

Auroral N₂ emissions and the effect of collisional processes on N₂ triplet state vibrational populations

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Abstract. Previous model results have shown that the N₂ triplet vibrational level populations in the aurora are strongly affected by cascade and quenching by atomic and molecular oxygen. As the aurora penetrates to lower altitudes (less than 100 km) the role of quenching by atomic oxygen becomes less important and processes involving N₂ collisions begin to play a more prominent part. We are developing a model which will yield steady state vibrational level populations for both the singlet and triplet valence states of N₂. The model currently provides results for the seven low-lying N₂ triplet states ($A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$, $D^3\Sigma_u^+$, and $E^3\Sigma_g^+$). These states are responsible for auroral emissions from the UV (Vegard-Kaplan (VK), second positive (2PG)) through the visible to the infrared (first positive (1PG), infrared afterglow (IRA), Wu-Benesch (WB)). We have included two additional collisional processes in the current model which were not treated previously. These are the intersystem collisional transfer of excitation (ICT) between the *B* state and the *A*, *W*, and *B'* states and vibrational redistribution within the *A* state vibrational manifold, both due to collisions with ground state N₂. The present work compares our current model results with those of a previous model as well as ground, airborne, and rocket observations. The comparison between N₂(*A*) (VK) and N₂(*B*) (1PG) vibrational level populations predicted by our model and a number of auroral observations indicate that the current model achieves a significant improvement in the fit between calculation and observation. In addition, the current model predicts a shift in the band intensity distribution of the 1PG $\Delta v = 3$ sequence from the infrared into the visible red at the lower altitudes (less than 90 km) as well as an overall enhancement in the entire 1PG system. Consequently, this provides a possible explanation of a dominant feature of type *b* aurora, the auroral red lower border.

1. Introduction

The nitrogen molecule, as a major component of the atmosphere, offers great potential as a diagnostic tool to examine energetics and composition in the lower thermosphere. This is largely due to its rich spectrum and the diverse and complex nature of its low-lying excited electronic states. The emission from these excited states in the aurora has long been observed from both the ground and space at wavelengths from the ultraviolet to the infrared. These emissions include the Vegard-Kaplan ($A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$) and second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) in the ultraviolet and the first positive ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$), infrared afterglow ($B'^3\Sigma_u^- \rightarrow B^3\Pi_g$), and Wu-Benesch ($W^3\Delta_u \rightarrow B^3\Pi_g$) in the visible and infrared. In the past the most comprehensive and well-known model of N₂ excited state vibrational level populations was developed by Cartwright *et al.* [1971, 1973] and Cartwright [1978]. In the present paper we will focus on a comparison between the results of our current model and those of this previous study.

The early work of Cartwright *et al.* [1971] was motivated in part by the observed altitude variation in the N₂(*A*) and N₂(*B*)

vibrational distributions inferred from VK and 1PG emission [Broadfoot and Hunt, 1964; Shemansky and Vallance Jones, 1968]. The work of Wu and Benesch [1968] and Benesch and Saum [1971] showed the importance of intrasystem cascading between the *W* and *B* states, and Gilmore [1969] addressed the potential for similar cascade from the high levels of the *A* state to the lower levels of the *B* state ("reversed" 1PG). The Cartwright *et al.* [1971] model incorporated the intrasystem cascade schemes although the N₂(*B'*) \leftrightarrow N₂(*B*) transitions were not included until the later model [Cartwright, 1978].

The significance of these cascades and other issues (e.g., the amount of 1PG cascade, etc.) was called into question [Shemansky and Broadfoot, 1973; Cartwright *et al.*, 1973]. The resulting controversy was resolved in favor of Cartwright *et al.* [1971, 1973] when quantitative measurements of the VK and 1PG by Vallance Jones [1974] and Vallance Jones and Gattinger [1976a, b, 1978] were compared by Cartwright [1978] with his later model results. In addition to questions about cascading there was also disagreement [Shemansky and Broadfoot, 1973; Cartwright *et al.*, 1973] on the relative magnitude of the cross sections for electron impact excitation of the low-lying N₂ excited electronic states [Stanton and St. John, 1969; McConkey and Simpson, 1969; Brinkmann and Trajmar, 1970; Cartwright, 1970; Shemansky and Broadfoot, 1971]. The electron beam studies of Cartwright *et al.* [1977a, b] and Chutjian *et al.* [1977] resolved this controversy in favor of the

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earlier electron beam work of *Brinkmann and Trajmar* [1970]. There have been some improvements to these cross sections [*Ajello and Shemansky*, 1985; *Trajmar et al.*, 1983], but these have not appreciably affected the relative magnitude of the N₂ excited state cross sections. However, there is evidence [*Zubek*, 1994; *Zubek and King*, 1994] that the cross sections for excitation of the N₂(C) state is approximately 20% larger than the values presented by *Trajmar et al.* [1983] and this could impact the interpretation of auroral and airglow 2PG observations.

The N₂ excited state vibrational level population model produced by *Cartwright* [1978] utilized the complex intrasystem cascading scheme, the *Cartwright et al.* [1977b] cross sections, and vibrational level dependent quenching by O, O₂, and N₂. Due to the fit between the above auroral observations and results of *Cartwright's* [1978] model, the N₂ vibrational level populations predicted by that study have remained a point of comparison with auroral observations since that time [*Valance Jones and Gattinger*, 1978; *Torr and Torr*, 1982; *Meier*, 1991].

Cartwright's [1978] model, and other models [*Gattinger and Vallance Jones*, 1979; *Solomon*, 1989; *Strickland et al.*, 1993] which predict vibrational level population of N₂ excited states, focus on radiative cascade and quenching by collisions with O, O₂, and N₂. *Cartwright* [1978] showed conclusively the importance of intrasystem cascade and vibrational level dependent quenching. However, he was forced to rely on both an incomplete set of radiative transition probabilities and less accurate quenching coefficients than are now available. Our current model uses more recent values for both transition probabilities associated with the N₂ triplet transitions [*Gilmore et al.*, 1992; *Piper et al.*, 1989; *Piper*, 1993] and N₂(A) quenching coefficients for collisions with O and O₂ [*Thomas and Kaufman*, 1985]. This model also incorporates two additional collisional processes not previously included in models of atmospheric N₂ emission: the intersystem collisional transfer of excitation (ICT) between vibrational levels of the low-lying N₂ triplet states and vibrational redistribution within the N₂(A) state manifold. The potential for the ICT in low-altitude aurora was addressed by *Cartwright et al.* [1971], *Cartwright* [1978], and *Vallance Jones and Gattinger* [1978], and discussed in detail by *Benesch* [1981, 1983]. As will be shown, by including these collisional processes and updated quenching coefficients and transition probabilities, we have been able to achieve significant improvements in the fit between model results and observations.

Of the two collisional processes the more significant is the intersystem collisional transfer of excitation. This process couples adjacent vibrational levels of overlapping electronic states. For the case of N₂ triplets, this involves the transfer of excitation (excited state population) between vibrational levels of the B³Π_g and the A³Σ_u⁺, W³Δ_u and B'³Σ_u⁻. The potential curves for these states appear in Figure 1, which shows the numerous overlapping vibrational levels which can participate in the ICT processes. We will discuss the details of this process below.

The other collisional process which we include vibrational redistribution within the N₂(A) state, reflects a more appropriate use of the coefficients for N₂(A) quenching by N₂(X) than that of *Cartwright* [1978]. The work on N₂(A) quenching [*Dreyer and Perner*, 1973; *Dreyer et al.* 1974] indicates that collisions between N₂(A, 2 ≤ v ≤ 8) and N₂(X, v = 0) lead to a loss of two N₂(A) vibrational quanta with increasing probability as the initial N₂(A) vibrational quantum number increases toward v = 8. *Dreyer and Perner* [1973] and *Dreyer et al.* [1974] also postulate that this loss of N₂(A) quanta results in the production of an N₂(X, v = 1) molecule. As we will discuss below, we have used

the assumption that two (or three) vibrational quanta are lost from the N₂(A) vibrational manifold during this kind of collision while at the same time the electronic energy of the N₂(A) state is retained by the excited molecule.

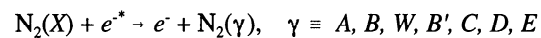
Including these two additional processes permits a more accurate treatment of the effects of collisions between N₂ ground and excited state molecules. Both of these processes are distinctly different from electronic quenching in that the electronic energy is not lost during the course of the collision. Under these kinds of collisions, either the excited molecule undergoes a transition to an adjacent vibrational level of an overlapping electronic state (ICT) or there is a loss of some number of excited state vibrational quanta (two or three) into a single ground state vibrational quantum. Here we present the preliminary results from our current model and compare them to both *Cartwright's* [1978] model and a number of ground, airborne, and rocket observations.

2. Details of the Vibrational Level Populations Model

2.1. Model Processes

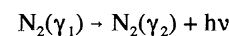
The following processes are included in the current model. The first three processes are generally understood and we will not focus on them in detail. These are the processes which were treated by *Cartwright* [1978].

(1) Electron impact

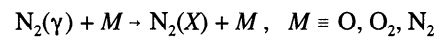


and e^* = an energetic electron.

(2) Radiative cascade and intrasystem cascading

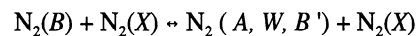


(3) Electronic quenching

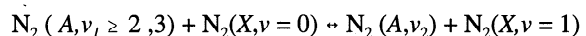


where we do not consider the end products in the quenching reaction, only that the electronic energy of state γ is permanently lost to the N₂ triplet manifold. The new processes are the following:

(4) Intersystem collisional transfer (ICT)



(5) Vibrational redistribution



with $v_2 = v_1 - 2, 3$

As to the first three processes, the following comments apply. For the current study we use the electron impact excitation rates calculated by *Cartwright* [1978] for altitudes between 100 and 130 km. These rates are a function of the flux and energy distribution of the auroral electrons as well as the energy-dependent cross sections for these excited electronic states [*Cartwright et al.*, 1977b]. The secondary electron spectrum used by *Cartwright* [1978] is based on the measured spectrum

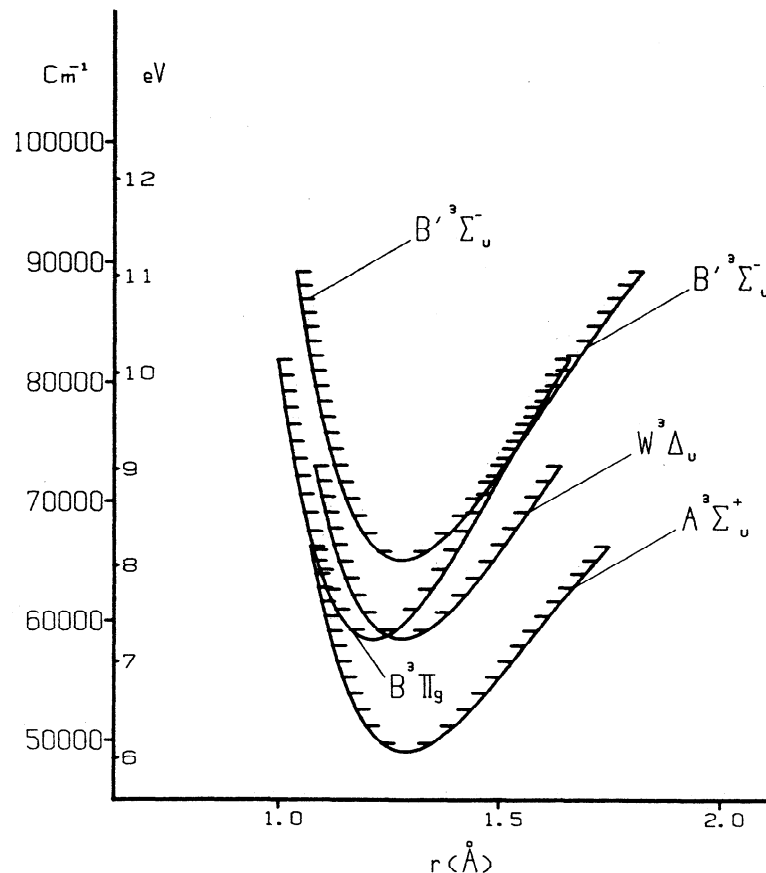


Figure 1. The most significant process which has been included in the current model is the intersystem collisional transfer of excitation (ICT) between the $B^3\Pi_g$ and the $A^3\Sigma_u^+$, $W^3\Delta_u$, and $B^3\Sigma_u^-$. This figure shows the potential curves for the four triplet states which are involved in the ICT process.

of *Feldman and Doering* [1975] for 8 to 100 eV and was extended to higher energies by use of the results of *Rees and Maeda* [1973]. The shape of the spectrum was held fixed but was decreased in magnitude at lower altitudes in a manner consistent with *Feldman and Doering* [1975]. The cascade scheme is the same as with *Cartwright* [1978] (see Table 1) except that we use the more recent transition probabilities of *Gilmore, et al.* [1992], *Piper* [1993], and *Piper et al.* [1989]. For the D -to- E transition we have used the calculated values for $\nu' = 0$ from *Cartwright's* original model (*D. C. Cartwright*, private communication, 1990).

The scheme for quenching by O, O₂, and N₂ is the same as that of *Cartwright* [1978] except for the N₂(A) state where we use the coefficients for the quenching of N₂(A) by N₂(X) as vibrational redistribution coefficients. We also use the coefficients for quenching by O and O₂ from the work of *Thomas and Kaufman* [1985] combined with the earlier work on O₂ done by *Dreyer et al.* [1974]. *Thomas and Kaufman's* values and the vibrational redistribution coefficients from *Dreyer et al.* [1974] appear in Figure 2, and the coefficients for quenching of the other excited states by N₂ appears in Figure 3 [*Dreyer and Perner*, 1972; *Cartwright*, 1978]. Quenching of the D and E states was taken to be identical with that of the B state. The vibrational-level-dependent rate coefficients for quenching of N₂(A) by O and O₂ were used for all seven triplet excited states, as with *Cartwright* [1978].

The stability of N₂ excited states with regard to O and O₂ quenching was discussed by *Cartwright* [1978]. At that time

coefficients for quenching by these species had been measured only for N₂(A). Based on stability arguments, *Cartwright* chose to use the quenching coefficients of N₂(A) by O and O₂ for all excited states. Since that time a number of measurements of quenching coefficients for N₂ singlets ($a^1\Pi_g$ and $a^1\Sigma_u^-$) by O₂

Table 1. Cascade Scheme

Transition	Common Name
<i>Normal Cascade</i>	
$A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$	Vegard-Kaplan
$C^3\Pi_u \rightarrow B^3\Pi_g$	Second positive
$D^3\Sigma_u^+ \rightarrow B^3\Pi_g$	Fourth positive
$D^3\Sigma_u^+ \rightarrow E^3\Sigma_g^+$	-----
$E^3\Sigma_g^+ \rightarrow A^3\Sigma_u^+$	Herman-Kaplan
$E^3\Sigma_g^+ \rightarrow B^3\Pi_g$	-----
$E^3\Sigma_g^+ \rightarrow C^3\Pi_u$	-----
<i>Intrasystem cascade</i>	
$B^3\Pi_g \leftrightarrow A^3\Sigma_u^+$	First positive (and reverse)
$B^3\Sigma_u^- \leftrightarrow B^3\Pi_g$	Infrared-afterglow
$W^3\Delta_u \leftrightarrow B^3\Pi_g$	Wu-Benesch

These are the ten transitions used in the current model. See text for discussion

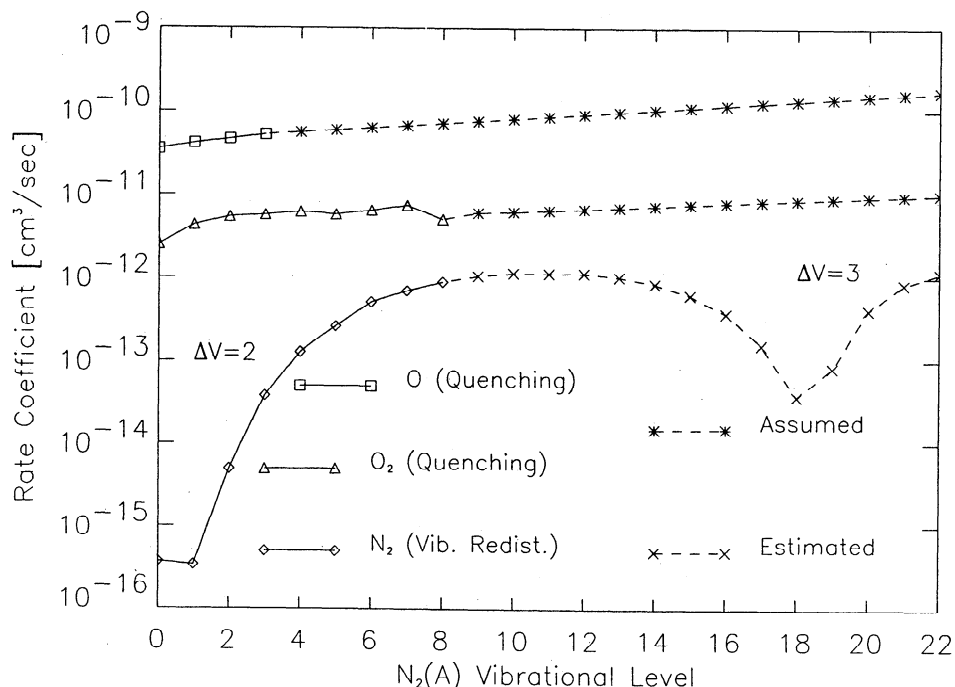


Figure 2. The quenching coefficients for the $A^3\Sigma_u^+$ used in the current model. The points connected by solid curves are measured values and those connected by dashed curves are extrapolated or estimated. Three major differences between the current values and those of *Cartwright* [1978] are (1) a slight increase of the O quenching coefficient, (2) an improvement in the O₂ quenching coefficients for $v = 1$ and 3 [*Thomas and Kaufman*, 1985], and (3) the use of the N₂ quenching coefficients for vibrational redistribution within the $A^3\Sigma_u^+$ vibrational manifold [*Dreyer et al.*, 1974].

have been done [*Marinelli et al.*, 1989; *Piper*, 1987]. The results indicate that the quenching coefficients for these two states are larger than originally assumed by *Cartwright* [1978] which carries the implications for similar increases for the triplet excited states. However, since the above studies do not distinguish between electronic quenching and collisional transfer they

must be interpreted carefully. Collisional transfer from the N₂(W) and N₂(A) states to the N₂(B) state, induced by collisions with O₂, has been observed by *Bachmann et al.* [1992, 1993]. Given that a focus of the current study is the addition of N₂ collisional processes to previous models and for comparison with the results of *Cartwright* [1978], we have chosen to use Cart-

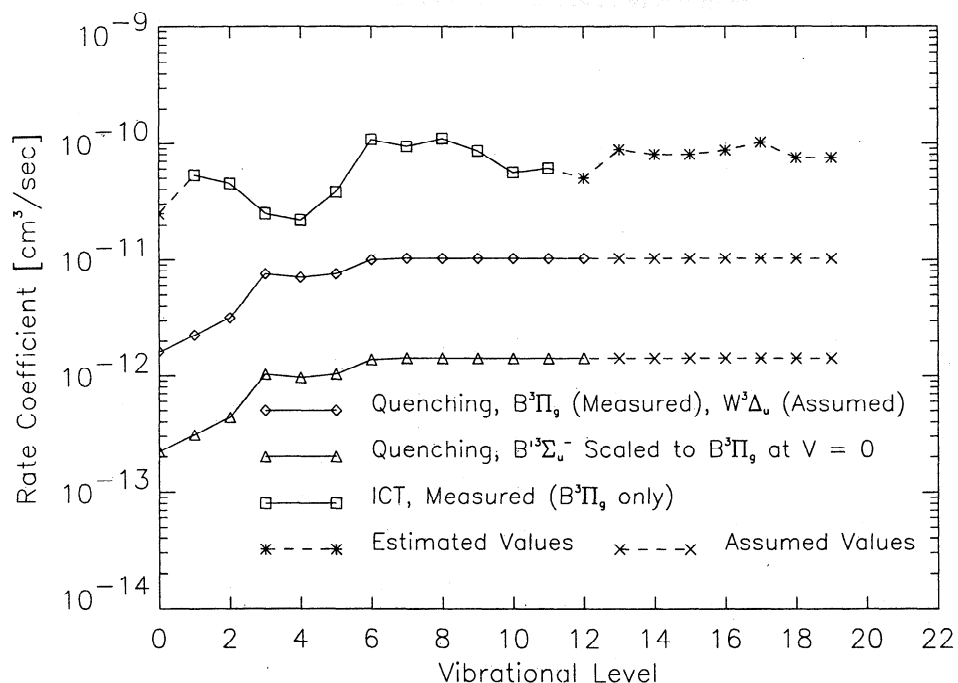


Figure 3. Comparison of the total collisional transfer rates from the $B^3\Pi_u$ with the quenching coefficients used by both the current model and *Cartwright's* [1978]. Also shown are the quenching rate coefficients for $W^3\Delta_u$ and $B^3\Sigma_u^-$.

wright's quenching scheme. Since we are mostly concerned with the effects at lower thermospheric altitudes where N₂ is the dominant species and the resulting intersystem collisional transfer rates are quite large, the impact of the uncertainties in the O and O₂ quenching coefficients will be small. This could effect the interpretation of observations at higher altitudes where atomic oxygen is the dominate collision partner and so warrants further examination.

2.2. Intersystem Collisional Transfer of Excitation

The ICT process couples vibrational level populations of overlapping electronic states and should not be considered a simple quenching process. The name is based on the fact that collisions transfer excitation (or population and thereby emission intensity) from one emission system (WB) to another (1PG). This process has been examined in numerous laboratory studies [Heidner *et al.*, 1976; Sadeghi and Setser, 1981; Rotem and Rosenwaks, 1983; Benesch and Fraedrich, 1984; Katayama, 1984; Ali and Dagdigian 1987; Morrill *et al.*, 1988; Bachmann, *et al.*, 1992, 1993 and references contained therein] but it has only recently been included in models of atmospheric emission [Morrill and Benesch, 1994, 1995; Eastes *et al.*, 1994].

Rate coefficients for this process have been measured [Rotem and Rosenwaks, 1983; Espy, 1986; Katayama and Dentamaro, 1989; Bachmann *et al.*, 1992, 1993; J. S. Morrill and W. M. Benesch, manuscript in progress] and the theoretical aspects of these transitions have also been examined [Alexander and Pouilly, 1983; Alexander and Corey, 1986; Ali and Dagdigian, 1987]. For the current model, the rate coefficients for collisional transfer between the N₂(B) state and the N₂(A), N₂(W), and N₂(B') states are based on the measured values of Rotem and Rosenwaks [1983]. We consider these rate coefficients to reflect the sum of rate coefficients for collisional transfer from the N₂(B) state to the N₂(A), N₂(W), and N₂(B') states. These coefficients are shown in Figure 3. In order to partition these rate coefficients from a given N₂(B) level to a set of nearby levels of the N₂(A), N₂(W), and N₂(B') states, we have assumed (1) that only transfers to the nearest vibrational levels of the overlapping N₂(A), N₂(W), and N₂(B') states are important and (2) that the rates scale as $(g_\gamma/g_B) \exp(-\Delta E)$. In the latter approximation, ΔE is the energy difference between the two vibrational levels involved in the transition and g_γ/g_B is the ratio of the degeneracies of the two states. The exponential term in the above approximation is used to weight more heavily, transitions between levels which have nearly the same energy. The return values from these three states to the N₂(B) were based on the formulation by Benesch and Fraedrich [1984] such that,

$$k_{WB} / k_{BW} = (Q_W / Q_B)(g_W / g_B) \sim (B_B / B_W)(g_W / g_B),$$

where the Q s are the rotational partition functions, the g 's are the electronic state degeneracies, and the B s are the rotational constants for the specific states and levels in question. We have used the simple model presented by Bachmann *et al.* [1992, 1993] to estimate rate coefficients for levels which have no measured values ($B, v = 0$ and $v \geq 12$, see Table 2).

The use of estimated rate coefficients does involve some uncertainty since the role of rotational energy levels in determining resonance between adjacent vibrational levels or the importance (or lack of importance) of the Franck-Condon factor between a given pair of adjacent levels is not yet completely

understood. Nonetheless, these recent values and current empirical estimates are of adequate quality to allow the inclusion of this process in our current model. However, the details of collisional transfer still require further experimental and theoretical examination.

During the study of the collisional transfer process [Rotem *et al.*, 1982; Benesch, 1983; Alexander and Pouilly, 1983;

Table 2. Intersystem Collisional Transfer Rate Coefficients

B ³ Π _g	A ³ Σ _u ⁺	W ³ Δ _u	B' ³ Σ _u ⁻			
0	7	7.83	0	17.2		
1	8	6.14	1	41.7		
	9	5.21				
2	10	22.0	2	22.7		
	11	8.57	3	9.06		
3	12	2.78	4	4.59		
	13	6.00	5	4.23		
	14	8.52	6	15.0	1	11.7
4	15	2.69				
	16	3.68	7	58.0	2	18.3
5	17	11.1	8	59.9	3	13.1
	18	9.75				
	19	35.3	9	43.4	4	14.1
6	20	6.97	10	6.77	5	3.52
	21	4.41	10	6.46	5	8.72
	22	36.9	11	10.2	6	3.58
7	23	4.18				
	24	3.93	11	6.46	6	4.62
	25	21.9	12	6.46	7	2.99
	26	3.24				
8	27	3.20	12	3.25	7	3.47
	28	18.9	13	22.5	8	3.43
	29	5.67				
9	30	1.31				
	31	5.67	14	28.2	8	2.08
	32	5.30			9	3.78
10	33	13.3				
	34		15	62.4	9	2.35
11			16	19.2	10	4.54
			16	45.5	10	2.11
			17	27.2	11	5.34
12			17	33.5	11	1.93
			18	38.4	12	6.14
13			18	24.9	12	1.82
			19	53.5	13	6.92
14			19	18.8	13	1.75
			20	73.8	14	7.60
15			21	65.7	14	1.72
					15	8.16

Intersystem collisional transfer rate coefficients from the N₂(B) state to the N₂(A), N₂(W), and N₂(B') states used in the current model. Rate coefficients are in units of 10⁻¹² cm³/molecule-s. The left most column is the N₂(B) state vibrational level. The columns of numbers under each other term symbol are the vibrational quantum numbers of the overlapping levels and the rate coefficient from the N₂(B) state. Return rate coefficients are scaled as discussed in the text.

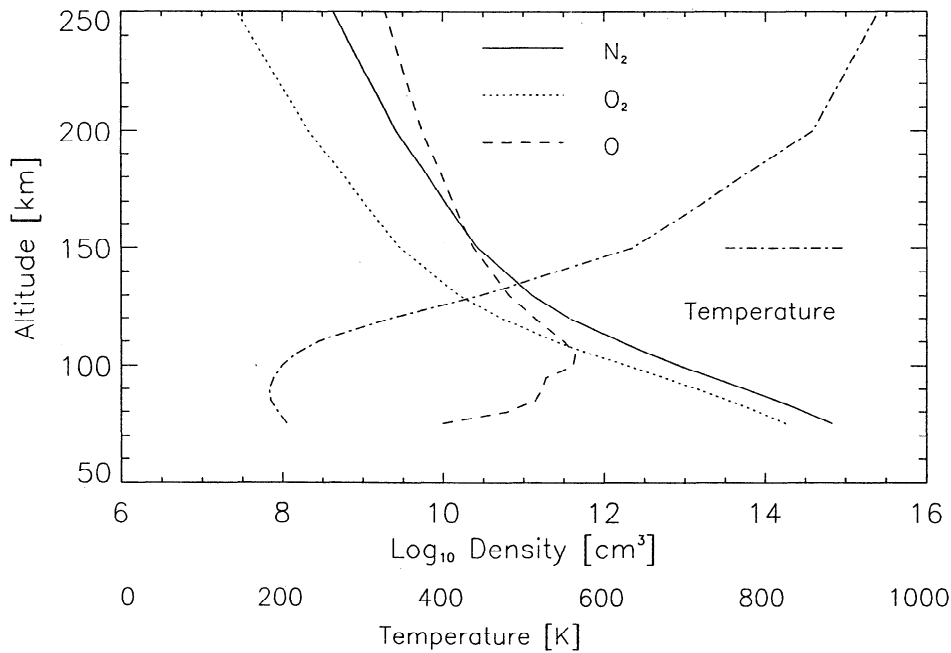


Figure 4. The atmospheric model used for the present results [Jursa, 1985] which was used for the density and temperature inputs required by the model. This model atmosphere is similar to that used by Cartwright [1978].

Katayama and Dentamaro, 1986; Ali and Dagdigian, 1987; Piper, 1988; Bachmann et al., 1992, 1993] a number of selection rules have come to light. These selection rules appear to be those for dipole allowed transitions ($\Delta\Lambda = 0, \pm 1, \Delta S = 0, g \leftrightarrow u, g(u) \leftrightarrow g(u)$). The consequence of these rules is that ICT transitions within the N₂ triplet manifold occur between the B³Π_g and the A³Σ_u⁺, W³Δ_u, and B³Σ_u⁻ but no transitions occur among the latter three states.

2.3. Vibrational Redistribution within the N₂(A) State

According to Dreyer and Perner [1973] and Dreyer et al. [1974] who studied quenching of N₂(A) by N₂(X), the loss of population from N₂(A, v₁) equals the gain in population into N₂(A, v₂) where v₁ - v₂ = 2 for 2 ≤ v₁ ≤ 7. They attributed this loss of two N₂(A) vibrational quanta to the production of N₂(X, v = 1) from N₂(X, v = 0). In addition, they note that as the N₂(A)

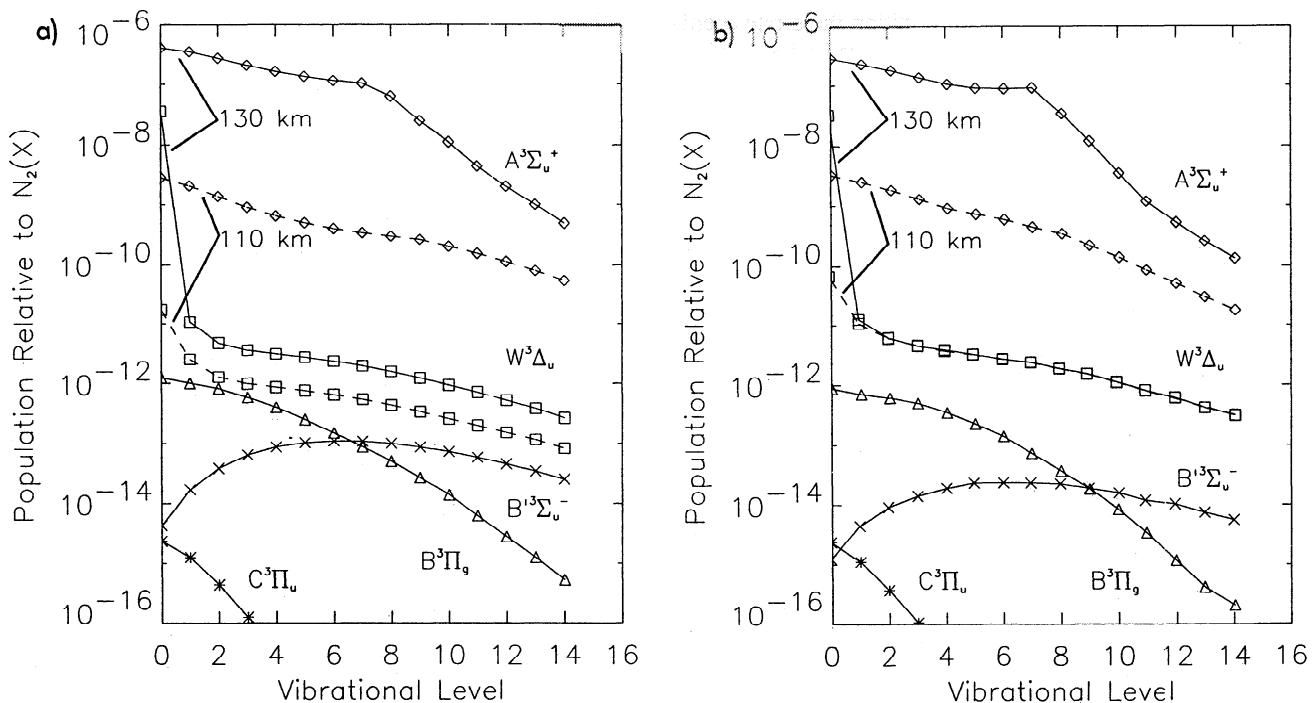


Figure 5. These figures compare results from (a) the current model with (b) those of Cartwright [1978] for 130 km (without quenching) and 110 km (with quenching only). The solid and dashed curves for A³Σ_u⁺ and W³Δ_u are for 130 and 110 km, respectively. Note that the curves for W³Δ_u at 130 and 110 km overlap in Figure 5b for v = 2 and above. The curves for B³Π_g, B³Σ_u⁻, and C³Π_u are for 130 km without quenching.

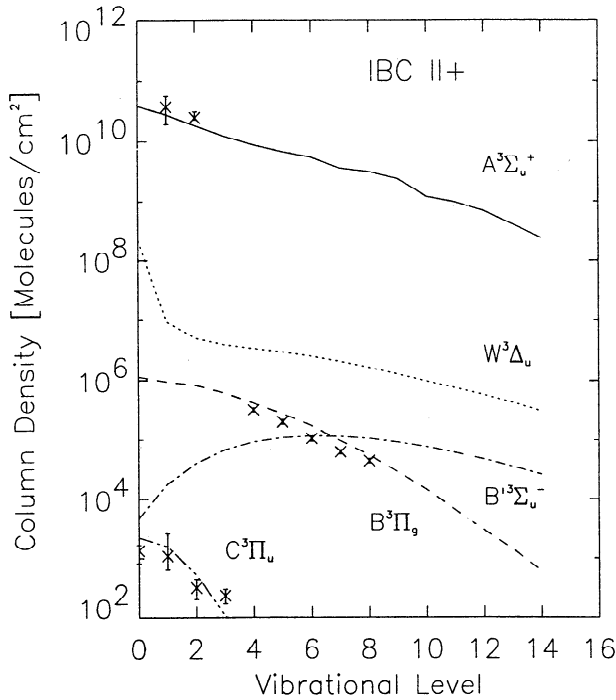


Figure 6. Column abundances predicted by the current model between 100 km and 250 km for the five indicated states. Also shown are the column abundances for N₂(A), N₂(B), and N₂(C) states implied by the observations of Rees et al. [1976] scaled to the current results.

vibrational level increases so does the resonance between $\Delta v = 2$ in the N₂(A) and the energy difference between the two lowest levels of N₂(X). Their data show a corresponding increase in rate coefficient with increasing vibrational level. In order to extrapolate to higher N₂(A) levels we have fit Dreyer and Perner's rate coefficients to a power series in $\exp(-|\Delta E|)$ where

$$\Delta E = [(E_{A,v1} - E_{A,v2}) - (E_{X,v=1} - E_{X,v=0})].$$

Since this function peaks between $v = 8$ and 12 for $\Delta v = 2$ we have used the resulting polynomial to estimate rate coefficients for higher N₂(A) vibrational levels ($v \geq 16$) using $\Delta v = 3$ in the N₂(A) state. The results appear in Figure 2. An important point to note is that Cartwright's [1978] use of the values for the quenching of N₂(A) by N₂(X) reduces the total N₂(A) population. Conversely, our use of the values in Figure 2 does not affect the total N₂(A) population but rather forces the vibrational distribution toward the lower levels.

2.4. Equations for Statistical Equilibrium

In order to determine the equilibrium vibrational level populations of the N₂ triplet excited states, we solve the equation for statistical equilibrium below. This is a master equation which is based on the processes mentioned above and is similar to the formulation used by Cartwright [1978]. For a given vibrational level v , in a given state α , the equation which describes the relative number density (n_v^α / n_{N_2}) at statistical equilibrium is

$$K_{ei,v}^\alpha + \sum_\beta \sum_I (A_{I,v}^{\beta\alpha} + K_{ICT,i,v}^{\beta\alpha} + \delta_{A\beta} \delta_{i,v+2(3)} K_{VR,i,v}^A) (n_i^\beta / n_{N_2}) = \{K_{qv}^\alpha + \sum_\gamma \sum_j (A_{j,v}^{\alpha\gamma} + K_{ICT,j,v}^{\alpha\gamma} + \delta_{A\gamma} \delta_{v,j+2(3)} K_{VR,j,v}^A)\} (n_v^\alpha / n_{N_2}) \quad (1)$$

where

- $K_{ei,v}^\alpha$ electron impact excitation rate (per N₂) of vibrational level v in state α ;
- $A_{I,v}^{\beta\alpha}$ transition probability from $\beta(I)$ to $\alpha(v)$;
- $K_{ICT,i,v}^{\beta\alpha}$ intersystem collisional transfer rate from $\beta(I)$ to $\alpha(v)$;
- $K_{VR,i,v}^A$ vibrational redistribution rate from $A(I)$ to $A(v)$;
- $K_{qv}^\alpha = k_{q(O);v}^\alpha(n_O) + k_{q(O_2);v}^\alpha(n_{O_2}) + k_{q(N_2);v}^\alpha(n_{N_2})$ total quenching rate;
- α, β, γ electronic states;
- i, j source and sink vibrational levels, respectively.

All rates are in Hertz. $K_{ei,v}^\alpha$ also includes enhancements due to elevated ground vibrational distributions [Morrill and Benesch, 1990]. The two Kronecker deltas insure the k_{VR} term (vibrational redistribution) applies only to the N₂(A) state and only for $\Delta v = 2$ or 3 . An important point about the ICT rates is that for any given $B^3\Pi_g$ vibrational level only the nearest (quasi-isoenergetic) vibrational levels of $A^3\Sigma_u^+$, $W^3\Delta_u$, $B^3\Sigma_u^-$ are involved in the ICT processes and so many of these terms are zero (see Table 2).

Currently, the model requires as inputs volume excitation rates (per N₂) for the seven excited states as well as temperature and density (O, O₂, N₂) from a model atmosphere. In order to present an effective comparison we have used the volume excitation rates from Cartwright [1978; Table 1] and the CIRA-72 model atmosphere for intermediate solar conditions and a 1000 K exospheric temperature [Jursa, 1985]. The model atmosphere we have used is shown in Figure 4. Calculations for altitudes above 130 km or below 100 km used the volume excitation rates at these altitudes, respectively, as well as the density and temperature provided by the model atmosphere for the specific altitude in question.

3. Results

The Figures 5a and 5b compare results from the current model with those of Cartwright [1978] for 130 km (without quenching) and 110 km (with quenching only). The solid and dashed curves for $A^3\Sigma_u^+$ and $W^3\Delta_u$ are for 130 and 110 km, respectively. The curves for $B^3\Pi_g$, $B^3\Sigma_u^-$, and $C^3\Pi_u$ are for 130 km without quenching. The major difference between the two Figures involves the stronger effect of quenching in the current model on the overall $W^3\Delta_u$ populations at 110 km. The current model also predicts an enhancement in the $B^3\Pi_g$ and $B^3\Sigma_u^-$ overall populations compared to the model of Cartwright [1978].

A rigorous test of any model of N₂ populations in the aurora involves its ability to predict the column abundances of the N₂ triplet state molecules. Calculated densities summed from 100 to 250 km are shown in Figure 6. Also shown are the abundances implied by the results of Rees et al. [1976] scaled to fit the predicted N₂(A), N₂(B), and N₂(C) state distributions. The excitation rates used for the model results are for an IBC II+ aurora (5577 Å > 10 kR) whereas the observation of Rees et al [1976] were made when the 5577 Å emission ranged from 5 to 7 kR. The fit between observation and model results is very good with the observations of Rees et al. [1976] being scaled up by a factor of 8.5. It should be noted that any effects of collisional processes at lower altitude are not expected to be seen in this type of observation due to the dominant role of the emission from the peak in the emission profile (approximately 110 km).

Figure 7 compares calculated $A^3\Sigma_u^+$ populations from our current model with Cartwright's [1978] model. Also shown are

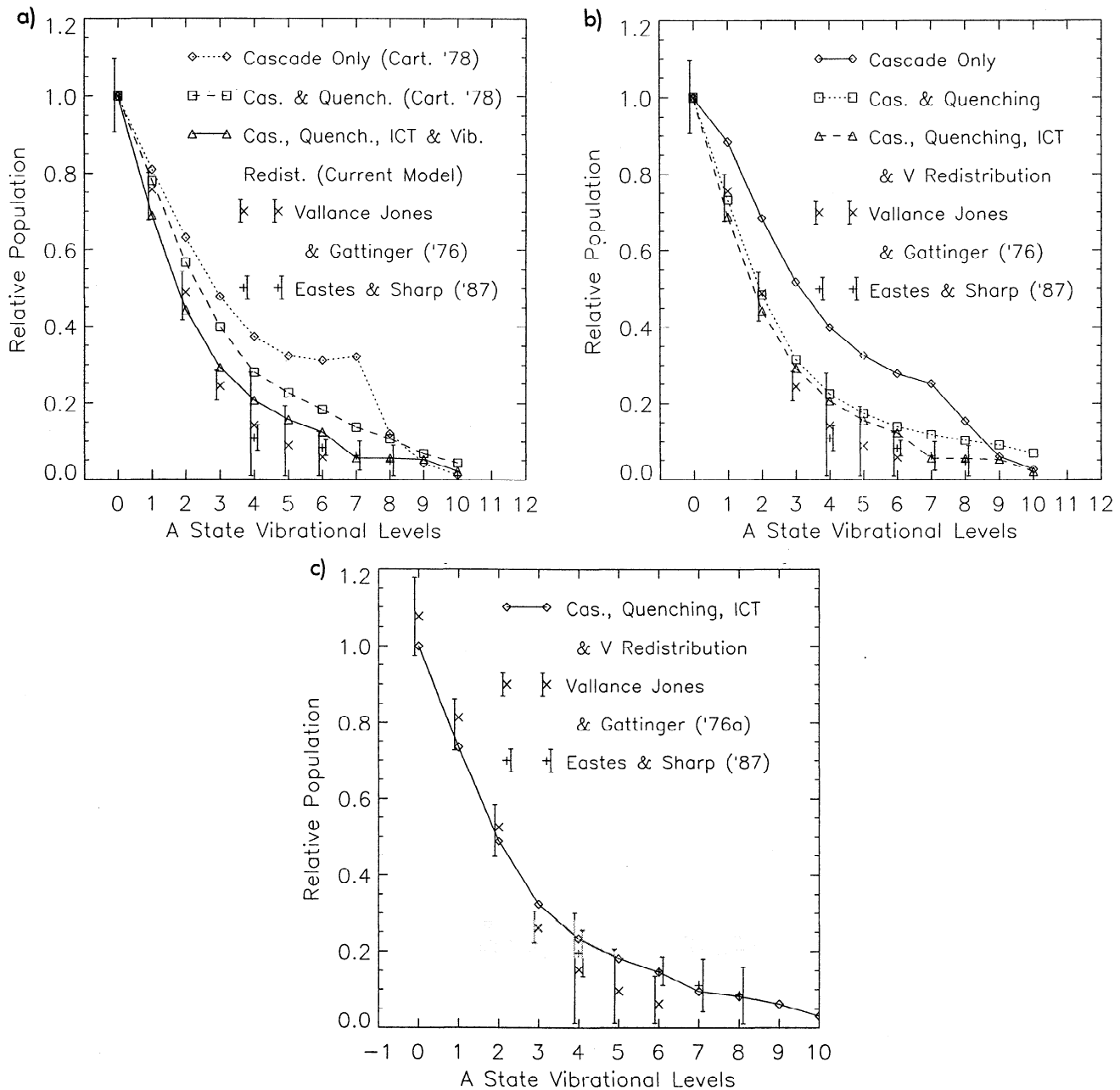


Figure 7. These three figures compare model $A^3\Sigma_u^+$ populations from our current model and *Cartwright's* [1978] with the observations of *Vallance Jones and Gattinger* [1976a] and *Eastes and Sharp* [1987]. Figure 7a compares *Cartwright's* [1978] results (with and without quenching) with the current model results with quenching, ICT, and vibrational redistribution all active. Figure 7b shows results from the current model alone and differentiates runs where various collisional processes were active. In Figure 7a and 7b the two data sets have been scaled to overlap at vibrational levels 4 and 6. Figure 7c compares the $A^3\Sigma_u^+$ column density distribution from Figure 5 with the above observations. Here both data sets have been scaled to the model distribution independently.

ground and rocket observations of relative N₂(A) populations from VK emissions [*Vallance Jones and Gattinger*, 1976a; *Eastes and Sharp*, 1987] (herein after referred to as VJ&G and E&S, respectively) which have been scaled using the recent transition probabilities of *Piper* [1993]. In this figure the model distributions are for 110 km as are the observations of E&S, whereas the VJ&G results are for integrated column emission. Figure 7a compares *Cartwright's* results (with and without quenching) with those of the current model when quenching, ICT, and vibrational redistribution are all active. This figure

shows a significant enhancement in the populations of the lower levels predicted by the current model. Figure 7b shows results from the current model alone at 110 km and displays the results of model runs where different collisional processes were active. For the lower vibrational levels, the enhancement of the populations is largely due to the use of improved transition probabilities and quenching coefficients for collisions with O and O₂. Vibrational redistribution appears to have only a slight effect on the relative populations of these levels at this altitude. The effect of ICT can be seen for $\nu = 7$ and above.

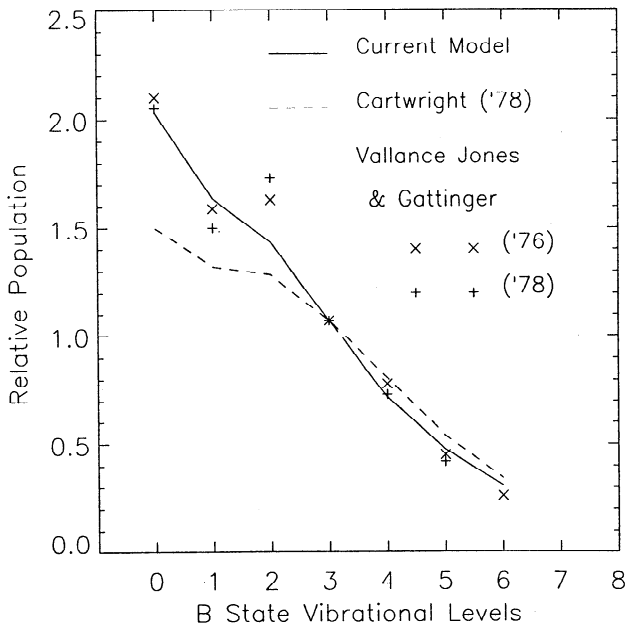


Figure 8. Comparison of $B^3\Pi_g$ populations predicted by the current model at 110 km with all collisional processes active and the model results of Cartwright [1978]. Also shown are the observations of Vallance Jones and Gattinger [1976, 1978].

The results in Figure 7c compare the N₂(A) predicted vibrational distribution implied by column emission (Figure 6) with the VJ&G and E&S data. This is a more comprehensive comparison of the VJ&G data with model results than is shown by Figures 7a and 7b. In Figure 7c the VJ&G and E&S data is scaled to the model distribution independently unlike the scaling on Figures 7a and 7b where the two distributions are scaled together at $\nu = 4$ and 6 and the $\nu = 0$ population is set to unity. The independent scaling is reasonable for Figure 7c since the E&S data fits equally well the relative distribution for $\nu = 4-8$ derived from either column densities measurements or emission spectra from a specific altitude.

Figure 8 compares $B^3\Pi_g$ populations predicted by the current model at 110 km, using all three collisional processes, with Cartwright's [1978] model results. Also shown are the observations of 1PG emission from Vallance Jones and Gattinger [1976b, 1978] scaled with the 1PG transition probabilities of Piper et al. [1989]. Model results indicate the best fit occurs when all three collisional processes (quenching, ICT, and vibrational redistribution) are active, although the full measure of the observed enhancement of $\nu = 2$ is not achieved by the current model.

The relative populations of the $B^3\Pi_g$ vibrational levels 3 through 9 at 130, 110, 95, and 80 km predicted by the current model is shown in Figure 9. Here all collisional processes are active. This figure shows that an enhancement of the higher vibrational levels is predicted at lower altitudes primarily due to the effect of collisional transfer (ICT) from the long-lived N₂(A) and N₂(W) states. Where such alterations occur, they give rise to an increase in the visually observed red emission from the 1PG. The effect is demonstrated in Figure 10 where the two spectra, that for 80 km and that for 130 km, have been scaled with the sensitivity function of the human eye [Gebel, 1964]. The total equilibrium population of the B state is the same for the two spectra shown here, but the solid spectrum, characterized by collisional rearrangement, embodies an enhancement in the total emission of visible red photons.

Figure 10 has been presented to emphasize the effect of the collisional redistribution of the emitted 1PG photons brought about by ICT. There is, however, the important additional consideration that most of the entire excitation of the B and the W is emitted as 1PG photons where ICT prevails. That is, when the W and B are collisionally coupled, 1PG transitions from the B to the A are far more probable than any optical transition from the W, and the 1PG constitutes the emission channel of choice for all of the W and B excitation. Since the W and B have roughly the same excitation rates in the aurora, the onset of ICT leads to a considerable augmentation of the overall 1PG intensity. Consequently, there is an enhancement of the 1PG over and above that produced by the combined effect of the redistributed B populations and the sensitivity of the human eye. This results

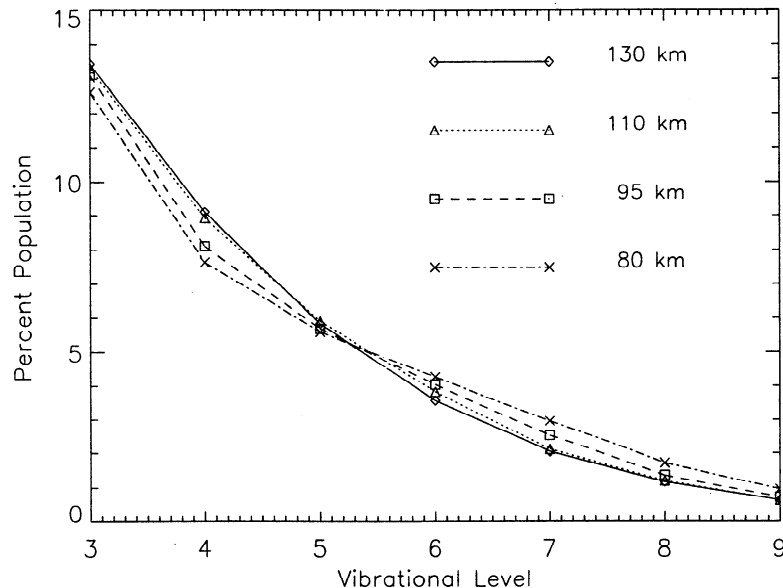


Figure 9. Percent population of the $B^3\Pi_g$ vibrational levels 3 through 9 at 130, 110, 95, and 80 km predicted by the current model with all collisional processes active. Note the enhancement in $\nu > 5$ for altitudes less than 90 km.

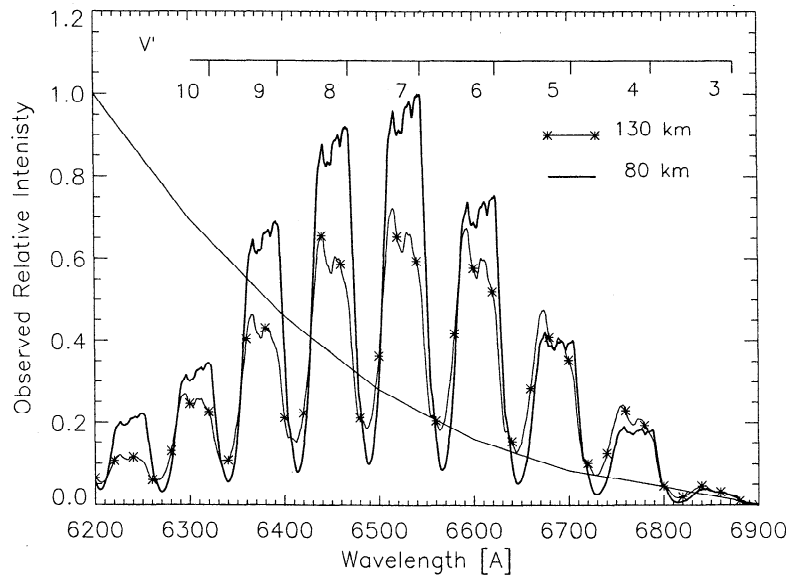


Figure 10. Model spectra of the 1PG $\Delta\nu = 3$ sequence predicted at 130 and 80 km produced by the distributions of Figure 9 and scaled with the sensitivity curve of the human eye. The resolution for these spectra is 9 Å. The total $B^3\Pi_g$ population for these two spectra is the same. This figure shows the predicted red enhancement to be observed visually as the aurora penetrates to lower altitudes (approximately 80 km).

in roughly a factor of 2 increase in the 1PG $\Delta\nu = 3$ volume emission rate due to ICT coupling primarily from the overlapping W state. Figure 11 shows the increase in the observed intensity due to both the enhancement in the B populations the sensitivity of the human eye [Gebel, 1964]. The populations of the B and W states at 80 km with and without ICT are shown in Figure 12. This figure shows the loss of W state population and corresponding gain in the B state population when ICT is included. As we have stated elsewhere [Benesch, 1981, 1983; Morrill *et al.*, 1988, 1991; Morrill and Benesch, 1990, 1994, 1995], we consider the effects of the ICT process to play a significant role in the variation of the $N_2(B)$ vibrational distribution and the production of the auroral red lower border.

4. Discussion

The considerations above address two distinct problems associated with auroral N_2 emission: the quenching of the $N_2(A)$ state, primarily by atomic oxygen, and the role of N_2 collisions in the variation of the $N_2(B)$ vibration populations.

Collisional deactivation of the $N_2(A)$ state has long been understood to be important [Broadfoot and Hunten, 1964; Shemansky *et al.*, 1971; Sharp, 1971] primarily because of its long radiative lifetime. Numerous values of the rate coefficients for the deactivation of $N_2(A)$ by O have been measured and compilations of these coefficients have appeared elsewhere [Cartwright, 1978; Torr and Torr, 1982; Meier, 1991] and

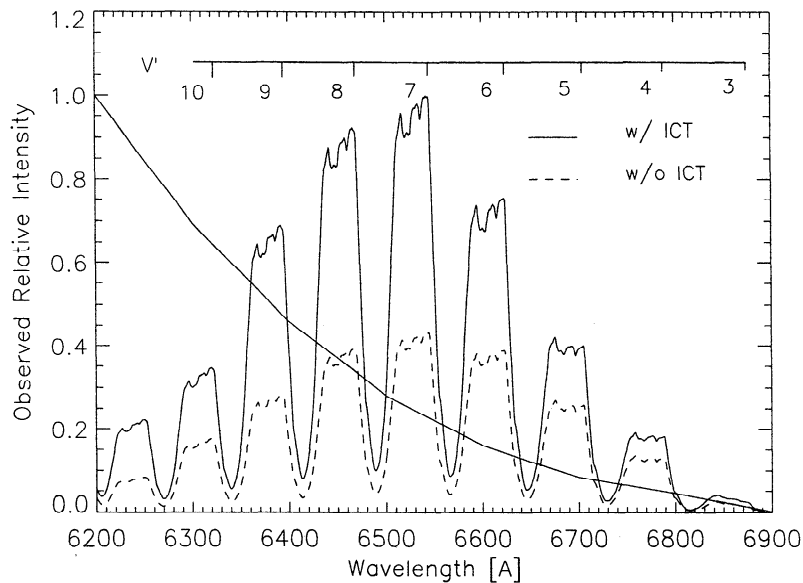


Figure 11. Comparison of $\Delta\nu = 3$ sequence predicted with and without ICT at 80 km. This figure includes the sensitivity of the eye (solid curve) and shows a significant enhancement ($>2X$) in the visible red intensity due to ICT.

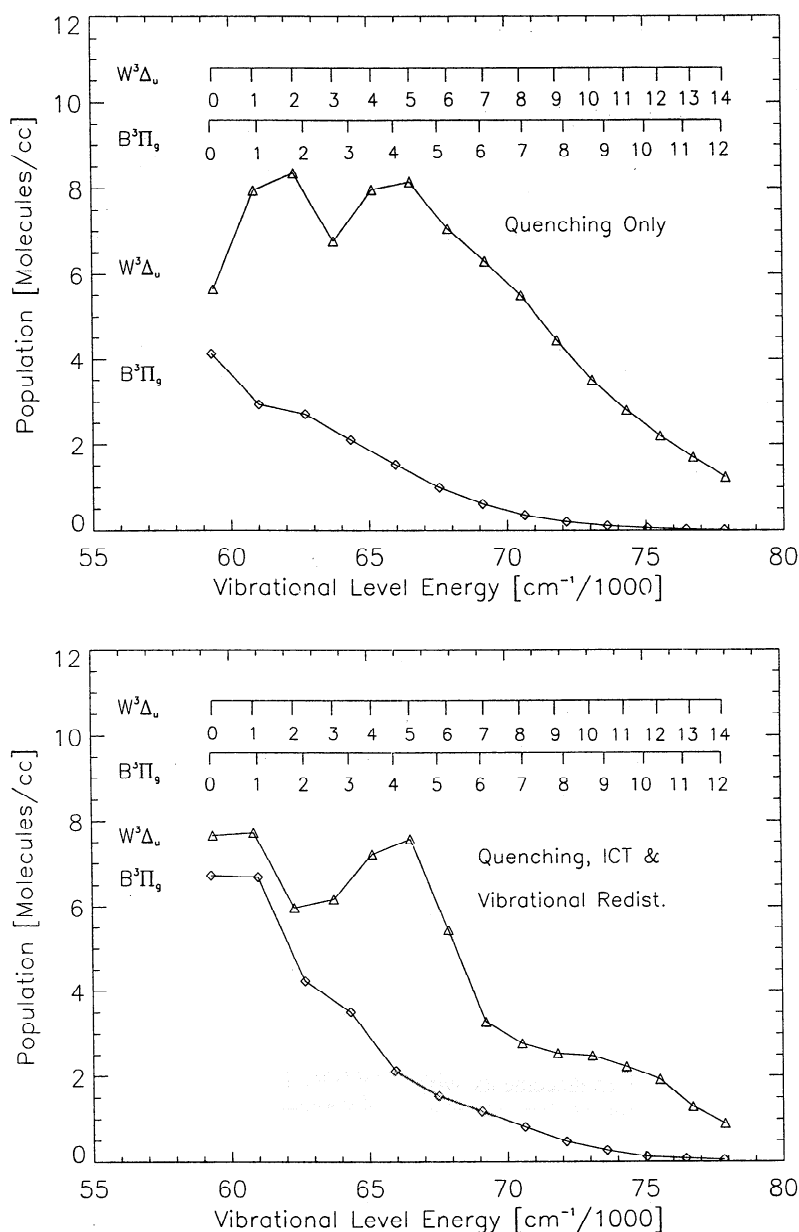


Figure 12. $B^3\Pi_g$ and $W^3\Delta_u$ vibrational distributions with and without ICT. The $W^3\Delta_u$ is a reservoir of population for the $B^3\Pi_g$ which can be accessed at lower altitudes with the increase in kinetic collisions. Note that for the case with ICT the $B^3\Pi_g$ and $W^3\Delta_u$ populations tend to draw together with increased resonance between vibrational levels.

range from 2×10^{-11} to 4×10^{-10} $\text{cm}^3/\text{molecule-second}$. The general tendency has been for the coefficients determined from atmospheric observations to be larger than the laboratory values by factors of 3 to 10. For the current study we have used the laboratory results of *Thomas and Kaufman* [1985] since their measurements cover the largest range of $N_2(A)$ vibrational levels. These results also include $N_2(A)$ quenching by O_2 which complement the earlier work by *Dreyer et al.* [1974] which was used by *Cartwright* [1978]. It is worth noting that *Thomas and Kaufman's* O -quenching coefficients are the largest of the recent values measured in the laboratory [*Piper et al.*, 1981; *Thomas and Kaufman*, 1985; *DeSouza et al.*, 1985] and this would contribute to our predicted column abundances of $N_2(A)$ being low compared to the observations of *Rees et al.* [1976] (see Figure 6). Given this comparison and the corroboration of the

smaller rate coefficients by recent laboratory measurements, we consider the coefficients determined from atmospheric observations to be overestimates of the correct values.

The discrepancy between rate coefficients determined from atmospheric observations and those of laboratory studies is likely due to a number of factors. These include inaccuracies in the O density used in calculation, use of older $N_2(A)$ lifetimes rather than the more recent values which are approximately 25% larger [*Piper*, 1993], and possible additional loss mechanisms in the atmosphere [*Torr and Torr*, 1982]. Coefficients determined via laboratory techniques are insensitive to the radiative lifetime and the measurement of O densities can be done with relatively high accuracy [*Piper et al.*, 1981; *Thomas and Kaufman*, 1985]. Consequently, the use of the laboratory coefficients offers the possibility of measuring thermospheric O density profiles from

VK/2PG intensity ratios using techniques described elsewhere [McDade and Llewellyn, 1984]. We will present the results of this type of analysis in a future publication.

As to variations in the N₂(B) vibrational distributions due to N₂ collisions, much of our previous work focuses on the corresponding spectral variations of the 1PG observed in laboratory N₂ discharges [Benesch and Fraedrich, 1984; Morrill et al., 1988, 1991; Morrill and Benesch, 1990]. These variations are produced by changes in experimental conditions, specifically, pressure or the repetition rate of the excitation pulse. Such changes in conditions lead to alterations in the electron temperature during the excitation pulse which, in turn, produces corresponding changes in the relative excitation rate of the excited states under present discussion. By far, the most significant spectral variations occur as a result of changes in pressure [Morrill et al., 1988] which reflects the molecular collision frequency. Of course, in the aurora, changes in altitude correspond to changes in collision frequency. For the long-lived N₂ triplet states, A³Σ_u⁺ and W³Δ_u, where the collision frequency exceeds the radiative lifetime, collisional transitions to the B³Π_g become more probable than emission. The N₂(A) and N₂(W) states represent a significant reservoir of excited state population which can be transferred to the N₂(B) state with the increasing N₂ collision frequency which occurs at lower altitudes. This transfer of population results in enhancements in the 1PG band intensities, primarily for bands with $\nu' = 6 - 8$ (see ICT rate coefficients in Figure 3 and Morrill et al. [1988]). This is shown for the case of the N₂(W) state in Figures 11 and 12.

As the results in Figure 9 show, collisional alterations in the N₂(B) vibrational distribution are not predicted to occur until approximately 80-90 km. This shift produces an increase in the visually observable red emission from the 1PG $\Delta\nu = 3$ sequence as discussed above. It should be noted that significant changes in the N₂(B, $\nu > 5$) populations are not predicted for 95 km and above in agreement with auroral observations of the 1PG by Gattinger et al. [1985]. Given the correlation of the predicted altitude and spectral region of the 1PG enhancements with observations of natural and man-made deep red lower borders [Stormer, 1955; Boquist and Synder, 1967], we consider the N₂ 1PG to be the probable source of this phenomenon. As noted by Gattinger and Vallance Jones [1979] there is historical evidence that red lower borders may occur at different heights with the ones near 100 km appearing "pink" and the ones near 80 km appearing "crimson." The present results apply specifically to the lower altitude "crimson" borders.

As early as 1938 Vegard observed the intense red lower border of type *b* aurora and remarked that they occur most frequently at sunspot minima [Vegard, 1938]. He presents spectra which show that enhancement of 1PG at the lower altitudes is a significant feature of type *b* red lower borders. One difficulty with verifying the spectral changes which our model calls for is that such features are often evanescent occurrences which move rapidly and unpredictably. Consequently, they are difficult to measure. However, a number of recent instruments [Rairden and Swenson, 1994; Sivjee, 1994] are beginning to make ground-based auroral measurements in the visible and near IR using CCD detectors. Such instruments collect time-resolved spectral images which contain altitude information. Thus they allow the repeated measurement of an entire spectrum of rapidly time-varying auroral forms which is a requirement for the capture of these elusive features.

5. Conclusions

Figures 5 through 12 display a number of results from the current model, some compared to observations. A comparison between the current model and Cartwright's [1978] model, using only cascade and quenching, shows that the results of the current model are in basic agreement with those of the earlier model, as shown in Figure 5. The current model also provides column abundances which fit well with simultaneous field observations of the N₂(A), N₂(B), and N₂(C) states. It appears that improvements in the O and O₂ quenching coefficients and updated transition probabilities both play a major role in improving the fit between model N₂(A) populations and observations (Figure 7c). In addition, vibrational redistribution provides a small but significant improvement in the prediction of N₂(A) state vibrational populations primarily because it forces the population toward lower levels without the loss of N₂(A) state molecules. Intersystem collisional transfer (ICT) strongly effects the vibrational level populations of the N₂(B) state. Model results show both an improvement in the fit with observations for the low N₂(B) state vibrational levels as well as an enhancement of the higher levels ($\nu = 6-9$) which is predicted to occur at lower altitudes (approximately 80-90 km). These latter changes in the N₂(B) populations shift the center of the intensity distribution of the 1PG $\Delta\nu = 3$ sequence from the near infrared into the visible red. It should be noted that appreciable changes in the N₂(B, $\nu > 5$) populations are not predicted until approximately 80-90 km, in agreement with 1PG observations at higher altitudes [Gattinger et al., 1985]. This behavior provides a probable explanation of the lower altitude deep-red lower border. Future plans for the model include the addition of the N₂ singlets and the estimation of thermospheric atomic oxygen density profiles using VK and 2PG band emission ratios.

Note added in proof. Recent interest in "Red Sprites", natural electric discharges appearing above the tops of thunderstorms, prompts us to call attention to the affinity of that phenomenon with the auroral red lower borders as discussed above. The spectrum of Red Sprites shows a dominant emission of molecular nitrogen 1PG, and the altitude domain of the Sprites impinges on that of the red lower border from below. Spectral observations of Sprites show an enhancement in the intensity of the bands in the $\Delta\nu = 3$ sequence of the 1PG over that observed in a normal aurora [Mende, et al., 1995; Hampton, et al., 1995]. This is consistent with the model outlined above which establishes that considerable intersystem collisional transfer of excitation occurs at pressures where Sprites are observed.

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