JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 85, NO. A2, PAGES 687–694, FEBRUARY 1, 1980

The Excitation and Collisional Deactivation of Metastable $N(^2P)$ Atoms in Auroras

E. C. ZIPF, P. J. ESPY, AND C. F. BOYLE

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

The concentration and altitude distribution of metastable $N(^2P)$ atoms has been measured in a diffuse IBC II^+ auroral arc. The dominant $N(^2P)$ source is shown to be the dissociative excitation of N_2 by electron impact with a minor contribution from the dissociative recombination of N_2^+ ions. The possibility that an ion-molecule process involving atomic oxygen and vibrationally excited N_2^+ ions, $(N_2^+)_{vib} + O \rightarrow NO^+ + N(^2P)$, is a significant $N(^2P)$ source is also explored. Atomic oxygen is found to be the principal $N(^2P)$ quenching agent, with O_2 contributing significantly below 120 km. By combining these observational results with recent laboratory studies on N_2 dissociative excitation the proportional yield of N^+, $N(^2P)$, $N(^2D)$, and $N(^4S)$ atoms from electron-impact dissociation of N_2 under optically thick conditions is found to be 0.135:0.165 0.30:0.40, respectively, at 100 eV.

INTRODUCTION

Comparatively little attention has been paid to the role of nitrogen atoms in the metastable $N(^2P)$ state in the upper atmosphere. This neglect has been fostered in part by the assumption that the $N(^2P)$ state is populated at a modest rate in comparison with the metastable $N(^2D)$ state which plays such a prominent role in the chemistry of nitric oxide and in part by the lack of in situ measurements of the concentration and altitude distribution of $N(^2P)$ atoms in the upper atmosphere. Until now the only observational data that have been available to modelers were derived from a limited number of ground-based spectral studies of auroral substorms [*Vallance Jones and Gattinger,* 1975, 1976*a,* 1978]. Laboratory work on the $N(^2P)$ state has also been quite limited and confined for the most part to investigations of its collisional deactivation at room temperature [*Golde and Thrusch,* 1972; *Husain et al.,* 1974; *Young and Dunn,* 1975]; there have been no laboratory measurements of the ^2P quantum yield from any source of aeronomic importance.

In this paper we present the results of an in situ study of the excitation and collisional deactivation of $N(^2P)$ atoms in an IBC II^+ aurora. The $N(^2P)$ concentration and altitude distribution from 110 to 195 km was determined from measurements of the intensity of the $NI(^4S - {}^2P;$ λ3466 Å) doublet. The optical data were obtained by a filtered photometer on board a Taurus-Orion sounding rocket (33.001 UA) that was launched into a bright auroral arc (0I(λ5577 Å) intensity of 40 kR) above Fort Churchill, Manitoba, on March 12, 1978, at 2240 CST. Complementary measurements of the intensity of the (0, 0) first negative band of N_2^+[λ3914 Å] and of the flux and energy distribution of the precipitating electrons in the 0–500 eV energy range were also made.

$N(^2P)$ EXCITATION MODEL

As part of their time-dependent studies of magnetospheric substorms, *Rees and Jones* [1973] have developed an excitation model for the $N(^2P)$ state based on the premise that dissociative ionization,

$$e + N_2 \rightarrow N(^2P) + N^+ + 2e \quad (1)$$

and dissociative recombination

$$N_2^+ + e \rightarrow N(^2P) + N \quad (2)$$

are the only $N(^2P)$ sources with 33% of the product atoms formed by these processes in the ^2P state. In this model the metastable $N(^2P)$ state is depopulated by radiation of the λ3466-Å and λ10,400-Å emission lines with effective transition probabilities of $5.4 \times 10^{-3} s^{-1}$ and $7.9 \times 10^{-2} s^{-1}$, respectively [*Chamberlain,* 1961] and is quenched by O_2, O_2^+, and NO with rate coefficients $k_1 = 5 \times 10^{-12}$ cm^3 s^{-1}, $k_2 = 2.2 \times 10^{-11}$ cm^3 s^{-1}, $k_3 = 1.8 \times 10^{-10}$ cm^3 s^{-1}, respectively. The fraction of nitrogen atoms formed in the ^2P state by electron-impact dissociation of N_2 in this model is approximately 5%. This modest quantum yield can be contrasted to estimates of the $N(^2D)$ production rate based on λ5200-Å airglow studies and from models of the odd-nitrogen chemistry of the earth and Mars, where $N(^2D)$ quantum yields in the 50–100% range seem to be required [*Frederick and Rusch,* 1977; *McElroy et al.,* 1976].

Although *Vallance Jones and Gattinger* [1978] have shown that this $N(^2P)$ excitation model is in good agreement with gound-based studies of λ3466-Å and λ10,400-Å emission in auroral substorms, the results from a number of laboratory experiments suggest that the success of the model is actually fortuitious. For example, the discovery that atomic oxygen quenches the $N(^2P)$ state efficiently [*Golde and Thrusch,* 1972; *Young and Dunn,* 1975] and that dissociative ionization (Process (1)) does not produce $N(^2P)$ atoms [*Ehrhardt and Kresling,* 1967] requires the $N(^2P)$ auroral model to be revised significantly. The revisions are necessary because the rapid quenching of the $N(^2P)$ state by O increases the required magnitude of the $N(^2P)$ source by nearly an order of magnitude, while the ineffectiveness of dissociative ionization as an $N(^2P)$ source shifts the burden to dissociative excitation,

$$e + N_2 \rightarrow N(^2P) + N \quad (3)$$

as the most likely $N(^2P)$ production mechanism.

OBSERVATIONAL RESULTS

In Figure 1 we have plotted the λ3644-Å and λ3914-Å intensity data obtained by the rocket-borne photometers which had bandwidths of 16 Å and 30 Å FWHM, respectively. The absolute sensitivity of the filtered photometers was determined by using an NBS standard lamp following the procedure described in detail by *Borst and Zipf* [1970]. The effective filter transmission for the λ3914-Å band was determined by

Paper number 9A1290.
0148-0227/80/009A-1290$01.00

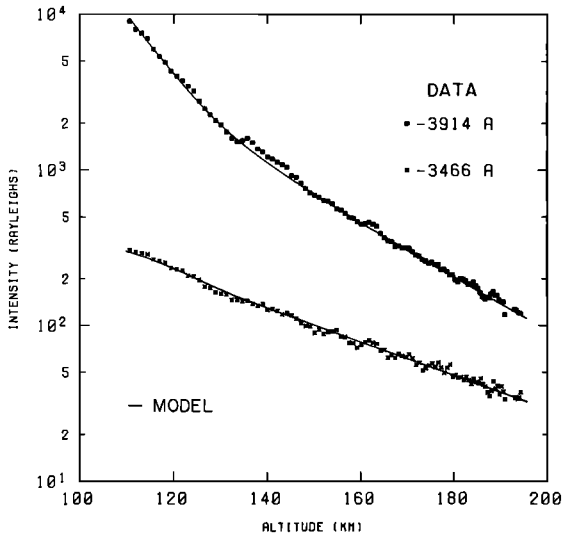

Fig. 1. Apparent column emission rates for the NI($^2P - {}^4S$; λ3466 Å) doublet (crosses) and the N_2^+(0, 0) 1NG band (λ3914 Å) (squares) in a stable IBC II$^+$ auroral arc. The solid curve fitted to the λ3466-Å intensity data was obtained in the model 1 analysis using (4) and (5), the parameters given in the text, and Model Atmosphere A of *Sharp* [1971].

calculating the wavelength position and line strengths of the individual rotational lines of the N_2^+ (0, 0) first negative band and then convoluting this structure with the measured filter transmission function. The λ3466-Å data were corrected for a small contribution (~10%) from the long-wavelength tail of the (1, 10) Vegard-Kaplan band [λ3426 Å]. In estimating this correction factor, we relied on laboratory VK spectral data for the (1, 10) band shape, while we used the VK (1, 10) and N_2^+(0, 1) band intensity data obtained by *Deans and Shepherd* [1978] in a stable, diffuse aurora of comparable 0I(λ5577 Å) brightness in order to estimate the intensity of the VK(1, 10) band under the conditions of our flight. The final photometry results shown in Figure 1 are probably reliable to within ±20%.

The N_2^+(λ3914 Å) data obtained in this flight are very similar in character to the results published by *Deans and Shepherd* [1978] and by *Feldman and Doering* [1975] which were also obtained in stable, diffuse auroras. A slight altitude-dependent modulation of the overhead intensity due to the precessional motion of the vehicle and to minor temporal and spatial fluctuations in the arc itself can be seen in the data readily. *Feldman* [1978] has shown that direct differentiation of intensity observations such as these tends to result in misleading volume emission rate values, and we have adopted his iterative procedure for inferring the local volume emission rates by fitting the integral measurements directly. The η(3914 Å) and η(3466 Å) values obtained in this manner are plotted in Figure 2.

ANALYSIS

Excitation Model With Temperature-Independent Quenching Coefficients

From the η(3914 Å) values and a suitable model atmosphere the N_2^+ loss rate from dissociative recombination, η_R, can be calculated as a function of altitude within the auroral arc by following the procedures outlined by *Jones and Rees* [1973] and *Vallance Jones* [1975]. In a similar manner the local atomic nitrogen production rate from dissociative excitation, η_d, can also be calculated from the λ3914-Å data by using the pertinent cross sections given by *Borst and Zipf* [1970] and by *Zipf and McLaughlin* [1978]. The λ3466-Å volume emission rate is related to these rates by the expression

$$\eta(3466\text{ Å}) = \frac{5.4 \times 10^{-3}\,[2f_R\eta_R + f_0\eta(3914)]}{0.0844 + k_4 n(\mathrm{O}) + k_1 n(\mathrm{O_2})} \tag{4}$$

where f_R is the ^2P quantum yield from process (2), and k_4 and k_1 are the rate coefficients for ^2P quenching by atomic oxygen and by O_2, respectively. For convenience the ^2P dissociative excitation source term, $f_d\eta_d$, has been expressed in terms of the local λ3914-Å volume emission rate, η(3914 Å), which was measured in this experiment; f_d is the ^2P quantum yield from process (3), and f_0 is a proportionality constant.

The overhead λ3466-Å intensity was then obtained by integrating (4):

$$I_z(3466\text{ Å}) = \int_z^\infty \eta(3466\text{ Å}; z')\,dz' \tag{5}$$

and the results compared with the observations given in Figure 1. Initially, the values of k_4 and k_1 given by *Young and Dunn* [1975] were adopted, and it was assumed that these coefficients were temperature independent; f_R and f_0 were used as adjustable parameters. The quality of the first-order fit to the overhead intensity data was further improved by making comparatively minor adjustments in the initial values for k_1, k_4, f_R, and f_0 until the solid λ3466-Å curve shown in Figure 1 was achieved with the following parameters: $k_1 = 2.0 \times 10^{-12}$ cm^3 s^{-1}; $k_4 = 1.2 \times 10^{-11}$ cm^3 s^{-1}; $f_0 = 4.1$; $f_R = 0.5$.

In this computation the O and O_2 densities were obtained from Sharp's Model Atmosphere A (1971) which is basically a CIRA 1965 model with $n(\mathrm{O}) = 7.6 \times 10^{10}$ cm^{-3} at 120 km. Since the fitting procedure that we have adopted effectively determines the products $k_4 n(\mathrm{O})$ and $k_1 n(\mathrm{O})$, the choice of a different model atmosphere will affect the specific values of k_4 and k_1 considerably, but not f_R and f_d. *Sharp* [1978] has ob-

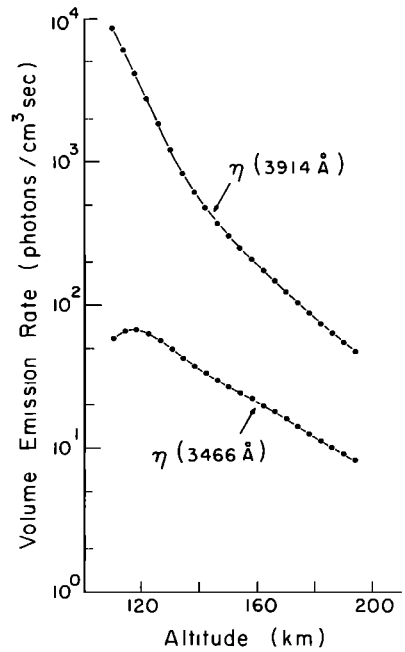

Fig. 2. The local λ3914-Å and λ3466-Å volume emission rates derived from the observed intensity data.

tained evidence based on a coordinated satellite-sounding rocket experiment [*Rees et al.*, 1977] that the atomic oxygen concentration in some auroral substorms is considerably lower (e.g., $n(O) = 2.8 \times 10^{10}$ cm^{-3} at 120 km) than those values adopted in this paper. If similar low $n(O)$ densities prevailed at the time of our experiment, the best fit k_4 value would increase to 3.6×10^{-11} cm^3 s^{-1}, which is significantly larger than the laboratory results of *Young and Dunn* [1975]. However, the new observational value would then be in good agreement with the preliminary laboratory work of *Golde and Thrusch* [1972].

The N(^2P) source functions inferred from this model are shown in Figure 3. The magnitudes of the rate coefficients k_1 and k_4 which have been derived from the in situ measurements are in good agreement with the laboratory work of *Young and Dunn* [1975]. The observational results show that atomic oxygen is the dominant N(^2P) quenching above 120 km, while O_2 contributes significantly to depopulating the N(^2P) state at E region altitudes. Dissociative excitation (3) is the dominant N(^2P) source, with N_2^+ dissociative recombination contributing less than 10% at altitudes below 195 km. Since the cross sections for the excitation of the N_2^+(0, 0) 1NG band,

$$e + N_2 \rightarrow N_2^+(B^2\Sigma_g^+) + 2e$$

$$N_2^+(B) \rightarrow N_2^+(X) + h\nu(\lambda 3914\ \text{Å})$$

and dissociative excitation (process (3)) are quite similar in shape [*Borst and Zipf*, 1970; *Zipf and McLaughlin*, 1978], the f_0 value of 4.1 implies an effective cross section for process (3) of approximately 7.2×10^{-17} cm^{-2} at 100 eV. Thus metastable N(^2P) atoms and N^+ ions are formed at comparable rates when 100-eV electrons impact on N_2, since the cross section for dissociative ionization

$$e + N_2 \rightarrow N^+ + N + 2e$$

has a value of 6.1×10^{-17} cm^2 at this energy.

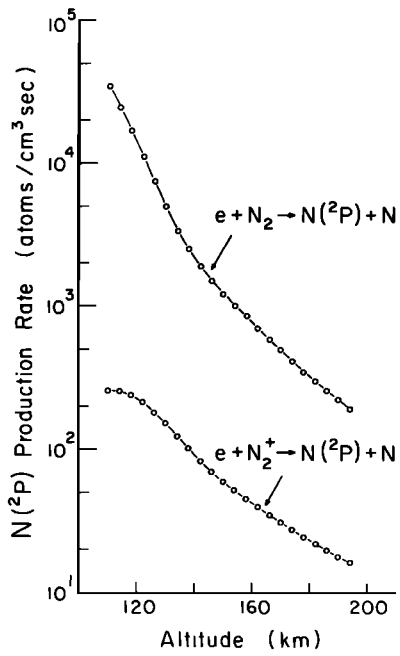

Fig. 3. The model 1 N(^2P) production rates from the dissociative excitation of N_2 by electron impact and from the dissociative recombination of N_2^+ ions.

Excitation Model With Temperature-Dependent Quenching Coefficients

Although the N(^2P) excitation model discussed in the preceding section (model 1) can reproduce the λ3466-Å observation data quite well, it is not without a number of problems. Firstly, the model 1 analysis concludes that N(^2P) atoms are formed by dissociative excitation with a comparatively large quantum yield (~17%). If this unexpectedly large value is verified by future experiments, it implies a considerably smaller N(^2D) yield than previously assumed by modelers. This reduction is a consequence of the discrete nature of the N_2 dissociative excitation process [*Zipf and McLaughlin*, 1978] which imposes conservation of energy constraints on the possible final atomic states that can be formed. The net effect of this constraint is than an enhanced N(^2P) yield is achieved at the expense of the ^2D state. Model 1 suggests that the N(^2D) quantum yield for process (3) is only 25%. This value is considerably smaller than current literature estimates based on nitric oxide studies [*Frederick and Rusch*, 1977; *McElroy et al.*, 1976] which are 2 to 4 times larger. Furthermore, the large implied N(^2P) quatum yield seems at variance with the estimates of the likely dissociation products based on spectroscopic arguments which strongly favor N(^2D) production [*Lofthus and Krupenie*, 1977]. These considerations suggest that model 1 considerably overestimates the N(^2P) yield from dissociative excitation of N_2. Second, the analysis also concludes that N(^2P) atoms are formed efficiently by the dissociative recombination of N_2^+ ions. However, this result is not compatible with recent theoretical studies of this process [*Michels*, 1979] nor with the findings of a preliminary plasma-spectroscopy experiment which indicates that the N(^2P) yield is less than 10% (E. C. Zipf, private communication, 1979). Third, it seems unlikely that the rate coefficient for N(^2P) quenching by atomic oxygen is independent of the temperature. Analogous processes involving metastable N(^2D) and O(^1S) atoms have a small but definite activation energy leading to Arrnehius exponential factors of exp (−500/RT) and exp (−610/RT), respectively [*Davenport et al.*, 1976; *Slanger and Black*, 1976]. If k_4 exhibits similar behavior, then the apparent agreement between model 1 and observation is purely fortuitous. This would imply that a significant source of N(^2P) atoms has been omitted from the analysis, a source that compensates for the loss of N_2^+ dissociative recombination as an effective ^2P production mechanism as well as for a diminished role for N_2 dissociative excitation.

In order to explore this possibility further, we assumed that k_4 does in fact have a modest temperature dependence,

$$k_4 = 2.8 \times 10^{-11} \exp(-500/\text{RT})$$

The preexponential factor has been chosen so that at room temperature (300°K), k_4 will have the measured laboratory value. Since the reaction of N(^2D) with O_2 exhibits very little temperature dependence [*Slanger et al.*, 1971], we assume that N(^2P) reacts with O_2 in a similar manner and therefore that the magnitude of k_1 is temperature independent. Having made these choices, the total $\eta(^2P)$ production rate can be readily calculated from the measured η(3466 Å) values plotted in Figure 2 and the relationship

$$\eta(^2P) = 185\eta(3466\ \text{Å})\,(0.0844 + k_4 n(O) + k_1 n(O_2)) \quad (6)$$

These results are compared with the $\eta_1(^2P)$ values from model 1 in Figure 4.

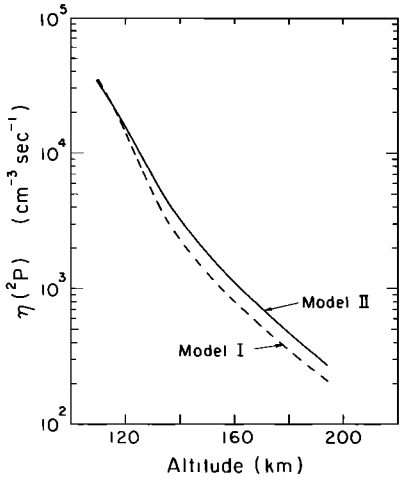

Fig. 4. Comparison of the total N(²P) production rates, η_I and η_{II}, inferred in models 1 and 2, respectively, from (6).

Since the altitude dependence of the ^2P dissociative excitation source function shown in Figure 3 is nearly the same as $\eta_I(^2P)$, the results of Figure 4 imply that the unidentified N(²P) source becomes progressively more important at high altitudes where it must supply 25% or more of the N(²P) atoms. Because this would require an effective production rate comparable to the λ3914-Å volume emission rate at these altitudes, processes involving direct excitation of ambient nitrogen atoms to the ^2P state can be ruled out, since they would require unrealistically large N densities. This suggests that the excited N(²P) atoms are formed as the by-products of an efficient, but overlooked, reaction or quenching process.

One intriguing possibility would be an ion-molecule reaction between vibrationally excited N_2^+ ions ($v' \geq 2$) and atomic oxygen:

$$N_2^+(v' \geq 2) + O \xrightarrow{k_5} NO^+ + N(^2P) \quad (7)$$

This exothermic process would be similar to the well-known N(²D) production mechanism

$$N_2^+(v' = 0) + O \xrightarrow{k_6} NO^+ + N(^2D) \quad (8)$$

which appears to have an N(²D) quantum yield near 100% [*Frederick and Rusch*, 1977]. Unfortunately, there have been no laboratory studies of reaction (7), so we have only indirect information to guide us in our speculation concerning the magnitude of k_5 and its dependence on the vibrational state of the N_2^+ ion. For example, in order to account for the rapid loss of N_2^+ ions in the sunlit ionosphere, *Biondi* [1978] suggested that the rate coefficient for process (7) might be considerably larger than that for the ground state ion-molecule reaction (process (8)). Reaction (7) would then behave in a manner analogous to the companion atom-transfer reaction

$$O^+ + N_2 \xrightarrow{k_7} NO^+ + N \quad (9)$$

which is slow for N_2 molecules in the $v' = 0$ vibrational level but exhibits a dramatic increase in rate coefficient when vibrationally excited molecules are involved. In this case the data of *Schmeltekopf et al.* [1968] show that the specific rate coefficients $k_7(v')$ have values near 4×10^{-10} cm^3 s^{-1} for the higher vibrational levels, and in the analysis that follows we have assumed that k_5 behaves similarly.

Of course, not all $N_2^+(v' \geq 2)$ ions formed by electron impact or by $O^+(^2D)$ quenching

$$O^+(^2D) + N_2 \xrightarrow{k_8} (N_2^+)_{excited} + O \quad (10)$$

in the aurora will result ultimately in the formation of an N(²P) atom, because reaction (7) must also compete with the excitation and charge transfer reactions

$$(N_2^+)_{vib} + N_2 \xrightarrow{k_9} N_2^+ + (N_2^+)_{vib} \quad (11)$$

and

$$N_2^+ + O_2 \xrightarrow{k_{10}} O_2^+ + N_2 \quad (12)$$

Reaction (12) and its temperature dependence have been studied by flowing afterglow and drift tube techniques [*Lindinger et al.*, 1974; *McFarland et al.*, 1974]. This process is a minor $(N_2^+)_{vib}$ loss mechanism except at E region altitudes. At this point, nothing definitive is known about the magnitude of k_9. However, preliminary drift tube work on vibrationally excited ions [*Lindinger et al.*, 1979] suggests that reaction (11) should be an efficient loss mechanism for vibrationally excited ions. For modeling purposes, we have arbitrarily adopted a k_9 value of 8×10^{-11} cm^3 s^{-1}.

One final loss mechanism for vibrationally excited N_2^+ ions needs to be considered; namely, dissociative recombination,

$$N_2^+(v') + e \xrightarrow{\alpha(v')} N + N \quad (13)$$

where $\alpha(v')$ is the specific recombination coefficient for ions in the v'th vibrational level. Based on an analysis of Atmospheric Explorer satellite data, *Orsini et al.* [1977] concluded that the dissociative recombination coefficients for the $v' = 1$ and 2 levels of the ground state are 22 and 35 times larger, respectively, than the $v' = 0$ value. Such large values would make reaction (13) a major sink for $(N_2^+)_{vib}$ under auroral conditions. However, *Zipf* [1979] has shown in a plasma spectroscopy experiment that the dissociative recombination coefficients for the $v' = 0$, 1, and 2 levels are nearly identical in magnitude and that the specific values are close to the averaged value reported by *Mehr and Biondi* [1969]. Thus when the laboratory results are combined with the ion chemistry developed for model 1, we find that dissociative recombination is not an important loss mechanism for vibrationally excited N_2^+ ions when compared with processes (7), (11), and (12).

The net N(²P) production rate from reaction (7) is related to the $N_2^+(v \geq 2)$ source term, $\eta[N_2^+(v' \geq 2)]$, by the expression

$$\eta'(^2P) = \eta[N_2^+(v' \geq 2)](k_5 n(O))/(k_5 n(O) + k_9 n(N_2) + k_{10} n(O_2) + \alpha n(e)) \quad (14)$$

In this model (model 2) we assume that there are two major sources of vibrationally excited N_2^+ ions under auroral conditions:

Electron impact and cascade

$$e + N_2 \rightarrow N_2^+(X^2\Sigma_g^+;\ v' \geq 2) + 2e \quad (15)$$

$$e + N_2 \rightarrow N_2^+(B^2\Sigma_u^+;\ A^2\pi_u) + 2e \quad (16)$$

$$N_2^+(B^2\Sigma_u^+;\ A^2\pi_u) \rightarrow N_2^+(X^2\Sigma_g^+;\ v' \geq 2) + h\nu \quad (17)$$

Charge transfer

$$O^+(^2D) + N_2 \xrightarrow{k_{11}} N_2^+(A^2\pi_u;\ X^2\Sigma_g^+) \quad (18)$$

The effective cross sections for the excitation of specific vibrational levels of the $N_2^+(X^2\Sigma_g^+)$ ground state due to direct excitation of the $B^2\Sigma_u^+$ and $A^2\pi_u$ states followed by the cascade emission of the N_2^+ first negative bands and the Meinel system can be calculated from the cross-section data and transition probabilities published for these states and band systems by *Shemansky and Broadfoot* [1971*a*, *b*], while the contribution due to direct excitation of the $N_2^+(X^2\Sigma_g^+)$ state can be estimated from Franck-Condon considerations, assuming that 30% of the N_2^+ total ionization cross section is identified with reaction (15) [*Shemansky and Broadfoot*, 1971*b*]. The effective excitation cross sections into specifically identified vibrational levels computed in this manner are given in Table 1. These results show that the $v' = 2$ level is excited at virtually the same rate as the λ3914-Å emission feature, while the total cross section for exciting $N_2^+(X^2\Sigma_g^+)$ ions to vibrational levels $v' \geq 2$ is nearly twice as large.

Vibrationally excited N_2^+ ions are also formed efficiently as the result of the $O^+(^2D) + N_2$ charge transfer reaction. In our model of this process, we assumed that $k_8 = 5 \times 10^{-10}$ cm^3 s^{-1}, and we used the method described by *Jones and Rees* [1973] to estimate the $O^+(^2D)$ production rate from the measured η(3914 Å) values. The actual distribution of excited states produced by reaction (18) is not known. There is some evidence, based on auroral spectral data, that reaction (18) results in enhanced $N_2^+(A^2\pi\ v' = 0, 1)$ population rates [*Vallance Jones and Gattinger*, 1978] which then excite the upper vibrational levels of the $X^2\Sigma_g^+$ state by cascade. Direct excitation of the $X^2\Sigma_g^+$ probably occurs to some extent too. For modeling purposes, we have assumed that the $v' = 1$ level of the $A^2\pi_u$ state is preferentially populated by reaction (18). With this assumption, about 24% of the $O^+(^2D)$ production rate results in the formation of $(N_2^+)_{vib}$ ions that can produce $N(^2P)$ atoms by reaction (7).

The $N(^2P)$ production due to vibrationally excited N_2^+ ions calculated from (14) is plotted in Figure 5. The contribution from dissociative excitation required to provide a good fit to the $\eta_{II}(^2P)$ values inferred from the measured η(3466 Å) data is also shown. In order to achieve a best fit in the least squares sense, an f_0 value of 3.9 was required. This value is immaterially different from the f_0 result deduced in model 1 (see section on analysis). Thus in spite of the reservations mentioned above, both models indicate that dissociative excitation of N_2 by electron impact is the primary ^2P excitation mechanism and that $N(^2P)$ atoms are formed by process (3) with a quantum yield approximately one half that for the $N(^2D)$ state.

TABLE 1. Effective Cross Sections for the Excitation of Vibrationally Excited $N_2^+(X^2\Sigma_g^+)$ Ions by Electron Impact

v'	Cross Section
2	1.77 (−17)*
3	7.01 (−18)
4	3.59 (−18)
5	9.51 (−19)
6	2.21 (−19)
7	6.22 (−20)
8	5.93 (−21)
Total	2.95 (−17)

*Read 1.77×10^{-17} cm^2.

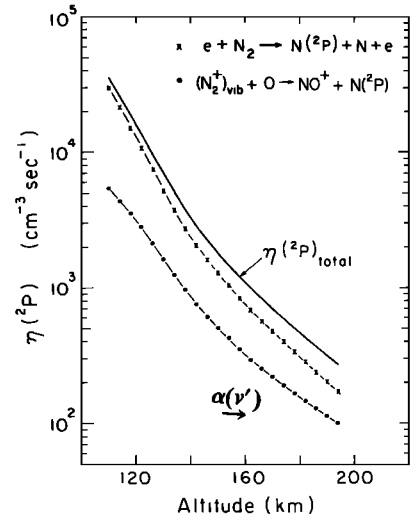

Fig. 5. The model 2 $N(^2P)$ production rates from the dissociative excitation of N_2 by electron impact and from reaction (7).

Specific Quantum Yields for Dissociation Excitation

The total cross section for electron impact dissociation of N_2,

$$e + N_2 \rightarrow N^+ + N + 2e \quad (19)$$

$$e + N_2 \rightarrow N + N + e \quad (20)$$

under optically thick conditions has a value of 2.2×10^{-16} cm^2 at 100 eV [*Zipf and McLaughlin*, 1978]. Dissociative ionization, which creates $N(^4S)$ and $N(^2D)$ atoms with equal probability but no $N(^2P)$ atoms [*Ehrhardt and Kresling*, 1967], accounts for 28% of this total (6.1×10^{-17} cm^2). Our observational results indicate that dissociative excitation forms $N(^2P)$ atoms with a 16% quantum yield (7×10^{-17} cm^2). Since the predissociation of N_2 $^1\pi$ and $^1\Sigma$ states with energies less than the dissociation limit for $N(^2P) + N(^2D)$ formation (15.7 eV) accounts for nearly 95% of the dissociative excitation cross section [*Zipf and McLaughlin*, 1978], the creation of $N(^2P)$ atoms by process (20) is accompanied almost always by an $N(^4S)$ atom. The predissociation of the $a^1\pi_g$ state and the numerous states belonging to the triplet systems of nitrogen (e.g., $C^3\pi_u$) leads only to the formation of $N(^4S)$ atoms. However, at 100 eV these dissociation channels contribute less than 1% to the total cross section.

Forty-two percent of the total cross section for N_2 dissociation remains to be accounted for. Once again, conservation of energy constraints limit the possible rate of $N(^2D)$ formation. Thus under the most favorable circumstances, ~85% of the predissociating singlet states will result in the formation of an $N(^4S) + N(^2D)$ pair, while the remaining states could in principal form two $N(^2D)$ atoms. Table 2 lists the specific cross sections for this optimum case at 100 eV.

The specific cross sections and excitation functions for the numerous $^1\pi$ and $^1\Sigma_u^+$ states that produce $N(^2D)$ and $N(^2P)$ atoms by predissociation are given in the paper by *Zipf and McLaughlin* [1978]. The excitation functions for $N(^2D)$ and $N(^2P)$ production by processes (19) and (20) can be evaluated

TABLE 2. Products of the Dissociation of N_2 by the Impact of 100-eV Electrons

	Specific Cross Sections ($\times 10^{-17}$ cm^2)			
	N^+	$N(^4S)$	$N(^2D)$	$N(^2P)$
Dissociation Channel				
$N^+ + N(^4S; ^2D)$	6.1	3.05	3.05	
$N(^4S) + N(^4S)$		~0.2		
$N(^4S + N(^2D)$		7.7	10.5	
$N(^4S) + N(^2P)$		7.2		7.2
Total	6.1	18.2	13.6	7.2
Quantum Yield	0.135	0.40	0.30	0.165

from these results by summing the contributions from the individual singlet states using the conservation of energy constraints and the auroral $N(^2P)$ measurements discussed above as a guide. The results of such an analysis are shown in Figure 6 and presented in detail in Table 3 in order to facilitate computational use.

DISCUSSION

The cross-section data presented in Figure 6 show that the net $N(^2D)$ and $N(^2P)$ production rates will vary with the character of the energy spectrum of the bombarding electrons. In the dayglow, low-energy photoelectrons will excite $N(^2D)$ atoms primarily by process (20), which is strongly dominated by the predissociation of the $N_2(b^1\pi_u)$ state. Under these conditions, dissociative ionization plays a minor role because it is effective only at high electron impact energies. Under auroral conditions, where there is an abundance of high-energy precipitating electrons, both excitation processes contribute.

The net $N(^2P)$ production rate depends also on the ultimate fate of the metastable $N(^2P)$ atoms which are formed efficiently by process (20). Above 200 km the majority of $N(^2P)$ atoms relax radiatively:

$$N(^2P) \rightarrow N(^2D) + h\nu(\lambda 10{,}400\ \text{Å})$$
$$\rightarrow N(^4S) + h\nu(\lambda 3446\ \text{Å})$$

with the formation of $N(^2D)$ atoms by cascade accounting for 94% of the $N(^2P)$ radiative loss rate. At lower altitudes, $N(^2P)$ quenching by O may also result in $N(^2D)$ formation either directly,

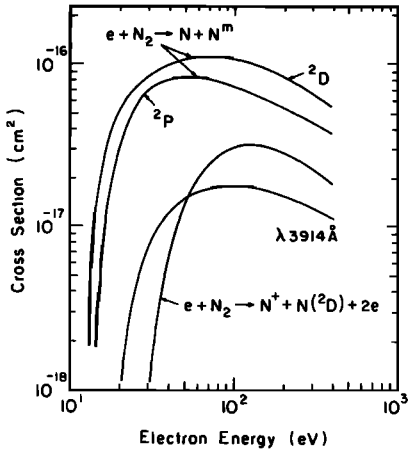

Fig. 6. Cross sections for the excitation of metastable $N(^2D)$ and $N(^2P)$ atoms by electron impact dissociation of N_2. The cross section for electron impact excitation of the N_2^+ (0, 0) first negative band (λ3914 Å) is plotted for comparison purposes.

$$N(^2P) + O \rightarrow N(^2D) + O \quad (21)$$

or indirectly by associative ionization [*Zipf*, 1978]:

$$N(^2P) + O \rightarrow NO^+ + e$$
$$NO^+ + e \rightarrow N(^2D) + O \quad (22)$$

Once again the net effect would be a $N(^2D)$ quantum yield equal to the sum of the specific ^2D and ^2P yields provided, of course, that the quenching process

$$N(^2P) + O \rightarrow N(^4S) + O \quad (23)$$

is a minor $N(^2P)$ loss mechanism. Below 120 km, $N(^2P)$ quenching by O_2 will decrease the effective $N(^2D)$ production, but since this process probably results in the formation of NO by chemical reaction,

$$N(^2P) + O_2 \rightarrow NO + O \quad (24)$$

the overall effect on nitric oxide production will still be as though the $N(^2D)$ quantum yield was equal to the total metastable yield from processes (19) and (20).

In order to investigate the dependence of the metastable quantum yield on the detailed shape of the secondary electron energy spectrum, we calculated the flux-averaged cross sections,

$$\bar{\sigma} = \frac{\int \sigma(\epsilon)\,\phi(\epsilon)\,d\epsilon}{\int \phi(\epsilon)\,d\epsilon}$$

for the specific excitation mechanisms (19) and (20) and for the total N_2 dissociation process using the cross-section data, $\sigma(\epsilon)$, from Table 3 and the measured auroral and photoelectron energy spectra, $\phi(\epsilon)$, published by *Feldman and Doering* [1975] and *Doering et al.* [1975], respectively. From these values we estimated the flux-averaged quantum yields which are given in Table 4. For comparison purposes we have also tabulated the quantum yields obtained for the auroral case using the theoretical secondary electron spectrum published by *Rees and Jones* [1973].

The results presented in Table 4 show that the net metastable yield [$^2D + ^2P$] is nearly independent of the spectral energy characteristics of the bombarding electrons. However, when the high-energy component of the secondary electron flux is reduced (compare the measured auroral and photoelectron fluxes), the N^+ yield decreases noticeably, while the $N(^2P)/N(^2D)$ ratio increases from 0.57 to 0.81. The flux-averaged quantum yield for $N(^2P)$ atoms under auroral conditions (17–20%) obtained in this study is in good agreement with the value of 20% reported by *Gerard and Harang* [1978] derived from ground-based studies of the ^2P multiplet radiation. However, the net metastable yield of about 47% is somewhat smaller than the values of 60–70% derived from auroral and mid-latitude nitric oxide models [*Rusch et al.*, 1978; *Cravens et al.*, 1979]. The results of both studies would be in still better agreement if the N^+ charge transfer reaction with O_2 formed $N(^2D)$ atoms efficiently,

$$N^+ + O_2 \rightarrow O_2^+ + N(^2D)$$

SUMMARY

From an analysis of λ3466-Å and λ3914-Å auroral data and from complementary laboratory studies of electron impact ex-

TABLE 3. Cross Sections for the Excitation of Metastable N(^2D) and N(^2P) Atoms by Electron Impact Dissociation of N_2

Energy, eV	^2D Cross Section, Process (20)	^2D Cross Section, Process (19)	Total ^2D Cross Section	Total ^2P Cross Section	Total N_2 Dissociation Cross Section*
10.5	...	...	...	...	1.27 (−18)
10.5	...	...	...	...	1.87 (−18)
11.0	...	...	...	...	2.49 (−18)
12.0	...	...	...	...	4.92 (−18)
13.0	...	...	...	...	1.12 (−17)
13.5	4.00 (−18)†	...	4.00 (−18)	...	1.60 (−17)
14.0	8.60 (−18)	...	8.60 (−18)	...	2.43 (−17)
14.5	1.25 (−17)	...	1.25 (−17)	2.20 (−18)	2.85 (−17)
15.0	1.67 (−17)	...	1.67 (−17)	3.50 (−18)	3.58 (−17)
15.5	2.04 (−17)	...	2.04 (−17)	5.40 (−18)	4.00 (−17)
16.0	2.42 (−17)	...	2.42 (−17)	8.00 (−18)	4.75 (−17)
17.0	3.12 (−17)	...	3.12 (−17)	1.27 (−17)	5.65 (−17)
18.0	3.75 (−17)	...	3.75 (−17)	1.83 (−17)	6.82 (−17)
19.0	4.37 (−17)	...	4.37 (−17)	2.38 (−17)	7.82 (−17)
20.0	4.91 (−17)	...	4.91 (−17)	2.90 (−17)	8.56 (−17)
22.0	5.85 (−17)	...	5.85 (−17)	3.92 (−17)	1.05 (−16)
24.0	6.67 (−17)	...	6.67 (−17)	4.78 (−17)	1.20 (−16)
26.0	7.35 (−17)	...	7.35 (−17)	5.56 (−17)	1.36 (−16)
28.0	7.82 (−17)	...	7.82 (−17)	6.22 (−17)	1.47 (−16)
30.0	8.23 (−17)	9.75 (−19)	8.33 (−17)	6.75 (−17)	1.58 (−16)
33.0	8.73 (−17)	2.05 (−18)	8.94 (−17)	7.22 (−17)	1.67 (−16)
36.0	9.12 (−17)	3.75 (−18)	9.50 (−17)	7.57 (−17)	1.75 (−16)
39.0	9.42 (−17)	5.40 (−18)	9.96 (−17)	7.77 (−17)	1.82 (−16)
42.0	9.70 (−17)	7.85 (−18)	1.05 (−16)	7.90 (−17)	1.88 (−16)
45.0	9.90 (−17)	9.60 (−18)	1.09 (−16)	8.00 (−17)	1.94 (−16)
50.0	1.02 (−16)	1.35 (−17)	1.16 (−16)	8.10 (−17)	2.03 (−16)
55.0	1.03 (−16)	1.70 (−17)	1.20 (−16)	8.07 (−17)	2.10 (−16)
60.0	1.04 (−16)	1.95 (−17)	1.24 (−16)	8.05 (−17)	2.16 (−16)
70.0	1.06 (−16)	2.35 (−17)	1.30 (−16)	7.95 (−17)	2.24 (−16)
80.0	1.08 (−16)	2.65 (−17)	1.35 (−16)	7.70 (−17)	2.27 (−16)
90.0	1.07 (−16)	2.90 (−17)	1.36 (−16)	7.42 (−17)	2.27 (−16)
100	1.05 (−16)	3.05 (−17)	1.36 (−16)	7.17 (−17)	2.24 (−16)
120	1.01 (−16)	3.15 (−17)	1.33 (−16)	6.63 (−17)	2.16 (−16)
140	9.60 (−17)	3.10 (−17)	1.27 (−16)	6.22 (−17)	2.05 (−16)
160	9.10 (−17)	3.03 (−17)	1.21 (−16)	5.85 (−17)	1.94 (−16)
180	8.65 (−17)	2.92 (−17)	1.16 (−16)	5.53 (−17)	1.86 (−16)
200	8.23 (−17)	2.80 (−17)	1.10 (−16)	5.25 (−17)	1.76 (−16)
250	7.25 (−17)	2.48 (−17)	9.73 (−17)	4.70 (−17)	1.65 (−16)
300	6.50 (−17)	2.22 (−17)	8.72 (−17)	4.30 (−17)	1.39 (−16)
350	5.85 (−17)	1.98 (−17)	7.83 (−17)	3.95 (−17)	1.25 (−16)
400	5.32 (−17)	1.83 (−17)	7.15 (−17)	3.70 (−17)	1.14 (−16)

*_Zipf and McLaughlin_ [1978].
†Read 4.00×10^{-18} cm^2.

citation of N_2 and of N_2^+ dissociative recombination, we have found the following:

1. The dominant N(^2P) source in auroras is electron impact dissociation of N_2. N^+, N(^2P), N(^2D), and N(^4S) atoms are formed by this process with a quantum yield of 0.135:0.165:0.30:0.40, respectively, under optically thick conditions.

TABLE 4. Flux-Averaged Quantum Yields for the Atomic Fragments Produced by Electron Impact Dissociation of N_2

Species	Aurora: Measured Secondary Electron Spectrum*	Aurora: Calculated Secondary Electron Spectrum†	Dayglow: Measured Photoelectron Energy Spectrum‡
N(^4S)	0.42	0.48	0.49
N(^2D)	0.30	0.27	0.27
N(^2P)	0.17	0.20	0.22
N^+	0.11	0.05	0.02

* _Feldman and Doering_ [1975].
†_Rees and Jones_ [1973].
‡_Doering et al._ [1975].

2. The dissociative recombination of N_2^+ ions is a minor (perhaps even negligible) N(^2P) source.

3. Indirect evidence that vibrationally excited $N_2^+(v' \geq 2)$ ions react rapidly with atomic oxygen to form N(^2P) atoms was obtained.

4. Atomic oxygen is the dominant N(^2P) quenching agent. At 300°K the rate coefficient for this loss process has a value of 1×10^{-11} cm^3 s^{-1} in agreement with recent laboratory studies.

5. Molecular oxygen contributes to the depopulation of the N(^2P) state in the auroral _E_ region, and this species becomes the dominant quenching agent in the _D_ region and below where the destruction of metastable N(^2P) atoms probably results in the formation of NO.

Acknowledgments. This research was supported in part by the Planetary Atmospheres program of the National Aeronautics and Space Administration under grants NGL 39-011-030 and NSG 6011 and by the National Science Foundation, Atmospheric Science section under grant ATM-7820538.

The Editor thanks P. D. Feldman, D. G. Torr, and W. E. Sharp for their assistance in evaluating this paper.

REFERENCES

Biondi, M. A., Objections to the $N_2^+ + e^-$ dissociative recombination coefficients inferred from analysis of Atmospheric Explorer measurements, *Geophys. Res. Lett., 5,* 661, 1978.

Borst, W. L., and E. C. Zipf, Cross section for electron-impact excitation of the (0, 0) first negative band of N_2^+ from threshold to 3 keV, *Phys. Rev. A., 1,* 834, 1970.

Chamberlain, J. W., *Physics of the Aurora and Airglow,* Academic, New York, 1961.

Cravens, T. E., J. C. Girard, A. I. Steward, and D. W. Rusch, The latitudinal gradient of nitric oxide in the thermosphere, *J. Geophys. Res., 84,* 2675, 1979.

Davenport, J. E., T. G. Slanger, W. E. Potter, and G. Black, The quenching of N(^2D) by O(^3P), *J. Geophys. Res., 81,* 12, 1976.

Deans, A. J., and G. G. Shepard, Rocket measurements of oxygen and nitrogen emissions in the aurora, *Planet. Space Sci., 26,* 319, 1978.

Doering, J. P., W. K. Peterson, C. O. Bostrom, and J. C. Armstrong, Measurement of low-energy electrons in the day airglow and dayside auroral zone from Atmospheric Explorer C, *J. Geophys. Res., 80,* 3934, 1975.

Ehrhardt, H., and A. Kresling, Die dissoziative Ionisation von N_2, O_2, H_2O, CO_2 und athan, *Z. Naturforsch., 22a,* 2036, 1967.

Feldman, P. D., Auroral excitation of optical emissions of atomic and molecular oxygen, *J. Geophys. Res., 83,* 2511, 1978.

Feldman, P. D., and J. P. Doering, Auroral electrons and optical emissions of nitrogen, *J. Geophys. Res., 80,* 2808, 1975.

Frederick, J. E., and D. W. Rusch, On the chemistry of metastable atomic nitrogen in the *F* region deduced from simultaneous measurements of the 5200-Å airglow and atmospheric composition, *J. Geophys. Res., 82,* 3509, 1977.

Girard, J. C., and O. E. Harang, The N(^2P) auroral excitation and quenching, paper presented at International Symposium on Solar-Terrestial Physics, Comm. on Space Res., Innsbruck, 1978.

Golde, M. F., and B. A. Thrusch, Faraday Disc. Chem. Soc., *53,* 233, 1972.

Husain, D., S. K. Mitra, and A. N. Young, Kinetic study of electronically excited nitrogen atoms, N(2^2D_J, 2^2P_J), by attenuation of atomic resonance radiation in the vacuum ultraviolet, *J. Chem. Soc. Faraday Trans. 2, 70,* 1721, 1974.

Jones, R. A., and M. H. Rees, Time dependent studies of the aurora, I, Ion density and composition, *Planet. Space Sci., 21,* 537, 1973.

Lindinger, W., F. C. Fehsenfeld, A. L. Schmeltekopf, E. E. Ferguson, Temperature dependence of some ionospheric ion-neutral reactions from 300° to 900° K, *J. Geophys. Res., 79,* 4753, 1974.

Lindinger, W., D. L. Albritton, and F. C. Fehsenfeld, Reactions of drift-induced, vibrationally excited ions, *Bull. Amer. Phys. Soc., 24,* 128, 1979.

Lofthus, A., and P. H. Krupenie, The spectrum of molecular nitrogen, *J. Phys. Chem. Ref. Data, 6,* 113, 1977.

McElroy, M. B., T. Y. Kong, Y. L. Yung, and A. O. Nier, Composition and structure of the Martian upper atmosphere: Analysis of the results from Viking, *Science, 194,* 1295, 1976.

McFarland, M., D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, Energy dependence and branching ratio of the $N_2^+ + O$ reaction, *J. Geophys. Res., 79,* 2925, 1974.

Mehr, F. J., and M. A. Biondi, Electron temperature dependence of recombination of O_2^+ and N_2^+ ions with electrons, *Phys. Rev., 181,* 264, 1969.

Michels, H. H., Electronic structure of excited states of selected atmospheric systems, in *The Excited State in Chemical Physics,* edited by J. W. McGowan, John Wiley, New York, 1979.

Orsini, N., D. G. Torr, H. C. Brinton, L. H. Brace, W. B. Hanson, J. H. Hoffman, and A. O. Nier, Determination of the N_2^+ rate coefficient in the ionosphere, *Geophys. Res. Lett., 4,* 431, 1977.

Rees, M. H., and R. A. Jones, Time dependent studies of the aurora, II, Spectroscopic morphology, *Planet. Space Sci., 21,* 1213, 1973.

Rees, M. H., A. I. Steward, W. E. Sharp, P. B. Hays, R. A. Hoffman, L. H. Brace, J. P. Doering, and W. K. Peterson, Coordinated rocket and satellite measurements of an auroral event, 1, Satellite observations and analysis, *J. Geophys. Res., 82,* 2250, 1977.

Rusch, D. W., J-C. Gerard, and W. E. Sharp, The reaction of N(^2D) with O_2 as a source of O(^1D) atoms in aurorae, *Geophys. Res. Lett., 5,* 1043, 1978.

Schmeltekopf, A. L., E. E. Ferguson, and F. C. Fehsenfeld, Reaction of atomic oxygen ions with vibrationally excited nitrogen molecules, *J. Chem. Phys., 48,* 2966, 1968.

Sharp, W. E., Rocket-borne spectroscopic measurements of the ultraviolet aurora: Nitrogen Vegard-Kaplan bands, *J. Geophys. Res., 76,* 987, 1971.

Sharp, W. E., NO_2 continuum in aurora, *J. Geophys. Res., 83,* 4373, 1978.

Shemansky, D. E., and A. L. Broadfoot, Excitation of N_2 and N_2^+ systems by electrons, I, Absolute transition probabilities, *J. Quant. Spectrosc. Radiat. Transfer, 11,* 1385, 1971*a*.

Shemansky, D. E., and A. L. Broadfoot, Excitation of N_2 and N_2^+ systems by electrons, II, Excitation cross sections and N 1PG low pressure afterglow, *J. Quant. Spectrosc. Radiat. Transfer, 11,* 1401, 1971*b*.

Slanger, T. G., and G. Black, O(^1S) quenching by O(^3P), *J. Chem. Phys., 64,* 3763, 1976.

Slanger, T. G., B. J. Wood, and G. Black, Temperature coefficients for N(^2D) quenching by O_2 and N_2O, *J. Geophys. Res., 76,* 8430, 1971.

Vallance Jones, A., A model for the excitation of electron aurora and some applications, *Can. J. Phys., 53,* 2267, 1975.

Vallance Jones, A., and R. L. Gattinger, Quantitative spectroscopy of the aurora, III, The spectrum of medium intensity aurora between 3100 Å and 4700 Å, *Can. J. Phys., 53,* 1806, 1975.

Vallance Jones, A., and R. L. Gattinger, Quantitative spectroscopy of the aurora, IV, The spectrum of medium intensity aurora between 8800 Å and 11,400 Å, *Can. J. Phys., 54,* 2128, 1976*a*.

Vallance Jones, A., and R. L. Gattinger, Quenching of the N_2 Vegard-Kaplan system in aurora, *J. Geophys. Res., 81,* 497, 1976*b*.

Vallance Jones, A., and R. L. Gattinger, Vibrational development and quenching effects in the $N_2(B^3\pi_g - A^3\Sigma_u^+)$ and $N_2^+(A^2\pi_u - X^2\Sigma_g^+)$ systems in aurora, *J. Geophys. Res., 83,* 3255, 1978.

Young, R. A., and O. J. Dunn, The excitation and quenching of N(^2P), *J. Chem. Phys., 63,* 1150, 1975.

Zipf, E. C., N(^2P) and N(^2D) atoms: Their production by *e*-impact dissociation of N_2 and destruction by associative ionization, *Eos Trans. AGU, 59,* 336, 1978.

Zipf, E. C., Dissociative recombination of vibrationally excited N_2^+ ions, *Bull. Amer. Phys. Soc., 24,* 129, 1979.

Zipf, E. C., and R. W. McLaughlin, On the dissociation of nitrogen by electron impact and by EUV photo-absorption, *Planet. Space Sci., 26,* 449, 1978.

(Received April 27, 1979;
revised August 15, 1979;
accepted September 4, 1979.)