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Nitrogen Ions In The Upper Atmosphere

R. B. NORTON

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Boulder, Colorado

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Nitrogen Ions In The Upper Atmosphere

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INSTITUTE FOR TELECOMMUNICATION SCIENCES AND AERONOMY
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Abstract

The chemistry for atomic and molecular nitrogen ions is discussed and detailed calculations for these ions are found to agree with rocket observations obtained between 140 and 240 km. Dissociative ionization of N_2 appears to be the major source of N^+ in this region but is adequate only if either the $N^+ + O_2$ rate coefficient is about $2 \times 10^{-10} cm^3 sec^{-1}$, or the cross section for dissociative ionization of N_2 by ultraviolet radiation is larger than the value measured by Weissler et al. [1959]. Charge exchange between $O^+(^2D)$ and N_2 may be an important source of N_2^+ in the F region. The column content of NO above 125 km is estimated to be about $7 \times 10^{12} cm^{-3}$ which is in reasonable agreement with observation. The atomic nitrogen concentration was estimated to be about $2.5 \times 10^7 cm^{-3}$ at 140 km and $8 \times 10^6 cm^{-3}$ at 240 km for daytime sunspot minimum conditions.

NITROGEN IONS IN THE UPPER ATMOSPHERE

R. B. Norton

1. Introduction

Holmes et al. [1965] have recently published the first experimental height profiles of N^+ and N_2^+. Prior to their publication, the concentration of these ions in the earth's upper atmosphere were only approximately known. Russian satellite experiments [Mirtov, 1961] indicated that the N^+ concentration was about 1% of the total ion concentration at 200 km and increased to 5 or 6% at 400 km. Airglow observations [Slipher, 1933] taken more than 3 decades ago, indicated that N_2^+ was present in the upper atmosphere and early rocket experiments indicated that its concentration in the F1 region was of the order of $10^3 cm^{-3}$.

Since N_2 is a major constituent of the atmosphere even at 200 km, it is not surprising that its ion should occur in the upper atmosphere. Indeed, the surprise might be that N_2^+ is a minor ion and that N^+ has a comparable concentration even though N is a minor constituent. The chemistry for these two ions is discussed in the following sections and detailed calculations for 130 to 240 km are compared with the observations of Holmes et al. [1965].

The neutral atmospheric model, presented in figure 1 and used in the calculations, is based mainly on the observations of Hedin et al. [1964] which were taken under approximately the same conditions as the ion data. However, the neutral atomic nitrogen and nitric oxide concentrations were calculated and are described in the following section. The solar ionizing flux was taken from Hinteregger et al. [1965]. The ionizing cross sections were taken from the tabulations of Norton et al. [1963], except for the

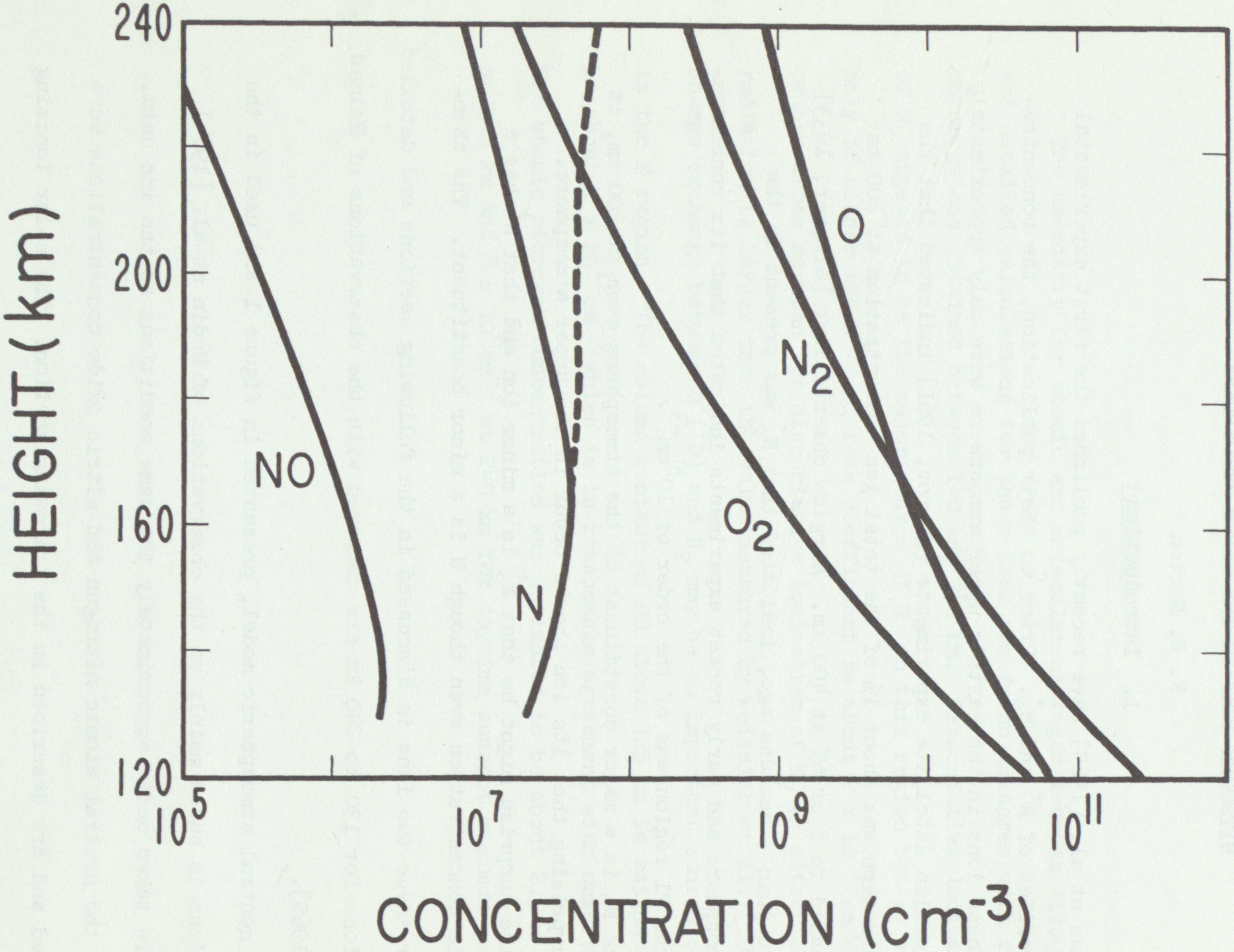

Figure 1. The neutral concentration is plotted against altitude. The O, O_2, and N_2 concentrations are based essentially on the observations of Hedin et al. [1964]. The N and NO concentrations were calculated and are described in the text.

atomic nitrogen cross sections which were obtained from Dalgarno and Parkinson [1960], Weissler et al. [1959], and Rapp et al. [1965]. The photoionization rates are shown in figure 2. The rate coefficients to be used are listed in table 1.

2. Atomic Nitrogen Ions

Bauer [1966], in a discussion of the N^+ ion, was primarily concerned with the concentration at much greater altitudes than we are considering here; however, he does argue that these ions in the F1 region are produced by direct photoionization of N. Earlier, Nicolet, and Swider [1963] in a comprehensive review of the ionospheric chemistry suggested that the N^+ was formed by dissociative ionization of N_2. We will demonstrate that this latter process is indeed the most significant. However, since there are no experimental data for atomic nitrogen, we must first estimate its concentration.

In the following sections the number density is indicated by brackets, thus [N] is the atomic nitrogen concentration. Neutral-neutral rate coefficients are designated by γ_{ij}; where the i and j denote the reactants and where 0, 1, 2, 3, and 4 represent O, O_2, N_2, NO, and N, respectively. Ion-neutral rate coefficients are denoted by k_{ij}, where the i refers to the ion and j to the neutral. This is the same notation used earlier [Norton et al., 1963]. The dissociate recombination rate coefficients are denoted by α_i and ionization rates are denoted q_i.

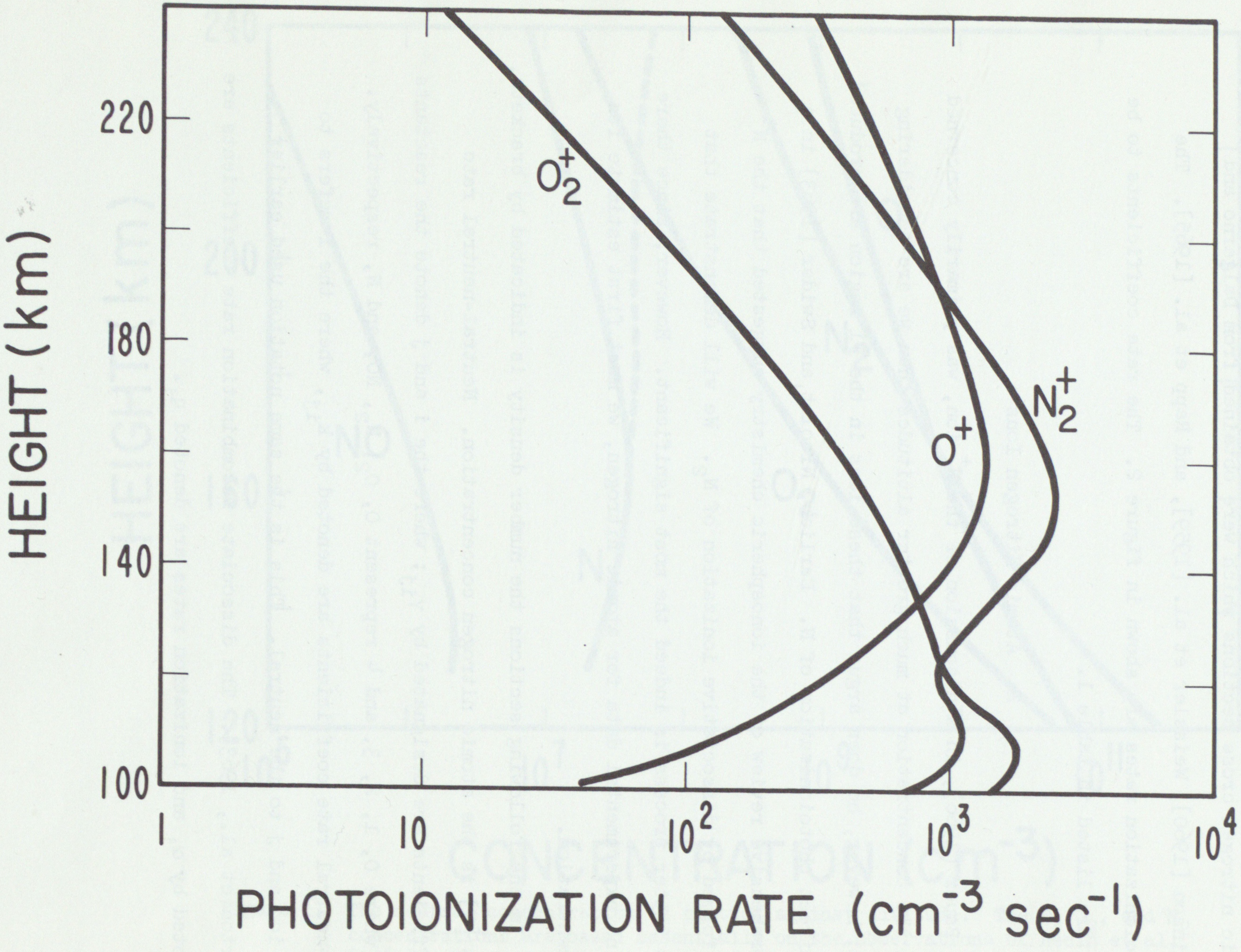

Figure 2. The photoionization rates for the major gases are plotted against altitude.

Table 1

Reaction	Rate	Coefficient ($cm^3 sec^{-1}$)	Reference
$N + NO \rightarrow N_2 + O$	γ_{43}	$1.5x10^{-12}\ T^{\frac{1}{2}}$	*
$N + O_2 \rightarrow NO + O$	γ_{41}	$2x10^{-13}\ T^{\frac{1}{2}}\ e^{-\frac{3000}{T}}$	*
$N^+ + O_2 \rightarrow NO^+ + O$	k_{41}	$\lesssim 5x10^{-10}$	Ferguson et al. [1965]
$N^+ + O_2 \rightarrow O_2^+ + N$	k'_{41}	$\sim 5x10^{-10}$	"
$N_2^+ + O \rightarrow NO^+ + N$	k_{20}	$2.5x10^{-10}$	"
$O^+ + N_2 \rightarrow NO^+ + N$	k_{02}	$3x10^{-12}$	"
$O_2^+ + N_2 \rightarrow NO^+ + NO$	k_{12}	$< 10^{-15}$	"
$NO^+ + e \rightarrow N + O$	α_3	$5x10^{-7}\ (300/T)^{1.3}$	†

† This value was obtained by comparing theoretical calculations of NO^+ with the observations of Holmes et al. [1965]. It agrees quite well with similar determinations by Ferguson et al. [1965] and Donahue [1966].

* These values were taken from a review by Nicolet [1965a].

The principal sources for N are

$$NO^+ + e \rightarrow N + O \tag{1}$$

$$N_2^+ + O \rightarrow NO^+ + N \tag{2}$$

$$O^+ + N_2 \rightarrow NO^+ + N \quad . \tag{3}$$

Photodissociation of neither N_2 nor NO contribute significantly at these altitudes, nor does dissociative recombination of N_2^+ contribute very much.

The main loss processes are

$$N + O_2 \rightarrow NO + O \tag{4}$$

$$N + NO \rightarrow N_2 + O \quad . \tag{5}$$

Direct recombination of atomic nitrogen in either a two-or three-body reaction is negligible at these heights, as are both the two- and the three-body reactions with atomic oxygen. The ion-neutral reaction with O_2^+ can be neglected to the first order.

In order to estimate the contribution of reaction (5) to the loss of N, we need to know the concentration of NO. Barth [1966] has determined, from rocket observations of the gamma band dayglow of NO, that the NO column content above 125 km was about $9 \times 10^{12} cm^{-2}$ and that its concentration at 125 km was about $3.6 \times 10^6 cm^{-3}$. However, there are no measurements of NO at greater heights and we must calculate the NO concentration. The main source for NO is reaction (4). The reaction suggested by Nicolet [1965b]

$$O_2^+ + N_2 \rightarrow NO^+ + NO \tag{6}$$

does not contribute significantly at these altitudes for k_{12} less than about $10^{-15} cm^3 sec^{-1}$. The main loss for NO is reaction (5); photodissociation and ionization of NO, and charge exchange with O^+, O_2^+, N^+, and N_2^+ are small in comparison. Thus the NO concentration is independent of N as originally suggested by Barth [1961].

The concentrations of N and NO calculated from reactions (1)-(5) and rate coefficients from table 1 are shown in figure 1. The ion densities used in these calculations were obtained from Holmes et al. [1965]. The column content of NO above 125 km is about $7 \times 10^{12} cm^{-2}$ which agrees reasonably well with Barth's measurement.

Two distributions are given for atomic nitrogen: one corresponding to the photochemical calculation and the other including a molecular diffusion correction. If the photochemical and diffusion time constants are compared, it is found that they are equal at about 150 km. Thus it was assumed that photochemistry determined the atomic nitrogen profile below this height and diffusion above this height. Diffusion does not significantly influence the nitric oxide distribution below about 230 km.

The possible sources for N^+ are

$$N + h\nu \rightarrow N^+ + e \qquad (7)$$

$$N + e \rightarrow N^+ + 2e \qquad (8)$$

$$N_2 + h\nu \rightarrow N^+ + N + e \qquad (9)$$

$$N_2 + e \rightarrow N^+ + N + 2e \qquad (10)$$

$$N_2^+ + N \rightarrow N^+ + N_2 \qquad (11)$$

$$He^+ + N_2 \rightarrow N^+ + N + He \quad . \qquad (12)$$

The electrons on the left-hand side of (8) and (10) are photoelectrons. If the cross sections of Dalgarno and Parkinson [1960] and the diffusion modified model for N are used, then the direct ionization of atomic nitrogen (Reaction (7)) produces N^+ at a rate which varies from 2 $cm^{-3}sec^{-1}$ at 160 km to less than 1 $cm^{-3}sec^{-1}$ at 240 km. According to Weissler et al. [1959], the cross section for dissociative ionization of N_2 by photons (Reaction (9)) to form N^+ is less than 1% of the cross section to form N_2^+, thus this process contributes N^+ at a rate of about 15 $cm^{-3}sec^{-1}$ at 160 km and about 1 $cm^{-3}sec^{-1}$ at 240 km.

However, Rapp et al. [1965] have reported that the cross section for dissociative ionization by electron impact (Reaction (8)) can be a large fraction of the total cross section, about 20-25% of the ionizing impacts lead to N^+. Photoelectrons produce about 20% of the total ionization between 160-240 km under the assumption that the photoelectrons are produced and ionize "locally." Therefore about 4% of the N_2 ionized by photoelectrons results in N^+ and thus q_{2D} is about 6 $cm^{-3}sec^{-1}$ at 240 km and nearly 95 $cm^{-3}sec^{-1}$ at 160 km.

The coefficient for charge exchange (k_{24}) between N_2^+ and N (Reaction (11)) has not been measured, but is expected to be less than about 10^{-12} cm^3sec^{-1}. This value of the coefficient leads to a production rate that is entirely negligible unless either k_{24} is much larger than $10^{-12} cm^3sec^{-1}$ or [N] much larger than estimated. Another process leading to N^+ formation involves the dissociative charge transfer between He^+ and N_2 (Reaction (12)). A production rate of N^+ of less than 1 $cm^{-3}sec^{-1}$ is estimated with the He concentration obtained from CIRA [1965] and a rate coefficient of 10^{-9} cm^3 sec^{-1}. It therefore seems that dissociative ionization is the major source of N^+ ions below 240 km, although direct ionization and dissociative charge exchange with He^+ contribute near 240 km. However, at great heights charge exchange between He^+ and N_2 probably dominates [Bauer, 1966].

The N^+ ions are lost mainly in a branching reaction with O_2

$$N^+ + O_2 \rightarrow NO^+ + O \qquad (13)$$

$$N^+ + O_2 \rightarrow O_2^+ + N \quad . \qquad (14)$$

The photochemical time constant is only 3 or 4 minutes even at 240 km so that diffusion should not be important at these heights and the steady state approximation should be quite adequate.

The calculation of N^+ in figure 3 for $k_{41} = 2 \times 10^{-10}$ agrees fairly well with the observations except that the calculated concentration decreases with increasing altitude more rapidly than does the observed. The significance of this discrepancy is not clear since Holmes et al. [1965] found it necessary to apply a height dependent correction to the total ion density in order to obtain agreement with the electron density. However, if the discrepancy is real, then k_{41} might decrease with increasing temperature or the other production mechanisms may be more important than estimated.

According to Rapp et al. [1965], the N^+ ions formed by dissociative ionization have considerable kinetic energy, .25 ev or more, and it might seem possible that the calculated profile could be altered, either through a more rapid diffusion or through an energy dependent rate coefficient, because of these hot ions. Spitzer [1962] has discussed the problem of a plasma containing two ions at different effective temperatures, and he defines a time constant τ_e for the ions to reach equilibrium. We have estimated that τ_e should be a few seconds, which is considerably smaller than the

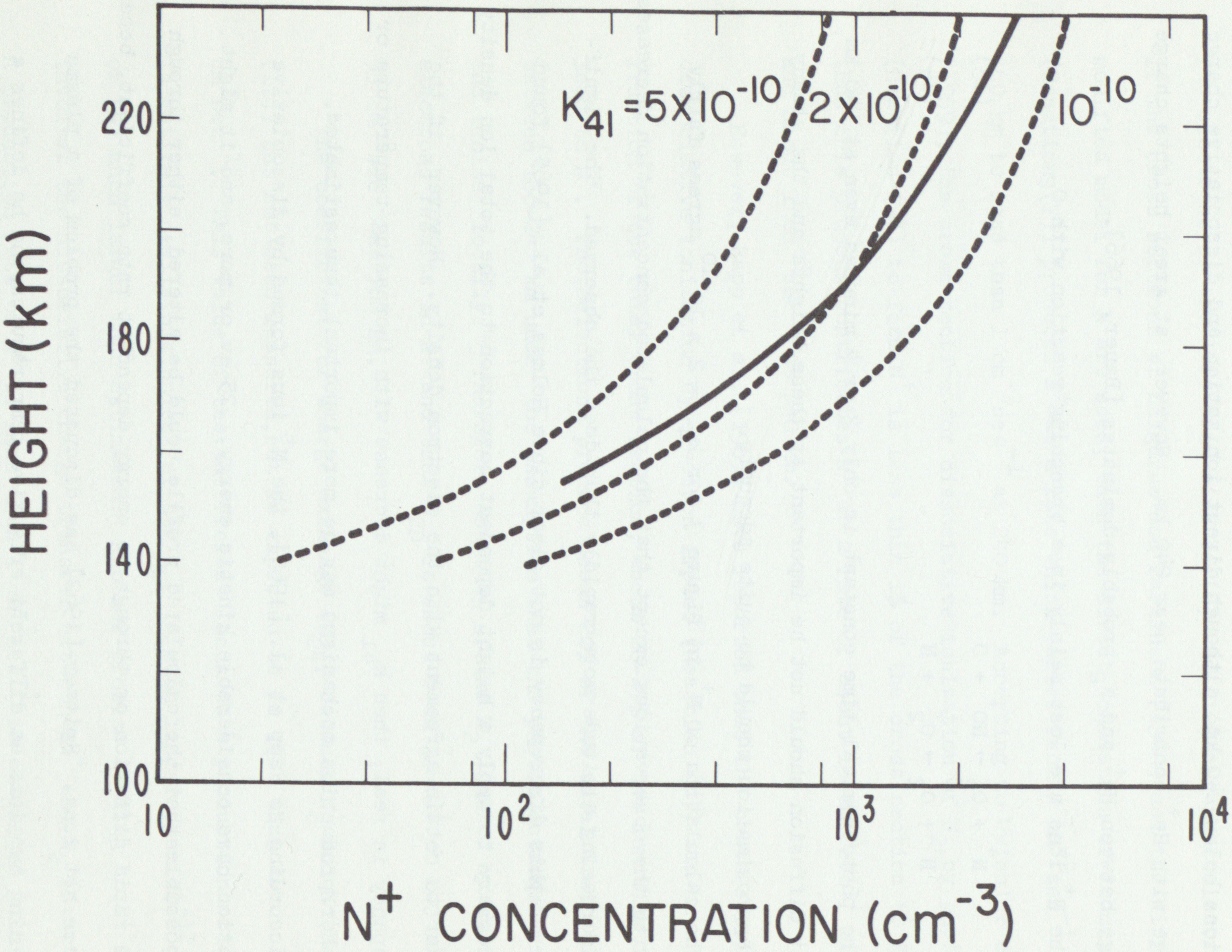

Figure 3. The curve (——) is the observed N^+ concentration [Holmes et al., 1965] plotted against altitude. For comparison with the observations, calculated N^+ concentrations (- -) for three values of k_{41} are plotted against altitude.

photochemical lifetimes except at the lowest heights.

The large difference in the dissociative ionization efficiencies (less than 1% for photons and 20% for energetic electrons) suggest that one of the measurements is in error. If the efficiency for dissociative ionization by energetic electrons is much smaller than the measured value [Rapp et al., 1965], then the problem of an adequate source for N^+ becomes serious. On the other hand, if the efficiency for dissociative ionization by photons is much larger than the measured value [Weissler et al., 1959], then the N^+ production rate is larger than estimated above and a larger value of the loss coefficient, k_{40}, more in agreement with laboratory measurements, should be used. McElroy [1966] recently suggested that the measured value of Weissler et al. [1959] is in error and that the efficiency for dissociative ionization by both UV radiation and photoelectrons is about 20%.

3. Molecular Nitrogen Ions

According to figure 2, there is more N_2^+ produced in the 130-to 240-km region than any other ion. Yet, according to mass spectrometer measurements, this ion is relatively minor in abundance, never being more than about 1% of the total ionization. Norton et al. [1963] argued that the reaction

$$N_2^+ + O \rightarrow NO^+ + N \qquad (15)$$

was necessary not only to reduce the N_2^+ to observable concentrations but also to provide a source capable of explaining the large concentrations of NO^+ observed. We have found that this reaction also provides a most important source of N. Donahue [1966] again investigated the ion chemistry in the light of some extremely important and timely laboratory measurements of the rate coefficients by Ferguson et al. [1965]. Donahue concluded, as had Ferguson et al. [1965], that the above reaction was indeed the major loss of N_2^+ in the F1 region. Donahue also concluded that the rate coefficient must decrease with temperature in order to explain the height variation of N_2^+. There are no laboratory measurements of the temperature dependence of this rate coefficient. We wish to suggest that there may be an additional source of this ion and that, if this source proves to be large enough, then a temperature dependent k_{20} may not be necessary. This reaction involves a charge transfer between $O^+(^2D)$ and N_2.

$$O^+(^2D) + N_2 \rightarrow N_2^+ + O \quad . \tag{16}$$

The reaction has been studied in the laboratory by Kaneko et al. [1966]. The rate coefficient is not very well determined, but appears to be greater than 10^{-11} $cm^3 sec^{-1}$.

According to the cross sections of Dalgarno et al. [1964], about 1/3 of the atomic oxygen ions produced by photoionization are left in the ^2D state. Some O^+ is left in more energetic states and should also contribute a small amount in reactions similar to (16). At low altitudes, near the F1 peak of production, the fractional contribution of (16) cannot be large since $q_2 > q_1$. However, at greater heights the inequality is reversed and (16) will contribute significantly to the N_2^+ formation unless $O^+(^2D)$ is deactivated by superelastic collisions with electrons. Seaton [1956] has given the collision strengths for electron deactivation, which leads to a rate coefficient, α_D, of approximately 2×10^{-8} $cm^3 sec^{-1}$ for electron temperatures near 2000°K.

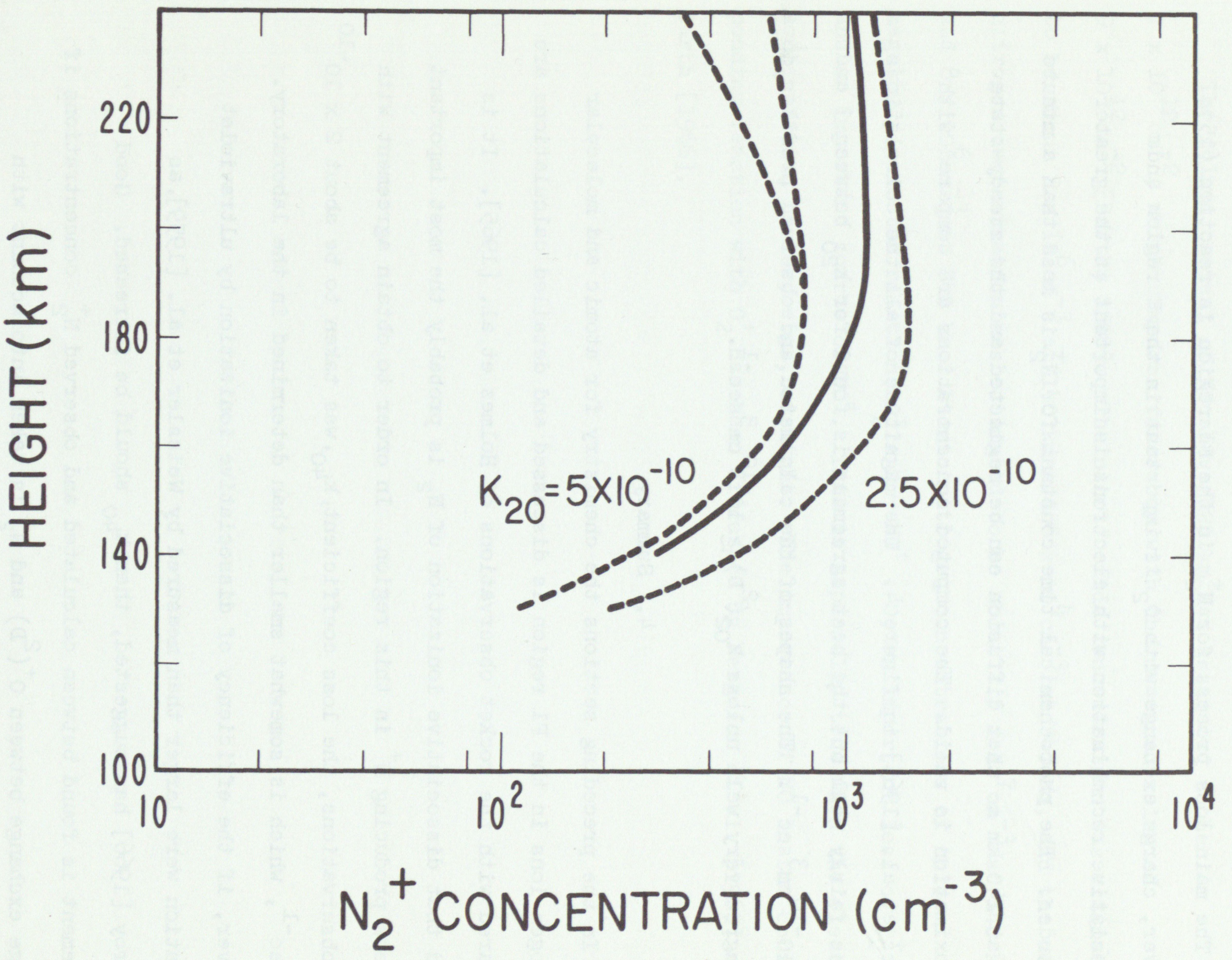

Figure 4. The curve (——) is the observed N_2^+ concentration plotted against altitude. For comparison with the observations, calculated N_2^+ concentrations (- -) for $k_{O2}(^2D) \geqq 10^{-10}$ $cm^3 sec^{-1}$ and two values of k_{2O} are plotted against altitude. The N_2^+ curve (-.-) is for $k_{O2}(^2D) = 0$.

The main loss process for N_2^+ in the F1 region is reaction (15); however, charge exchange with O_2 is important in the E region and dissociative recombination with electrons is important at the greater altitudes. The photochemical time constant for N_2^+ is less than a minute even at 240 km so that diffusion can be neglected and the steady-state approximation is valid. The computed concentrations are compared with Holmes et al. [1965] in figure 4. The magnitude of all the calculations agrees fairly well but the best agreement is found for k_{20} between 3 and $4 \times 10^{-10} cm^3 sec^{-1}$. The shapes of the calculated and observed profiles do not agree very well unless $k_{02}(^2D) \gtrsim 10^{-10} cm^3 sec^{-1}$.

4. Summary

In the preceding sections the chemistry for atomic and molecular nitrogen ions in the F1 region is discussed and detailed calculations are compared with the rocket observations of Holmes et al. [1965]. It is found that dissociative ionization of N_2 is probably the most important process producing N^+ in this region. In order to obtain agreement with the observations, the loss coefficient, k_{40}, was taken to be about 2×10^{-10} $cm^3 sec^{-1}$, which is somewhat smaller than determined in the laboratory. However, if the efficiency of dissociative ionization by ultraviolet radiation were larger than measured by Weissler et al. [1959], as McElroy [1966] has suggested, then k_{40} should be increased. Good agreement is found between calculated and observed N_2^+ concentrations if charge exchange between $O^+(^2D)$ and N_2 is taken into account with $k_{02}(^2D) \gtrsim 10^{-10} cm^3 sec^{-1}$.

The column content of NO above 125 km was estimated to be $7 \times 10^{12} cm^{-2}$, which compares favorably with the measured value of $9 \times 10^{12} cm^{-2}$ [Barth, 1966]. The nitric oxide concentration was estimated to be about $2 \times 10^{6} cm^{-3}$ at 140 km and $6 \times 10^{4} cm^{-3}$ at 240 km, and the atomic nitrogen concentration was estimated to be about $2.5 \times 10^{7} cm^{-3}$ at 140 km and $8 \times 10^{6} cm^{-3}$ at 240 km. Atomic nitrogen concentrations of this magnitude make the reaction, $O_2^+ + N \rightarrow NO^+ + O$, an important loss of O_2^+ and an important source of NO^+. This is especially true when the electron concentration is low, e.g., at night. The importance of NO in the corresponding reaction with O_2^+ has been discussed by Ferguson et al. [1965] and Barth [1966].

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