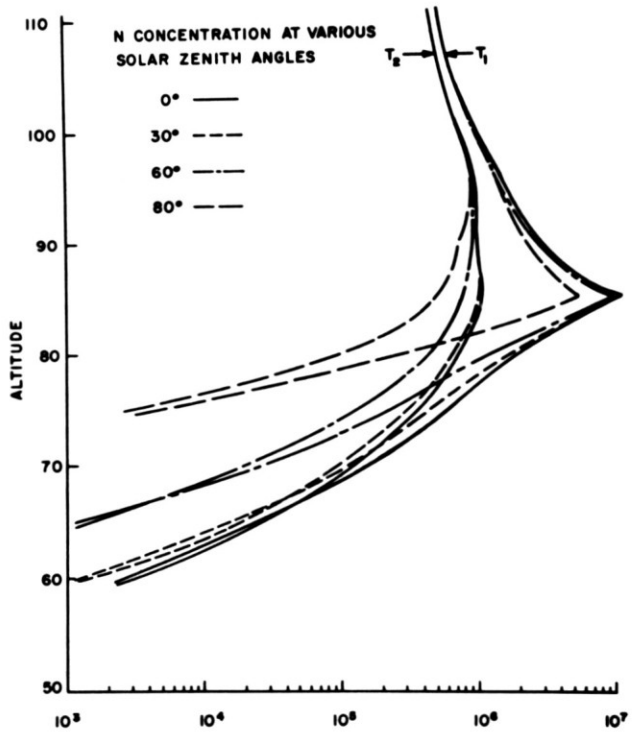


Fig. 9. Equilibrium nitrogen concentrations below the E layer.

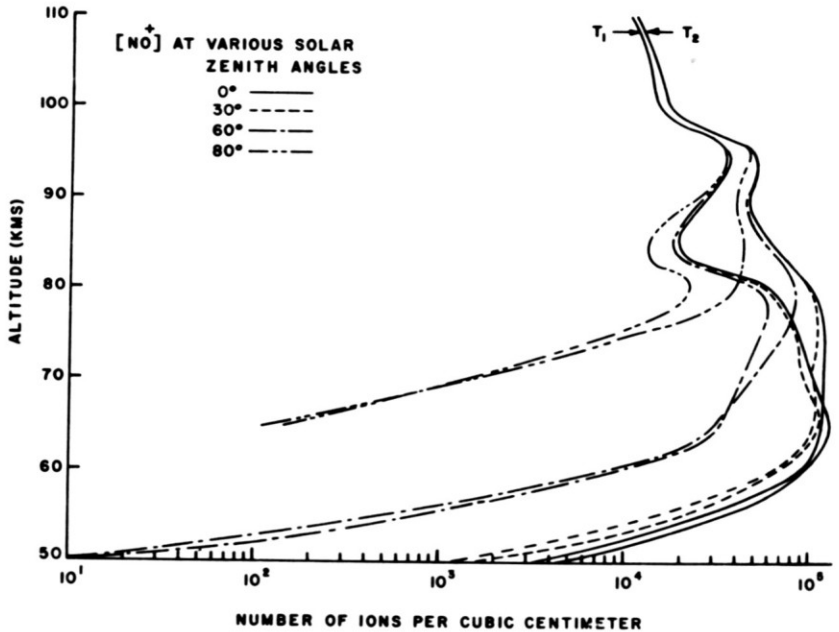
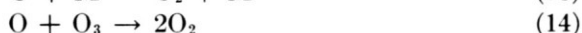


Fig. 10.

WET OZONE PHOTOCHEMISTRY

There have been many suggestions that water vapor plays a significant role in reduction of atmospheric ozone. The first comprehensive examination of photochemical behavior of wet ozone, a study by Forbes and Heidt,¹⁴ had as a partial aim the assessment of whether or not ozone in the atmosphere could be regarded as a tracer for water vapor.

While Heidt's work outlined the problem and much has been accomplished in the intervening years, final details of the processes of wet ozone photochemistry await elucidation. Useful information has been obtained by Norrish *et al.*^{15, 15a} from flash photolysis of dry and wet ozone. Their scheme of reactions invokes production of singlet D oxygen atoms by photolysis of ozone as a prime agent in the catalytic processes for dry and wet ozone. A relatively large number of reactions is involved in the atmospheric processes. Bates¹⁶ and Krassovsky^{17, 17a} have presented arguments concerning the pertinent reactions, and, in addition to the oxygen system of Eqs. (11) to (15), Eqs. (16) to (47) are relevant.

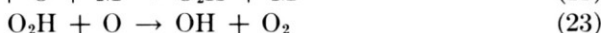
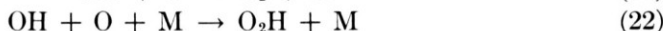
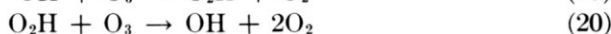
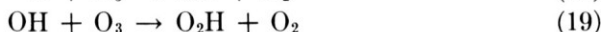


The wet ozone chain reactions include the following:

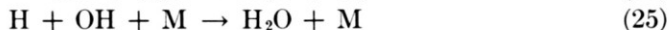
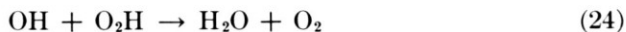
Initiation



Propagation



Termination



Ancillary reactions not directly descriptive of initiation or propagation are given as



or, perhaps

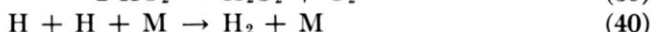


Other reactions occur, including many of relatively minor significance.

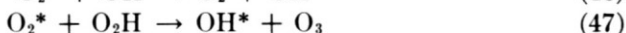
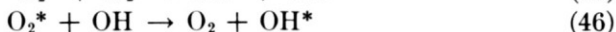
Initiation



Termination



Reactions involving excited states have been termed important by Krassovsky.



Bates has reviewed the relative importance of most of the reactions, and many can be dismissed as unimportant. For example, terminating reactions (36), (39), (41), and (42) can be disregarded; (36) is almost neutral; (37), (39), and (41) are inhibited by steric hindrance; and (45) involves breaking the hydrogen bond and should be slower than the reverse reaction to (44).

In discussing the high-altitude system, Wallace¹⁸ comes to the conclusion that the equilibrium concentration of high-altitude ozone is controlled by the hydrogen, hydroxyl reactions. He does not consider many of the reactions given above; reactions (19) and (20) are conspicuously absent from his scheme. It is difficult to dismiss them as unimportant at low altitudes since the very large quantum efficiencies obtained by Heidt can be explained only by a catalytic chain involving (19) and (20). Since these reactions increase the effect of hydroxyl, hydrogen control on high-altitude ozone, this does not invalidate Wallace's general conclusion.

A complete solution to the high-altitude problem appears difficult because of the complexity of the reactions and the lack of information on some of the reaction rates. A most important question is whether photochemistry of low-altitude ozone is affected by water vapor. From the meteorological point of view, the low-altitude problem may be more important since the solar energy absorbed is much higher.

In assessing the significance of the catalytic chain, reactions (18), (19), and (20) may be assumed to dominate at low altitudes. A simplified solution to the equilibrium ozone concentration can be sought under these conditions for the

reaction scheme represented by reactions (16), (17), (24), (25), (26), and (30), in addition to (18), (19), and (20).

It appears likely that reaction (24) is the fastest recombination reaction since 25 is a three-body reaction. If either (16) is sufficiently fast or (26) sufficiently slow, the propagation chain is controlled by (19) and (20). Although the reaction rates are not known, two limiting conditions can be given. For both initiation occurs via (16) and (17). Propagation in one case is via (19) and (20), and in the other case via (18), (19), and (26). Termination occurs through either (24) or several three-body reactions. Although the propagation reactions have dissimilar rates, an assumption that the slowest rate dominates the reaction system should make possible a qualitative appraisal. Assuming that the propagating reactions have similar rates and that one terminating reaction occurs, the equilibrium ozone concentration may be given by Eq. (48).

$$\left. \begin{aligned} [\text{O}_3] &= \frac{2Q_A - AQ_B}{\frac{AQ_B 2K_4}{d \cdot K_6 [\text{H}_2\text{O}] + K_p} + \frac{Q_c + AQ_B}{K_T}} \\ A &= \frac{d \cdot K_6 [\text{H}_2\text{O}]}{K_2[\text{O}_2][\text{M}] + d \cdot K_6 [\text{H}_2\text{O}]} \end{aligned} \right\} \quad (48)$$

Q_A , Q_B , Q_C are the number of photodissociating quanta absorbed per cu cm per sec in oxygen, ozone, and water vapor. K_p , K_T , K_4 , K_6 , K_2 are reaction rates for the propagating and terminating reactions and for reactions (14), (16), and (12).

$$d = \left\{ \frac{1}{1 + \frac{3.2 \times 10^{-18}}{K_6 W}} \right\}$$

where W is the water vapor mixing ratio, and allows for the decay of singlet D atoms through collision deactivation. Expression (48) holds only at low altitudes where $K_2 [\text{O}_2] [\text{M}] \gg K_4 [\text{O}_3]$.

Equilibrium ozone was calculated by use of the data on solar flux, ozone absorption coefficient and oxygen reaction rates given by Craig¹⁹ and the value derived by Granath²⁰ for the oxygen absorption coefficient. The purpose of the calculation was to ascertain the conditions under which water vapor substantially modified the equilibrium ozone concentration. K_p and K_T were taken as 10^{-15} and the effect of singlet D oxygen reactions was disregarded. (Assuming that $K_6 \sim 10^{-15}$, A becomes significant only at very high altitudes where the expression itself is invalid. In addition, the ozone concentration was evaluated by assuming K_T to be a three-body reaction and the reaction rate 10^{-34} .)

Using the water vapor distribution of Fig. 11 produced the concentrations shown in Fig. 12. In curves A , B , C , and D the chain is terminated by two- and three-body reactions, respectively. Eucken and Patat's value²⁰ for K_4/K_6 is used in curves A and C , while their highest measured value 9.2×10^{-18} is used in curves B and D . Additional calculations were carried out with Benson and

Axworthy's data.²² Craig's figures for equilibrium ozone are inserted for comparison (curve *E*). Hydroxyl concentrations for the reaction schemes involving two- and three-body termination reactions are shown in Fig. 13.

In using the values of 10^{-15} for the hydroxyl radical reactions, the object was to define the character of the effects. Clearly, the reaction $H + O_3$ is much faster. (It probably does not matter much which oxygen atom is closest to the hydrogen atom in the collision.) The hydroxyl, perhydroxyl reactions ($OH + O_3$), ($O_2H + O_3$) are bound to be slower than the hydrogen reaction, but this is probably offset by the fact that the terminating reaction $OH + O_2H$ must be slow. Which direction the O_2H molecule faces is important if it is to have an effective collision with an oncoming hydroxyl radical. Moreover, if O_2H is readily photolyzed, chain termination by day must be through $H + OH + M$, and this is a very slow reaction at high altitude.

The values of hydroxyl content which are quoted may be misleading. Since the hydroxyl reaction with ozone is likely to proceed faster than the perhydroxyl reaction, the hydroxyl concentration required for the degree of ozone catalysis quoted should be smaller than the values given. Hence, the radio observation of a maximum hydroxyl content less than $10^{16}/\text{cm}^2$ column is not necessarily significant.

In the absence of accurate values for reaction rates, Fig. 12 serves only to illustrate the possibility of catalytic action of water vapor - ozone photolysis. Craig's analysis was used for simplicity since it afforded a readily available set of computations. This analysis contains several deficiencies, one of the most notable of which is a very inaccurate temperature profile. K_6 is much smaller than the values given by Craig when the true lower temperatures are substituted.

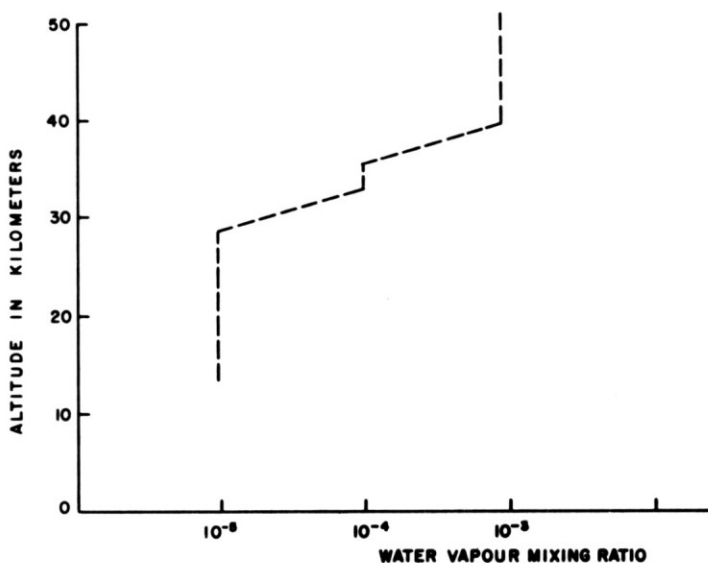


Fig. 11. Assumed water vapor distribution in the stratosphere.

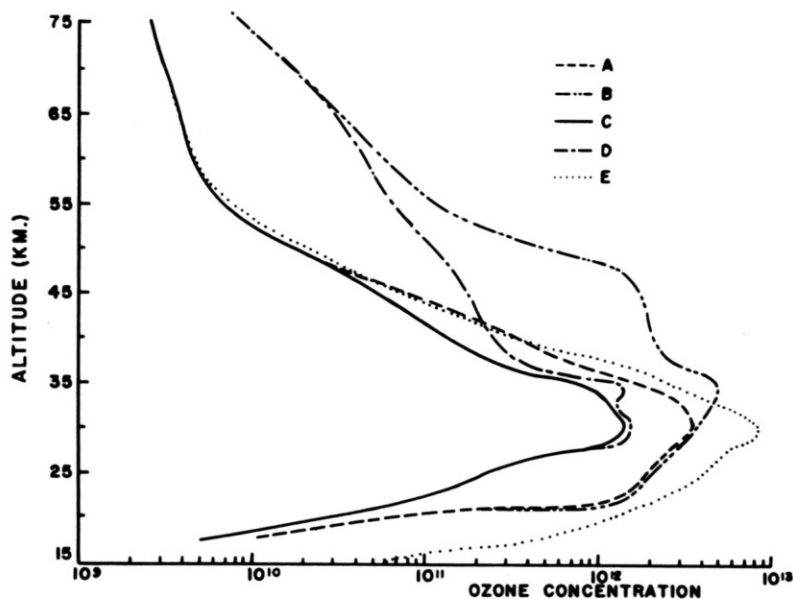


Fig. 12. Equilibrium ozone concentrations for a wet ozone layer (zenith angle $\cong 0^\circ$).

Consequently, equilibrium ozone deduced from the oxygen system is substantially larger than he predicts.

Since recombination by night is likely to be a two-body process, even if photolysis of perhydroxyl makes three-body recombination more important by day, the equilibrium hydrogen hydroxyl content should be considered to be defined by two-body processes. Thus, if reasonable values have been chosen for the limiting reaction rates, curve *B* (Fig. 12) is likely to be closer to the atmospheric values than the others.

Deduction of the complete process solely from a knowledge of water - ozone concentration can hardly prove possible in view of the incomplete nature of our knowledge of the reaction system. In order to make a check of the system, one should know the hydroxyl content. A clue to the latter might be obtained if an assessment of total neutral hydroxyl content were available. Chamberlain²³ has derived the theoretical ratio of the band intensities. If the 1.0 band is relatively much weaker than predicted, one must assume that the fundamental is absorbed by neutral hydroxyl radicals in the atmosphere. The amount of absorption can be gaged from the ratio of the actual to the theoretical intensities of the bands.

Since both the emission and the absorption bands have lines whose shape is controlled primarily by doppler broadening, calculation of the product of hydroxyl content and line intensity is simple.

Assuming that the overlapping of lines can be neglected at the very low pressure involved, the transmission is given by

$$T = \frac{2 \int_0^\infty \frac{N_T}{\alpha_D} \frac{K}{\sqrt{\pi}} \exp\left[-\frac{(\nu-\nu_0)^2}{\alpha_D}\right] \exp\left[\frac{uK}{\alpha_D}\right] e^{-\left[\frac{\nu-\nu_0}{\alpha_D}\right]^2} d\nu}{2 \int_0^\infty \frac{N_T K}{\alpha_D \sqrt{\pi}} \exp\left[-\frac{(\nu-\nu_0)^2}{\alpha_D}\right] d\nu}$$

By expanding the second term in the numerator and integrating term by term, we may give the transmission as

$$T = 1 - \frac{p}{\sqrt{2}} + \frac{p^2}{2\sqrt{3}} - \frac{p^3}{12} + \frac{(-p)^{n-1}}{(n-1)! \sqrt{n}}$$

when

$$T = 0.8$$

$$p = \frac{Ku}{\alpha_0 \sqrt{\pi}} = \frac{1}{3}$$

$$\alpha_D = \text{line half width} = \frac{1}{\lambda_0} \left(\frac{2kT}{m} \right)^{\frac{1}{2}}$$

$K, k, T,$ and M = line intensity, Boltzmann's constant, ambient temperature, and mass of hydroxyl radical, respectively

ν_0, λ_0 = frequency and wavelength of the line center

u = thickness of absorbing path

If the line intensity is 10^{15} c/sec per g cm², the thickness of the total hydroxyl layer is approximately 10^{16} molecules per cm² column. Assuming a uniform distribution, the total content in a vertical path would be 10^{15} per cm² column. This value is in fair agreement with the estimate shown for the two-body recombination of Fig. 13, allowing for the fact that the perhydroxyl content should be much greater than the hydroxyl content.

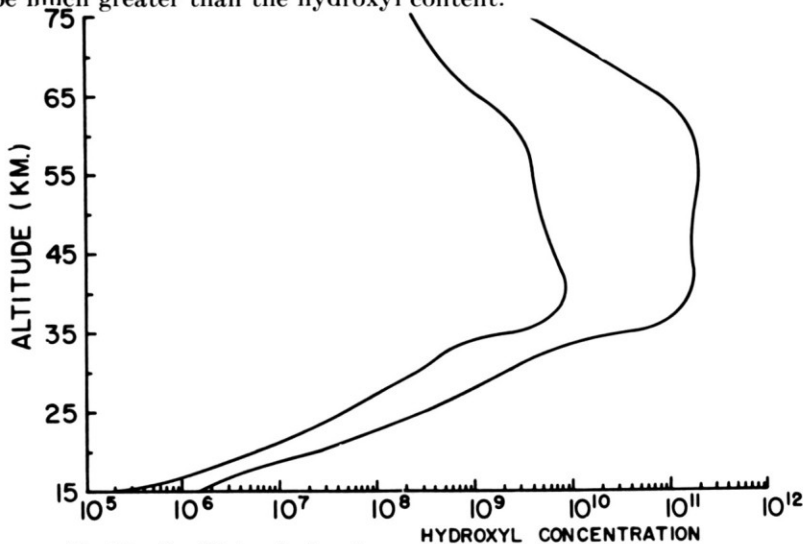


Fig. 13. Equilibrium hydroxyl concentrations in the ozone layer.

More accurate measurement of the band intensities may make possible deductions on the behavior of wet ozone, but present predictions are subject to considerable uncertainty because the precise excitation mechanisms have not been evaluated.

If the hydroxyl airglow comes from reaction (18), as suggested by Herzberg and Bates, the temporal and spatial variation can be used to deduce active hydrogen, ozone behavior. Krassovsky has concluded from Friedman's data²⁴ on hydrogen atom concentration above 100 km, and from an inference by Kaufman²⁵ that the three-body reaction (30) is extremely fast, that the hydrogen atom concentration below 100 km is much too small for (18) to be the responsible reaction. However, Kaufman's list of reactions (21), (23), and (25) is hardly complete, and the reactions $H + O + M$ and $OH + M$ may, with (21), provide an adequate catalytic chain. The crucial test is whether hydroxyl emission is observed by day, as well as by night, because three of the processes given by Krassovsky (45), (46), and (47) are bound to be more effective by day. The fourth reaction that he postulates (20) may be of relatively greater importance during the day if perhydroxyl is readily photolyzed. However, this latter reaction is not sufficiently energetic to provide the highly excited vibrational levels seen in the airglow.

Two of our airglow spectrometer measurements extended into the dawn, and the intensity of the signal appeared to diminish below the noise level of the instrument. It is likely that the change in signal was due to a change in performance of the detector rather than to a genuine reduction in hydroxyl emission. Additional experiments are required.

In the event that reaction (18) is the responsible reaction, it is clear that the height of peak hydroxyl emission must increase during the night. When atomic oxygen is fully converted to ozone, (18) removes hydrogen from the atmosphere and there is no mechanism for recreating it. The experimental data of Fig. 1 may reflect this behavior for the observation was made 9 hours after sunset.

CONCLUSION

Since wet ozone is readily photolyzed, one would expect atmospheric water vapor to affect the ozone distribution and ozone to be a tracer for water vapor. More importantly, water vapor may act as a thermostat for the ozone layer. Any increase in temperature, assuming an available reservoir of water, must lead to an increased water vapor mixing ratio and reduced equilibrium ozone. The resultant decrease in energy absorbed lowers the temperature. Thus, in the presence of a reservoir of water vapor, the peak temperature in the ozone layer cannot be high.

Although from the meteorological point of view this property is essentially conservative, variability in water vapor may lead to considerable fluctuation in the energy input to the stratosphere since a reservoir of water is unlikely to be a permanently stable feature of the stratosphere. The variability in water-vapor measurements reflects this point. It is easy to show that an instantaneous change in the local water-vapor mixing ratio from 10^{-5} to 10^{-2} in the 40-km region should

lead to a drastic change in heating, corresponding over one day to a temperature drop of several degrees.

There have been several studies of the correlation between solar activity and meteorological parameters. Some of these have discussed solar activity in the ozone layer.²⁶ The experimental data, which show the changes in ultraviolet solar flux to be small, mitigate against the thesis that such a correlation exists. However, if catalytic decomposition of ozone by water vapor can produce significant changes in ozonospheric heating, such a correlation may occur.

Studies similar to these have been carried out which appear to indicate a nitric oxide layer in the atmosphere, and some features of hydroxyl content and hydroxyl emission may have an important bearing on the energy balance of the upper stratosphere. However, the fact that several features have been seen and not identified and the small number of results obtained denote that we are only at the rudimentary beginnings of infrared studies of the upper atmosphere and the bulk of the problems lie hidden awaiting improved observation and inference. Order-of-magnitude improvements in existing equipment are feasible. Such measurements as temporal variation over short time intervals of the rotational temperature of hydroxyl emission are necessary and feasible.

One pertinent question remains. What is the value of these investigations to the aeronautical sciences? To understand the parameters controlling sustained commercial or military flying in the stratosphere, relevant data on temperature, winds, turbulence, ozone, corrosion effects, etc., can and must be gathered through measurement. Although such measurements do not require an understanding of the phenomena, an accurate appraisal of the energy input and resulting dynamics would be of great value in assembling them. The suggestion in this paper is that there is a requirement for improved meteorological studies of the stratosphere. Dynamic studies based on temperature and pressure fields are not enough. Is it more appropriate to assume that the thermal incline above the tropopause produces stability in the lower stratosphere, or that such stability is inferred from the mechanism which creates the thermal incline? If ozone concentrations are greatly affected by water vapor and thus the latter catalytically controls stratosphere temperature, the study of wet ozone photolysis will prove extremely rewarding.

It is a reflection on meteorological interest in the chemistry of the ozone layer that Heidt's experiments, made a generation ago, appear to have evoked no interest on the part of meteorologists and hardly rate mention in contemporary literature.

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