THE ALTITUDE DEPENDENCE OF THE OH(X²Π) VIBRATIONAL DISTRIBUTION IN THE NIGHTGLOW: SOME MODEL EXPECTATIONS

IAN C. McDADE

Space Physics Research Laboratory, Department of Atmospheric, Oceanic and Space Sciences,
University of Michigan, Ann Arbor, MI 48109, U.S.A.

Abstract—A number of different OH Meinel band excitation models are used to investigate the extent to which quenching and vibrational deactivation processes could cause the nightglow OH vibrational distributions to vary with altitude. The various models, which are based upon those described by McDade and Llewellyn (1988, *Planet. Space Sci.* **36**, 897), are used to calculate the steady state OH vibrational distributions throughout the 80–100 km region. The results of the calculation show that, irrespective of the basic model assumptions, the OH vibrational distributions should not be strongly altitude dependent and that the emission profiles of the Meinel bands from the v' levels 1 through 9 should not differ in altitude by more than one or two kilometers. The results of some recent laboratory studies pertaining to the Meinel band excitation mechanism are also discussed and it is shown that stepwise collisional vibrational deactivation is unlikely to play a major role in controlling the observed nightglow OH vibrational distribution.

1. INTRODUCTION

In spite of many years of observational and theoretical study very little is known about the altitude dependence of the OH vibrational distributions in the nightglow. In a limited number of rocket experiments (Rogers *et al.*, 1973; Lopez Moreno *et al.*, 1987; McDade *et al.*, 1987) attempts have been made to measure simultaneously the altitude profiles of different OH vibrational levels. These experiments have all been performed using broad-band radiometers that captured emission from a number of different v' levels, but the results of these experiments have suggested that the lower vibrational levels peak at a lower altitude than the higher vibrational levels. A number of theoretical calculations have also been reported and these studies have indicated that the vibrational distribution should shift towards higher vibrational levels at higher altitudes (Nagy *et al.*, 1976; Llewellyn *et al.*, 1978; Battener and Lopez-Moreno, 1979; Takahashi and Batista, 1981; Şivjee and Hamwey, 1987; Lopez and Moreno *et al.*, 1987). These theoretical calculations, however, were largely based upon assumed excitation mechanisms and/or reaction rate coefficients that are now considered to be of questionable validity (Finlayson-Pitts and Kleindienst, 1981; Greenblatt and Wiesenfeld, 1982; McDade and Llewellyn, 1987; Meriwether, 1989).

In this paper we reconsider the question of the altitude dependence of the OH vibrational distributions and use a number of different OH Meinel band excitation models to examine how quenching and vibrational deactivation processes could cause the vibrational distributions to vary with altitude. We show that the altitude dependence of the OH vibrational distribution should not be very strong and that the emission profiles of the various v' levels of the Meinel band system should not differ in altitude by more than one or two kilometers across the entire vibrational manifold.

2. THE MEINEL BAND EXCITATION MODELS

It is now generally accepted that the reaction between ozone and atomic hydrogen, first suggested by Bates and Nicolet (1950),

$$H + O_3 \xrightarrow{k_1} OH(v \leqslant 9) + O_2 \qquad (1)$$
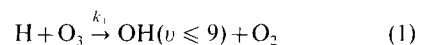
is the major source of vibrationally excited OH in the nightglow and that the $HO_2 + O$ reaction does not make a major contribution (Kaye, 1988; Meriwether, 1989). However, the factors which control the nightglow OH vibrational distributions have still not been established. The main outstanding problems concern the extent to which collisions between the vibrationally excited OH radicals and the major atmospheric species O_2, N_2 and O contribute to the production and loss of each level. It is known that reaction (1) preferentially produces vibrationally excited OH in the levels $v = 7$, 8 and 9 and that the lower levels, which are responsible for most of the Meinel band
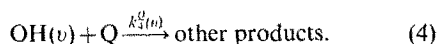
emission, must be populated as the result of either radiative cascade from the higher levels

$$OH(v') \xrightarrow{A(v',v'')} OH(v'') + hv \qquad (2)$$
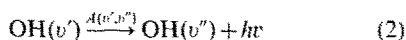
or stepwise collisional deactivation processes

$$OH(v') + Q \xrightarrow{k_3^Q(v',v'')} OH(v'') + Q. \qquad (3)$$
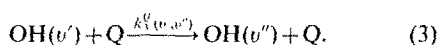
The loss of each vibrational level may be controlled by either of these two processes or by reactions that remove the vibrationally excited species

$$OH(v) + Q \xrightarrow{k_4^Q(v)} \text{other products.} \qquad (4)$$

If the collisional processes (3) and (4) were not important at nightglow altitudes then the OH vibrational distribution would be invariant with respect to altitude and geophysical conditions and all of the Meinel bands would have the same vertical distribution profile. However, the nightglow distributions are known to vary (Krassovsky *et al.*, 1961) and the mean distribution differs from that which would result from reaction (1) and a purely radiative cascade mechanism (Llewellyn *et al.*, 1978; Turnbull and Lowe, 1983). This implies that the collisional processes must be important and that the OH vibrational distributions will be, to some extent, altitude dependent. However, the nature and strength of the altitude variations will depend critically upon the roles played by O_2, N_2 and O in reactions (3) and (4).

McDade and Llewellyn (1987) have previously considered how these reactions might control the OH vibrational populations and they used the mean OH vibrational distribution observed from the ground to derive kinetic parameters pertinent or two quite distinct excitation models. In the first case which McDade and Llewellyn considered, stepwise vibrational deactivation, i.e. reaction (3), was assumed to dominate and to proceed via single quantum steps. This model is known as the "collisional cascade model". For the alternative model, known as the "sudden death model", it was assumed that the collisional losses of each level were dominated by reaction (4) and that stepwise vibrational deactivation did not contribute significantly to the production of each level. In a subsequent paper (McDade and Llewellyn, 1988) the parameters for these two basic models were further refined to accommodate upper and lower limits for parameters describing the oxygen atom quenching process which was assumed to proceed via chemical reaction and/or multi-quantum vibrational deactivation to the $v = 0$ level.

Since the four models described by McDade and Llewellyn (1988) represent extreme limiting cases that should bracket the details of the actual mechanism, we have used these models to investigate how the OH vibrational distributions might change with altitude throughout the OH airglow layer. These four models are referred to in this paper as (a) collisional cascade with no O-atom quenching, (b) collisional cascade with maximum O-atom quenching, (c) sudden death with no O-atom quenching and (d) sudden death with maximum O-atom quenching.

2.1. *The model formulation*

Under steady state conditions in the nightglow the number density of each vibrational level of OH may be expressed as

$$[OH(v)] =$$

$$\frac{p(v) + \sum_{v^*=v+1}^{9} [OH(v^*)]\{A(v^*,v) + \sum_Q k_3^Q(v^*,v)[Q]\}}{\{A(v) + \sum_Q k_L^Q(v)[Q]\}}, \qquad (5)$$

where $p(v)$ represents the nascent volume production rate of the level v in the $H + O_3$ reaction and $k_L^Q(v)$ represents the total rate coefficient for collisional removal of the level v by the species $Q = Q_2$, N_2 or O in reactions (3) and (4). In their assessment of the potential importance of these two reactions McDade and Llewellyn (1987) chose to avoid making any assumptions about the absolute Meinel band transition probabilities which were highly controversial at that time. Consequently, each of the kinetic parameters which they derived from the observed mean OH vibrational distribution, and a constraint imposed at $v = 9$ by the laboratory experiments of Finlayson-Pitts and Kleindienst (1981), was obtained in the form of the quotient of the relevant rate coefficient and the inverse radiative lifetime of the $v = 9$ level, $A(9)$. Under this formulation the relative population in each vibrational level of OH, normalized to that in the level $v = 9$, may be obtained from the expression

$$N(v) =$$

$$\frac{F(v)\{1 + K_L^{O_2, N_2}(9)[O_2] + K_L^O(9)[O]\}}{+ \sum_{v^*=v+1}^{9} N(v^*)\{a(v^*,v) + K_3^{O_2, N_2}(v^*,v)[O_2]\}}{\{a(v) + K_L^{O_2, N_2}(v)[O_2] + K_L^O(v)[O]\}}, \qquad (6)$$

where $F(v) = p(v)/p(9)$; $a(v^*,v) = A(v^*,v)/A(9)$; $K_L^O(v) = k_L^O(v)/A(9)$; and $K_L^{O_2, N_2}(v)$ and $K_3^{O_2, N_2}(v^*,v)$ correspond to the kinetic parameters $\{k_L^{O_2}(v) +$

$Rk_L^{N_2}(v)\}/A(9)$ and $\{k_3^{O_2}(v^*,v) + Rk_3^{N_2}(v^*,v)\}/A(9)$ described by McDade and Llewellyn (1988) with $R(\approx 4)$ representing the mean $N_2 : O_2$ number density ratio in the mesopause region.

To investigate how the OH vibrational distributions would vary with altitude for each of the proposed limiting case models we have used equation (6), together with the model parameters listed in Tables 1 and 2 and the $[O_2]$ and $[O]$ profiles given by the CIRA 1972 Mean Reference Atmosphere, to calculate the altitude profiles of the fractional populations in each OH vibrational level. The results of these calculations are discussed below.

3. THE MODELLED VIBRATIONAL DISTRIBUTIONS

3.1. *The "collisional cascade with no O-atom quenching" case*

The fractional population profiles calculated for the "no O-atom quenching" limit of the collisional cascade model are shown in Fig. 1. Clearly, the vibrational distributions calculated for this model are only weakly altitude dependent and this weak dependence would not result in any significant differences between the emission profiles of the various v' Meinel bands. The calculated vibrational distributions do shift slightly towards lower vibrational levels at higher altitudes. This may at first seem surprising since one might expect the distributions for a collisional cascade model to become less relaxed, or "hotter", as the densities of O_2 and N_2 decrease. However, the "collisional cascade with no O-atom quenching" parameters were chosen to reproduce the observed mean OH vibrational distribution in the 85–90 km region (McDade and Llewellyn, 1987). The mean OH

vibrational distribution considered by McDade and Llewellyn is "hotter", or less relaxed, than the distribution that would result from a purely radiative cascade mechanism. This radiative cascade distribution is determined only by the nascent product state distribution of the $H + O_3$ reaction and the relative Meinel band transition probabilities. Since the vibrational distributions calculated for any viable "collisional cascade with no O-atom quenching" model must reproduce the "hotter" OH distribution in the 85–90 km region and approach the "colder" radiative cascade distribution at high altitude, the distributions calculated for such a model must, by necessity, shift towards lower vibrational levels as the O_2 and N_2 densities decrease. We do note, however, that if the mean OH distribution was in fact more relaxed than the radiative cascade distribution then any viable collisional model that does not include O-atom quenching would predict a shift towards higher vibrational levels at higher altitudes.

3.2. *The "sudden death with no O-atom quenching" case*

The fractional population profiles calculated for the "no O-atom quenching" limit of the sudden death model are shown in Fig. 2. Here again we note that the vibrational populations shift towards the lower vibrational levels at higher altitudes and this effect is stronger than that observed in the "collisional cascade with no O-atom quenching" case. Under the sudden death assumptions radiative decay of the higher lying levels is the only source of the lower levels and the collisional loss of each level does not feed the level immediately below. Consequently, the lower vibrational levels and their precursors are both quenched

TABLE 1. REACTIONS AND ADOPTED COEFFICIENTS

Reaction	Coefficient	Reference
$H + O_3 \xrightarrow{p(v)k_1} OH(v) + O_2$	$p(9) = 0.32$	Ohoyama *et al.* (1985)*
	$p(8) = 0.29$	Ohoyama *et al.* (1985)*
	$p(7) = 0.19$	Ohoyama *et al.* (1985)*
	$p(6) = 0.06$	Ohoyama *et al.* (1985)*
	$p(5) = 0.06$	Ohoyama *et al.* (1985)*
	$p(4) = 0.06$	Ohoyama *et al.* (1985)*
$OH(v') \xrightarrow{A(v',v'')} OH(v'') + hv$	$a(v',v'') = A(v',v'')/A(9)$	Murphy (1971)
$OH(v') + Q \xrightarrow{k_3^Q(v',v'')} OH(v'') + Q$	$Q = O_2, N_2$	See text and Table 2
$OH(v) + Q \xrightarrow{k_L^Q(v)} $ all products	$Q = O_2, N_2, O$	See text and Table 2

* Adjusted using the relative transition probabilities of Murphy (1971) as described by McDade and Llewellyn (1987).

TABLE 2. MODEL PARAMETERS

	Collisional cascade with no O-atom quenching	Collisional cascade with maximum O-atom quenching
	all $k_L^O(v)/A(9) = 0$	all $k_L^O(v)/A(9) = 6 \times 10^{-13}$
	all $k_L^Q(v)/A(9) = k_3^Q(v, v-1)/A(9)$	all $k_L^Q(v)/A(9) = k_3^Q(v, v-1)/A(9)$
v	$\{k_3^{O_2}(v, v-1) + Rk_3^{N_2}(v, v-1)\}/A(9)$	$\{k_3^{O_2}(v, v-1) + Rk_3^{N_2}(v, v-1)\}/A(9)$
9	5.3×10^{-14}	5.3×10^{-14}
8	8.9×10^{-14}	8.8×10^{-14}
7	13.4×10^{-14}	12.9×10^{-14}
6	9.8×10^{-14}	9.0×10^{-14}
5	5.9×10^{-14}	4.8×10^{-14}
4	4.1×10^{-14}	2.9×10^{-14}
3	3.3×10^{-14}	1.8×10^{-14}
2	2.5×10^{-14}	0.9×10^{-14}
1	1.4×10^{-14}	0

	Sudden death with no O-atom quenching	Sudden death with maximum O-atom quenching
	all $k_L^O(v)/A(9) = 0$	all $k_L^O(v)/A(9) = 1.5 \times 10^{-13}$
	all $k_3^Q(v', v'')/A(9) = 0$	all $k_3^Q(v', v'')/A(9) = 0$
v	$\{k_L^{O_2}(v) + Rk_L^{N_2}(v)\}/A(9)$	$\{k_L^{O_2}(v) + Rk_L^{N_2}(v)\}/A(9)$
9	5.3×10^{-14}	5.3×10^{-14}
8	4.5×10^{-14}	4.3×10^{-14}
7	5.1×10^{-14}	4.9×10^{-14}
6	1.1×10^{-14}	1.0×10^{-14}
5	0.1×10^{-14}	0
4	0.15×10^{-14}	0
3	0.15×10^{-14}	0
2	0.25×10^{-14}	0
1	0.15×10^{-14}	0

All coefficients are cm^3 molec^{-1} units and taken from McDade and Llewellyn (1987, 1988).
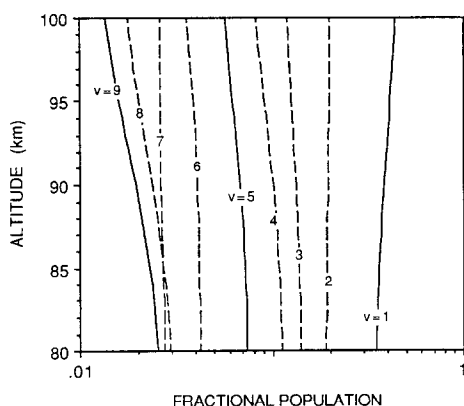

FIG. 1. THE ALTITUDE PROFILES OF THE FRACTIONAL POPULATIONS IN THE OH VIBRATIONAL LEVELS $v = 1$–9 CALCULATED FOR THE "COLLISIONAL CASCADE WITH NO O-ATOM QUENCHING" MODEL.
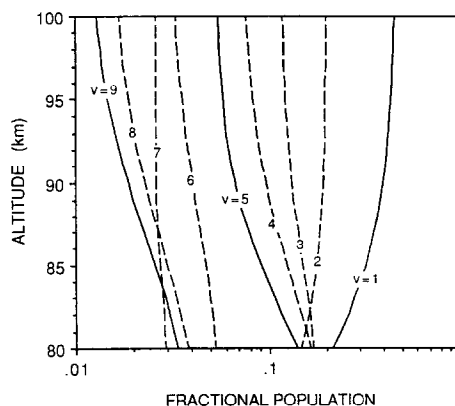

FIG. 2. THE ALTITUDE PROFILES OF THE FRACTIONAL POPULATIONS IN THE OH VIBRATIONAL LEVELS $v = 1$–9 CALCULATED FOR THE "SUDDEN DEATH WITH NO O-ATOM QUENCHING" MODEL.
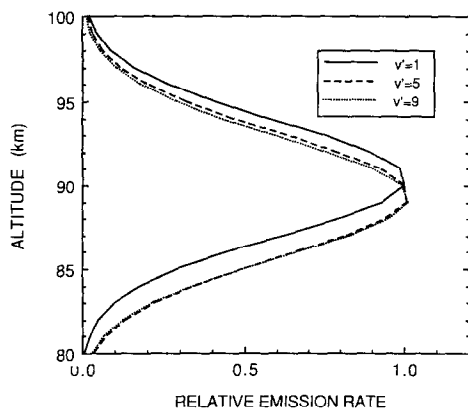
FIG. 3. THE EMISSION PROFILES OF THE OH MEINEL BANDS FROM THE v' LEVELS 1, 5 AND 9 CALCULATED FOR THE "SUDDEN DEATH WITH NO O-ATOM QUENCHING" MODEL AND A GAUSSIAN VIBRATIONALLY EXCITED OH DENSITY PROFILE CENTRED ON AN ALTITUDE OF 90 km.
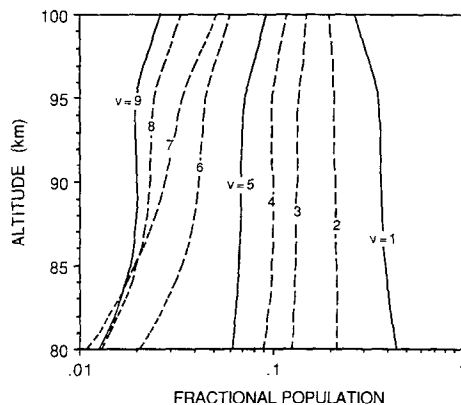

FIG. 4. THE ALTITUDE PROFILES OF THE FRACTIONAL POPULATIONS IN THE OH VIBRATIONAL LEVELS $v = 1$–9 CALCULATED FOR THE "SUDDEN DEATH WITH MAXIMUM O-ATOM QUENCHING" MODEL.

by O_2 and/or N_2. This results in a cumulative quenching effect and the populations in the lower levels are selectively eroded at lower altitudes. It should also be noted that although the magnitudes of the "collisional cascade with no O-atom quenching" parameters decrease with vibrational level (see Table 2), the effective quenching coefficients for the levels below $v = 6$ increase relative to the inverse radiative lifetimes and this tends to amplify the effects of the cumulative quenching process.

The altitude dependence of the OH vibrational distributions calculated for the "sudden death with no O-atom quenching" model would lead to a small shift in the altitude profiles of the Meinel bands from different v' levels. For example, if the total vibrationally excited OH density profile was a simple Gaussian layer centred on an altitude of ~90 km, then the emission profiles shown in Fig. 3 would result and the $v' = 1$ emission bands would peak approximately 1 km above the $v' = 9$ bands.

3.3. The "sudden death with maximum O-atom quenching" case

The fractional population profiles calculated for the "maximum O-atom quenching" limit of the sudden death model are shown in Fig. 4. Clearly, when the possible effects of OH quenching by atomic oxygen are considered we see a reversal of the trends obtained in the "no O-atom quenching" limit. Throughout the 80–100 km region the vibrational distributions now shift towards higher vibrational levels at higher altitudes. This effect is mostly due to cumulative quenching by atomic oxygen which erodes the populations

in the lower vibrational levels at higher altitudes. We note, however, that for the "sudden death with maximum O-atom quenching" case the levels below $v = 6$ are not assumed to be quenched by O_2 or N_2 (see Table 2) and the populations in the lower levels are not eroded at lower altitudes. The structure in the fractional population profiles shown in Fig. 4 is a reflection of the structure in the adopted CIRA 1972 oxygen density profile and the profiles shown in this figure are only meant to represent the trends that would be expected for this model. Nevertheless, the calculations do indicate that a small shift in the altitude profiles of the various Meinel bands would result from this excitation mechanism and the magnitude of this shift will depend upon the local atomic oxygen density profile.

3.4. The "collisional cascade with maximum O-atom quenching" case

The fractional population profiles calculated for the "maximum O-atom quenching" limit of the collisional cascade model are shown in Fig. 5. The behaviour of the OH vibrational distributions calculated for this model is qualitatively similar to that obtained for the "sudden death with maximum O-atom quenching" case. However, in the "collisional cascade" case the oxygen atom quenching parameters, $k_v^O(v)/A(9)$, are substantially larger and this results in enhanced erosion of the populations in the lower vibrational levels at higher altitudes.

The "collisional cascade with maximum O-atom quenching" model clearly leads to the strongest altitude variation in the OH vibrational distributions. This altitude dependence would result in a small shift
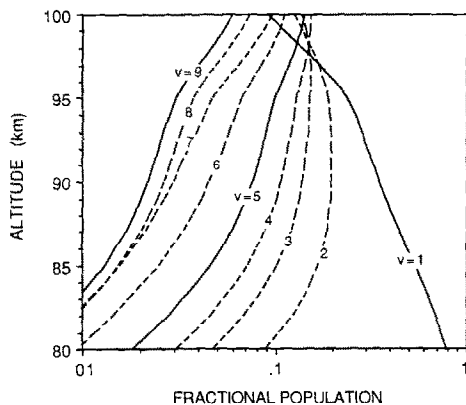
FIG. 5. THE ALTITUDE PROFILES OF THE FRACTIONAL POPU-
LATIONS IN THE OH VIBRATIONAL LEVELS $v = 1–9$ CALCULATED
FOR THE "COLLISIONAL CASCADE WITH MAXIMUM O-ATOM
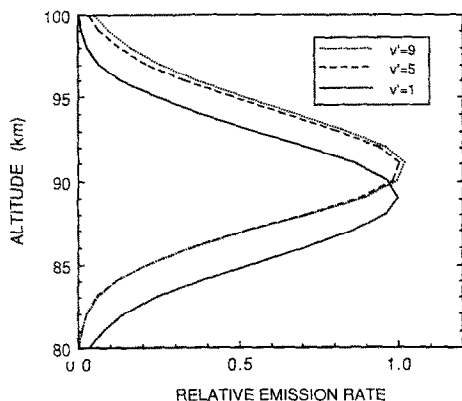QUENCHING" MODEL.

FIG. 6. THE EMISSION PROFILES OF THE OH MEINEL BANDS
FROM THE v' LEVELS 1, 5 AND 9 CALCULATED FOR THE
"COLLISIONAL CASCADE WITH MAXIMUM O-ATOM QUENCHING"
MODEL AND A GAUSSIAN VIBRATIONALLY EXCITED OH DENSITY
PROFILE CENTRED ON AN ALTITUDE OF 90 km.

in the altitude profiles of the various Meinel bands
and the magnitude of this shift will depend upon the
local atomic oxygen density profile. For the CIRA
1972 oxygen atom densities the Meinel bands with
$v' = 9$ would peak ~ 2 km above those with $v' = 1$ as
shown in Fig. 6.

4. DISCUSSION

In the previous section we have shown that stepwise
vibrational deactivation or sudden death quenching
by O_2, or N_2, could cause the nightglow OH
vibrational distributions to shift towards lower

vibrational levels at higher altitudes but that quen-
ching by atomic oxygen would tend to cancel or
reverse this effect. We have also shown that the alti-
tude dependence of the OH vibrational distributions
would be strongest for an OH excitation mechanism
that involved collisional cascade with strong oxygen
atom quenching. However, even for such a mechanism
the altitude dependence of the distribution would be
fairly weak near the peak of the OH layer and would
not cause the peak heights of the Meinel bands to
vary by more than 2 km across the entire vibrational
manifold.

The validity of these conclusions does, however,
depend upon the extent to which the adopted limiting
case models really do embrace the actual kinetics of
OH formation and loss in the nightglow. The model
parameters which we have utilized in this study were
obtained by McDade and Llewellyn (1987) from a
particular set of Meinel band intensity ratios using
the product state distribution of the $H + O_3$ reaction
reported by Ohoyama et al. (1985) and the relative
Meinel band transition probabilities of Murphy
(1971). Since there is now some discussion in the
literature about (a) the appropriateness of the
Murphy (1971) relative transition probabilities and
(b) the accuracy of the Ohoyama et al. (1985) branching
ratios we have considered how the adoption of alter-
native transition probabilities and branching ratios
might alter the basic model parameters.

New measurements of the branching ratios for the
production of $OH(v = 6–9)$ in the $H + O_3$ reaction
have been reported by Klenerman and Smith (1987)
and we have repeated the McDade and Llewellyn
(1987) analysis using these branching ratios in place
of those of Ohoyama et al. (1985). The kinetic par-
ameters thus obtained for the collisional cascade and
sudden death excitation models are compared with
those originally presented by McDade and Llewellyn
(1987) in Figs 7 and 8. The revised parameters
(labelled "case A" in Figs 7 and 8) differ slightly from
those originally obtained using the Ohoyama et al.
(1985) data but the altitude profiles of specific
vibrational levels calculated using these parameters
do not differ significantly from those presented in Figs
1 and 2.

Alternative sets of Meinel band transition prob-
abilities have been presented by Mies (1974), Langhoff
et al. (1986), Turnbull and Lowe (1989) and Nelson
et al. (1990). Unfortunately, the calculations by
Langhoff et al. (1986) and Nelson et al. (1990) do not
extend to $\Delta v = 6$ transitions and therefore they can
not be used for any re-evaluation of the McDade and
Llewellyn analysis which requires knowledge of the
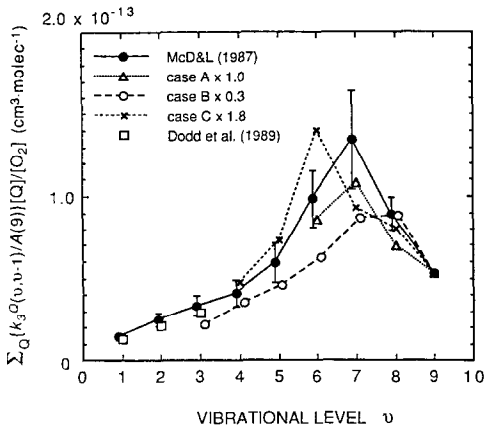$A(9,3)/A(9)$ transition probability ratio. Conse-

FIG. 7. THE COLLISIONAL CASCADE $\Sigma_Q\{k_3^Q(v,v-1)/A(9)\}$ [Q]/[O$_2$] PARAMETERS ORIGINALLY PRESENTED BY McDADE AND LLEWELLYN (1987) (SOLID CIRCLES) AND THE PARAMETERS OBTAINED AS DESCRIBED IN THE TEXT USING ALTERNATIVE BRANCHING RATIOS AND TRANSITION PROBABILITIES.

The parameters labelled "case A" were obtained using the branching ratios of Klenerman and Smith (1987) and the transition probabilities of Murphy (1971). The parameters labelled "case B" were obtained using the branching ratios of Ohoyama *et al.* (1985) and the transition probabilities of Turnbull and Lowe (1989). The parameters labelled "case C" were obtained using the branching ratios of Ohoyama *et al.* (1985) and the transition probabilities of Mies (1974). Each set of alternative parameters has been normalized to those of McDade and Llewellyn at $v = 9$ using the indicated factors. The open squares show the $k_3^{O_2}(v,v-1)$ coefficients reported by Dodd *et al.* (1990) scaled as described in the text using $A(9) = 10 \text{ s}^{-1}$.
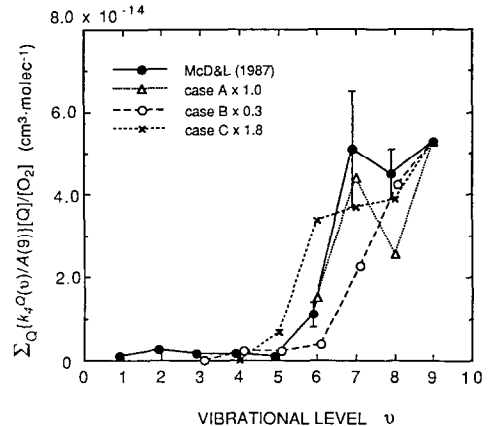

FIG. 8. THE SUDDEN DEATH $\Sigma_Q\{k_4^Q(v)/A(9)\}$ [Q]/[O$_2$] PARAMETERS ORIGINALLY PRESENTED BY McDADE AND LLEWELLYN (1987) (SOLID CIRCLES) AND THE PARAMETERS OBTAINED AS DESCRIBED IN THE TEXT USING ALTERNATIVE BRANCHING RATIOS AND TRANSITION PROBABILITIES.

The parameters labelled "case A" were obtained using the branching ratios of Klenerman and Smith (1987) and the transition probabilities of Murphy (1971). The parameters labelled "case B" were obtained with the branching ratios of Ohoyama *et al.* (1985) and the transition probabilities of Turnbull and Lowe (1989). The parameters labelled "case C" were obtained with the branching ratios of Ohoyama *et al.* (1985) and the transition probabilities of Mies (1974). Each set of alternative parameters has been normalized to those of McDade and Llewellyn at $v = 9$ using the indicated factors.

quently, we only consider here the impact of adopting the probabilities of Mies (1974) or Turnbull and Lowe (1989). If the relative transition probabilities of Murphy (1971) are to be replaced with relative probabilities derived from the Einstein coefficients of either Mies (1974) or Turnbull and Lowe (1989) then several aspects of the McDade and Llewellyn (1987) analysis must be reconsidered. For example, the mean OH nightglow vibrational distribution used in the analysis must correspond to the distribution that would be inferred from airglow observations using the alternative probabilities. Similarly, the key input parameter $k_{l^-}^{O_2}(9)/A(9)$, which is based on the laboratory measurements of Finlayson-Pitts and Kleindienst (1981), must be changed to take into account any revision of the $A(9,3)/A(9)$ branching ratios (see Appendix B of McDade and Llewellyn, 1987). In the case of the Mies (1974) probabilities $k_{l^-}^{O_2}(9)/A(9)$ must be decreased from $5.3 \times 10^{-14} \text{ cm}^3$ to $2.9 \times 10^{-14} \text{ cm}^3$ and in the case of the Turnbull and Lowe (1989) probabilities $k_{l^-}^{O_2}(9)/A(9)$ has to be increased from $5.3 \times 10^{-14} \text{ cm}^3$ to $1.5 \times 10^{-13} \text{ cm}^3$. To examine the

impact of adopting the Turnbull and Lowe (1989) probabilities we have repeated the calculations of McDade and Llewellyn (1987) using a revised value for $k_{l^-}^{O_2}(9)/A(9)$ of $1.5 \times 10^{-13} \text{ cm}^3$ and a mean OH vibrational distribution derived from the array of Meinel band intensities presented in Table 3 of Turnbull and Lowe's paper. The collision cascade and sudden death model parameters thus obtained are shown in Figs 7 and 8 and are labelled "case B". These revised parameters are larger than those obtained with the transition probabilities of Murphy (1971) but they do exhibit the same general vibrational level dependence. The parameters obtained with the Turnbull and Lowe (1989) probabilities would imply stronger quenching of all levels of vibrationally excited OH but the vibrational distributions calculated using these parameters do not differ significantly from those presented in Section 3. The collision cascade and sudden death model parameters obtained using the transition probabilities of Mies (1974) and a mean OH vibrational distribution based on these probabilities [see Table 4 of Turnbull and Lowe (1989)] are shown in Figs 7 and 8 and labelled "case C". These revised

parameters are smaller than those obtained with the transition probabilities of Murphy (1971) and the "collisional cascade" coefficients maximize at $v = 6$ rather than $v = 7$. However, the altitude profiles of specific vibrational levels calculated using these revised parameters are qualitatively similar to those presented in Figs 1 and 2. Clearly, the model parameters do vary depending upon which transition probabilities and branching ratios are used but our main conclusions concerning the altitude dependence of the OH vibrational distributions are not particularly sensitive to these assumptions.

Unfortunately, it is not yet possible to identify which of the four limiting case models considered in this work most closely resembles the actual Meinel band excitation mechanism. McDade and Llewellyn (1987) have previously noted that the collisional cascade parameters exhibit a very unusual vibrational level dependence and they suggested that a sudden death model should, perhaps, be preferred. The results of some very recent laboratory experiments would now seem to strongly support this view. Rensberger et al. (1989) have used a two-laser pump-and-probe technique to measure the total rate coefficients for the removal of $OH(v = 2)$ by O_2 and N_2 and they have reported that $k_L^{O_2}(2)$ is 2.6×10^{-13} cm^3 s^{-1} and that $k_L^{N_2}(2)$ is less than 1×10^{-14} cm^3 s^{-1}. Dodd et al. (1990) have analysed time resolved $H + O_3$ chemiluminescence measurements using a single quantum relaxation model and they have reported values for $k_3^{O_2}(1,0)$, $k_3^{O_2}(2,1)$ and $k_3^{O_2}(3,2)$ of 1.3×10^{-13} cm^3 s^{-1}, 2.1×10^{-13} cm^3 s^{-1} and 2.9×10^{-13} cm^3 s^{-1} respectively. The vibrational trend in the $k_3^{O_2}(v, v-1)$ coefficients reported by Dodd et al. is remarkably similar to that of the collisional cascade parameters deduced by McDade and Llewellyn (1987) (see Fig. 7) and the two sets of coefficients would be in excellent agreement if $A(9)$ was ~ 10 s^{-1}. However, it seems very unlikely that $A(9)$ could be so small since the theoretical calculations of Mies (1974), Langhoff et al. (1986), Turnbull and Lowe (1989) and Nelson et al. (1990) all strongly favour values of $A(9)$ lying between 200 s^{-1} and 300 s^{-1}. Furthermore, McDade and Llewellyn (1987) have pointed out that the collisional cascade parameters would conflict with the Spenser and Glass (1977) rate coefficient for quenching of $OH(v = 1)$ by atomic oxygen if $A(9)$ had a value less than ~ 170 s^{-1}. Consequently, unless there are serious problems with both the Spenser and Glass measurements and the theoretical OH radiative lifetimes, the single-quantum deactivation coefficients required to explain the nightglow with a collisional cascade model are much larger than those which have been inferred from the laboratory studies of Dodd et

al. (1990) and the appropriateness of the collisional cascade model must be seriously questioned.

The alternative sudden death models would, therefore, appear to be more viable and the combined laboratory measurements of Spenser and Glass (1977) and Rensberger et al. (1989) suggest that the "maximum O-atom quenching" limit of this model should be preferred. The ratio of the rate coefficients $k_L^O(1)$ and $k_L^O(2)$ reported by Spenser and Glass (1977) and Rensberger et al. (1989) is $\sim 400 : 1$. Near the peak of the OH layer the $[O_2] : [O]$ density ratios are typically $\sim 100 : 1$. Therefore, if the rate coefficients $k_L^O(v)$ and $k_L^{O_2}(v)$ are not strongly v dependent below $v = 6$ then the collisional loss of these levels must be dominated by atomic oxygen rather than O_2 or N_2. This is basically consistent with the "sudden death with maximum O-atom quenching" model but would not be consistent with the "sudden death with no O-atom quenching" model. We should also point out that the sudden death model does not preclude the possibility that the processes studied by Rensberger et al. (1989) and Dodd et al. (1989) represent single quantum vibrational deactivation since such a weak background vibrational relaxation process would not play a significant role in controlling the nightglow OH vibrational distributions. To remain viable, however, the sudden death model still requires that the levels above $v = 6$ are strongly quenched by O_2, or N_2, in a sudden-death manner and evidence to support this has been presented by Sappey and Copeland (1990). Sappey and Copeland report that the $v = 12$ level of OH is removed by O_2 and N_2 with rate coefficients of 1.6×10^{-11} cm^3 s^{-1} and 2.5×10^{-12} cm^3 s^{-1} respectively. These total loss rate coefficients would be consistent with the vibrational trend in the sudden death parameters if $A(9)$ was ~ 300 s^{-1} as the theoretical calculations cited above suggest.

5. CONCLUSIONS

We have used a number of limiting case OH Meinel band excitation models to examine how sudden death quenching and stepwise vibrational deactivation processes would cause the nightglow OH vibrational distributions to vary with altitude. These model calculations show that the altitude dependence of the OH vibrational distributions should be relatively weak and that the emission profiles of the various v' Meinel bands should not differ in altitude by more than one or two kilometers. We have also shown that some recent laboratory experiments suggest that the nightglow Meinel band emission is best explained by a mechanism that involves sudden death quenching

of the higher vibrational levels rather than stepwise single quantum vibrational deactivation.

REFERENCES

Bates, D. R. and Nicolet, M. (1950) The photochemistry of atmospheric water vapour. *J. geophys. Res.* **55**, 301.

Battencr, E. and Lopez-Moreno, J. J. (1979) Time and altitude variations of vibrationally excited states of atmospheric hydroxyl. *Planet. Space Sci.* **27**, 1421.

CIRA (1972) *COSPAR International Reference Atmosphere*. Akademie, Berlin.

Dodd, J. A., Lipson, S. J. and Blumberg, W. A. M. (1990) Vibrational relaxation of $OH(X^2\Pi_i, v = 1-3)$ by O_2. *J. chem. Phys.* **92**, 3387.

Finlayson-Pitts, B. J. and Kleindienst, T. E. (1981) The reaction of hydrogen atoms with ozone as a source of vibrationally excited $OH(X^2\Pi_i)_{v=9}$ for kinetic studies. *J. chem. Phys.* **74**, 5643.

Greenblatt, G. D. and Wiesenfeld, J. R. (1982) Time-resolved emission studies of vibrationally excited hydroxyl radicals: $OH(X^2\Pi, v = 9)$. *J. geophys. Res.* **87**, 11145.

Kaye, J. A. (1988) On the possibly role of the reaction $O + HO_2 \rightarrow OH + O_2$ airglow. *J. geophys. Res.* **93**, 285.

Klenerman, D. and Smith, I. W. M. (1987) Infrared chemiluminescence studies using a SISAM spectrometer. *J. chem. Soc., Faraday Trans. 2*, **83**, 229.

Krassovsky, V. I., Shefov, N. N. and Yarin, V. I. (1961) On the OH airglow. *J. atmos. terr. Phys.* **21**, 46.

Langhoff, S. R., Werner, H.-J. and Rosmus, P. (1986) Theoretical transition probabilities for the OH Meinel system. *J. molec. Spectrosc.* **118**, 507.

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

Lopez-Moreno, J. J., Rodrigo, R., Moreno, F., Lopez-Peurtas, M. and Molina, A. (1987) Altitude distribution of vibrationally excited states of atmospheric hydroxyl at levels $v = 2$ to $v = 7$. *Planet. Space Sci.* **35**, 1029.

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

McDade, I. C. and Llewellyn, E. J. (1988) Mesospheric oxygen atom densities inferred from nighttime OH Meinel band emission rates. *Planet. Space Sci.* **36**, 897.

McDade, I. C., Llewellyn, E. J., Murtagh, D. P. and Greer, R. G. H. (1987) ETON 5: simultaneous rocket measurements of the OH Meinel (8,3) band and $\Delta v = 2$ sequence in the nightglow. *Planet. Space Sci.* **35**, 1137.

Meriwether, J. W. (1989) The photochemistry of nightglow emissions of the mesopause region. *J. geophys. Res.* **94**, 14629.

Mies, F. H. (1974) Calculated vibrational transition probabilities of $OH(X^2\Pi)$. *J. molec. Spectrosc.* **53**, 150.

Murphy, R. E. (1971) Infrared emission of OH in the fundamental and first overtone bands. *J. chem. Phys.* **54**, 4852.

Nagy, A. F., Lui, S. C. and Baker, D. J. (1976) Vibrationally-excited hydroxyl molecules in the lower atmosphere. *Geophys. Res. Lett.* **3**, 731.

Nelson, D. D., Schiffman, A., Nesbitt, D. J., Orlando, J. J. and Burkholder, J. B. (1990) $H + O_3$ Fourier-transform infrared emission and laser absorption studies of $OH(X^2\Pi)$ radical: an experimental dipole moment function and state–to–state Einstein A coefficients. *J. chem. Phys.* **93**, 7003.

Ohoyama, H., Kasai, T., Yoshimura, Y., Kimura, H. and Kuwata, K. (1985) Initial distribution of vibration of the OH radicals produced in the $H + O_3 \rightarrow OH(X^2\Pi) + O_2$ reaction. *Chem. Phys. Lett.* **118**, 263.

Rensberger, K. J., Jeffries, J. B. and Crosley, D. R. (1989) Vibrational relaxation of $OH(X^2\Pi_i, v = 2)$. *J. chem. Phys.* **90**, 2174.

Rogers, J. W., Murphy, R. E., Stair, A. T., Ulwick, J. C., Baker, K. D. and Jensen, L. L. (1973) Rocket-borne radiometric measurements of OH in the auroral zone. *J. geophys. Res.* **78**, 7023.

Sappey, A. D. and Copeland, R. A. (1990) Collisional dynamics of $OH(X^2\Pi_i, v = 12)$. *J. chem. Phys.* **93**, 5741.

Sivjee, G. G. and Hamwey, R. M. (1987) Temperature and chemistry of the polar mesopause OH. *J. geophys. Res.* **92**, 4663.

Spencer, J. E. and Glass, G. P. (1977) Some reactions of $OH(v = 1)$. *Int. J. Chem. Kinetics*, **9**, 111.

Takahashi, H. and Batista, P. P. (1981) Simultaneous measurements of OH(9,4), (8,3), (7,2), (6,2) and (5,1) bands in the airglow. *J. geophys. Res.* **86**, 5632.

Turnbull, D. N. and Lowe, R. P. (1983) Vibrational population distribution in the hydroxyl night airglow. *Can. J. Phys.* **61**, 244.

Turnbull, D. N. and Lowe, R. P. (1989) New hydroxyl transition probabilities and their importance in airglow studies. *Planet. Space Sci.* **37**, 723.