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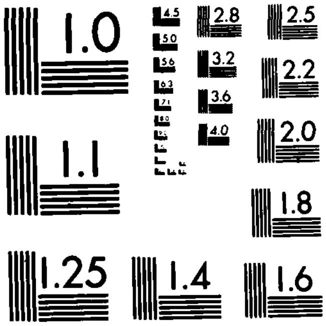

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COCHISE Observations of O_3 Formed by Three-Body Recombination of O and O_2

W.T. RAWLINS
R.A. ARMSTRONG

17 September 1982

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OPTICAL PHYSICS DIVISION PROJECT 2310
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Alva T Stair, Jr.

DR. ALVA T. STAIR, Jr
Chief Scientist

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Infrared spectra of the v_3 mode of ozone formed in the three-body recombination of O-atoms and O_2 have been observed in the cryogenic COCHISE facility. Temperature and pressure effects have been investigated. Correlations with field experiments are presented along with high-altitude LWIR emission implications.

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Contents

Illustrations

COCHISE Observations of O_3 Formed by Three-Body Recombination of O and O_2

1. INTRODUCTION

Ozone is now well-established as a major source of LWIR emission in the upper atmosphere, principally through its asymmetric stretch (ν_3) vibrational band near 10 μm.[1] Most of the atmospheric ν_3-band emission arises from resonant excitation by absorption of earth radiation, a process that significantly populates only the first vibrational level and thus does not produce significant O_3 emission at wavelengths longer than ~10 μm.[2] However, the recombination of atomic and molecular oxygen,

$$O + O_2 + M \rightarrow O_3(v) + M \quad , \tag{1}$$

has been shown to produce sufficient vibrational excitation in the $O_3(v)$ product to give rise to significant ν_3-band emission between 10 and 12 μm.[3,4,5] Indeed, this effect is dramatically illustrated in the rocketborne SPIRE observations of earth-limb radiation, which show major contributions to the total ν_3-band intensity near 80-100 km from the 10-12 μm "hot-bands," especially during the daytime when the total band radiation is reduced due to photochemical destruction of ozone.[6,7] In addition, the rocketborne HIRIS auroral observations indicate a

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(Received for publication 16 September 1982)

Because of the large number of references cited above, they will not be listed here. See References, page 19.

substantial and hitherto unexpected auroral enhancement in both band intensity and vibrational excitation in a strong aurora.[8, 9, 10] The mechanism for this effect is unknown, but most likely does not involve the O_2 recombination reaction (Eq. (1)). Possible excitation processes include direct excitation of O_3 by electron impact or by energy transfer from aurorally excited forms of O_2, N_2, or O; however, none of these processes have been identified in the laboratory.

The COCHISE facility has been used to study the vibrational excitation of ozone in electrically discharged O_2/Ar mixtures.[11, 12, 13] Our initial experiments,[11] the first spectrally resolved laboratory measurements of $O_3(v)$ emission, established a lower bound for the extent of the initial excitation due to reaction (Eq. (1)). Furthermore, the data at higher O_2 mixing ratios showed evidence of an additional excitation mechanism analogous to that suggested by the HIRIS auroral observations. This preliminary work had a limited dynamic range due to poor signal/noise ratio and marginal thermal performance of the cryogenic system. The analysis was further hampered by an imprecise knowledge of the vibrational spectroscopy of highly excited $O_3(v)$.

After extensive modifications and refurbishment of the COCHISE facility,[14] we have achieved order-of-magnitude improvements in the sensitivity and efficiency of the system, such that it is now worthwhile to repeat these $O_3(v)$ experiments over wider ranges of O_2 mixing ratio, gas temperature, and spectral resolution. Reducing the O_2 mixing ratio decreases the effects of collisional deactivation and thus allows a closer approach to the nascent distribution from Eq. (1), which is a critical parameter set for modeling the atmospheric O_3 emission. Variation of

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[8] Green, B.D., Rawlins, W.T., and Nadile, R.M. (1982) Diurnal variability of vibrationally excited ozone in the mesosphere, J. Geophys. Res. (to be submitted).

[9] Adler-Golden, S.M., Armstrong, R.A. (1982) Spectroscopic Parameters for Ozone From Infrared and Ultraviolet Techniques, AFGL-TR-82-0231, (In preparation).

[10] Rawlins, W.T. (1982) Chemistry of Vibrationally Excited Ozone in the Upper Atmosphere (manuscript in preparation).

[11] Rawlins, W.T., Caledonia, G.E., and Kennealy, J.P. (1981) Observation of spectrally resolved infrared chemiluminescence from vibrationally excited $O_3(\nu_3)$, J. Geophys. Res. 86:5247.

[12] Rawlins, W.T., Piper, L.G., Green, B.D., Wilemski, G., Goela, J.S., and Caledonia, G.E. (1980) LABCEDE and COCHISE Analysis II, Vol. I (Final Report) PSI-TR 207A, Physical Sciences Inc., Andover, MA 01801.

[13] Rawlins, W.T., Piper, L.G., Caledonia, G.E., and Green, B.D. (1981) COCHISE Research, PSI-TR 298, Physical Sciences Inc., Andover, MA 01801.

[14] Rawlins, W.T., Murphy, H.C., Taylor, R.L., and Caledonia, G.E. (1980) Final Report on COCHISE Refurbishment, PSI-TR 222, Physical Sciences Inc., Andover, MA 01801.

the reaction temperature allows the identification of effects of recombination and collisional deactivation, as well as other excitation processes that might occur. Lastly, improvement in the spectral resolution will permit more conclusive identification of vibrational band centers, enabling the construction of a more accurate spectral model for the emission.

We have recently conducted a series of experiments to address these issues. While the data analysis is still in an embroyonic stage, these new data are highly enlightening and provide observations that are important to the atmospheric infrared community. The features of the experimental results and their relevance to the modeling of high-altitude LWIR emission from O_3 will be reported here.

2. EXPERIMENTAL

The design and operation of the COCHISE facility have been described in detail elsewhere.[11-17] In brief, the entire radiative environment of the experiment is maintained at a base temperature of ~20 K, which effectively eliminates background radiation within the 2-20 μm operating range of the apparatus. The detection system consists of a scanning grating monochromator and a liquid-helium-cooled Si:As detector. Reagent gases are introduced through temperature-controlled feed lines to the reaction cell as shown in Figure 1. A flowing O_2/Ar mixture at ~1 *torr* passes through four parallel microwave discharges (2450 MHz, 50 w) prior to expending into a low-pressure (~3 mt), cryogenically pumped interaction volume. A counterflow gas (usually O_2) enters the volume from the opposite side to combine with the discharged gas in a stagnation region near the axis of the cell, which coincides with the axis of the cylindrical field-of-view of the detector. In some cases (for example, Kennealy et al[16]), this interaction consists of a chemical reaction under nearly single-collision conditions. However, in the present experiments, reaction (Eq. (1)) is too slow to occur significantly in the interaction zone at 3 mt, and all the O_3 emission observed arises from processes occurring in the

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15. Kennealy, J. P., DelGreco, F. P., Caledonia, G. E., and Rawlins, W. T. (1979) COCHISE: Laboratory spectroscopic studies of atmospheric phenomena with high-sensitivity cryogenic instrumentation, Proc. Soc. Photo-Opt. Instrum. Eng. (G. A. Vanesse, ed.), 191:151.

16. Kennealy, J. P., DelGreco, F. P., Caledonia, G. E., and Green, B. D. (1978) Nitric oxide chemiexcitation occurring in the reaction between metastable nitrogen atoms and oxygen molecules, J. Chem. Phys. 69:1574.

17. Caledonia, G. E., Green, B. D., Simons, G. A., Kennealy, J. P., Robert, F. X., Corman, A., and DelGreco, F. P. (1977) COCHISE Studies I: Fluid Dynamical and Infrared Spectral Analyses, AFGL-TR-77-0281, AD A053218.

discharge sidearms. This is readily confirmed by substituting non-reactive counterflow gases and obtaining no change in the observed emission intensity.

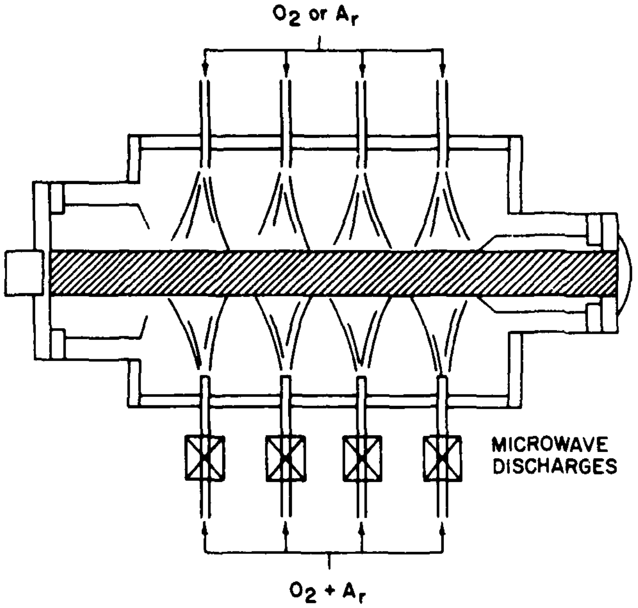

Figure 1. COCHISE Reaction Chamber. The cross-hatched region delineates the field-of-view of the detector (not shown)

In the experiments reported here, the reagent gases were introduced at temperatures of 80-150 K; most of the experiments were conducted at 80-90 K. In the discharged gas, the Ar flow rate was held at 640 μmole/s, and the O_2 flow rate was varied from 2.3-86 μmole/s (0.3-12 percent O_2). Under these conditions, the residence time in the chemically active portion of the sidearm is ~2 ms, and vibrational deactivation of $O_3(v)$ occurs mainly via collisions with O and, to a lesser extent, with O_2 and the surface of the discharge tube.[11]

Vibraluminescence from $O_3(v)$ was observed with spectral resolutions of 0.027-0.080 μm (2.7-8.0 cm^{-1}). All spectral data were acquired by an on-line computer and were corrected to radiometric units using blackbody calibrations of the spectral responsivity of the detection system.

3. $O_3(v)$ OBSERVATIONS

As described in Section 2, the formation of $O_3(v)$ occurs in the sidearms containing the microwave-excited plasma. Some of the O_2 in the incoming O_2/Ar mixture is dissociated via electron impact and/or energy transfer from Ar metastables. The O-atoms thus formed recombine with the remaining O_2, in the presence of Ar as a stabilizing third body, to give O_3 in some nascent distribution of vibrational (and rotational) states. Further collisions in the sidearm with O, O_2, Ar, and the tube walls serve to partially relax this distribution of states, resulting in the "arrested relaxation" spectrum, which is finally observed in the low-pressure zone. As the number density of the relaxation partners O and O_2 is decreased, we would expect to see an increase in the relative emission contributions from the higher vibrational levels of O_3. In this way, it may be possible to approach more closely the nascent state distribution for reaction Eq. (1).

The effects of initial O_2 level on the observed spectral distributions are illustrated in Figure 2. For the low-O_2 cases ($\leq$3 percent O_2), the spectra exhibit a characteristic intensity degradation to long wavelengths. This behavior is indicative of a Boltzmann or pseudo-Boltzmann vibrational state-population distribution, where the state populations decrease uniformly with increasing energy. This type of distribution would be expected for the recombination/relaxation steady-state, since Reaction (Eq. (1)) probably populates states fairly uniformly throughout the ν_3 manifold. Furthermore, the vibrational "temperature" is seen to increase as we progress to lower O_2 levels (as we expect) due to decreased collisional relaxation of the nascent $O_3(v)$. The "hottest" distribution occurs at the lowest O_2 flow that was measurable in these experiments, $\leq$0.3 percent O_2. When these spectra are spectrally analyzed to determine the vibrational state distributions, they will provide a much-improved lower bound for the initial excitation due to reaction (Eq. (1)).

At the higher O_2 levels, 4-12 percent O_2, a dramatically different spectral distribution appears, which suggests a population inversion at vibrational levels radiating between 10 and 11 μm. The growth of this effect with increasing O_2 strongly suggests that a second mechanism is coming into play, perhaps involving direct excitation of O_3 by energy transfer from discharge-excited O_2 or O. This type of process is similar to possible auroral excitation mechanisms (see Section 4).

Note that for the entire range of flow conditions and excitation distributions, the $O_3(v)$ radiation is confined to wavelengths shorter than ~ 11 μm (the features appearing at 11.1 and 11.5 μm are Rydberg transitions of Ar - see Rawlins, et al[13]). This is difficult to understand, since the bound vibrational states of the ν_3 mode should radiate up to about 12 μm. The absence of emission from states having transitions between 11 and 12 μm could occur if

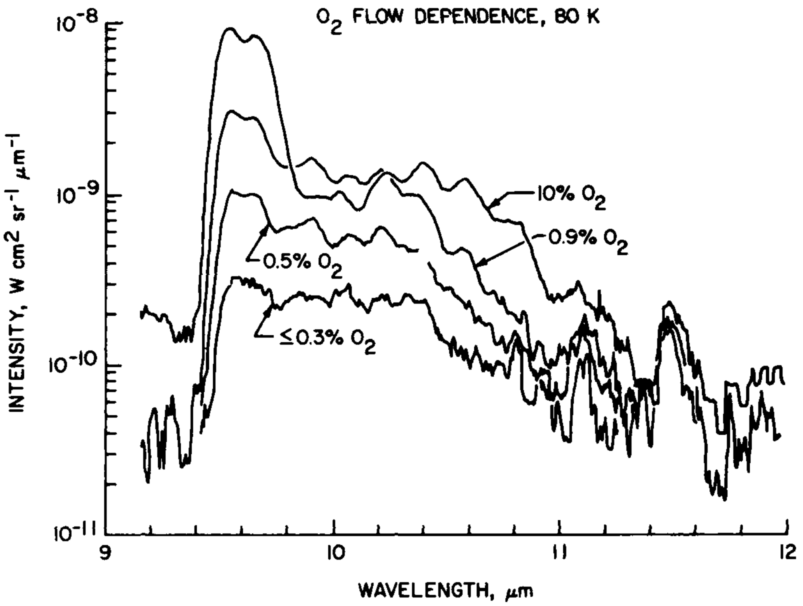

Figure 2. Effect of O_2 Level in Discharged O_2/Ar Mixtures on Observed Spectral Distributions. (No counterflow, 80 K, 640 μmole/s Ar, 0.08-μm resolution)

(1) the excitation processes do not form $O_3(v)$ in these higher levels ($v_3 > 6$),
(2) the Einstein transition probabilities cease to increase with increasing vibrational energy owing to higher order state-coupling effects,
(3) the high vibrational levels undergo very rapid collisional deactivation, or
(4) the levels $v > 6$ behave ergodically[18] and the vibrational energy is "scrambled".

Even though we do not yet understand the chemical dynamic reasons for this observation, these results have significant bearing on predictions of high altitude radiation in discrete LWIR bandpasses. Namely, it appears that vibrationally-excited $O_3(\nu_3)$ at high altitudes can give rise to significant radiation between 10 and 11 μm under the right conditions, but is surprisingly unlikely to do so between 11 and 12 μm.

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[18] Hansel, K.D. (1979) On the Dynamics of Multiphoton Dissociation of Polyatomic Molecules II Application to O_3 in Laser Induced Processes in Molecules, K. L. Kompa and S. D. Smith (eds.), Springer Series in Chemical Physics, Volume 6, Springer, Berlin.

The dependence of the observed spectral emission upon sidearm temperature was examined to further elucidate the excitation and deactivation kinetics. Sample results for a low-O_2 case are shown in Figure 3. The band intensity decreases uniformly with increasing temperature, closely matching the ~exp (500/T) temperature dependence observed[19] for reaction (Eq. (1)) near 300 K. The gross spectral distribution does not change significantly, but the resolvable structures present at 80 K do not appear at 135 K. The latter effect could be due to higher rotational temperature or to increases $\nu_3 \rightleftarrows \nu_1$ collisional coupling at the higher temperatures. The results shown in Figure 3 suggest that nearly all of the observed temperature effect is due to reaction (Eq. (1)) and that the temperature dependences of the major collisional deactivation processes are very weak. With more complete analysis, this type of data will allow improved estimates of temperature effects on collisional excitation and deactivation processes at high altitudes.

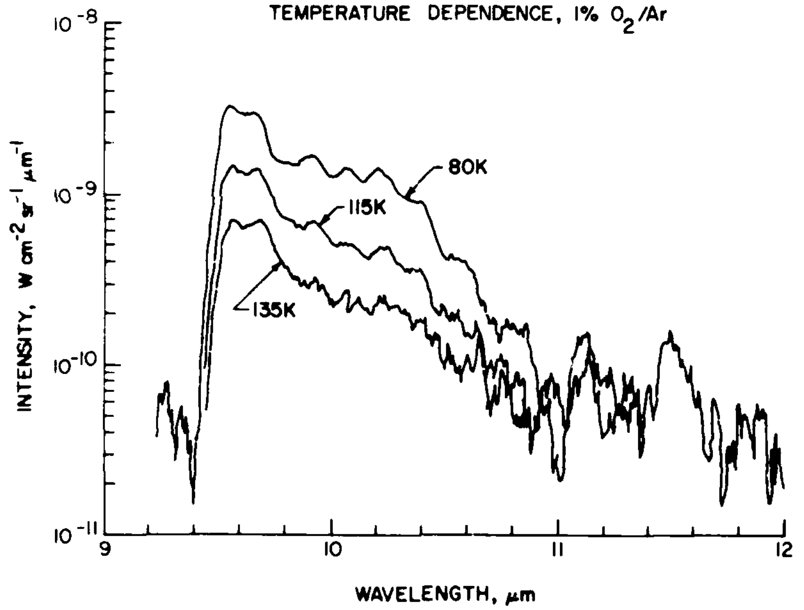

Figure 3. Effect of Temperature, Low-O_2 Case. (No counterflow, 640 μmole/s Ar, 1-percent O_2, 0.08-μm resolution)

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[19] Huie, R.E., Herron, J.T., and Davis, D.D. (1972) Absolute rate constants for the reaction of $O + O_2 + M \rightarrow O_3 + M$ over the temperature range 200-346 K, J. Phys. Chem. 76:2653.

The effects of temperature for a high-O_2 case are illustrated in Figure 4. The emission from the lowest vibrational level (near 9.6 μm) behaves as one would expect for the O_2 recombination mechanism, but the behavior at higher vibrational levels (9.9-11.0 μm) is remarkably different. While this complex behavior cannot be explained without considerable spectral analysis and kinetic interpretation, it presents clear evidence that a secondary excitation mechanism is present at highter O_2 levels.

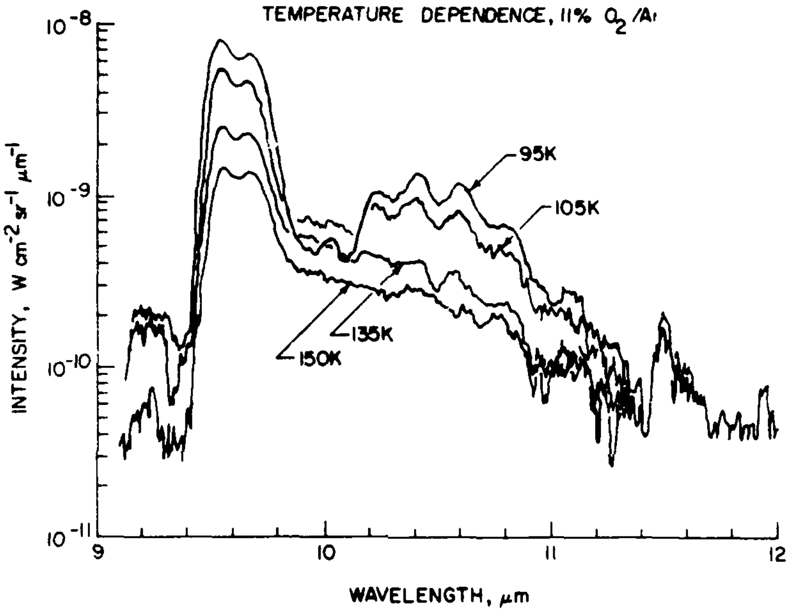

Figure 4. Effect of Temperature, High-O_2 Case. (No counter-flow, 640 μmole/s Ar, 11-percent O_2, 0.08-μm resolution)

Detailed spectral and kinetic analysis of the new O_3(v) data base is in progress. An important component of the spectral analysis will be to attempt to identify the band centers of the observed vibrational transitions. Several high-resolution O_3(v) spectra were obtained for this purpose. Particular attention will be given to the possible effects of Darling-Dennison coupling on the vibrational frequencies and transition probabilities,[9] and to possible contributions from $\nu_1 + \nu_3$ combination states. The objectives of the spectral analysis are to obtain a firm lower bound on the nascent O_3(v) distribution from O_2 recombination and data on the kinetic behavior of each vibrational state as functions of O_2 level and temperature. The data thus obtained will be interpreted in terms of a kinetic model of the processes likely to be occurring in the discharge plasma. In this way we hope to derive further information about the kinetics of reaction (Eq. (1)), the deactivation processes, and the hitherto unidentified secondary excitation of $O_3(v)$.

4. IMPLICATIONS FOR HIGH-ALTITUDE LWIR EMISSION

The COCHISE experiments on the O_2 recombination reaction yield steady-state vibrational distributions that are remarkably similar to those observed in the upper atmosphere. The earlier COCHISE results of Rawlins, et al[11] are compared in Figure 5 to distributions obtained from rocketborne measurements.[9, 20]

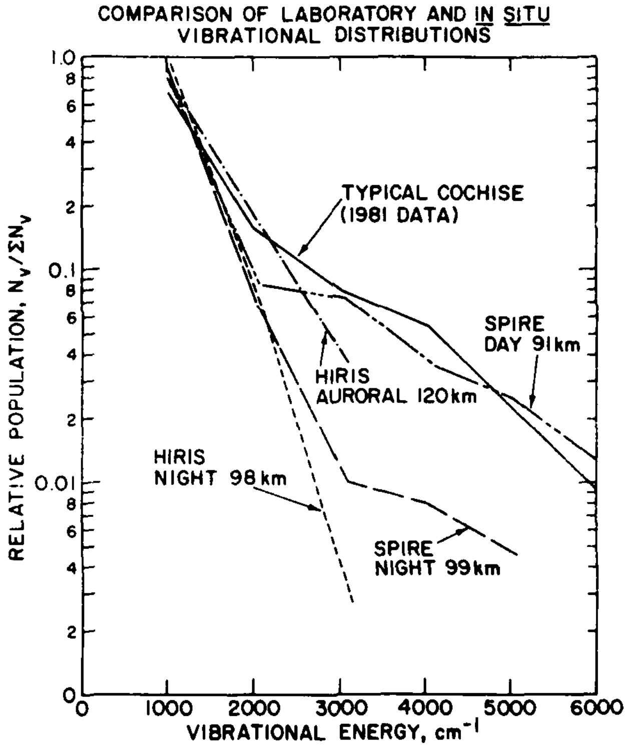

Figure 5. Comparison of Relative Vibrational State-Population Distributions for COCHISE, HIRIS, and SPIRE. Populations in each distribution are normalized to ΣN_v

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20. Rawlins, W.T., Caledonia, G.E., Gibson, J.J., and Stair, A.T. Jr. (1982) HIRIS rocketborne spectra of infrared fluorescence in the $O_3(\nu_3)$ band near 100 km (manuscript in preparation).

Vibrational distributions such as these are the principal observable quantities in IR spectro-radiometric measurements in the upper atmosphere; however, their interpretation requires considerable modeling of the detailed, vibrational-state-dependent kinetics of the system. Until very recently, no such modeling has been attempted for $O_3(v)$, owing largely to the formidable dearth of information on the excitation and deactivation of vibrationally-excited ozone. However, the information required to assess the presence of $O_3(v)$ in the upper atmosphere is essentially the same as that required to interpret the COCHISE laboratory data. Accordingly, we have begun to develop and exercise a steady-state kinetic model for high-altitude $O_3(v)$ that obtains much of its format and many fundamental parameters from information gleaned from COCHISE experiments as presented. The initial stage of this model is described in detail elsewhere[9, 10]; we will discuss here the major implications and how the modeling relates the laboratory and field measurements to each other, in order to present a comprehensive picture of the high-altitude radiative processes.

The kinetic processes involving formation and destruction of $O_3(v)$ in the upper atmosphere are outlined schematically in Figure 6. We represent the initial formation as recombination of O and O_2 into the ν_3 mode; this is followed by rapid $\nu_3 \rightarrow \nu_1$ transfer and relatively slow $\nu_3, \nu_1 \rightarrow \nu_2$ transfer, as well as by collisional and radiative cascade relaxation. The lowest vibrational states are also populated by absorption of earth radiation by O_3. The major modeling difficulties are, first, expressing the initial vibrational distribution for the O_2 recombination reaction, and, second, extending kinetic and spectroscope data for low-lying vibrational states to very high quantum levels. The COCHISE results, showing spectral distributions as functions of $[O_2]$ and temperature, provide the insight necessary to address these problems. In particular, we have used two different assumptions for the nascent $O_3(v)$ distribution: (1) the ~2000 K lower bound given by the earlier COCHISE data of Rawlins, et al[11] (this lower bound will be increased significantly upon analysis of the new data presented here); and (2) a "statistical" distribution computed assuming maximum entropy change (that is, zero surprisal) for an O_2-O recombination. The principal modeling results to date are: (1) collisional deactivation is at most a minor process above ~ 80 km, although the effects of atomic oxygen are highly uncertain; and (2) since the first vibrational level is populated mainly via earthshine absorption by ground-state O_3 and the higher levels are formed exclusively by reaction of O with O_2, the predicted vibrational state distributions are governed largely by the assumed O and O_3 density profiles, thus offering a means of determining these critical atmospheric properties from high altitude IR spectral data.

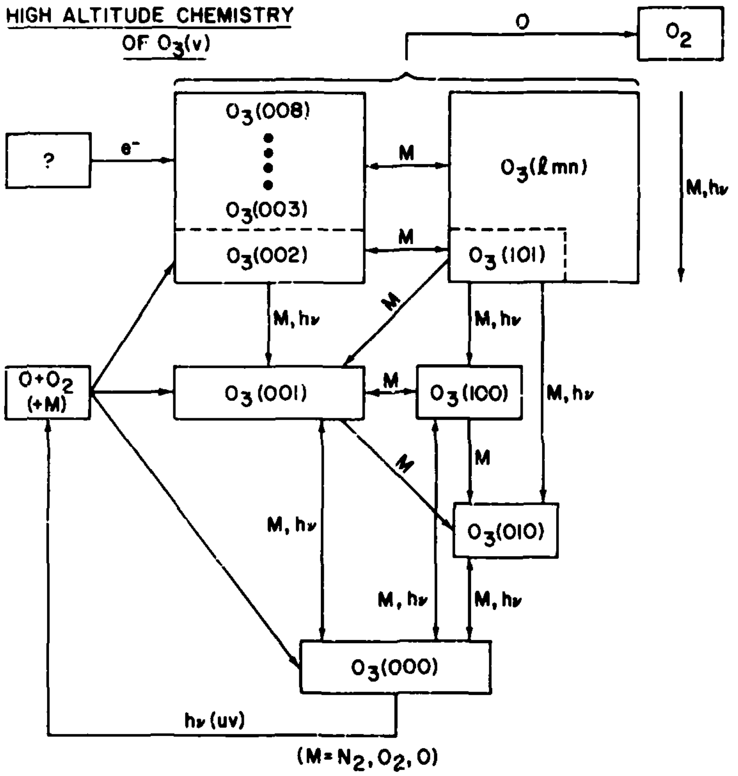

Figure 6. Schematic Diagram of the High-Altitude Chemistry of Vibrationally-Excited Ozone

In general, the model predictions and field observations are in excellent agreement for the quiescent sunlit and dark atmosphere, and the spectra observed in situ clearly can be explained in terms of the O_2 recombination mechanism. However, limited observations by HIRIS[9, 20, 21] of dramatic enhancements in band intensity and vibrational excitation during an intense aurora cannot be explained by this model, and an additional excitation mechanism must be postulated. This mechanism may involve direct energy transfer to ground-state O_3 from an aurorally excited form of O, O_2, or N_2 in a process similar to the secondary excitation reaction evidenced in the COCHISE high-O_2 experiments.

The modeling points to a number of crucial parameters that still need to be determined by fundamental experimental or theoretical studies. These include the

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21. Stair, A.T. Jr., Pritchard, J., Coleman, I., Bohne, C., Williamson, W., Rogers, J. and Rawlins, W.T. (1982) The rocketborne cryogenic (10 K) high resolution interferometer spectrometer flight-HIRIS: Atmospheric and auroral infrared emission spectra, Applied Optics (to be submitted).

true nascent vibrational distribution of $O_3(v)$ formed in O_2 recombination, the radiative transition probabilities for the higher vibrational levels, and the detailed kinetics of the $O + O_3(v)$ interaction. In addition, there remain questions about the degree of intermode versus intramode energy transfer, and about the possibility of electronically excited precursors to the $O_3(\nu_3)$ signatures actually observed. Further COCHISE experiments are being planned to address most of these issues. For example, we intend to survey the IR spectrum of recombining O_2 from 2-16 μm in search of evidence for the ν_1 (9 μm), ν_2 (14 μm), $\nu_1 + \nu_3$ (4.7 μm), and $3\nu_3$ (3.2 μm) bands, as well as for possible transitions[3] involving electronically-excited ozone. In particular, a spectral analysis of the $\nu_1 + \nu_3$ combination band will assist greatly in the delineation of the effects of $\Delta v_3 = 1$ transitions from combination states at 10 μm, and will serve to verify model predictions and field observations of the 4.7-μm band radiance at high altitudes. In addition, we are presently engaged in a feasibility study for a new type of COCHISE experiment aimed at directly observing the nascent $O_3(v)$ from recombination in the center of the reaction chamber. In this approach, Ar/N_2O mixtures will be passed through the microwave discharges to produce O, and O_2 will be present only in the counterflow gas. However, these measurements will require operation of the cell at elevated pressure (10-30 mt) and temperature (~40 K), conditions that have not been used before but which are well within the capabilities of the apparatus. Our feasibility calculations indicate that, if the ratio $[O]/[O_2]$ can be increased enough, it may be possible to assess the effects of the $O + O_3(v)$ process.

5. SUMMARY

Recent COCHISE observations of LWIR radiation from O_2 recombination ($O + O_2 + Ar$) in O_2/Ar discharge plasmas have greatly increased the laboratory data base on the spectroscopy and kinetics of vibrationally excited O_3. These data provide both direct and indirect information that can be used in modeling high-altitude IR radiation and in interpreting the in situ data base. Indeed, the earlier COCHISE results have been used to construct a successful steady-state model for $O_3(v)$ near the mesopause.

The current COCHISE data described here will be analyzed to obtain lower bounds for the nascent $O_3(v)$ distribution, improved values for band centers of the "hot band" transitions, and information on intermode transfer and collisional relaxation kinetics. In addition, we will closely examine and kinetically model the high-O_2 cases in an attempt to identify the secondary excitation mechanism responsible for the observed distributions. Additional experiments will be performed as necessary to verify and extend the present results.

Future COCHISE experiments will continue to address aspects of the high-altitude $O_3(v)$ problem. In the near term, spectral surveys of all IR emission from O_2/Ar discharges (2-16 μm) will delineate any other O_3 band systems that can be excited in recombination. Longer range experiments, utilizing discharged N_2O as a source of O in the absence of O_2, are being planned in order to directly observe nascent $O_3(v)$ formed in the interaction zone at elevated reaction cell pressures.

The principle unknowns in modeling and assessing high-altitude radiation from $O_3(v)$ are the nascent $O_3(v)$ distribution from O_2 recombination, the identity of the auroral mechanism for $O_3(v)$ excitation, the collisional quenching effects of O and, to a lesser extent, O_2 and N_2, and the radiative properties of $O_3(v)$. The COCHISE experiments address each of these problems either directly or indirectly, and are likely to contribute a great deal of information toward solving these problems. However, the major difficulty that is least-directly addressed in COCHISE is that of the radiative transition probabilities of $O_3(v)$. This parameter set is crucial for the determination of state populations from laboratory and field data, for kinetically modeling $O_3(v)$ relaxation, which is in or near the radiative limit above 80 km, and for predicting band radiances from kinetically-modeled $O_3(v)$ state distributions. In particular, it is important to learn whether the behavior of the transition probabilities at high vibrational energy could be responsible for the surprising 11 μm "cutoff" observed in our experiments. Thus, experimental and/or theoretical efforts directed toward determination of the upper-level transition probabilities are sorely needed.

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