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

Jeff S. Morrill
E. O. Hulburt Center for Space Research, Naval Research Laboratory, Washington, D.C.

William M. Benesch
Institute for Physical Science and Technology, University of Maryland, College Park

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 3Σ⁺, B 3Πₗ, W3Δₗ, B 3Σ⁺, C3Πₗ, D 3Σ⁺, and E 3Σ⁻). 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 Δν = 3 sequence from the infrared into the visible red at 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 dominate 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 3Σ⁺ → X 3Σ⁺) and second positive (C 3Πₗ → B 2Πₗ) in the ultraviolet and the first positive (B 3Πₗ → A 3Σ⁺), infrared afterglow (B 3Σ⁺ → B 3Πₗ), and Wu Benesch (W3Δₗ → B 3Πₗ) 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 Huntten, 1964; Shemansky and Vallance Jones, 1968]. The work of Wu and Renesch [1968] and Renesch 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) → 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 Gattiner [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 Traynar, 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
earlier electron beam work of Hinkmann 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 $N_2$ excited state cross sections. However, there is evidence [Zubek, 1994; Zubek and King, 1994] that the cross sections for excitation of the $N_2(C)$ 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 $N_2$ 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 $O$, $O_2$, and $N_2$. Due to the fit between the above auroral observations and results of Cartwright's [1978] model, the $N_2$ 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 $N_2$ excited states, focus on radiative cascade and quenching by collisions with $O$, $O_2$, and $N_2$. 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 $N_2$ triplet transitions [Gilmore et al., 1992; Piper et al., 1989; Piper, 1993] and $N_2(A)$ quenching coefficients for collisions with $O$ and $O_2$ [Thomas and Kaufman, 1983]. This model also incorporates two additional collisional processes not previously included in models of atmospheric $N_2$ emission: the inter-system collisional transfer of excitation (ICT) between vibrational levels of the low-lying $N_2$ triplet states and vibrational redistribution within the $N_2(A)$ 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 those 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 inter-system collisional transfer of excitation. This process couples adjacent vibrational levels of overlapping electronic states. For the case of $N_2$ triplets, this involves the transfer of excitation (excited state population) between vibrational levels of the $B^1\Sigma_u^+$ and the $A^2\Sigma_u^+$, $B^3\Delta_u$, and $A^3\Sigma_u^-$ states. 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 $N_2(A)$ state, reflects a more appropriate use of the coefficients for $N_2(A)$ quenching by $N_2(X)$ than that of Cartwright [1978]. The work on $N_2(A)$ quenching [Dreyer and Perner, 1973; Dreyer et al. 1974] indicates that collisions between $N_2(A, z < 3.3)$ and $N_2(X, v = 0)$ lead to a loss of two $N_2(A)$ vibrational quanta with increasing probability as the initial $N_2(A)$ vibrational quantum number increases toward $v = 3$. Dreyer and Perner [1973] and Dreyer et al. [1974] also postulate that this loss of $N_2(A)$ quanta results in the production of an $N_2(X, v = 1)$ molecule. As we will discuss below, we have used the assumption that two (or three) vibrational quanta are lost from the $N_2(A)$ vibrational manifold during this kind of collision while at the same time the electronic energy of the $N_2(A)$ state is retained by the excited molecule.

Including these two additional processes permits a more accurate treatment of the effects of collisions between $N_2$ 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

$$N_2(X) + e^- \rightarrow N_2(\gamma), \quad \gamma = A, B, W, B', C, D, E$$

and $e^-$ an energetic electron.

(2) Radiative cascade and intrasystem cascading

$$N_2(\gamma_i) \rightarrow N_2(\gamma_j) + \nu$$

(3) Electronic quenching

$$N_2(\gamma) + M \rightarrow N_2(X) + M, \quad M = O, O_2, N_2$$

where we do not consider the end products in the quenching reaction, only that the electronic energy of state $\gamma$ is permanently lost to the $N_2$ triplet manifold. The new processes are the following:

(4) Intersystem collisional transfer (ICT)

$$N_2(A) + N_2(X) \rightarrow N_2(A, W, B') + N_2(X)$$

(5) Vibrational redistribution

$$N_2(A, v_i > 3) \rightarrow N_2(X, v = 0) + N_2(A, v_j) + N_2(X, v = 1)$$

with $v_j = v_i - 2.3$

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.
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. [1988]. For the D-to-E transition we have used the calculated values for ν’ = 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'Πₚ and a'Σ⁺ₚ) by Oₐ

<table>
<thead>
<tr>
<th>Table 1. Cascade Scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
</tr>
<tr>
<td>A''Σ⁺ₚ → A'Σ⁺ₚ</td>
</tr>
<tr>
<td>B''Πₚ → B'Πₚ</td>
</tr>
<tr>
<td>D''Σ⁺ₚ → E''Σ⁺ₚ</td>
</tr>
<tr>
<td>D''Σ⁺ₚ → E''Σ⁺ₚ</td>
</tr>
<tr>
<td>E''Σ⁺ₚ → B''Πₚ</td>
</tr>
<tr>
<td>E''Σ⁺ₚ → C''Πₚ</td>
</tr>
</tbody>
</table>

Intrastem cascade

B''Πₚ → A''Σ⁺ₚ. First positive (and reverse)
H''Σ⁺ₚ → B''Πₚ Infrared-afterglow
W''Δₚ → B''Πₚ Win-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 in the $O$ quenching coefficient, (2) an improvement in the $O_2$ quenching coefficients for $v = 1$ and $3$ (Thomas and Kaufman, 1985), and (3) the use of the $N_2$ quenching coefficients for vibrational redistribution within the $A^3\Sigma_u^+$ vibrational manifold (Dreyer et al., 1974).

have been done (Marnelli 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 $N_2(W)$ and $N_2(A)$ states to the $N_2(R)$ state, induced by collisions with $O_2$, has been observed by Bachmann et al. [1992, 1993]. Given that a focus of the current study is the addition of $N_2$ 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 \( \text{N}_2 \) is the dominant species and the resulting inter-system collisional transfer rates are quite large, the impact of the uncertainties in the \( \text{O} \) and \( \text{O}_2 \) 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 Friedrick, 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; Easter 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 \( \text{N}_2(\text{B}) \) state and the \( \text{N}_2(\text{A}), \text{N}_2(\text{W}), \) and \( \text{N}_2(\text{H}) \) 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 \( \text{N}_2(\text{B}) \) state to the \( \text{N}_2(\text{A}), \text{N}_2(\text{W}), \) and \( \text{N}_2(\text{H}) \) states. These coefficients are shown in Figure 3. In order to partition these rate coefficients from a given \( \text{N}_2(\text{B}) \) level to a set of nearby levels of the \( \text{N}_2(\text{A}), \text{N}_2(\text{W}), \) and \( \text{N}_2(\text{H}) \) states, we have assumed (1) that only transfers to the nearest vibrational levels of the overlapping \( \text{N}_2(\text{A}), \text{N}_2(\text{W}), \) and \( \text{N}_2(\text{H}) \) states are important and (2) that the rates scale as \( g_i/g_0 \) \( \exp \Delta E \). In the latter approximation, \( \Delta E \) is the energy difference between the vibrational levels involved in the transition and \( g_i/g_0 \) 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 \( \text{N}_2(\text{B}) \) were based on the formulation by Benesch and Friedrick [1984] such that,

\[
k_w / k_y = (Q_w / Q_0)(g_w / g_0) - (B_w / B_0)(g_w / g_0),
\]

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>
<thead>
<tr>
<th>( B'\pi )</th>
<th>( A'2\Sigma^+ )</th>
<th>( W'\Delta )</th>
<th>( B'2\Sigma^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7</td>
<td>7.83</td>
<td>17.2</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>6.14</td>
<td>41.7</td>
</tr>
<tr>
<td>9</td>
<td>5.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>22.0</td>
<td>22.7</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>8.57</td>
<td>9.06</td>
</tr>
<tr>
<td>12</td>
<td>2.78</td>
<td>4.59</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>0.95</td>
<td>2.33</td>
</tr>
<tr>
<td>13</td>
<td>6.00</td>
<td>5.423</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>8.52</td>
<td>15.0</td>
</tr>
<tr>
<td>15</td>
<td>2.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>3.68</td>
<td>58.0</td>
</tr>
<tr>
<td>16</td>
<td>28.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>17</td>
<td>11.1</td>
<td>59.9</td>
</tr>
<tr>
<td>8</td>
<td>18</td>
<td>9.75</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>19</td>
<td>35.3</td>
<td>43.4</td>
</tr>
<tr>
<td>20</td>
<td>6.97</td>
<td>10.677</td>
<td>5.352</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>4.41</td>
<td>10.646</td>
</tr>
<tr>
<td>21</td>
<td>36.9</td>
<td>11.102</td>
<td>6.358</td>
</tr>
<tr>
<td>22</td>
<td>4.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>22</td>
<td>5.93</td>
<td>11.646</td>
</tr>
<tr>
<td>23</td>
<td>21.9</td>
<td>12.646</td>
<td>7.299</td>
</tr>
<tr>
<td>24</td>
<td>3.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>24</td>
<td>3.20</td>
<td>12.325</td>
</tr>
<tr>
<td>25</td>
<td>18.9</td>
<td>13.225</td>
<td>3.433</td>
</tr>
<tr>
<td>26</td>
<td>5.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>1.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>26</td>
<td>5.67</td>
<td>14.282</td>
</tr>
<tr>
<td>27</td>
<td>5.30</td>
<td>9.378</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>15</td>
<td>62.4</td>
<td>9.235</td>
</tr>
<tr>
<td>16</td>
<td>19.2</td>
<td>10.434</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>16</td>
<td>45.5</td>
<td>10.211</td>
</tr>
<tr>
<td>17</td>
<td>27.2</td>
<td>11.534</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>17</td>
<td>33.5</td>
<td>11.193</td>
</tr>
<tr>
<td>18</td>
<td>38.4</td>
<td>12.614</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>18</td>
<td>24.9</td>
<td>12.182</td>
</tr>
<tr>
<td>19</td>
<td>53.5</td>
<td>13.692</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>19</td>
<td>18.8</td>
<td>13.175</td>
</tr>
<tr>
<td>20</td>
<td>73.8</td>
<td>14.760</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>21</td>
<td>65.7</td>
<td>14.172</td>
</tr>
<tr>
<td>15</td>
<td>8.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Intersystem collisional transfer rate coefficients from the \( \text{N}_2(\text{B}) \) state to the \( \text{N}_2(\text{A}), \text{N}_2(\text{W}), \) and \( \text{N}_2(\text{H}) \) states used in the current model. Rate coefficients are in units of \( 10^{-16} \text{ cm}^3/\text{molecule-s} \). The leftmost column is the \( \text{N}_2(\text{B}) \) 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 \( \text{N}_2(\text{B}) \) state. Return rate coefficients are scaled as discussed in the text.
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 (ΔΛ = 0, ±1, ΔS = 0, 
g - u, g(u) - g(u)). The consequence of these rules is that ICT transitions within the N₂ triplet manifold occur between the \( \Pi \) and the \( \Sigma \) states, \( W^3 \Delta \), and \( B^3 \Sigma \) but no transitions occur among the latter three states.

2.3. Vibrational Redistribution within the \( N_2(A) \) State

According to Dreyer and Perner [1973] and Dreyer et al. [1974] who studied quenching of \( N_2(A) \) by \( N_2(X) \), the loss of population from \( N_2(A, \nu) \) equals the gain in population into \( N_2(A, \nu') \) where \( \nu' = 2 \nu - 2 \) for \( 2 \leq \nu \leq 7 \). They attributed this loss of two \( N_2(A) \) vibrational quanta to the production of \( N_2(X, \nu = 1) \) from \( N_2(X, \nu = 0) \). In addition, they note that as the \( N_2(A) \)

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 \( \Lambda^3 \Sigma^+ \) and \( W^3 \Delta \) are for 130 and 110 km, respectively. Note that the curves for \( W^3 \Delta \) at 130 and 110 km overlap in Figure 5b for \( \nu = 2 \) and above. The curves for \( B^3 \Pi \) and \( C^3 \Pi \) are for 130 km without quenching.
vibrational level increases so does the resonance between $\Delta v - 2$ in the $N_2(4)$ and the energy difference between the two lowest levels of $N_2(X)$. Their data show a corresponding increase in rate coefficients with increasing vibrational level. In order to extrapolate to higher $N_2(A)$ levels we have fitted Dreyer and Perner’s rate coefficients to a power series in $\exp(-\Delta E)$ where

$$\Delta E = [(F_{v^2} - F_{v^1}) \cdot (F_{X^{v+1}} - F_{X^{v-1}})].$$

Since this function peaks at $v = 8$ and 12 for $\Delta v = 2$ we have used the resulting polynomial to estimate rate coefficients for higher $N_2(A)$ vibrational levels ($v \geq 16$) using $\Delta v = 3$ in the $N_2(A)$ 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 $N_2(A)$ by $N_2(X)$ reduces the total $N_2(A)$ population. Conversely, our use of the values in Figure 2 does not affect the total $N_2(A)$ 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 $N_2$ 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 $\alpha$, the equation which describes the relative number density $(n_{v,\alpha}/n_{N_2})$ at statistical equilibrium is

$$K_{e^{-}\alpha} + \sum_{\beta} (A_{v^2} \cdot A_{v^1} + K_{ICT,v^2} \cdot \delta_{j^1} \cdot \delta_{j^2} + K_{CR,v^2} \cdot \delta_{j^1} \cdot \delta_{j^2}) (n_{v^1}/n_{N_2}) =$$

$$K_{\alpha^*} \sum_{\beta} (A_{v} \cdot K_{\alpha^*}) + \sum_{j} (A_{v^1} \cdot K_{\alpha^*}) + \delta_{\alpha} \cdot \delta_{j^1} \cdot \delta_{j^2} (K_{\alpha\alpha} + \delta_{\alpha}) (n_{v^2}/n_{N_2})$$

where

- $K_{e^{-}\alpha}$ electron impact excitation rate (per $N_2$) of vibrational level $v$ in state $\alpha$;
- $A_{v^2}$ transition probability from $\beta$($I$) to $\alpha(v)$;
- $K_{ICT,v^2}$ intersystem collisional transfer rate from $\beta$($I$) to $\alpha(v)$;
- $K_{CR,v^2}$ vibrational redistribution rate from $\alpha(v)$ to $\alpha(v)$;
- $K_{\alpha^*}$ total quenching rate;
- $\alpha, \beta, \gamma$ electronic states;
- $i, j$ source and sink vibrational levels, respectively.

All rates are in Hertz. $K_{e^{-}\alpha}$ also includes enhancements due to elevated ground vibrational distributions [Morrill and Benesch, 1990]. The two Kronecker deltas inside the $k_{\alpha\alpha}$ term (vibrational redistribution) applies only to the $N_2(A)$ state and only for $\Delta v = 2$ or 3. An important point about the ICT rates is that for any given $B^3\Pi_0$, vibrational level only the nearest (quasi-isoinertial) 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 $N_2$) for the seven excited states as well as temperature and density ($O$, $O_3$, $N_2$) from a model atmosphere. In order to present an effective comparison we have used the volume excitation rates from Cartwright [1978] as Table 1] and the CIRA72 model atmosphere for intermediate solar conditions and a 1000 K exospheric temperature [Jura, 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 $B^3\Pi_0$, $B^3\Sigma_u^-$, and $C^3\Pi_0$ 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 $B^3\Pi_0$ and $B^3\Sigma_u^-$ populations compared to the model of Cartwright [1978].

A rigorous test of any model of $N_2$ populations in the aurora involves its ability to predict the column abundances of the $N_2$ 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 $N_2(A)$, $N_2(B)$, and $N_2(C)$ 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 $A^2\Sigma_u^+$ 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 $A^2\Sigma_u^+$ 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 $N_2(A)$ 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 O$_2$. 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 $v = 7$ and above.
Figure 8 compares $B^3\Pi_u$ 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 $N_2(A)$ predicted vibrational distribution implied by column emission (Figure 6) with the VI&G and E&S data. This is a more comprehensive comparison of the VI&G data with model results than is shown by Figures 7a and 7b. In Figure 7c the VI&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 $v = 4$ and 6 and the $v = 0$ 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 $v = 4$ & 8 derived from either column densities measurements or emission spectra from a specific altitude.

Figure 8 shows that the $B^3\Pi_u$ 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 $v = 2$ is not achieved by the current model.

The relative populations of the $B^3\Pi_u$ 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 $N_2(A)$ and $N_2(W)$ 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 $R$ excitation. Since the $W$ and $R$ 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 $B^3\Pi_u$ 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 $v > 5$ for altitudes less than 90 km.
in roughly a factor of 2 increase in the 1PG $\Delta v = 3$ 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
range from $2 \times 10^{15}$ to $4 \times 10^{16}$ cm$^{-3}$/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, 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 corroborative 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

**Figure 12.** $B^3\Pi_u$ and $W^3\Delta_v$ vibrational distributions with and without ICT. The $W^3\Delta_v$ is a reservoir of population for the $B^3\Pi_u$, which can be accessed at lower altitudes with the increase in kinetic collisions. Note that for the case with ICT the $B^3\Pi_u$ and $W^3\Delta_v$ populations tend to draw together with increased resonance between vibrational levels.
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 $N_2(A), N_2(B),$ and $N_2(C)$ states. It appears that improvements in the $\Omega$ and $\Omega_2$ quenching coefficients and updated transition probabilities both play a major role in improving the fit between model $N_2(A)$ populations and observations (Figure 7c). In addition, vibrational redistribution provides a small but significant improvement in the prediction of $N_2(A)$ state vibrational populations primarily because it forces the population toward lower levels without the loss of $N_2(A)$ state molecules.

Intersystem collisional transfer (ICT) strongly affects the vibrational level populations of the $N_2(B)$ state. Model results show both an improvement in the fit with observations for the low $N_2(B)$ 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 $N_2(B)$ 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 $N_2(B, \nu \gtrsim 5)$ 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 boundary. Future plans for the model include the addition of the $N_2$ singlets and the estimation of thermospheric atomic oxygen density profiles using 1PG 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.

Acknowledgments. This material is based on work supported in part by the National Science Foundation under grant number ATM-8912154 and NASA grant NAGW 2168. The computer time was supported by the Upper Atmospheric Physics Branch and Solar Physics Branch, Space Science Division, Naval Research Laboratory. The authors would like to thank David Cartwright for his helpful and encouraging comments and for providing us with a copy of his $N_2$ excited state model, Eric Buescha for his helpful and enjoyable conversations, and Susan Queen for her patience and critical review of the manuscript.

The editor thanks I. C. McDade and A. L. Broadfoot for their assistance in evaluating this paper.
References


Benesch, W. Mechanism for the auroral red lower border, J. Geophys. Res. 86, 9065, 1981.


Espy, P. J., A spectroscopic investigation of the infrared molecular band systems of N2 and O2 resulting from low energy electron impact excitation, Ph.D. dissertation, Utah State Univ., Logan, 1968.


Katayama, D. H., Collision induced electronic energy transfer between the AΠ (v = 4) and Σ(4Π) (v = 8) rotational manifolds of N2, J. Chem. Phys. 81, 3495, 1984.


Solomon, S. C., Auroral excitation of the N$_2$ 2P(0,0) and VK(0,9) bands, J. Geophys. Res., 94, 17,215, 1989.


Vegard, L., Altitude effects in the red part of the auroral spectrum and the two types of red auroras, Nature, 141, 200, 1938.

