Metastable $N(^{2}P)$ Atoms in the Aurora

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Auroral spectra have been obtained in the 3380- to 3560-Å region to study the [NI] ${}^{4}S^{-2}P$ doublet at 3466 Å. The [NI] 3466 Å/N₂ Vegard-Kaplan ratio is found to remain constant. This is in agreement with the results of a model calculation showing that the dominant source of N(${}^{2}P$) atoms is dissociative excitation of N₂ by fast electrons, and the major quenching agent is atomic oxygen. A value of about 5 × 10⁹ cm⁻³ s is deduced for the ratio of the N(${}^{2}P$) quantum yield to the atomic oxygen deactivation coefficient.

INTRODUCTION

The N(²D) metastable state has received considerable attention in recent years as a consequence of the major role played by these atoms in the production of thermospheric nitric oxide through the reaction N(²D) + O₂ \rightarrow NO + O. Substantial progress in the N(²D) chemistry has been made with the observations of the [NI] ⁴S-²D 5200-Å emission in the airglow [*Frederick and Rusch*, 1977] and aurora [*Rusch and Gérard*, 1980], and new sets of quantum yields and quenching coefficients have been obtained. By contrast, little is known about the sources and sinks of N(²P) atoms in the thermosphere. For example, no laboratory measurement of the yield of N(²P) in the dissociation of N₂ by fast electrons is available. A few deactivation coefficients have been measured, but no attempt has been made to apply them to airglow or auroral observations.

So far no systematic study has been made of the [NI] 3466-Å intensity and variations relative to other emissions. The posibility of using the ${}^{2}D{}^{2}P$ 10400-Å relative intensity as an indicator of the height of the aurora has recently been pointed out by *Vallance-Jones and Gattinger* [1979]. This paper presents the analysis of spectrometric observations in the vicinity of the 3466-Å emission and discusses the implications of these measurements on the determination of the efficiency of the production and loss of N(${}^{2}P$) atoms in the thermosphere.

OBSERVATIONS

Nighttime auroral spectra in the region extending from 3380 to 3560 Å were recorded during new moon periods from January to March 1978 from the optical station of the University of Tromsö in Skibotn (magnetic latitude: 66°N) using a 0.5-m grating spectrometer in the photon-counting mode. The measurements were made along the magnetic field line which at this location has an inclination of about 12°. The resolution was approximately 4.5 Å, and the spectral range was scanned in about 50 s. Bright spectra were analyzed individually, provided that the intensity of the aurora did not vary significantly during the scan, while weaker spectra were summed up to increase the signal to noise ratio. A series of 4 sums is shown in Figure 1, where the main features are identified. A synthetic spectrum of the same region for a resolution of 3.5 Å by Vallance-Jones and Gattinger [1975] (VJG) is also plotted at the bottom of Figure 1 for comparison. The good agreement be-

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tween the observed and the synthetic spectra indicates that no other emission contributes significantly to the spectrum with the exception of two weak features which we identify as the (2, 5) and (6, 7) Herzberg I bands at 3450 and 3479 Å. These bands appear in the spectra during periods of weak auroral activity. Degen [1977] gives typical nightglow emission rates of 13 R and 15 R, respectively. As may be seen in Figure 1, the emissions partly overlap in this section of the auroral spectrum. In order to determine the intensity of each feature, the synthetic spectrum of Vallance-Jones and Gattinger [1975] was used to estimate the various contributions. Finally, the intensity was obtained by integrating the intensity of the line or bands over their profile. Since the atmospheric extinction does not vary by more than 20% over this limited spectral region and since only relative intensity values are used, no attempt has been made to correct the intensities for this effect.

Variations of the [N I] 3466 Å/N₂2P (1, 2) ratio ranging between 0.24 and 2.5 are present in our measurements. Since the $N_2 2P$ (1, 2) emission rate is 0.18 that of N_2^+ (4278 Å) [Vallance-Jones and Gattinger, 1975], our observations give a I(4278 Å)/I(3466 Å) ratio varying between 2 and 21. The average ratio usually observed in medium-intensity aurorae is of the order of 12. This variability is illustrated in Figure 2a, where the intensity during the course of one night of the [N I] 3466-Å doublet and V-K (1, 10) band are plotted versus the N_22P intensity. Different symbols have been used for the points obtained from individual spectra or from the sums. The arrows connect data points consecutive in time. The scatter in the V-K/2P and [N I]/2P ratios is interpreted as a consequence of changes in the incident particle mean energy. It is, however, striking that the figure described by the [N I] and V-K intensities are almost parallel to each other. To examine this point further, the [N I] 3466-Å intensities are plotted in Figure 2b versus the V-K intensity by using the same set of data as in Figure 2a. In this case the scatter is greatly reduced, indicating a similar response of the two emissions to the variation of the energy spectrum. This is confirmed by the statistical analysis shown in Figure 3, where all of the measurements available have been used to plot the [N I] 3466-Å emission rate versus V-K (1, 10). A linear regression was fitted to the data, giving a [N I] 3466-Å/V-K (1, 10) slope of 0.54 and a correlation coefficient of 0.98. The curvature in the linear fit of Figure 3 is due to the use of the logarithmic scale and a nonzero intercept. Consequently, the proportionality of the two



Fig. 1. Comparison between 4 sums of auroral spectra and synthetic spectrum from Vallance-Jones and Gattinger [1975].

emissions is clearly established over 2 orders of magnitude of brightness.

N(²P) Sources and Sinks

The potential sources of $N(^{2}P)$ atoms in the aurora are

Dissociation of N₂ by fast electrons

$$N_2 + e_j \xrightarrow{f_1} N({}^4S, {}^2D, {}^2P) + N({}^4S, {}^2D, {}^2P) + e_j$$
 (1)

Dissociative ionization of N₂ by fast electrons

$$N_2 + e_i \stackrel{f_2}{\to} N^+ + N({}^4S, {}^2D, {}^2P) + 2e_i$$
(2)

Dissociative recombination of N₂⁺ ions

$$N_2^+ + e \xrightarrow{f_3} N + N({}^4S, {}^2D, {}^2P)$$
(3)

Charge transfer of N⁺ on nitric oxide

$$N^{+} + NO \frac{14}{k} N(^{4}S, ^{2}D, ^{2}P) + NO^{+}$$
 (4)

where f_1, f_2, f_3 , and f_4 denote the fractions of atoms produced in the ²P state. These fractions are unknown, but the total dis-



Fig. 3. Correlation between [N I] 3466-Å and V-K (1, 10) emission rates. The solid curve is a linear least square fit to the data.

sociative recombination coefficient α_{N_2+} as well as the total dissociation cross section of N₂ by fast electrons [Winters, 1966] have been measured. Incidentally, the N₂⁺ + O reaction and the NO⁺ dissociative recombination, which are among the three major sources of N(²D), are not energetically able to yield N(²P) atoms.

The sinks of $N(^2P)$ are mainly

$$N(^{2}P) + O_{2} \xrightarrow{\sim} O_{2} NO + O(^{3}P, ^{1}D)$$
(5)

$$N(^{2}P) + O \xrightarrow{\sim_{O}} N(^{4}S, ^{2}D) + O(^{3}P, ^{1}D)$$
 (6)

$$N(^{2}P) + e \stackrel{k_{e}}{\to} N(^{4}S, ^{2}D) + e$$
(7)

$$N(^{2}P) + NO \xrightarrow{NO} N_{2} + O$$
(8)

$$N(^{2}P) \rightarrow N(^{2}D, \,^{4}S) + h\nu \tag{9}$$

Table 1 lists the available results of the few laboratory measurements of the quenching coefficients of reactions (5), (6), and (8). The agreement between the available measurments is satisfactory for quenching by O₂ and NO, but for atomic oxygen a discrepancy of almost an order of magnitude exists between the two measurements. In the calculations, we have adopted $k_{O_2} = 2.6 \times 10^{-12}$ cm³ s⁻¹, $k_{NO} = 2.8 \times 10^{-11}$ cm³ s⁻¹,



Fig. 2. (a) Vertical intensities of the V-K (1, 10) band and [N I] 3466-Å doublet versus the intensity of the N_2 (1, 2) second positive band measured during one night. The arrows connect consecutive data. Intensities are in arbitrary units. (b) [N I] 3466-Å intensity versus V-K (1, 10) band intensity for the same data as in part (a).

and we leave k_0 as a parameter. The quenching coefficient by electrons and its temperature dependence are assumed to be the same as for N(²D) [Frederick and Rusch, 1977], and we assume arbitrarily $f_3 = 0.5$ and $f_4 = 1$. As is shown below, this choice has no consequence, since reactions (3) and (4) are negligible sources of N(²P). Consequently, the unknown parameters for the reactions controlling the production and loss of N(²P) are the quantum yields f_1 and f_2 and the deactivation coefficient by O. In fact, processes (1) and (2) have the same altitude dependence, and the ratio of their total rates is equal to 0.32 [Kieffer and Dunn, 1966], which is the ratio of the dissociative ionization cross section to the dissociation cross section of N₂. Thus it is impossible to determine the contribution of the two sources separately. The combined production rates of N(²P) by (1) and (2) may be written as

$$(N^2 P) = (2f_1 + 0.32f_2)D[N_2]$$

= $2f^*D[N_2]$

where D is the dissociation rate of N₂ by fast electrons and f^* is the effective quantum yield equal to $f_1 + 0.16f_2$. Under these assumptions, the equation governing the N(²P) density is

$$\eta(N^2 P) = 2f^* D[N_2] + \alpha_{N_2} f_3[N_2^+][e] + k_1 f_4[N^+][NO]$$

- [N(²P)] {k₀₂[O₂] + k₀[O] + k_e[e] + k_{N0}[NO]
+ A₃₄₆₆ + A₁₀₄₀₀}

where A_{3466} and A_{10400} are the Einstein coefficients for the ⁴S- ^{2}P and $^{2}D^{-2}P$ transitions, respectively. A time-dependent model solving for all major ions as well as NO, $N(^4S)$, $N(^2D)$, and $N(^{2}P)$ was used to investigate the source and sinks of $N(^{2}P)$ atoms. The model is basically identical to that described by Gérard and Barth [1977] except for the inclusion of $N(^{2}P)$ and the update of some of the reaction coefficients. The ionization profiles for various electron energies are calculated following the method used by Gérard and Rusch [1979]. The neutral atmosphere is a Jacchia [1971] model with an exospheric temperature of 1100°K smoothly connected below 120 km to CIRA (1965). The energy distribution of the electrons at the top of the atmosphere is assumed to have the form $F(E) \sim N_0 E \exp(-E/E_0)$, having an average energy of $2E_0$. The time constants involved in the ion and metastable chemistry are of the order of tens of seconds. An exception is the NO build up, which takes time of the order of hours or days. The results illustrated below are obtained after 5 min of precipitation. The relative intensity of the [N I] 3466-Å emission was calculated to study its dependence on the energy of the primary electrons and parameters described before.

Only a few quantitative measurements of the [N I] 3466-Å doublet have been reported in the literature. Moreover, the energy characteristics of the precipitated electrons are generally not known. Consequently, any comparison between observations and model are subject to large uncertainties. Valance-Jones and Gattinger [1975] observed a ratio R = I(4278 Å)/I(3466 Å) of 12.5 in medium intensity aurorae. Dick [1970], using airborne photometers, measured values of R between 8 and 100, and noticed that the I(6300 Å)I(3466 Å) ratio was constant (~18). In their observations of the N₂ auroral emissions, Rees et al. [1976] measured R = 25 in an aurora with a characteristic energy of 2.8 ± 0.4 keV. Finally, Sharp [1970] observed the 3466-Å doublet with a rocket-borne UV spectrometer and measured R = 23 below the region of precipitation. Since his ionization profile peaks near 105 km, we

TABLE 1. Laboratory N(²P) Quenching Coefficients

k_{O_2}	k _o	k _{NO}
2.6×10^{-12}		3.2×10^{-11}
$\leq 2 \times 10^{-12}$	7×10^{-11} 1×10^{-11}	2.8×10^{-11}
	$\frac{k_{O_2}}{2.6 \times 10^{-12}} \le 2 \times 10^{-12}$	$\frac{k_{O_2}}{2.6 \times 10^{-12}} \frac{k_0}{7 \times 10^{-11}} \le 2 \times 10^{-12} 1 \times 10^{-11}$

Values are in cubic centimeters per second.

deduce $E_0 \simeq 5$ keV. The results of the observations are plotted in Figure 4 versus the characteristic energy E_0 for comparison with the model calculations. The characteristic energy of the auroral electrons for the VJG and our observations is set to 3 ± 1 keV, a typical value for the diffuse aurora of the type observed here [Venkatarangan and McEwen, 1979]. The scatter in the values is fairly large and most likely to be due to measurement errors and large uncertainties in the deduced electron energies. The solid curve in this figure is a plot of the to tal vertical ratio R obtained from the model calculations using $f^* = 50\%$ and $k_0 = 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Table 2 lists the sources and sinks of $N(^{2}P)$ for this set of parameters. It is clear that the electron impact on N₂ is the dominant source of $N(^{2}P)$ with a contribution from $N_{2}^{+} + e$ at high altitude. Provided that $k_0 \ge 1 \times 10^{-12}$ cm³ s⁻¹, quenching by atomic oxygen dominates over other quenching processes at altitudes above the peak of $N(^{2}P)$. Reaction (5) is marginally important at low altitudes, and reactions (7) and (8) are always negligible. Radiative deexcitation becomes increasingly important at high altitudes.

Obviously, this choice of parameters is not unique. Since approximately one 4278-Å photon is produced for 45 N_2^+ ions created [Borst and Zipf, 1970] and since the N_2^+ production rate and the N_2 dissociation rates are almost equal [Winters, 1966], the volume emission rates of the two emissions are given by

$$\eta(4278 \text{ Å}) = \frac{D[N_2]}{45}$$

and

$$\eta(3466 \text{ Å}) = \frac{2f^* D[N_2] A_{3466}}{k_0[O] + k_{02}[O_2] + k_e[e] + A_{3466} + A_{1040}}$$

Thus limiting to the dominant terms and assuming that radiative deexcitation remains small in comparison with quench-

 $\begin{array}{c} 60 \\ (9950) \\ 10 \\ 0 \\ 1 \\ 2 \\ 3 \\ 20 \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \end{array}$

Fig. 4. Vertical N₂⁺ (4278 Å)/[N I] 3466-Å intensity ratio as a function of the characteristic energy of a Maxwellian electron flux. Solid curve: model calculation for $f^* = 0.5$ and $k_0 = 1 \times 10^{-10}$ cm³ s⁻¹; observations: (1) Sharp [1970], (2) Vallance-Jones and Gattinger [1975], (3) Rees et al. [1976], (4) these measurements.

Z, km	Sources, $cm^{-3} s^{-1}$		Loss Frequency, s ⁻¹				
	$N_2 + e$	$N_2^+ + e$	$\overline{N(^2P)+O_2}$	$N(^2P) + O$	$N(^2P) + e$	$N(^2P) + NO$	$A_{3466} + A_{10400}$
100	6.4 (3)*	1.6 (0)	5.2 (0)	5.0(1)	1.3 (-4)	1.4 (-3)	8.3 (-2)
120	2.9 (4)	2.7 (2)	2.0 (–1)	7.6 (Ó)	4.6 (-4)	1.1 (-3)	8.3 (-2)
140	1.0 (4)	3.5 (2)	2.5 (-2)	2.2 (0)	4.9 (–4)	2.0 (–4)	8.3 (-2)
160	3.7 (3)	2.4 (2)	6.8 (-3)	9.8 (-1)	5.1 (-4)	6.8 (-5)	8.3 (-2)
180	1.5 (3)	1.4 (2)	2.3 (-3)	5.4 (–1)	4.0 (-4)	2.8 (~5)	8.3 (-2)
200	6.7 (2)	7.4 (l)	9.4 (–4)	3.2 (–1)	3.0 (4)	1.4 (-5)	8.3 (-2)
250	1.3 (2)	1.5 ÌÌ	1.4 (-3)	1.1 (–1)	1.0 (-4)	2.6 (–6)	8.3 (–2)
300	2.8 (1)	3.1 (0)	2.9 (-5)	5.1 (-2)	4.2 (-5)	4.4 (-7)	8.3 (-2)

TABLE 2. N(²P) Production and Loss

*Read as 6.4×10^{3} .

ing by atomic oxygen,

$$\frac{\eta(4278A)}{\eta(3466A)} \simeq 1.1 \times 10^{-2} \frac{k_0[O]}{\int^* A_{3466}}$$

The comparison with observations gives an estimate for the f^*/k_0 ratio at about 5 × 10⁹ cm⁻³ s¹. Thus if Young and Dunn's [1975] value is accepted, one deduces $f^* \simeq 5\%$. This is compatible with Zipf's [1978] estimates of $f_1 = 0.25$ which gives k_0 of the order of 5×10^{-11} cm³ s⁻¹, a value mid-way between the two laboratory determinations. Figure 5 shows the volume emission rate of 4278 Å and 3466 Å for an aurora characterized by $E_0 = 2.3$ keV, a flux of 3.3×10^8 cm⁻² s⁻¹, f* = 50%, and $k_0 = 1 \times 10^{-10}$ cm³ s⁻¹. At this point and until new laboratory results become available, there is no possibility of deducing values of k_0 and f^* separately. Another uncertainty arises from the choice of the neutral model atmosphere. Our model is very similar to the MSIS [Hedin et al., 1977] model for the place and dates considered here. However, recent measurements have indicated that the atomic oxygen density tends to be overestimated by the MSIS model when they are compared with in situ measurements [Sharp et al., 1979; Deans and Shepherd, 1978]. In this case our derived value of the f^*/k_0 ratio probably represents an upper limit. The fact that the ratio of the V-K bands to the 3466-Å emission remains constant over a large range of conditions suggests that the two emissions have a similar altitude distribution. It has been shown [Sharp, 1970] that the N₂($A^{3}\Sigma$)



Fig. 5. N₂⁺ (4278-Å) and [N I] 3466-Å volume emission rates for a model aurora (see text).

production rate is porportional to the 2P emission rate and thus to the dissociation rate of N₂. Consequently, both features have the same altitude distribution for their production rates. Analysis of the altitude distribution of the V-K band emission rate has shown [*Beiting and Feldman*, 1979, and references therein] that N₂($A^3\Sigma$) molecules are mainly quenched by atomic oxygen with a rate coefficient between 0.7 and 4 × 10⁻¹⁰ cm³ s⁻¹. Consequently, since the two metastables have identical sources and quenching agent, their intensity ratio remains independent of the primary electron energy, in agreement with the observations described above.

The products of the $N(^{2}P)$ quenching by atomic oxygen are unknown. If the nitrogen atoms are left in the ^{2}D state, these results imply that virtually all the atoms produced in the ^{2}P state transit through the ^{2}D state. Consequently, the effective branching ratio for the production of $N(^{2}D)$ by electron impact on N_{2} would be equal to the sum of the fractions of atoms created in the $N(^{2}D)$ and $N(^{2}P)$ states.

CONCLUSIONS

Observations of a limited region of the ultraviolet auroral spectrum at medium resolution have provided a systematic study of the [N I] ${}^{4}S{}^{2}P$ doublet at 3466 Å and neighboring N₂ Vegard-Kaplan and second positive bands. They show that the relative intensities of the 3466-Å and second positive bands are variable, whereas the V-K band is covariant with the [N I] 3466-Å emission. Since the two emissions have sources which vary proportionally to the N₂ ionization rate, it is concluded that $N(^{2}P)$ is also mainly deactivated by atomic oxygen. Comparison of the measurement with model calculations has shown that dissociative excitation of N_2 is the dominant source of $N(^{2}P)$ atoms, and quenching by atomic oxygen is the major sink in the thermosphere. The ratio of the quantum yield of $N(^{2}P)$ in the N₂ dissociation to the quenching coefficient by O is of the order of 5×10^9 cm⁻³ s, a value in agreement with recent laboratory measurements of deactivation coefficients and other estimates of the quantum yield of $N(^{2}P)$ in the N_{2} dissociation.

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