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The Vibrational Distribution of N_2^+ in the Terrestrial IonosphereJ. L. FOX¹ AND A. DALGARNO*Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts*

The densities and vibrational distributions of N_2^+ in the $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ states in the daytime terrestrial ionosphere are computed for both low and high solar activity. Altitude profiles of the relative populations of the vibrational levels of $N_2^+X^2\Sigma_g^+$ are presented. The fraction of vibrationally excited N_2^+ varies from 5% at 100 km to 50% at 450 km. Several models are examined in which loss of $N_2^+(v)$ is enhanced for $v > 0$ and in which various assumptions are made about the vibrational distributions produced in charge transfer reactions. The N_2^+ densities are significantly reduced if $N_2^+(v)$ reacts with O at rates which are near gas-kinetic. Vibrational distributions of the $A^2\Pi_u$ and $B^2\Sigma_u^+$ states are also presented, as well as volume emission rates and integrated overhead intensities of the major bands of the Meinel and first negative systems.

INTRODUCTION

The vibrational distribution of N_2^+ in the terrestrial ionosphere has been of interest to aeronomers for more than three decades. Bates [1949] sought to explain the intensities of the first negative ($B^2\Sigma_u^+ - X^2\Sigma_g^+$) system of N_2^+ in sunlit aurorae and the twilight sky. His study included electron impact on N_2 and fluorescent scattering from $N_2^+(X^2\Sigma_g^+)$ as sources of $N_2^+(B^2\Sigma_u^+)$. He found that fluorescent scattering raises the vibrational temperature of the ground state ions, which in turn affects the intensity distribution of the N_2^+ band systems. Broadfoot [1967, 1971] expanded the work of Bates [1949] to include new information. He studied the first negative and Meinel ($A^2\Pi - X^2\Sigma_g^+$) band systems of N_2^+ in aurorae, sunlit aurorae, twilight glow, and dayglow. He reported relative populations of the vibrational levels of the $X^2\Sigma_g^+$, $A^2\Pi$, and $B^2\Sigma_u^+$ states of N_2^+ as a function of the ion lifetime. Degen [1981] updated Broadfoot's work and pointed out the role of fluorescence induced by low-energy electrons in producing the observed vibrational enhancement of the first negative system in both sunlit and nonsunlit aurorae. The vibrational distribution of ground state ions has recently become of interest, since the vibrational state of an ion has been shown to influence its chemical reactivity [cf. Albritton, 1979] as well as the fluorescence of the band systems.

In this work we report vibrational distributions of the $X^2\Sigma_g^+$, $A^2\Pi$, and $B^2\Sigma_u^+$ states of N_2^+ in the nonauroral daytime terrestrial ionosphere from 100 to 450 km for conditions of both high and low solar activity. We then discuss the effects of the vibrational distribution of ground state N_2^+ on its chemistry. Finally, we report volume emission rates and overhead intensities for the major bands of the first negative and Meinel systems of N_2^+ .

THE MODEL

We considered two model atmospheres. For the densities of O, O₂, N₂, and He and the neutral temperatures, the models of Hedin [1979] for $F_{10.7} = 75$ (low solar activity) and $F_{10.7} = 200$ (high solar activity) were adopted. The electron temperature profile for low solar activity was taken from the

measurements from AE-C orbit 457 (upleg), as reported by Oppenheimer *et al.* [1976]. The electron temperatures for high solar activity and the ion temperatures for both values of the solar activity were adopted from Banks and Kockarts [1973]. The solar fluxes used were the SC#21 and F79050N spectra of Hinteregger [1976] [see Torr *et al.*, 1979] which are appropriate to periods of low and high solar activity, respectively. The solar zenith angle is 45°. For photoionization of He, N₂, O, and O₂, the cross sections of Kirby *et al.* [1979] were employed. The cross sections were extended to 14 Å using the values for inner shell ionization of atoms reported by Weisheit [1974] and Daltabuit and Cox [1972]. Photoionization of atomic nitrogen was included using the cross section of Le Dourneuf *et al.* [1976]. Photoelectron impact excitation and ionization were included as discussed by Victor *et al.* [1976].

The populations of the vibrational levels of N_2^+ were computed assuming photochemical equilibrium, which is a valid approximation over the altitude range considered. The chemical lifetime of N_2^+ at 400 km is about 18 s, in comparison with a diffusion lifetime of 5×10^3 s. The numbers of vibrational levels included for the X, A, and B states are 6, 6, and 4, respectively.

The sources and sinks of N_2^+ in the terrestrial ionosphere are summarized in Table 1. N_2^+ is produced by photoionization and electron impact ionization of N₂ and in a few charge transfer reactions. The branching ratios for the production of the electronic states of N_2^+ are given by Samson *et al.* [1977] for photoionization and by Cartwright *et al.* [1975] for electron impact ionization. The individual vibrational levels are assumed to be populated according to the Franck-Condon factors of Nicholls [1962]. For neutral N₂ we adopted a Boltzmann distribution of vibrational levels characterized by a temperature of 1000 K. Values between 320 and 2200 K have been calculated for the lower thermosphere by Breig *et al.* [1973]. The computed vibrational distribution of N_2^+ is not, however, sensitive to the assumed vibrational temperature of N₂ [cf. Broadfoot, 1967].

The charge transfer reaction

energetically can populate vibrational levels to $v = 5$ in the $X^2\Sigma_g^+$ state and to $v = 1$ in the $A^2\Pi$ state. The analogous reaction for $O^+(^2P)$

can populate up to $A^2\Pi$, $v = 8$. Reaction of He⁺ with N₂

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TABLE 1. Sources and Sinks of N_2^+ in the Terrestrial Ionosphere

Reaction	Rate Coefficient	Reference
(R1) $N_2 + h\nu \rightarrow N_2^+ + e$	see text	see text
(R2) $N_2 + e \rightarrow N_2^+ + 2e$	see text	see text
(R3) $O^+(^2D) + N_2 \rightarrow N_2^+ + O$	8×10^{-10}	<i>Johnsen and Biondi</i> [1980]; <i>Rowe et al.</i> [1980]
(R4) $O^+(^2P) + N_2 \rightarrow N_2^+ + O$	1.35×10^{-10}	see text
(R5) $He^+ + N_2 \rightarrow N_2^+ + He$	5.6×10^{-10}	<i>Rakshit et al.</i> [1978]; <i>Adams and Smith</i> [1976]
(R6) $N_2^+ + e \rightarrow N + N$	$3.5 \times 10^{-7} (300/T_e)^{0.5}$	<i>Mul and McGowan</i> [1979]
(R7) $N_2^+ + O \rightarrow NO^+ + N$	$1.4 \times 10^{-10} (300/T_e)^{0.44}$	<i>McFarland et al.</i> [1974]
(R8) $N_2^+ + O \rightarrow O^+ + N_2$	$9.8 \times 10^{-12} (300/T_e)^{0.23}$	<i>McFarland et al.</i> [1974]
(R9) $N_2^+ + O_2 \rightarrow O_2^+ + N_2$	5.1×10^{-11}	<i>Smith et al.</i> [1978]
(R10) $N_2^+ + NO \rightarrow NO^+ + N_2$	3.3×10^{-10}	<i>Fehsenfeld et al.</i> [1970]

(reaction (R5)) produces N_2^+ about 40% of the time [*Adams and Smith*, 1976]. $N_2^+(C^2\Sigma_u^+)$ $v = 3$ and $v = 4$ are preferentially populated in the reaction [*Govers et al.*, 1977], but these levels are mostly predissociated [*Erman*, 1976]. The distribution of states of N_2^+ produced is unknown and is complicated by cascading. All the levels we consider here are accessible. In the standard model we assume that all the states that can be populated are equally probable in all the charge transfer reactions.

The rate coefficient for (R3) has been measured by *Johnsen and Biondi* [1980] and by *Rowe et al.* [1980]. They report that $k_3 = 8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. For (R4) we arbitrarily adopt a rate coefficient of 1.35×10^{-10} . Charge transfer from O^{++} to N_2 may also produce vibrationally excited N_2^+ , but the products of the reaction are unknown and the densities of O^{++} are small in comparison with those of $O^+(^2D)$. We therefore ignore the reaction.

N_2^+ is lost in dissociative recombination (reaction (R6)) and in reactions with neutral species. *Zipf* [1980] has reported that the dissociative recombination rate is a weakly increasing function of the vibrational energy level. We have scaled the rate coefficient measured by *Mul and McGowan* [1979] by the relative values for $v = 0-2$ measured by *Zipf* [1980] and extrapolated the measurements to obtain rate coefficients for $v = 3-5$. N_2^+ will charge transfer to O, O_2 , and NO (reactions (R7), (R8), (R9), and (R10)). Reaction with O produces NO^+ 93% of the time and O^+ 7% of the time [*McFarland et al.*, 1974].

In the low solar activity model, photoionization (reaction (R1)) and electron impact ionization (reaction (R2)) of N_2 are the major sources of N_2^+ below 235 km. Above this altitude, charge transfer from $O^+(^2D)$ (reaction (R3)) dominates. For high solar activity the altitude at which the two sources are equal is about 270 km. Loss of N_2^+ is dominated by reaction with O ((R7) and (R8)) below 260 km in the low solar activity case and below 270 km in the high solar activity model. Above 270 km the major loss is by dissociative recombination.

In addition to the reactions that cause net production or destruction of N_2^+ , there are several processes which change the distribution of N_2^+ among the vibrational levels without altering the total concentration of N_2^+ . These are enumerated below:

In fluorescent scattering and electron-induced fluorescence, ground state N_2^+ ions are excited to the $A^2\Pi_u$ or $B^2\Sigma_u^+$ state by the absorption of a photon or by electron impact. These states then decay by the emission of a photon. The oscillator strengths for excitation of the A and B states are taken from *Cartwright* [1973] and *Degen* [1977]. *Degen* [1981] has computed the solar fluxes averaged over the bands from measurements reported by *Arveson* [1969]. The electron impact cross sections were computed by scaling the cross section for excitation of the $B^2\Sigma_u^+(v' = 0)$ state of *Crandall et al.* [1974] by the factors given by *Degen* [1981]. The transition probabilities for the Meinel (A-X) and first negative (B-X) bands are given by *Cartwright* [1973] and *Degen* [1977], respectively. Vibrationally excited N_2^+ may lose vibrational quanta in collisions with neutrals. Reaction with N_2 probably proceeds by charge transfer:

The rate coefficient for this reaction has been measured by *Lindinger et al.* [1981], *Smith and Adams* [1981], and *Mahan et al.* [1982]. They report values ranging from 4×10^{-10} to $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. *Mahan et al.* [1982] found that $N_2^+(v = 2)$ is quenched much less efficiently than $N_2^+(v = 1)$, although they do not give a quantitative estimate for the effect. We chose values of $6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $v = 1$ and $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $v > 1$. The rate coefficient for quenching by atomic oxygen (reaction (R12)) has not been measured. The standard model assumes that $k_{12} = 1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. We discuss the effect of larger or smaller values both on the resulting vibrational distribution and on the chemistry. The rate coefficient for quenching of $N_2^+(v \neq 0)$ by O_2 (reaction (R13)) has been reported by *Kemper and Bowers* [1984].

The degree of vibrational excitation of N_2^+ may affect the total density if the reaction rates for vibrationally excited N_2^+ are significantly different from the rates for N_2^+ in the ground vibrational state. The internal energy state of an ion can affect its reactivity [*Albritton*, 1979]. Both energy resonance and Franck-Condon effects appear to play a role in determining the rates of reaction for different vibrational states, although neither appears to be always important [cf. *Govers et al.*, 1977; *Anderson et al.*, 1982; *Smith et al.*, 1983].

The measured concentrations of N_2^+ in the terrestrial ionosphere are smaller than models indicate by about a factor of 2 [*Abdou et al.*, 1982, 1984; *Breig et al.*, 1983, 1984]. Enhanced loss of vibrationally excited N_2^+ in the reaction

has been proposed to account for the discrepancy [Biondi, 1978; Johnsen and Biondi, 1980]. This reaction is analogous to the reaction

which has been found to proceed faster for vibrationally excited N_2 [Schmeltekopf *et al.*, 1968]. Torr *et al.* [1981] have suggested that vibrationally excited N_2^+ may charge transfer to O faster than ground state N_2^+ . Abdou *et al.* [1984] have examined the effect of increasing the rate for this reaction and have found that the models can be made to agree with the data if a rate coefficient of $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ is assumed for the back reaction. Abdou *et al.* [1982] have suggested that charge transfer of $O^+(^2D)$ to N_2 (reaction (R3)) preferentially produces $N_2^+(X^2\Sigma_g^+ v = 5)$ and that because of the near resonance the back reaction proceeds at the same rate. Ferguson [1984] has pointed out that the rate coefficient for the back reaction is probably no more than one fourth that of the forward reaction because of the difference in the statistical weights of the reactants and products and the slight energy defect. Abdou *et al.* [1984] have subsequently revised their analysis to include a more realistic rate for the back reaction. They obtain agreement only if all the N_2^+ produced in (R3) is formed in $v = 5$. We will consider several models in which plausible assumptions are made about the production or loss of N_2^+ in different vibrational levels and examine the effect of these assumptions on radiation in the N_2^+ band systems, on the vibrational distribution of N_2^+ , and on the total ion densities.

We consider six sets of models which are summarized in Table 2. Model A is the standard model. In this model we employ the rate coefficients shown in Table 1 and in the appendix. Except for dissociative recombination the reactions of vibrationally excited ions are assumed to proceed at the same rate as those of ground state ions. In reactions which produce N_2^+ , all the energetically accessible vibrational levels are assumed to be populated with equal probability. Models B1, B2, and B3 examine the effects of an enhanced rate for

The reaction of ground state N_2^+ with O produces mainly NO^+ . In models C1 and C2, vibrationally excited N_2^+ is assumed to produce $NO^+ + N(^2D)$ or $NO^+ + N(^2P)$ in reaction with atomic oxygen. Models D1 and D2 probe the consequences of preferential production of $N_2^+ X v = 5$ in charge transfer of $O^+(^2D)$ to N_2 (reaction (R3)). For D1 the back reaction (R8) proceeds with a rate coefficient of $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. D1 is similar to model 3 of Abdou *et al.* [1984]. In models E1 and E2 we vary the rate coefficient for quenching of $N_2^+(v > 0)$ by O (reaction (R2)) from 1.4×10^{-11} to 5×10^{-10} . Oppenheimer *et al.* [1976] found that agreement between the measured and model densities of N_2^+ could be obtained if the reaction

proceeds with a rate coefficient of $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. In model F we compute the effects of increasing the quenching coefficient (reaction (R14)) from $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ to $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

VIBRATIONAL DISTRIBUTIONS OF THE $N_2^+ X^2\Sigma_g^+$ STATE

Broadfoot [1967, 1971] did the first detailed study of the vibrational distribution of the X, A, and B states of N_2^+ as a

TABLE 2. Reaction Rate Coefficients Differing From the Standard Model A

Model	Reactions	Rate Coefficients, $\text{cm}^3 \text{ s}^{-1}$
B1		$1 \times 10^{-10} (300/T)^{0.23}$
B2	$N_2^+(v > 0) + O \rightarrow O^+ + N_2$	$2 \times 10^{-10} (300/T)^{0.23}$
B3		$5 \times 10^{-10} (300/T)^{0.23}$
C1	$N_2^+(v > 0) + O \rightarrow NO^+ + N(^2D)$	$5 \times 10^{-10} (300/T)^{0.44}$
C2	$N_2^+(v = 1) + O \rightarrow NO^+ + N(^2D)$	$5 \times 10^{-10} (300/T)^{0.44}$
	$N_2^+(v \geq 2) + O \rightarrow NO^+ + N(^2D)$	$5 \times 10^{-10} (300/T)^{0.44}$
D1	$O^+(^2D) + N_2 \rightarrow N_2^+(v = 5) + O$	8×10^{-10}
	$N_2^+(v = 5) + O \rightarrow O^+ + N_2$	2×10^{-10}
D2	$O^+(^2D) + N_2 \rightarrow N_2^+(v = 5) + O$	8×10^{-10}
E1	$N_2^+(v'' > 0) + O \rightarrow N_2^+(v'' - 1) + O$	1.4×10^{-11}
E2		5×10^{-10}
F	$O^+(^2D) + O \rightarrow O^+(^4S) + O$	1×10^{-10}

function of ion chemical lifetime τ . Since he assumed that τ is independent of vibrational level, he did not take into account quenching of $N_2^+ v > 0$ or differences in the chemical reactivities of the individual vibrational levels. Degen [1981] used Broadfoot's basic model with new radiative and collisional cross sections and added the effect of fluorescence induced by low-energy electron impact on N_2^+ . He computed the vibrational distributions of the X, A, and B states but only reported values for the B state.

Altitude profiles of the sources of $N_2^+ X^2\Sigma_g^+ v = 1$ are shown in Figure 1a. The single most important source of $v = 1$ is fluorescence from the A and B states of N_2^+ . Collisional excitation of $N_2^+(X, v = 0)$ by impact with N_2 is the second most important source from 130 to 210 km, and quenching by atomic oxygen is the next most important source from 175 to 275 km. Fluorescence, collisional excitation, and quenching are processes that interchange different states of N_2^+ but do not produce net N_2^+ . The vibrational distribution does not therefore directly reflect the vibrational states populated in the production of N_2^+ . The major sources which affect the total amount of N_2^+ are photoionization and electron impact ionization below 180 km and charge transfer from $O^+(^2D)$ to N_2 (reaction (R3)) above 180 km. The standard model assumes that all of the energetically accessible states included in the model are populated equally in chemical reactions. Charge transfer from $O^+(^2P)$ (reaction (R4)) is a minor source of $N_2^+ X v = 1$ at all altitudes if k_4 is near $1.35 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, as we have assumed. Rusch *et al.* [1977] have proposed that k_4 is closer to $4.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, but an increase of this magnitude in the rate coefficient will have little effect on the vibrational distributions.

Altitude profiles of the sinks of $N_2^+ X v = 1$ for low solar activity are presented in Figure 1b. Below 250 km the most important loss processes are quenching by N_2 and O. Of the two, N_2 is the dominant quencher below 275 km. Above 250 km, fluorescent scattering is the major loss process. Of the loss processes for $v = 1$ that also destroy total N_2^+ , the reaction

is the most important below about 260 km and dissociative recombination is the most important above this altitude. Simple charge transfer of N_2^+ to O (reaction (R8)) is a minor sink over the entire altitude range.

The relative populations of the vibrational levels of $N_2^+(X^2\Sigma_g^+)$ from 0 to 3 as a function of altitude for both low and high solar activities are shown in Figure 2. The fraction of N_2^+ in the ground state for low solar activity varies from

from 44% in the standard model to 47% in model E1 and 37% in model E2.

Enhanced chemical loss rates for vibrationally excited N_2^+ will also change the steady state vibrational distribution. In model B3 the rate for

which is $9.8 \times 10^{-12} (300/T)^{0.23} \text{ cm}^3 \text{ s}^{-1}$ [McFarland *et al.*, 1974] for $v=0$, is assumed to increase to $5.0 \times 10^{-10} (300/T)^{0.23} \text{ cm}^3 \text{ s}^{-1}$ for $v > 0$. The effect is most important over the same range where quenching of N_2^+ by O is important. The degree of vibrational excitation at 300 km in models B3 and E2 is 37%. Both models provide loss processes of similar magnitudes, but in model B3 the $N_2^+(v)$ is converted to O^+ . The vibrational distributions produced in models C1 and C2 are similar to those of model B3.

These vibrational distributions are similar to those of Torr and Torr [1982], whose model includes enhanced destruction of $N_2^+(v > 0)$, by reaction with O, but no quenching by atomic oxygen. In models D1 and D2 we assume that (R3) produces $N_2^+(v=5)$ exclusively as Abdou *et al.* [1982, 1984] have suggested. This has a large effect on the vibrational distribution above 200 km where the reaction is an important source of N_2^+ , both for D1, where the back reaction

is assumed to proceed with a rate coefficient of $2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, and for D2, where no back reaction is assumed. At 300 km the degree of vibrational excitation increases from 44% in the standard model to 56% and 59% in models D1 and D2, respectively. As is shown in Table 3, above $v=2$, the relative concentrations of $N_2^+(v)$ ions increase with increasing vibrational quantum number. The concentration of $N_2^+(X(v=5))$ ions in models D1 and D2 is 4–5 times that of the standard model. Such a perturbed vibrational distribution should be observable in the first negative and Meinel bands that arise in fluorescent scattering from the $X^2\Sigma_g^+ v=5$ state. In order to model this effect properly, it would be necessary to take several more vibrational levels into account.

Fig. 2. Relative vibrational populations of $N_2^+(X, {}^2\Pi_u, v=0-3)$ as a function of altitude for the standard low and high solar activity models (model A).

TABLE 3. Relative Populations of the Vibrational Levels of $N_2^+ X^2\Sigma_g^+$ at 300 km for Different Models

Model	Solar Activity	Vibrational Level					
		0	1	2	3	4	5
A	high	65	15	9.2	5.1	3.7	2.8
	low	56	18	11	6.6	4.8	4.0
B1	high	65	15	8.2	5.1	3.7	2.8
	low	59	17	10	6.2	4.5	3.6
B2	high	67	14	7.6	4.7	3.5	2.7
	low	61	16	9.5	5.9	4.3	3.6
B3	high	74	11	5.6	3.6	2.8	2.3
	low	63	15	8.6	5.5	4.3	3.7
C1	high	71	13	6.6	4.1	3.2	2.5
	low	62	16	9.1	5.7	4.2	3.5
C2	high	71	13	6.6	4.1	3.2	2.5
	low	62	16	9.1	5.7	4.2	3.5
D1	high	57	12	5.9	3.5	5.5	16
	low	44	14	8.3	4.1	6.1	24
D2	high	53	12	5.9	3.8	6.5	19
	low	41	14	8.4	4.2	6.6	26
E1	high	63	15	8.6	5.4	4.1	3.2
	low	53	19	11	7.0	4.9	4.6
E2	high	71	14	6.5	3.9	2.6	1.6
	low	63	16	9.0	5.6	3.9	2.7
F	high	65	15	8.2	5.1	3.7	2.8
	low	57	18	10	6.0	4.3	3.5

See Table 2 for an explanation of the models.

EFFECT OF THE VIBRATIONAL DISTRIBUTION ON THE CHEMISTRY

In the standard model, no enhanced loss of vibrationally excited N_2^+ is assumed, except for the slight increase in the rate of dissociative recombination with vibrational quantum number. With the inclusion of this effect the N_2^+ profile changes slightly at high altitudes in both absolute values of the density and slope. At 300 km the density is reduced by 8%, and at 400 km, by 10% over the values obtained by ignoring the vibrational excitation of N_2^+ . The N_2^+ densities at several altitudes for the standard and other models considered are presented in Table 4. Figure 3 illustrates the density profiles for models A, B3, and C1.

The density profile in the standard model is not sensitive to the assumed value for the rate coefficient for quenching of $N_2^+(v)$ by atomic oxygen (reaction (R12)), as models E1 and E2 show. In models B1, B2, and B3 we adopt larger rate coefficients for loss of vibrationally excited N_2^+ in (R8). The N_2^+ density at 300 km decreases by 8% in model B1, by 15% in B2, and by 29% in B3, in comparison with the standard model.

These values are dependent on the value assumed for the quenching coefficient of $N_2^+(v)$ by O (reaction (R12)). If the quenching coefficient is reduced by a factor of 10 to $1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, the N_2^+ reduction in B3 increases slightly to 31% at 300 km. If the quenching coefficient is increased to $5.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, the N_2^+ density is reduced by only 26%.

In model B3, k_9 at 300 km is about $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in comparison with the Langevin rate coefficient of $6.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for reaction of N_2^+ with O. The N_2^+ density reduction is therefore significant only if the rate coefficient is of the order of the Langevin limiting value. The O^+ densities will also increase if the rate for (R8) is larger for $v > 0$. The production rate of $O^+(^4S)$ increases by 58% at 200 km and by 25% at 300 km in model B3.

In models C1 and C2 the reaction of $N_2^+(v)$ with O (reac-

TABLE 4. N_2^+ Densities at Several Altitudes for the Standard and Alternate Models (Low Solar Activity)

Altitude, km	A	B3	C1	D1	E1	E2	F
150	7.60(2)	6.33(2)	6.68(2)	7.53(2)	7.60(2)	7.60(2)	7.51(2)
200	2.26(3)	1.56(3)	1.76(3)	2.21(3)	2.26(3)	2.26(3)	2.15(3)
250	1.36(3)	8.09(2)	1.01(3)	1.26(3)	1.36(3)	1.38(3)	1.23(3)
300	4.96(2)	3.00(2)	3.97(2)	4.23(2)	4.93(2)	5.04(2)	4.67(2)
350	1.48(2)	9.34(1)	1.28(2)	1.22(2)	1.47(2)	1.49(2)	1.48(2)
400	3.61(1)	2.40(1)	3.34(1)	3.07(1)	3.60(1)	3.63(1)	4.11(1)
450	8.61(0)	6.02(0)	8.26(0)	7.63(0)	8.60(0)	8.63(0)	1.10(1)

tion (R7)) is assumed to be faster for $v > 0$, but the products are $NO^+ + N(^2D)$ for C1; in C2, the products are $NO^+ + N(^2D)$ for $v = 1$ and $NO^+ + N(^2P)$ for $v = 2$. The reduction in N_2^+ densities is about the same for these models as for model B3, but the O^+ production rates are unaffected. The computed NO^+ densities change slightly. At 200 km they increase by 4%, and at 300 km, by 23%. The $N(^2D)$ densities do not change appreciably because the increase in the rate coefficient for (R7) is offset by the decrease in the N_2^+ density. If $N(^2P)$ is produced for $v \geq 2$, this reaction is an important source of the metastable atom above 200 km. The other sources are photodissociation and electron impact dissociation of N_2 . In photodissociation we assume an optically thin yield of $N(^2P)$ of 22% [cf. Fox, 1982]. On this basis, (R7) is the dominant source of $N(^2P)$ above 260 km in the low solar activity case. At these altitudes the major loss process is radiation to $N(^2D)$ at 10,400 Å. The volume emission rates will increase substantially at altitudes above 250 km. At 300 km the $N(^2P)$ density, and hence the volume emission rate, in model C2 is nearly double that in the standard model. Since the maximum densities of $N(^2P)$ occur below 200 km, the total overhead intensity will not be as greatly affected. We find that the integrated overhead intensity at 10,400 Å increases from 3.1 to 4.7 kR for low solar activity and from 11 to 16 kR for high solar activity from the standard model A to model C2. In models D1 and D2, (R3) is assumed to preferentially populate $N_2^+(v = 5)$. If no back reaction takes place (model D2), the N_2^+ densities at 300 km are only 9% less than in the standard model. If the back reaction occurs with a rate coefficient of $2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, the N_2^+ densities are reduced by 19%. As was shown in the discussion of the vibrational distributions, the assumptions in models D1 and D2 result in significant vibrational excitation of N_2^+ at high altitudes. If we combine this with enhanced loss of vibrationally excited N_2^+ , as in model B3, the N_2^+ depletion at 300 km increases to 42%.

The effect on the N_2^+ densities near 300 km of increasing the rate coefficient for

from $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ to $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (model F) is about the same as for model D1, although the N_2^+ densities fall off faster with increasing altitude in model D1. Thus for orbits considered by Oppenheimer et al. [1976], their models and those of Abdou et al. [1982, 1984] are equally successful in predicting the N_2^+ densities. Models D1 and F, however, show very different degrees of vibrational excitation. As we shall show in the next section, the volume emission rates of 3914-Å radiation and the (1, 0) Meinel band at 9181 Å differentiate these models.

VIBRATIONAL DISTRIBUTIONS OF THE $N_2^+ A^2\Pi_u$ AND $B^2\Sigma_u^+$

The $N_2^+ A^2\Pi_u$ and $B^2\Sigma_u^+$ states of N_2^+ are the origin of the Meinel and first negative band systems. The intensities of these band systems have been measured in aurorae and airglow by ground-based methods and from rockets [cf. Gattinger and Vallance Jones, 1973; Vallance Jones and Gattinger, 1978; Wallace and McElroy, 1966; Feldman, 1973; Wallace and Broadfoot, 1969]. Because these emissions are produced both by direct ionization of N_2 and by fluorescent scattering of $N_2^+(X^2\Sigma_g^+)$, the intensities are indicative both of the ionization rate and of the densities of N_2^+ . Following the suggestion that (R3) is a near resonance for N_2^+ produced in the $A^2\Pi_u$, $v = 1$ state [Omholt, 1957], Dalgarno and McElroy [1965] computed the effect of a preferential population of this state on the Meinel band intensities. They found that the intensity of bands originating from $v = 1$ in the dayglow is comparable to that anticipated from fluorescence. Gattinger and Vallance Jones [1973] and Vallance Jones and Gattinger [1978] derived the relative population rates of the vibrational levels of the $A^2\Pi_u$ state from ground-based measurements of the Meinel bands in aurorae and found no evidence for an enhanced production of $v = 1$. Wallace and McElroy [1966] and Feldman [1973] examined rocket data of the (0, 0) band of the first negative system at 3914 Å and compared the measurements with model calculations. They demonstrated the importance of (R3) as a source of N_2^+ . Broadfoot [1967] showed how the vibrational distributions are affected if (R3) is

Fig. 3. Altitude profiles of N_2^+ densities for models A, B3, and C1. Only the low solar activity case is shown.

Fig. 4. Altitude profiles of the sources of $N_2^+ A^2\Pi_u v = 0$ for the standard model.

responsible for half the ionization and produces only $v = 1$ of the $A^2\Pi$ state of N_2^+ . Degen [1981] reported vibrational distributions of the B state for sunlit and nonsunlit aurorae.

The sources of $N_2^+ A^2\Pi_u v = 0$ for the standard model are shown in Figure 4. In this model one eighth of the charge transfer reactions of $O^+(^2D)$ with N_2 (reaction (R3)) and one twelfth of the reactions of $O^+(^2P)$ with N_2 (reaction (R4)) populate this state. For low solar activity the major source is photoionization below 180 km and fluorescent scattering above this altitude. For high solar activity, both the photoionization and fluorescent scattering rates are higher, but photoionization dominates to about 200 km. Reaction (R3) is a secondary source of $N_2^+ A v = 0$ which exceeds fluorescent scattering below 150 km and photoionization above 230 km. Reaction (R3) cannot populate $v \geq 2$. For $v = 2$ the transition from photoionization to fluorescent scattering occurs at about the same altitude, near 230 km for low solar activity and near 250 km for high solar activity. The only important loss process above 100 km is radiation. Pendleton and Weaver [1973] report a rate coefficient of about $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for quenching of the $N_2^+ A^2\Pi_u v = 2$ level by N_2 . Using this value, at 100 km the quenching time is $3.0 \times 10^{-4} \text{ s}$, whereas

the radiative lifetime is $1.2 \times 10^{-5} \text{ s}$. The quenching rates for the other vibrational levels are similar [Pendleton and Weaver, 1973; Gray *et al.*, 1972; Mitchell, 1970]. Cartwright *et al.* [1975] found that quenching becomes comparable to radiation at about 85 km.

The resulting vibrational distributions at 100, 200, 300, and 400 km are shown in Table 5 for low and high solar activity. The fraction of ions in $v = 0$ varies from 34% at 100 km to 44% at 400 km. The values for high solar activity vary from 35% to 45%, which is not appreciably different, since the relative production rates of the vibrational levels in photoionization and fluorescent scattering do not depend on solar activity. Our results are similar to those of Broadfoot [1971] for his case in which (R3) is not assumed to preferentially populate the $A v = 1$ state.

The volume emission rates of the (1, 0) Meinel band at 9181 Å are shown in Figure 5. The integrated overhead intensities are 2.1 kR and 6.5 kR for the low and high solar activity models, respectively.

The $B^2\Sigma_u^+$ state of N_2^+ is populated appreciably only in photoionization of N_2 and fluorescent scattering by $N_2^+ X^2\Sigma_g^+$. Charge transfer of He^+ to N_2 energetically can produce

TABLE 5. Vibrational Distributions of the $A^2\Pi_u$ and $B^2\Sigma_u^+$ States at Four Altitudes

Level	100 km		200 km		300 km		400 km	
	Low Solar Activity	High Solar Activity	Low Solar Activity	High Solar Activity	Low Solar Activity	High Solar Activity	Low Solar Activity	High Solar Activity
$A^2\Pi_u$								
0	34	35	44	43	45	45	44	45
1	32	33	32	33	29	31	27	31
2	18	17	14	14	13	12	14	12
3	9.4	8.9	6.3	6.4	6.5	5.8	7.6	6.3
4	4.5	4.3	2.9	3.0	3.8	3.0	4.6	3.6
5	2.0	2.0	1.4	1.4	2.3	1.7	2.9	2.2
$B^2\Sigma_u^+$								
0	85	85	72	73	56	63	53	55
1	13	13	20	19	23	22	24	23
2	1.2	1.2	5.5	5.9	13	9.5	15	13
3	0.089	0.089	2.6	2.4	7.6	5.3	8.6	8.1

Fig. 5. Volume emission rates of the (1, 0) Meinel band for the standard models, both low and high solar activity. The volume emission rate for model D1, low solar activity, is shown for comparison.

Fig. 7. Volume emission rates of the (0, 0) first negative band at 3914 Å for the standard models, both low and high solar activity. The volume emission rate for model D1, low solar activity, is shown for comparison.

ions in the B state, but the He^+ densities are low in this altitude range, and the branching ratio for production of the B state is small [Govers *et al.*, 1977]. Tinsley *et al.* [1982] have suggested that charge transfer of $O^+(^2P)$ to N_2 (reaction (R4)) could be a source of $N_2^+ B v=0$, but this is true only for energetic ions, since the reaction is short 0.14 eV.

The sources of $v=0$ for high and low solar activities are shown in Figure 6. Photoionization is the major source of $v=0$ and $v=1$ below 170 km. Fluorescent scattering is more important above this altitude. For high solar activity the transition altitude is near 180 km.

Loss of the $B^2\Sigma_u^+$ state is primarily by radiation above 100 km. The coefficients for quenching by N_2 have been measured

by Jolly and Plain [1983] as $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $15 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for the $v=0$ and $v=1$ states. At 100 km the radiative lifetimes of both levels are about $6 \times 10^{-8} \text{ s}$ compared with quenching lifetimes of $3.0 \times 10^{-4} \text{ s}$ and $1.6 \times 10^{-4} \text{ s}$, respectively.

The resulting vibrational distributions at 100, 200, 300, and 400 km for low and high solar activities are shown in Table 5. The distributions for high solar activity are very similar, since the relative populations, even more so than in the $A^2\Pi_u$ state, are determined by quantities which do not depend on solar activity: Franck-Condon factors, g values, and transition probabilities. Only the relative importance of photoionization and fluorescent scattering at a given altitude will be different.

Fig. 6. Altitude profiles of the sources of $N_2^+ B^2\Sigma_u^+ v=0$.

The fraction of ions in the ground state varies from 0.85 at 100 km to 0.53 at 400 km for low solar activity and from 0.85 to 0.55 for high solar activity. Broadfoot [1971] reported values of 87 to 50%. His long-lifetime values correspond to altitudes that are higher than any we consider here.

The computed volume emission rates of the (0, 0) 3914-Å band of the first negative system ($B^2\Sigma_u^+ - X^2\Sigma_g^+$) of N_2^+ for both values of the solar activity are shown in Figure 7. The integrated overhead intensities are 2.0 kR for low solar activity and 6.1 kR for high solar activity. The profile for low solar activity compares favorably with the measurements of Feldman [1973], which were taken on July 31, 1968, when $F_{10.7}$ was 135.

Broadfoot [1967] found the B state to be little affected by the charge transfer of $O^+(^2D)$ to N_2 (reaction (R3)) if the reaction is assumed to produce $A v = 1$ exclusively. If the product of (R3) is $N_2^+ X v = 5$, as Abdou *et al.* [1982, 1984] suggest (model D2), the vibrational distribution of the X state is altered appreciably, and therefore at high altitudes where fluorescent scattering is the major source of $N_2^+ B^2\Sigma_u^+$ and $A^2\Pi_u$, the vibrational distributions of the B and A states are also affected. An increase in the vibrational excitation of the B state decreases fluorescence in the (0, 0) first negative band and the (1, 0) Meinel band. Figures 5 and 7 show also the volume emission rates of the 3914-Å and 9181-Å bands for model D2, low solar activity. The computed values for model D2 are significantly less than for the standard model above 200 km for the 3914-Å emission and above 150 km for the (1, 0) Meinel band. Measurements of the volume emission rate of N_2^+ at 3914 Å or 9181 Å may therefore provide some indication of the vibrational distribution of ground state N_2^+ . In particular, models D1 and F may be distinguished. The volume emission rate of 3914-Å photons at 300 km is 50% larger in model F than in model D1.

SUMMARY

We have computed the densities and vibrational distributions of N_2^+ in the $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ states for both high and low solar activities in the daytime ionosphere. Altitude profiles of the relative populations of the vibrational levels of $N_2^+ X^2\Sigma_g^+$ are presented. Near 100 km, quenching limits the fraction vibrationally excited to 0.05. By contrast, at 450 km, 50% are vibrationally excited. We have examined several models in which loss of N_2^+ is enhanced for vibra-

Fig. 8. Steady state densities of the major ions for the standard (model A) low solar activity case.

tionally excited N_2^+ and in which various assumptions are made about the production of different vibrational levels of N_2^+ in charge transfer of $O^+(^2D)$ to N_2 . An enhanced rate for (R7) or (R8) can significantly decrease the N_2^+ densities if the rates are near gas-kinetic. If (R7) produces $N(^2P)$, it is the most important source above 260 km. The assumed quenching rate for $N_2^+(v)$ by O (reaction (R12)) is important in determining the densities of N_2^+ if an enhanced loss is assumed. The vibrational distributions at 300 km are given for the different models.

Volume emission rates and integrated overhead intensities of the major bands of the Meinel and first negative systems are reported. Abdou *et al.* [1984] have suggested that (R3) may produce $N_2^+(v = 5)$ exclusively. This seems unlikely, but if it occurs, the effect could be seen in bands that arise from fluorescent scattering from the $X^2\Sigma_g^+ v = 5$ state. The decreased population of $v = 0$ would be evidenced in reduced intensities of the 3914-Å (0, 0) first negative band and the (1, 0) Meinel band, although not as dramatically. Altitude profiles of these emissions would be especially helpful in distinguishing the models, as would laboratory measurements of the rate coefficients both for reaction of $N_2^+(v > 0)$ with O ((R7) and (R8)) and for quenching by O (reaction (R12)).

TABLE 6. Standard Chemical Reaction Scheme

Reaction	Rate Coefficient, $\text{cm}^3 \text{s}^{-1}$	Reference
$N_2^+ + \text{NO} \rightarrow N_2 + \text{NO}^+$	3.3×10^{-10}	Fehsenfeld <i>et al.</i> [1970]
$N_2^+ + \text{O}_2 \rightarrow N_2 + \text{O}^+$	5.1×10^{-11}	Smith <i>et al.</i> [1978]
$N^+ + \text{O}_2 \rightarrow \text{N}(^2D) + \text{O}_2^+$	3.1×10^{-10}	Albritton <i>et al.</i> [1979]
$N^+ + \text{O}_2 \rightarrow \text{O} + \text{NO}^+$	2.5×10^{-10}	Albritton <i>et al.</i> [1979]
$N^+ + \text{O}_2 \rightarrow \text{O}^+ + \text{NO}$	3.7×10^{-11}	Albritton <i>et al.</i> [1979]
$N^+ + \text{NO} \rightarrow \text{N} + \text{NO}^+$	6×10^{-10}	Fahey <i>et al.</i> [1981]
$\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$	4.8×10^{-10}	Smith <i>et al.</i> [1978]
$\text{He}^+ + \text{O}_2 \rightarrow \text{O}^+ + \text{O} + \text{He}$	8×10^{-10}	Rakshit <i>et al.</i> [1978]
$\text{O}^+ + \text{O}_2 \rightarrow \text{O} + \text{O}_2^+$	$2.1 \times 10^{-11}(300/T)^{0.83}$	Mauclaire <i>et al.</i> [1979]
$\text{O}^+(^2D) + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$	7×10^{-10}	Johnsen and Biondi [1980]
$\text{O}^+(^2P) + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$	1.3×10^{-10}	Glosik <i>et al.</i> [1978]
$\text{O}^+(^2P) + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$	6.5×10^{-10}	Mauclaire <i>et al.</i> [1979]
$\text{N}(^4S) + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$8.2 \times 10^{-11} \exp(-410/T)$	Hampson [1980]
$\text{N}(^4S) + \text{O}_2 \rightarrow \text{O} + \text{NO}$	$4.4 \times 10^{-12} \exp(-3220/T)$	Hampson [1980]
$\text{N}(^2D) + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$3.5 \times 10^{-13} T^{1/2}$	Schofield [1979]
$\text{N}(^2P) + \text{O}_2 \rightarrow \text{NO} + \text{O}$	3.5×10^{-12}	Iannuzzi and Kaufman [1980]

APPENDIX

The chemical reaction scheme employed includes the reactions listed by Fox and Dalgarno [1979], Fox and Victor [1981], Fox [1982], and Breig *et al.* [1984]. To them are added those shown in Table 6. If we assume no vibrational excitation, the resulting altitude profiles for the major ions for low solar activity are those shown in Figure 8. The O^+ profile has been constructed to approximate the measurements of orbit 594U of Atmosphere Explorer C reported by Oppenheimer *et al.* [1977]. The neutral atmosphere for this orbit is similar to the mass spectrometer/incoherent scatter model for low solar activity used here.

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