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ABSTRACT

Recent rocket observations of the N_2 V-K (Vegard Kaplan) system in the aurora have been reinterpreted using an atmospheric model based on mass spectrometer measurements in an aurora of similar intensity at the same time of year. In contrast to the original interpretation, we find that population by cascade from the C $^3\Pi_u$ and B $^3\Pi_g$ states in the A $^3\Sigma_u^+$ v = 0,1 levels, as calculated using recently measured electron excitation cross sections, accurately accounts for the observed relative emission rates ($I_{V-K}/I_{2PG_{0,0}}$). In addition there is no need to change the production rate of A $^3\Sigma_u^+$ molecules relative to that of C $^3\Pi_u$ v = 0 as a function of altitude in order to fit the profile of the deactivation probability to the atmospheric model. Quenching of A $^3\Sigma_u^+$ molecules at high altitudes is dominated by atomic oxygen. The rate constants for the v = 0 and v = 1 levels are $8 \times 10^{-11} cm^3 sec^{-1}$ and $1.7 \times 10^{-10} cm^3 sec^{-1}$ respectively, as determined using the model atmosphere mentioned above. Recent observations with a helium cooled mass spectrometer suggest that conventional mass spectrometer measurements tend to underestimate the atomic oxygen relative concentration. The rate coefficients may therefore be too

large by as much as a factor of 3. Below 130 km we find that it is possible to account for the deactivation in bright auroras by invoking large nitric oxide concentrations, similar to those recently observed mass spectrometrically and using a rate constant of $8 \times 10^{-11} cm^3 sec^{-1}$ for both the v = 0 and v = 1 levels. This rate constant is very nearly the same as that measured in the laboratory ($7 \times 10^{-11} cm^3 sec^{-1}$). Molecular oxygen appears not to play a significant role in deactivating the lower $A\ ^3\Sigma_u^+$ levels.

I. INTRODUCTION

The A $^3\Sigma_u^+$ state of N_2 is populated efficiently in the aurora by direct electron excitation and by cascade from higher states. The resultant radiation in the Vegard-Kaplan (V-K) system, (A $^3\Sigma_u^+$ - X $^1\Sigma_g^+$), would make this the brightest spectral feature of the aurora-15 kR in the spectral range from 1500Å to 4000Å for an IBC I aurora according to Shemansky et al.(1971) if most of the molecules excited to the A $^3\Sigma_u^+$ state were not quenched by collisions. In this article we discuss the excitation and deactivation of the A $^3\Sigma_u^+$ state.

It appears to have been established that the dominant excitation modes of the A $^3\Sigma_u^+$ $v < 3$ levels due to electron bombardment of N_2X $^1\Sigma_g^+$ are radiative transitions from the B $^3\Pi_g$ state in the $N_2$1P (first positive) system (cf. Broadfoot and Hunten, 1964, Shemansky and Broadfoot 1971a). The electron cross-section of the A $^3\Sigma_u^+$ state is comparable to that of the B $^3\Pi_g$ state according to recent estimates (cf. Shemansky and Broadfoot, 1971a), but virtually all of the production by this mode goes into the higher A $^3\Sigma_u^+$ ($v > 3$) levels. The relative production rates of the A $^3\Sigma_u^+$ state levels due to the combined modes are roughly comparable for levels $v = 0$ to $v \approx 12$, according to Shemansky et al 1971. Furthermore, the relative production rates of the C $^3\Pi_u$, B $^3\Pi_g$ and A $^3\Sigma_u^+$ states should be essentially independent of the auroral electron energy distribution. The calculated relative production rates of the N_2C $^3\Pi_u$, N_2B $^3\Pi_g$, N_2^+A $^2\Pi_u$ and N_2^+B $^2\Sigma_u^+$ states using the electron excitation cross-sections estimated by Shemansky and Broadfoot (1971a) do in fact compare well with average auroral observations (Shemansky et al, 1971). The question then is whether the observed auroral emission in the N_2V-K system is consistent with this simple electron excitation scheme of direct excitation combined with cascade contributions from the $C\ ^3\Pi_u$ and $B\ ^3\Pi_g$ states in the $N_2$1P and $N_2$2P (second positive) systems. According to our interpretation of the evidence, this is actually the case.

Observations of the N_2 V-K transitions have been limited to the v'<3 levels with some uncertain identification of transitions from v'=4,5 (Chamberlain, 1961). Thus the only levels that have been observed in the aurora are those populated by radiative transitions from the $B\ ^3\Pi_g$ state. The apparent absence of transitions from the higher $A\ ^3\Sigma_u^+$ levels according to the present analysis, is probably due to a combination of the distribution of band transition probabilities and spectral positions, along with moderately higher quenching rates. Deactivation by N_2 $X\ ^1\Sigma_g^+$ molecules becomes significant for $A\ ^3\Sigma_u^+$ v>5 levels, according to Shemansky and Broadfoot (1971a). Auroral rocket observations (Miller et al, 1963, Isler and Fastie, 1965, Peek, 1970) in the appropriate wavelength region (1500Å - 1900Å) appear not to be of sufficiently high quality for identification of the higher level transitions.

The $A\ ^3\Sigma_u^+$ v<3 - $X\ ^1\Sigma_g^+$ transitions have been throughly studied from the ground by Broadfoot and Hunten (1964)(cf. Hunten, 1965) in the 3100Å - 3700Å region. This work produced evidence for considerable variability in emission rates of N_2V-K relative to the $N_2$2P system, associated with auroral brightness. Volume production rates of the observed $A\ ^3\Sigma_u^+$ levels predicted from emission rates in the $N_2$1P and $N_2$2P systems are generally an order of magnitude larger than the observed emission rates in the N_2V-K system. Thus quenching clearly plays a large part in controlling the $A\ ^3\Sigma_u^+$ population. Recent rocket observations by Sharp (1971) have produced valuable measurements of the N_2V-K, v'<2, volume emission rates in the 100km - 200km region. These measurements are of considerable interest since they allow calculation of the altitude dependence of quenching. The analysis given below differs in two respects with the original interpretation by Sharp. First of all, we suggest that the simple excitation scheme discussed above accurately predicts the production rates of the A $^3\Sigma_u^+$ v < 2 levels, and the additional population modes proposed by Sharp, involving both radiative and collisional transitions from the A $^3\Sigma_u^+$ v > 6 and W $^3\Delta_u$ levels, are not significant contributors. Secondly, we propose that in that particular aurora the dominant deactivators of A $^3\Sigma_u^+$ v < 2 molecules were a combination of nitric oxide and atomic oxygen rather than the original combination suggested by Sharp, molecular and atomic oxygen. Deactivation by atomic oxygen is dominant above 130km. The rate constants are 8.5 x $10^{-11}cm^3sec^{-1}$ and 1.7 x $10^{-10}cm^3sec^{-1}$ for the v' = 0,1 levels, roughly the same as those obtained by Sharp, but 2 orders of magnitude larger than the laboratory estimate by Meyer et al. (1969). Part of the discrepancy could be due to difficulties associated with measurement of the atomic oxygen concentration in the laboratory, but there is also a suggestion that the mass spectrometer measurements of atmospheric concentration may be underestimated by as much as a factor of 3 (Offermann and Von Zahn, 1971). The interpretation of deactivation in the altitude region below 130km is based on recent rocket borne mass spectrometer measurements (Zipf et al, 1970) which indicate large densities of nitric oxide associated with the brighter auroras. The use of a rate constant, 8.5 x $10^{-11}cm^3sec^{-1}$ for the v' = 0,1 levels, slightly larger than the value measured in the laboratory by Young et al (1969), accurately accounts for the observed deactivation probability. Deactivation by O_2 may not be significant under any auroral condition if we accept the rate constants estimated in the laboratory (Young et al, 1969, Meyer et al, 1969, Gutcheck and Zipf, 1971). The variations in relative emission rate of the N_2 V-K bands associated with auroral brightness as observed from the ground (Broadfoot and Hunten, 1964) are thus likely to be due to variations in atmospheric composition in the lower auroral altitudes coupled with auroral altitude variations, rather than a result of variations in the excitation mechanism of the $N_2B\ ^3\Pi_g$ state.

II. DISCUSSION

We assume the populations (N_v) of the $N_2A\ ^3\Sigma_u^+$ vibrational levels are determined by the equation.

$$d\,N_v/dt = -N_v(\overline{A}_v + D_v) + gVK_v, \tag{1}$$

where $\overline{A}_v$ is the mean transition probability for spontaneous emission, D_v is the quenching probability and g_v is the population rate of level v.

We apply the steady state version of Eq. 1 to relate volume emission rate (I) in the Vegard Kaplan bands to the population rate, and thus assume that transient variations have been removed from the data:

$$IVK_{v'v''} = (\overline{A}_{v'v''}/\overline{A}_{v'})\ gVK_{v'}\ SV_{v'} \tag{2}$$

where

$$SV_v = 1/(1 + D_{v'}/\overline{A}_{v'}) \tag{3}$$

is the Stern-Volmer quenching factor.

The volume emission rate (Eq. 2) is thus determined by the product of the two principle quantities required for an understanding of the auroral characteristics. In principal one can obtain a measure of production rate (g_v) through extrapolation of the observations to zero pressure. However, auroral excitation conditions are never well behaved and we require a direct measure of the source function variations in order to obtain a reasonable measure of altitude dependence of the Stern-Volmer factor. Thus the analysis depends critically on an independent measure of the altitude variation of g_v. An independent measure of the absolute g_v is obviously preferable. Our calculations of the production and deactivation profiles depend entirely on the Sharp (1971) rocket measurements. Unfortunately these observations do not provide a direct measure of the B $^3\Pi_g$ populations which directly determine the production rates of the A $^3\Sigma_u^+$ $v \leq 3$ levels. The monitor of the source function in this case is the measured volume emission rate of the $N_2 2PG_{0,0}$ band. The calculation of $gVK_{v<3}$ as a function of altitude then depends on the production rates of the B $^3\Pi_g$ levels ($g1PG_v$) as determined from the measured $I2PG_{0,0}$. Our interpretation of the production modes of the B $^3\Pi_g$ levels differs with that of Sharp. The calculations are therefore discussed in detail below.

A. Determination of Population Rates gVK_v

The population rate gVK_v can be written

$$gVK_v = \sum_{v'} I1PG_{v',v} + [N_2] \int (QVK_v) \; \Phi \; dE \tag{4}$$

where Q is the excitation cross section, Φ is differential electron flux and E is electron energy. The first term on the right side of this equation represents the population rate due to radiation in the first positive system, B $^3\Pi_g$ - A $^3\Sigma_u^+$. The second term represents the population rate due to direct electron excitation, A $^3\Sigma_u^+$ - X $^1\Sigma_g^+$. The contribution of the second term to levels v < 3 is negligible and $gVK_{v<3}$ is determined entirely by the emission rate of the $N_2$1PG (cf. Shemansky and Broadfoot 1971a). The populations of the first three vibrational levels of the B $^3\Pi_g$ state in fact determine the population rates of the first three A $^3\Sigma_u^+$ levels; about 70% of the population in the A $^3\Sigma_u^+$ v < 3 levels is contributed by the B $^3\Pi_g$ v = 0,1 levels and about 95% from the B $^3\Pi_g$ v = 0,1,2 levels. We believe there is general agreement with the above statements concerning the nature of Eq. 4. However, the present work differs with the Sharp (1971) analysis in the population modes of the B $^3\Pi_g$ state. According to Shemansky et al. (1971) and the present analysis the populations of the B $^3\Pi_g$ state are effectively determined by two processes; direct electron excitation in the B $^3\Pi_g$ - X $^1\Sigma_g^+$ system and radiative transitions in the $N_2$2P (C $^3\Pi_u$ - B $^3\Pi_g$) system. This is represented formally by the equation

$$g1PG_v = \sum_{v'} I2PG_{v',v} + [N_2] \int (Q\ 1PG_v)\ \Phi\ dE, \qquad (5)$$

where the C $^3\Pi_u$ state is populated entirely by direct electron excitation in the C $^3\Pi_u$ - X $^1\Sigma_g^+$ system:

$$g2PG_v = [N_2] \int (Q2PG_v)\ \Phi\ dE \qquad (6)$$

The Stern-Volmer factors for the $N_2$1P and 2P systems are expected to be very nearly unity for normal auroras since the lifetimes of the B $^3\Pi_g$

and C $^3\Pi_u$ states are less than 10^{-5}sec. As we have noted in the introduction, the ratio $gVK_v/g1PG_v/g2PG_v$ as determined by Eqs. 4, 5 and 6 does not have a significant dependence on variations in the energy spectrum of the auroral electrons (Shemansky et al.1971). The reduction of Eqs. 4, 5, 6 in a form appropriate to the Sharp rocket observations can be obtained with the use of appropriate transition probabilities (Shemansky 1969, Shemansky and Broadfoot, 1971b) and the relative auroral population rates predicted by Shemansky et al.(1971):

$$gVK_0 = 5.9\ I2PG_{0,0} \tag{7}$$

$$gVK_1 = 5.7\ I2PG_{0,0} \tag{8}$$

Eqs. 7 and 8 are thus determined by the electron excitation cross-section $Q2PG_v$ and $Q1PG_v$ as measured by Shemansky and Broadfoot (1971a).

The equivalent of Eq. 5 in the Sharp analysis contains three additional population modes; radiative contributions in the A $^3\Sigma_u^+$ $v > 6$ – B $^3\Pi_g$ and W $^3\Delta_u$ – B $^3\Pi_g$ systems and collision transfer, A $^3\Sigma_u^+$ $v > 6 \rightarrow$ B $^3\Pi_g$, through collisions of A $^3\Sigma_u^+$ $v > 6$ molecules with ground state N_2. In his rocket observations carried out in an IBC II aurora over Fort Churchill, Manitoba in March, 1969 Sharp measured the emission rate of the (0,0) band of the N_2 second positive system as well as $IVK_{0,v}$ and $IVK_{1,v}$ for the Vegard-Kaplan system. The relationships (7) and (8) permit us to calculate gVK_0 and gVK_1 from his second positive observations. Provided we know the transition probabilities involved we can use his observations of $IVK_{0,v}$ and $IVK_{1,v}$ to determine from Eq. 2 what quenching rates D_0 and D_1 are needed to produce the resulting ratios of I_v to g_v. However, before we discuss the transition probabilities and deactivation rates, we wish to address ourselves to the question of why we believe that adoption of the scheme just described to compute the rates $g2PG_v$, $g1PG_v$ and gVK_v based on the Shemansky and Broadfoot (1971a) cross sections is to be preferred to the mechanisms chosen by Sharp. We shall show that the latter scheme grossly overestimates the auroral intensity of bands of the first positive relative to bands of the second positive system while our procedure predicts correctly the observed ratios.

In Table 1 we show the population rates g_v for the C $^3\Pi_u$, B $^3\Pi_g$ and A $^3\Sigma_u^+$ states calculated according to our procedure by Shemansky et al (1971). The B $^3\Pi_g$ state rates contain both the direct and cascade contributions. The upper levels of the A $^3\Sigma_u^+$ state are produced mainly by direct electron impact excitation, the lower levels by radiative decay of the B $^3\Pi_g$ and C $^3\Pi_u$ states as we have already pointed out. We can use these results to predict ratios of various emission features for comparison with auroral data. The predicted ratios $I1PG_{5,2}/I(2PG)$, $I1PG_{0,0}/I1PG_{5,2}$ and $I1PG_{0,0}/I1PG_{1,0}$ are compared with observed values in Table 2. The observations on which this comparison is based are discussed in detail in our paper on the electron energy spectrum (Shemansky et al, 1971). The point we wish to make here is that our calculation predicts the correct ratio of first to second positive excitation rates and the correct distribution of rates within the B $^3\Pi_g$ state. It is to assure ourselves about the latter point that we make the comparison of different first positive band intensities.

On the other hand the excitation cross section (Cartwright, 1970) for the B $^3\Pi_g$ state used by Sharp is a factor of 2.5 smaller than the Shemansky and Broadfoot value used here. Because additional excitation of lower $B\ ^3\Pi_g$ state levels was then needed to feed the lower $A\ ^3\Sigma_u^+$ state levels and produce the observed ratios of Vegard-Kaplan to second positive emission rates, it was assumed that upper vibrational levels ($v > 6$) of the $A\ ^3\Sigma_u^+$ state and levels of the $W\ ^3\Delta_u$ state radiatively populated these lower $B\ ^3\Pi_g$ state levels at a high rate. We find that this scheme underestimates the excitation rates of the upper levels of the $B\ ^3\Pi_g$ state relative to the $C\ ^3\Pi_u$ state leading to a predicted ratio of $I1PG_{5,2}$ to I2PG lower than the observed by a factor of 2. It overestimates the population of low $B\ ^3\Pi_g$ state levels relative to high levels leading to predicted ratios $I1PG_{0,0}/I1PG_{5,2}$ and $I1PG_{0,0}/I1PG_{1,0}$ too high by factors of about 3 and 1.5. Apart from this strong indication from auroral measurements it is difficult to produce much other evidence theoretical or experimental for or against the Cartwright scheme. The inclusion of the additional excitation modes in the Sharp calculations was not due to any direct evidence for significant contributions by these processes. The relative contribution of the radiative $A\ ^3\Sigma_u^+\ v > 6 - B\ ^3\Pi_g$ transitions depends on whether the transition probabilities are larger or smaller than the corresponding $A\ ^3\Sigma_u^+ - X\ ^1\Sigma_g^+$ probabilities. A crude estimate can be made by extrapolation of the $B\ ^3\Pi_g - A\ ^3\Sigma_u^+$ electronic transition moment. However this provides little information of value other than the suggestion that the $A\ ^3\Sigma_u^+\ v > 6 - B\ ^3\Pi_g$ probabilities are in the order of magnitude region of those of the $A\ ^3\Sigma_u^+ - X\ ^1\Sigma_g^+$ transition (Shemansky and Broadfoot 1971a). Thus one could not expect to observe the effect of the A - B transition on the $B\ ^3\Pi_g$ state in the laboratory due to removal of the $A\ ^3\Sigma_u^+$ molecules by a combination of heterogenous and homogenous collisional deactivation. Combined transient and steady state low pressure measurements in the laboratory (Shemansky and Broadfoot 1971a) display no evidence of processes other than those determining the predicted numbers given in Tables 1 and 2 and a low pressure afterglow effecting the higher B $^3\Pi_g$ levels. We must then rely on the auroral measurements for evidence of significant contributions from the A - B and W - B transitions. If we accept the Shemansky and Broadfoot cross-section measurements, the values in Table 2 suggest there are no significant additional contributions to the B $^3\Pi_g$ $v < 5$ populations.

Shemansky and Broadfoot (1971a) claim to observe a low pressure afterglow in N_2 excited by low energy electrons, due to collision transfer to B $^3\Pi_g$ $v > 4$ levels through the reaction

$$N_2A\ ^3\Sigma_u^+\ v > 6 \ + \ N_2X\ ^1\Sigma_g^+ \ \rightarrow \ N_2B\ ^3\Pi_g \ + \ N_2X\ ^1\Sigma_g^+ \quad ,$$

The afterglow displays some of the characteristics of the Lewis-Rayleigh afterglow; peak population rates occur at B $^3\Pi_g$ $v = 6$ and B $^3\Pi_g$ $v = 12$, and no levels B $^3\Pi_g$ $v > 12$ are observed. The B $^3\Pi_g$ $v < 5$ levels were not measurably affected by the process. We estimate that collision transfer to the B $^3\Pi_g$ $v = 6$ and 12 levels at 100 km would contribute fractions of ~ 10% and ~ 100% of the electron population rates, respectively. The estimate is based on crude values of the collision transfer rate coefficient given by Shemansky and Broadfoot (1971a), and on the assumption of gas kinetic rates for deactivation of the higher A $^3\Sigma_u^+$ levels by [NO] and [O] (see below). The contributions to either of the B $^3\Pi_g$ levels would be very difficult to detect in the aurora; transitions from the B $^3\Pi_g$ $v = 12$ level are barely observable (cf. Chamberlain, 1961) and factor of 2 variations would go unnoticed. The only published evidence suggesting auroral variations in the upper B $^3\Pi_g$

vibrational populations (Shemansky and Vallance Jones, 1968) indicates a decrease in vibrational development with decreasing altitude, rather than the increase one would expect from the collision transfer process.

A further possibility of collision induced vibrational cascade within the A $^3\Sigma_u^+$ state appears to be remote even for levels $v < 6$ where electronic deactivation by $[N_2]$ would be slow; analysis of the N_2 afterglow (Shemansky 1971) suggests that A $^3\Sigma_u^+$ $v < 3$ levels are not populated significantly by this process, and that A $^3\Sigma_u^+$ $v > 1$ levels are removed electronically at a higher rate.

In Table 1 the total rates Σg_v shown are the predicted column emission rates in kR for the second positive, the first positive and the Vegard-Kaplan systems in an IBC I aurora in the absence of quenching. We also show the rates of population of the first three vibrational levels of the A $^3\Sigma_u^+$ state calculated from the observations of Broadfoot and Hunten (1964) and Sharp (1971). These values are all normalized to the same rate calculated in Column 3 for $v = 0$ in an IBC I aurora. We have used the data in Table 1 to predict the ratio of volume excitation rate in the $v = 0$ level of the A $^3\Sigma_u^+$ state to the volume emission rate in the $N_2 2PG_{0,0}$ band and show this rate also in Table 2. It has the value of 5.9 already given in Eq. (7). The ratio of emission rates $IVK_0/I2PG_{0,0}$ observed by Sharp at 200 km was 4.8. If this value is corrected for a roughly estimated collisional quenching rate of 0.2 sec^{-1} the deduced population rate ratio would be 6.6 as shown. The quenching rate 0.2 sec^{-1} is the probability predicted from our calculated deactivation profile which we discuss below. Thus at 200km, quenching is not severe and the Stern-Volmer factor is as large as $SV_0 \approx 0.7$.

B. Transition Probabilities of the A $^3\Sigma_u^+$ State

According to Shemansky (1969) the A $^3\Sigma_u^+$ sub-states have two distinct lifetimes. The transition probabilities applied to the N_2V-K bands examined here must then be mean values dependent on the relative populations of the sub-states. In the laboratory case where the relative sub-state populations are maintained in thermal equilibrium (Shemansky, 1969), one can apply an invariant mean transition probability, $\bar{A}_v$. However the auroral condition presents the possibility of a variable $\bar{A}_v$. The excitation transitions for production of A $^3\Sigma_u^+$ are symmetrical and the sub-states are populated at approximately equal rates, with the exception of the first few rotational levels. However, due to the double lifetime, rotational thermal equilibrium in the excitation source will not be reflected in the sub-state distribution of the A $^3\Sigma_u$ state unless there are enough relaxation collisions during the radiative lifetime. We may have a condition in which the sub-state populations are characterized by the production rates in the 200 km region where there are few or no collisions in the radiative lifetimes, while at lower altitudes the sub-states would be in thermal equilibrium. The lifetimes of the sub-states differ by a factor of 2. However it can be shown that the mean transition probability $\bar{A}_v$ cannot vary by more than about 10% in the aurora, and a calculation using reasonable values for the relaxation and radiationless deactivation rate coefficients suggest a variation of less than 2% at altitudes ranging from 200 km down to the 100 km region (Appendix). According to Shemansky (1969) (cf. Shemansky and Carleton, 1969) the lifetimes of the A $^3\Sigma_u^+$ v = 0 levels are 1.27 sec for $\Sigma = 0$ sub-state levels and 2.5 sec for $\Sigma = 1, -1$ levels. The mean transition probabilities are $\bar{A}_0 = 0.52$ sec^{-1}, $\bar{A}_1 = 0.51$ sec^{-1},

$\bar{A}_2 = 0.50 \text{ sec}^{-1}$, for the first three vibrational levels.

C. Quenching Probability, D_v, of the A $^3\Sigma_u^+$ State

We are now in a position to calculate the quenching rates (Eq. 2) as determined from the ratios of the observed IVK_0 and IVK_1 to the calculated production rates obtained from Eqs. (7) and (8). The values of D_v required to explain Sharp's results are plotted in Fig. 1. The change in curvature at 180 km is not real in our opinion, and is assumed to reflect minor systematic differences, ~ 5% - 20%, between the predicted population rates gVK_v and the values determined by extrapolation, of the measured IVK_v, to zero pressure. Minor errors in the ratio gVK_v/IVK_v tend to produce large errors in the calculated deactivation probability, D_v, at high altitudes where the ratio is close to unity: D_v is given according to Eqs. 2, 3 by

$$D_v = \bar{A}_v \left[\frac{gVK_v}{IVK_v} - 1 \right] . \qquad (9)$$

Radiationless deactivation dominates below 150km and reaches values $D_0 \approx D_1 \approx 100\text{sec}^{-1}$ at 100km. We must rely to some extent on laboratory measurement in order to remove ambiguity in determining the deactivating species. Deactivation of the lower vibrational levels A $^3\Sigma_u^+$ v = 0,1 by N_2 can be ignored since it is well known to be a very slow process (Noxon, 1962), with a rate constant of about $10^{-20}\text{cm}^3/\text{sec}$. The recent mass spectrometer measurements by Zipf et al. (1970) on NASA rocket flight 4.309, showing large quantities of [NO], leads to the suggestion that this species may be an important deactivator below 130 km in the brighter aurorae. The mass spectrometer observations indicate a non-linear relationship between auroral intensity and [NO]; significant quantities of [NO] are not observed in IBC I aurorae. The model atmosphere shown in Fig. 2 is based on the flight 4.309 measurements in an IBC II aurora in March 1970. The second most abundant species in this aurora in the 100 km - 115 km region was [NO]. Since both the Sharp (1971) and Zipf et al. (1970) observations were made at the same time of year and in aurorae of similar brightness, we apply the model atmosphere of Fig. 2 to the Sharp observations.

In Fig. 3 we plot $D_v/[0]$ using the estimated average D_v. This figure shows that atomic oxygen cannot account for the observed deactivation below 130 km, but at higher altitudes the constancy of the ratio $D_v/[0]$ suggests that the quenching agent is this species. The [0] profile in Fig. 2 is quite similar to the profile observed in atmospheres having no significant quantities of [NO]. The assumption that $[0_2]$ is the major deactivator below 130 km would require a rate constant of about $10^{-10}cm^3/sec$, which would vary by a factor of about 2 between 100 km and 110 km for both of the A $^3\Sigma_u^+$ levels. However, calculations using [NO] lead to a much more satisfactory fit to the deactivation profile; compare the relative number densities $[0_2]/[0]$ and $[NO]/[0]$ plotted in Fig. 2. This is supported by the laboratory deactivation measurements. Young et al. (1969) estimate the ratio $k_{NO}/k_{0_2} \approx 18$, and Meyer et al. (1969) measurements give a value of $k_{NO}/k_{0_2} \approx 19$. However the two experimental measurements differ in the absolute values--Young et al obtain $k_{NO} = 7 \times 10^{-11}cm^3/sec$ and Meyer et al give $k_{NO} = 2.3 \times 10^{-11}cm^3/sec$. The recent laboratory measurements by Gutcheck and Zipf (1971), $k_{0_2} = 3 \times 10^{-12}cm^3/sec$, tend to support the Young et al measurements, $k_{0_2} = 3.8 \times 10^{-12}cm^3/sec$. If we assume that $[0_2]$ plays an insignificant role in deactivation of A $^3\Sigma_u^+$ v = 0,1, with a rate coefficient $k_{0_2} \approx 3 \times 10^{-12}cm^3/sec$, the combination of values

$k_{NO}(v)$, $k_0(v)$ that best fit the auroral deactivation profiles are

$$A\ {}^3\Sigma_u^+ \quad v = 0$$

$$k_0(0) = 8.5 \times 10^{-11} \text{cm}^3/\text{sec}$$

$$k_{NO}(0) = 8.5 \times 10^{-11} \text{cm}^3/\text{sec}$$

$$k_{O_2}(0) = 3 \times 10^{-12} \text{cm}^3/\text{sec}$$

and

$$A\ {}^3\Sigma_u^+ \quad v = 1$$

$$k_0(1) = 1.7 \times 10^{-11} \text{cm}^3/\text{sec}$$

$$k_{NO}(1) = 8.5 \times 10^{-11} \text{cm}^3/\text{sec}$$

$$k_{O_2}(1) = 3 \times 10^{-12} \text{cm}^3/\text{sec}$$

The circled points shown in Fig. 3 are calculated from Eq. 3 using the rate constants given above and the model atmosphere of Fig. 2. The agreement with observation is clearly quite satisfactory. The major uncertainty in these calculations arises in the use of mass spectrometer measurements obtained in a different aurora than the optical observations, although both sets of observations were in aurorae of about the same brightness and at the same time of year. However, circumstantial evidence appears to support the use of the present model atmosphere; the use of a rate constant, k_{NO}, close to the value measured by Young et al appears to give the most satisfactory explanation of the observed deactivation profile below 130 km.

The rate coefficient k_0 estimated from the auroral measurements above 130 km is two orders of magnitude larger than the Meyer et al (1969) laboratory estimate. If the Meyer et al set of measurements were normalized to those of

Young et al, the estimated k_0 would still be an order of magnitude smaller than the auroral estimate. However, Offermann and Von Zahn (1971) suggest, on the basis of observations with a helium cooled mass spectrometer, that uncooled mass spectrometer measurements may underestimate the relative abundance of atomic oxygen by as much as a factor of 3. If this were indeed the case the Meyer et al ratios $k_{NO}/k_{O_2}/k_O$ (= 100/5.2/14) would give a reasonable approximation to the auroral observations. We therefore have the possibility that the values of k_0 given above may be too large by as much as a factor of 3.

D. Deactivation of the Higher A $^3\Sigma_u^+$ Vibrational Levels

A number of recent laboratory observations of direct electron excitation, A $^3\Sigma_u^+$ ← X $^1\Sigma_g^+$, suggest that the population rates of the higher A $^3\Sigma_u^+$ vibrational levels given in Table 1 should be within a factor of 2 of the correct values (Shemansky and Broadfoot 1971a). The direct excitation process makes significant contributions to the A $^3\Sigma_u^+$ $v > 3$ levels, such that all of the levels up to about $v = 13$ are populated at comparable rates. However, transitions from the A $^3\Sigma_u^+$ $v > 2$ levels are very seldom observed in emission and A $^3\Sigma_u^+$ $v > 6$ levels have never been observed either in the laboratory or in the aurora. The explanation for this lack of observation probably lies in a combination of higher deactivation rates and the characteristics of the transition. Transitions of the A $^3\Sigma_u^+$ $v = 3, 4, 5, 6$ levels are fairly uniformly distributed throughout the Deslandres table and no single transition is dominant. As a result these transitions are relatively difficult to observe. Many of the bands are impossible to observe from the ground due to atmospheric extinction. The A $^3\Sigma_u^+$ $v > 6$ transitions of the $v'' = 0$ progression tend to dominate, and if quenching were neglected, these bands in the 1500Å - 1700Å region would be roughly as detectable as the N_2 L-B-H bands falling in the same wavelength region. We use the ratio of peak differential brightness to brightness as a measure of detectability; on this basis an N_2 L-B-H band is about 4 times more easily observed than a N_2 V-K band of the same brightness, for a spectral resolution of $\Delta\lambda \simeq 5Å$. The quality of the spectra obtained so far (Isler et al, 1965, Miller et al, 1968, Peek, 1970) in our judgment is such that these bands would be very difficult to detect if one takes into account a moderate amount of radiationless deactivation. According to Shemansky and Broadfoot (1971a) the A $^3\Sigma_u^+$ $v > 6$ levels are subject to significant deactivation rates by $N_2X\ ^1\Sigma_g^+$. Crude estimates of the rate coefficients vary from gas kinetics to $10^{-11}cm^3/sec$ for the A $^3\Sigma_u^+$ $v = 13 - 27$ levels. If we assume values in the region of $\sim 10^{-11}cm^3/sec$ for the A $^3\Sigma_u^+$ $v = 7 - 13$ levels, and gas kinetic rates for [O] and [NO], then $D_{v > 6} \approx 0.7\ sec^{-1}$ at 200 km and $D_{v > 6} \approx 500\ sec^{-1}$ at 100 km. The best conditions for observations appear to prevail in the 200 km region in spite of lower volume production rates. The bands suffering the least deactivation by $N_2X\ ^1\Sigma_g^+$ should be the (8,0) and (12,0) transitions according to the data given by Shemansky and Broadfoot (1971a).

E. Auroral Variability of the N_2 V-K System

The dependence of radiationless deactivation of the $N_2A\ ^3\Sigma_u^+$ state on [NO] in the lower auroral altitudes should contribute to the variability of the ratio I2PG/IV-K as observed from the ground. A weak aurora producing negligible quantities of [NO] would leave D_v almost entirely dependent on [O], and one would expect values of $D_0 \approx 20\ sec^{-1}$, $D_1 \approx 40\ sec^{-1}$, at 100 km rather than $\sim 100\ sec^{-1}$, as observed in brighter aurorae. Thus variations in D_v at a given altitude coupled with auroral height variations may well determine the observed variations in I2PG/IV-K. Lower I2PG/IV-K ratios are associated with weaker aurorae (Broadfoot and Hunten 1964, Hunten, 1955), as we would predict in the present analysis. One may also expect variations in apparent relative gVK_v due to the factor of 2 differences in the $k_0(0)$ and $k_0(1)$ values. Weak aurorae should then have an enhanced A $^3\Sigma_u^+$ v = 0 relative population. However, the Broadfoot and Hunten observations suggest a variation in the opposite direction. The 0,10 band, on which the Broadfoot and Hunten measurements are based, is difficult to observe due to an apparent continuum background and low transition probability. This may have some effect on their observations. The average apparent relative population rates (g_v SV_v) calculated from the Broadfoot and Hunten observations using the Shemansky (1969) transition probabilities, are shown in Table 1. The agreement with the predicted rates appears to be much better than one would expect from their observations of apparent variability. Thus we predict a ratio $SV_0/SV_1 < 1$ from the observations of variability as a function of brightness and, in contrast, a ratio $SV_0/SV_1 \simeq 1$ from the average relative emission rates. The source of this discrepancy is not obvious. The apparent relative population rates (g_vSV_v) obtained from the Sharp (1971) rocket measurements at 120 km are also shown in Table 1. The value for g_2SV_2 is not considered reliable according to a private communication with Sharp.

CONCLUSION

According to the present work the population rates of the N_2A $^3\Sigma_u^+$ v < 2 levels in the aurora are accurately determined by radiative cascade from the N_2C $^3\Pi_u$ and B $^3\Pi_g$ states, excited by direct electron impact, and a major role in quenching the lower vibrational levels of the A state is taken by NO in some bright auroras. The conclusions are based on a number of relevant auroral observations in combination with calculations using electron cross section and transition probability measurements by Shemansky and Broadfoot (1971a, 1971b). Earlier work by Sharp (1971) using cross sections given by Cartwright (1970) suggested additional significant contributions in the radiative systems, W $^3\Delta_u$ - B $^3\Pi_g$ and A $^3\Sigma_u^+$ - B $^3\Pi_g$ because of the small B state cross sections employed. However, the auroral observations do not compare satisfactorily with the resultant relative population rates. The collision transfer process A $^3\Sigma_u^+$ v > 6 → B $^3\Pi_g$ (Shemansky and Broadfoot, 1971a) may contribute marginally to the B $^3\Pi_g$ v > 5 populations in the aurora, but it is doubtful that the effect would be measurable. The only direct evidence for variation of the relative B $^3\Pi_g$ v > 3 population rates (Shemansky and Vallance Jones, 1968) is in opposition to the variation predicted by the collision transfer process.

The quenching probability D_v, for the A $^3\Sigma_u^+$ v = 0,1 levels calculated from the Sharp (1971) rocket observations in an IBC II aurora, conforms rather well to the calculated probability based on a model atmosphere determined from mass spectrometer measurements in a similar aurora (Zipf et al. 1970). Deactivation dominated by [NO] below 130 km and by [O] at higher altitudes provides an accurate fit to the deactivation profile. The auroral observations and laboratory measurements (Young et al, 1969; Meyer et al, 1969, Gutcheck and Zipf, 1971) are consistent with a low deactivation rate coefficient for [O_2]. The rate coefficients estimated from the auroral measurements are, in units of cm^3/sec,

$N_2A\ ^3\Sigma_u^+\ v = 0$

$k_0 = 8.5 \times 10^{-11}$

$k_{NO} = 8.5 \times 10^{-11}$

$N_2A\ ^3\Sigma_u^+\ v = 1$

$k_0 = 1.7 \times 10^{-11}$

$k_{NO} = 8.5 \times 10^{-11}$

The estimated value of k_{NO} is in good agreement with the laboratory estimate by Young et al, $7 \times 10^{-11} cm^3/sec$, but is an order of magnitude larger than that of Meyer et al. The present values for k_0 are two orders of magnitude larger than the Meyer et al laboratory measurement. Part of this discrepancy may be due to underestimation of relative atomic oxygen abundance in the upper atmosphere (Offermann and Von Zahn, 1971).

The [NO] concentration has a non linear relationship with the auroral brightness, and as a result one would expect variations of as much as a factor of 5 in the deactivation probability in the 100 km region; weaker aurorae would be associated with a lower deactivation probability. Deactivation by $[O_2]$ with a rate coefficient of ~ $3 \times 10^{-12} cm^3/sec$ (Young et al, 1969, Gutcheck and Zipf, 1971), appears not to play a significant role even in weak aurorae. The variability of the deactivation probability at the lower altitudes due to the exchange of dominance by [NO] and [O] may thus make a significant contribution to variations in the ratio I2PG/IV-K as observed from the ground (Broadfoot and Hunten, 1964, Hunten 1955). The present analysis would also predict variations in the apparent relative population rates within the A $^3\Sigma_u^+$ state due to deactivation, but in the opposite sense to the variations suggested by the Broadfoot and Hunten observations.

The higher vibrational levels of the A $^3\Sigma_u^+$ state are expected to have population rates comparable to those of the v = 0,1 levels. However transitions from these levels have not been observed. This may be due to a combination of small transition probabilities, higher deactivation rates, and blends with other emissions. The N_2V-$K_{12,0}$ and 8,0 bands at 1536Å and 1654Å may be the best prospects for observation due to lower predicted deactivation rates for $[N_2]$.

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APPENDIX

Rotational Disequilibrium in the $N_2A\ ^3\Sigma_u^+$ State Due to Double Lifetime

The equations determining the populations of the sub-states may be written

$$dN_v^i/dt = -N_v^i\ (A_v^i + 2\ [M]k_r + D_v) + (N_v^j + N_v^k)\ [M]k_r + g_v/3. \qquad \text{(A1)}$$

where i, j, k refer to the sub-states, g_v is the total population rate of level v, and k_r is the rate coefficient for sub-state relaxation.

We have

$$A_v^2 = 2A_v^1 = 2A_v^3$$

and therefore

$$N_v^1 = N_v^3 \quad ,$$

since the population rates of the three sub-states are equal. The three equations (A1) reduce to two, and in equilibrium we have

$$N_v^1\ (A_v^1/[M]k_r + 1 + D_v/[M]k_r) - N_v^2 = g_v/3[M]k_r \qquad \text{(A2)}$$

$$-N_v^1 + N_v^2\ [A_v^1/[M]k_r + 1 + D_v/2[M]k_r] = g_v/6[M]k_r \qquad \text{(A3)}$$

we write

$$A_v^1/[M]k_r + 1 = a, \qquad \text{(A4)}$$

$$D_v/[M]k_r = b \tag{A5}$$

$$g_v/3[M]k_r = c \tag{A6}$$

Then

$$N_v^1 = N_v^3 = c[(a + b/2) + 1/2]/[(a + b)\ (a + b/2) - 1], \tag{A7}$$

$$N_v^2 = c[(a + b)/2 + 1]/[(a + b)\ (a + b/2) - 1] \tag{A8}$$

$$N_v^1/N_v^2 = N_v^3/N_v^2 = (2a + b + 1)/(a + b + 2), \tag{A9}$$

and

$$\overline{A}_v = 2[(N_v^1/N_v^2 + 1)/(2N_v^1/N_v^2 + 1)]A_v^1 \tag{A10}$$

In the extreme case of high relaxation rate,

$$a \rightarrow 1$$
$$N_v^1/N_v^2 = 1$$
$$\overline{A}_v = 1.33\ A_v^1.$$

The other extreme of low relaxation rate gives

$$a \rightarrow \text{large}$$
$$N_v^1/N_v^2 = 2$$
$$\overline{A}_v = 1.20\ A_v^1$$

We thus have a possible variation of $\overline{A}_v$ of only about 10%.

We expect sub-state relaxation to go at about the same rate as rotational relaxation in the A $^3\Sigma_u^+$ state due to the close spacing of the sub-states (Hunds case b coupling). A reasonable value for k_r would then be ~ 3 x $10^{-10} cm^3/sec$, the gas kinetic rate. At 200 km we estimate

$$D_0 = 0.2\ sec^{-1}$$

$$[M]k_r = 1.5\ sec^{-1}$$

$$a = 1.26$$

$$b = 0.13$$

$$N_v^1/N_v^2 = 1.07$$

$$\overline{A}_0 = 1.32\ A_0^1$$

At low altitude,

$$\overline{A}_0 \rightarrow 1.33\ A_0^1$$

and we have a variation in the region of 1%.

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Table I

Relative Population Rates of the N_2 C $^3\Pi_u$, B $^3\Pi_g$, A $^3\Sigma_u^+$ States

[a] Predicted rates by Shemansky et al. (1971), from cross sections by Shemansky and Broadfoot (1971b). The total population rates (Σg_v) are the estimated emission rates in kR for an IBC I aurora for transitions from the (C $^3\Pi_u$, B $^3\Pi_g$) states which do not suffer radiationless deactivation. The population rates for the B $^3\Pi_g$ and A $^3\Sigma_u^+$ states include cascade processes.

[b] Average apparent (g_v SV_v) relative rates calculated from the ground based measurements of Broadfoot and Hunten (1964), using transition probability tables by Shemansky (1969).

[c] Average apparent (g_v SV_v) relative rates calculated from rocket borne measurements by Sharp (1971) at 120 km.

Table II

Predicted and Observed Relative Emission Rates of N_2 Systems

[a] Sharp (1971) measurements at 200 km, corrected for estimated radiationless deactivation rate of 0.2 sec^{-1}.

[b] From averages of measurements by Hunten (1955), Petrie and Small (1952), of N_2 2PG relative to N_2^+ 1N, and measurements on NASA rocket flights 4.163, 4.217, 4.309, and aircraft observation by Gattinger and Vallance Jones (1971) of N_2 $1PG_{5,2}$ relative to N_2^+ $1N_{0,0}$ (cf. Shemansky et al. 1971).

[c] From averages of measurements by Harrison (1969) of N_2 $1PG_{0,0}$ relative to N_2^+ $1N_{0,0}$ and the observations of $N_2 1PG_{5,2}$ relative to N_2^+ $1N_{0,0}$ given in (b) above.

[d] From measurements of $N_2 1PG_{0,0}$ and $N_2 1PG_{1,0}$ by Hunten (1958).

Table I

Relative Population Rates of the N_2 $C\ ^3\Pi_u$, $B\ ^3\Pi_g$, $A\ ^3\Sigma_u^+$ States

v	[a] $C\ ^3\Pi_u$	[a] $B\ ^3\Pi_g$	[a] $A\ ^3\Sigma_u^+$	[b] $A\ ^3\Sigma_u^+$	[c] $A\ ^3\Sigma_u^+$
0	0.52	0.73	1.50	1.5	1.5
1	0.28	0.98	1.45	1.3	1.2
2	0.10	1.15	1.20	1.1	2.5
3	0.029	1.07	1.00		
4		0.83	0.92		
5		0.57	0.92		
6		0.35	0.93		
7		0.21	0.93		
8		0.11	0.92		
9		0.060	0.87		
10		0.030	0.80		
11		0.015	0.70		
12		0.007	0.59		
13			0.50		
Σg_v	0.93	6.1	15.2		

Table II

Predicted and Observed Relative Emission Rates of N_2 Systems

	$IV\text{-}K_0/I2PG_{0,0}$	$I1PG_{5,2}/I2PG$	$I1PG_{0,0}/I1PG_{5,2}$	$I1PG_{0,0}/I1PG_{1,0}$
Shemansky et al. (1971)	5.9	0.19	2.4	0.61
Observed	6.6 [a]	0.23 [b]	2.5 [c]	0.63 [d]

FIGURE CAPTIONS

Figure 1

Deactivation Probability of the $N_2A\ ^3\Sigma_u^+$ v = 0,1 Vibrational Levels as a Function of Altitude.*

*Calculated from volume emission rates of the $N_2$2PG and N_2V-K systems measured in the rocket borne experiment by Sharp (1971).

Figure 2

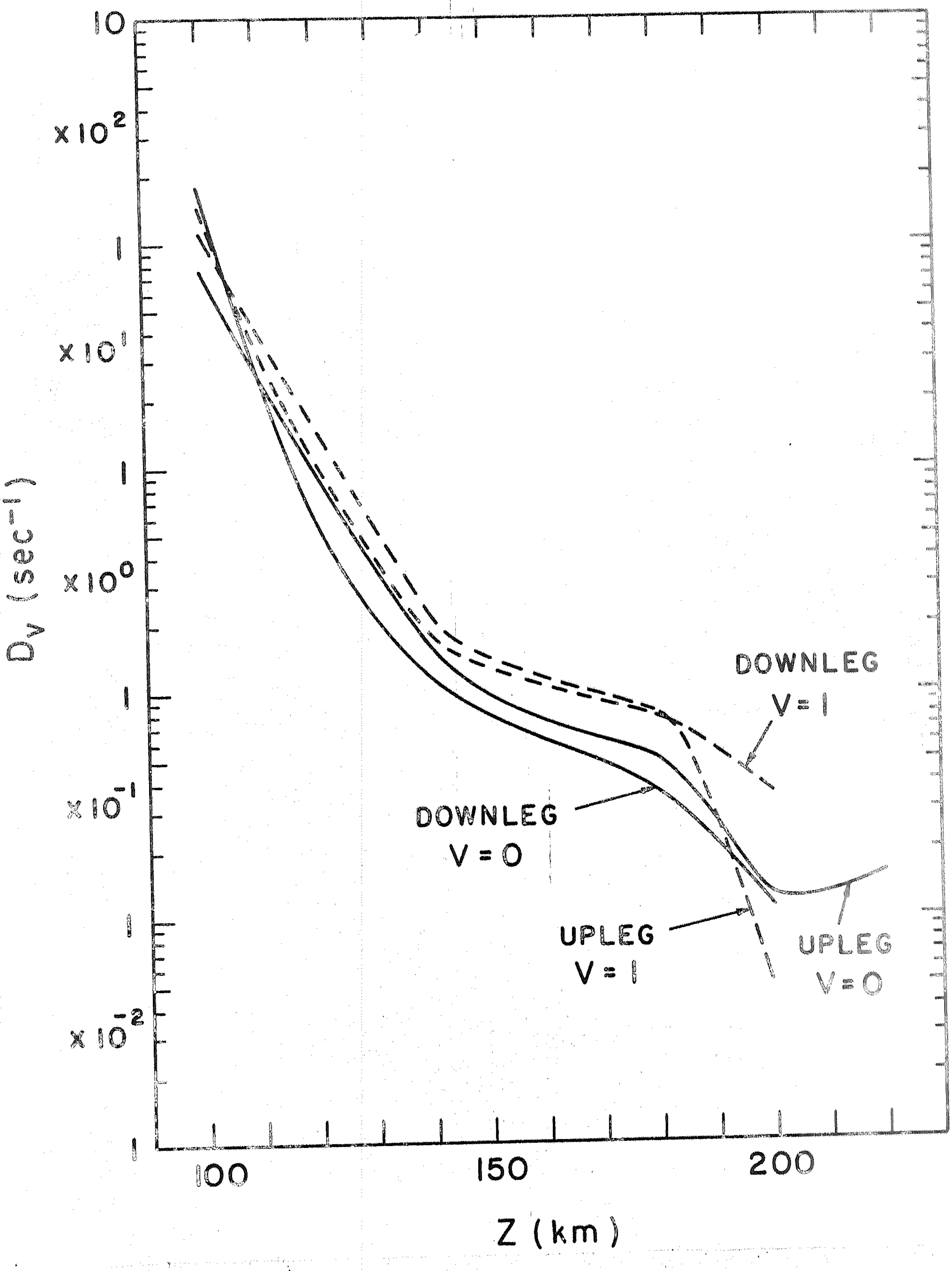
Model Atmosphere*

*Based on mass spectrometer measurements by Zipf et al (1970).

Figure 3

Ratio of Deactivation Probability to [0] as a Function of Altitude.*

*The continuous curves are calculated from the average measured D_v and the model atomsphere given in Fig. 2. The plotted points are calculated using the rate coefficients shown in the Figure and the relative number densities given in Fig. 2.



10
x10²
1
x10¹
1
x10⁰
1
x10⁻¹
1
x10⁻²
1
D_V (sec⁻¹)
DOWNLEG
V=1
DOWNLEG
V=0
UPLEG
V=1
UPLEG
V=0
100
150
200
Z (km)

Figure 1

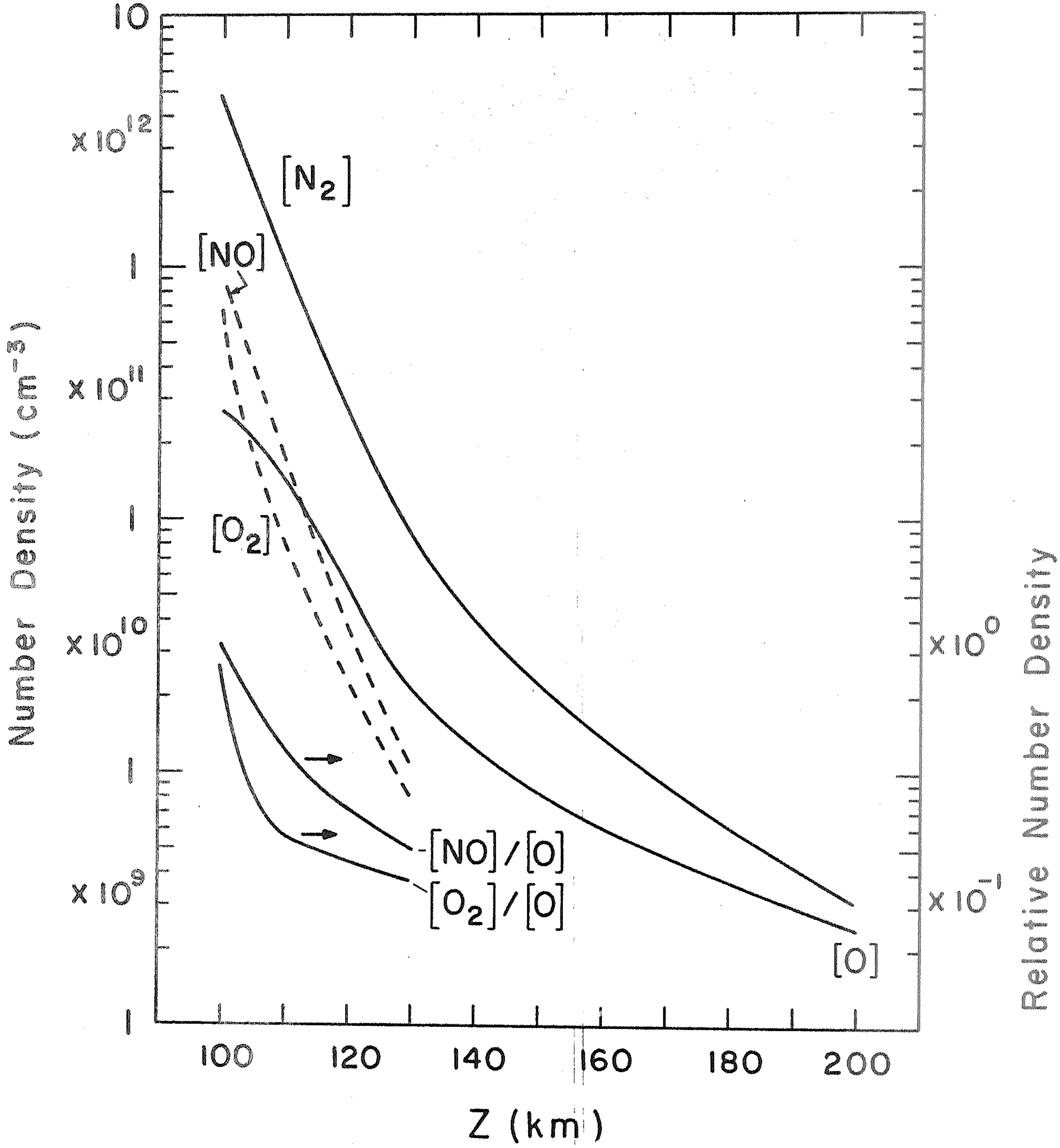
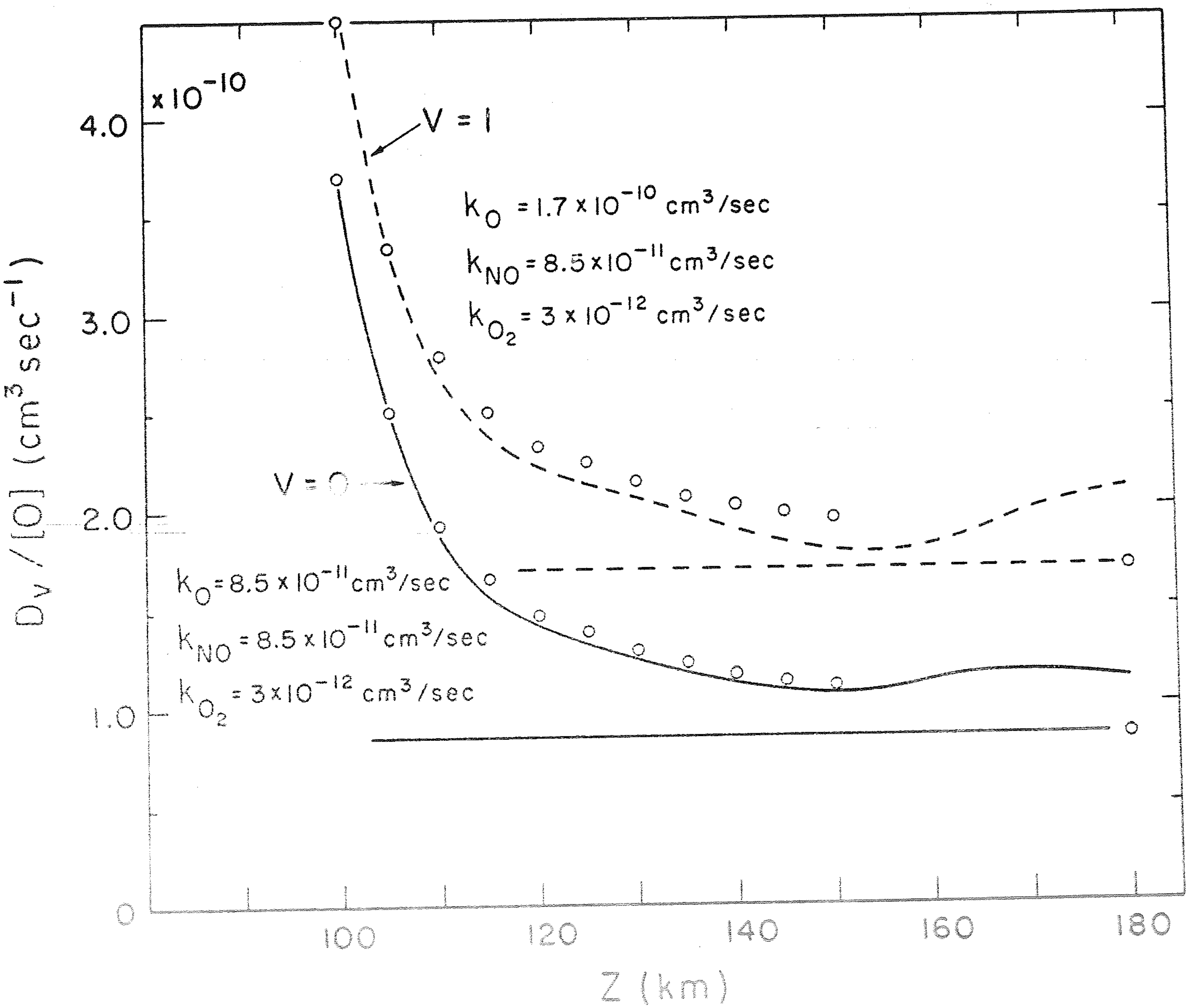

10
x 10^12
1
x 10^11
1
x 10^10
1
x 10^9
1
Number Density (cm^-3)
[N2]
[NO]
[O2]
[NO]/[O]
[O2]/[O]
[O]
x 10^0
x 10^-1
Relative Number Density
100
120
140
160
180
200
Z (km)

Figure 2



x 10^-10
4.0
3.0
2.0
1.0
0
V = 1
V = 0
k_O = 1.7 x 10^-10 cm^3/sec
k_NO = 8.5 x 10^-11 cm^3/sec
k_O2 = 3 x 10^-12 cm^3/sec
k_O = 8.5 x 10^-11 cm^3/sec
k_NO = 8.5 x 10^-11 cm^3/sec
k_O2 = 3 x 10^-12 cm^3/sec
D_v / [O] (cm^3 sec^-1)
100
120
140
160
180
Z (km)

Figure 3