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Ar⁺ in the Terrestrial Ionosphere

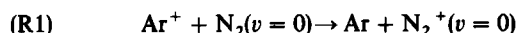
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The Ar⁺ densities in the terrestrial ionosphere are computed for both low and high solar activity models. The reaction N₂⁺(*v* > 0) + Ar → N₂ + Ar⁺ is found to be a significant source of Ar⁺, nearly equal to photoionization and electron impact ionization in the high solar activity model. Peak densities of Ar⁺ of 11 cm⁻³ near 190 km and 22 cm⁻³ near 220 km are predicted for the low and high solar activity models. It is suggested that a simultaneous measurement of Ar⁺ and Ar densities would provide a test for the presence of vibrationally excited N₂⁺ in the terrestrial ionosphere.

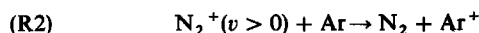
INTRODUCTION

The charge transfer reaction of Ar⁺ with N₂ in its ground vibrational level to produce N₂⁺ in its ground vibrational level



is exothermic by 0.18 eV. The values of the rate coefficient measured prior to 1980 were scattered over nearly 2 orders of magnitude from 1×10^{-12} cm³ s⁻¹ to 6.6×10^{-11} cm³ s⁻¹ (see references in the work of Lindinger *et al.* [1981]).

Lindinger *et al.* [1981], however, have used a drift tube and Smith and Adams [1981] have used a SIFT apparatus to show that the reaction has a true rate coefficient of about 1×10^{-11} cm³ s⁻¹ at room temperature, the very small rate coefficients previously measured for (R1) arising from interference by the reverse reaction:



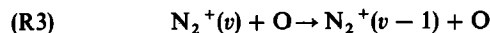
[Lindinger *et al.*, 1981]. Smith and Adams [1981] found that two thirds of the N₂⁺ ions produced in (R1) are vibrationally excited even at low (~300 K) temperatures. For N₂⁺ ions in the vibrational ground state, the charge transfer to Ar (reaction (R2)) proceeds with a rate coefficient of $1.7\text{--}2.0 \times 10^{-13}$ cm³ s⁻¹ at room temperature. For *v* > 0 the reaction proceeds at near gas kinetic rates, with a rate coefficient of 4×10^{-10} cm³ s⁻¹ [Lindinger *et al.*, 1981; Smith and Adams, 1981; Kato *et al.*, 1982]. Just as the large difference in the reactivities of N₂⁺(*v* = 0) and N₂⁺(*v* > 0) with Ar has made Ar⁺ useful as a "monitor ion" in laboratory settings, the ratio of Ar⁺ to Ar should provide a test for the presence of vibrationally excited N₂⁺ in the terrestrial ionosphere.

THE MODEL

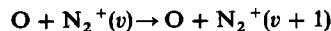
Fox and Dalgarno [1985] have computed the vibrational distribution of N₂⁺ in the terrestrial ionosphere for two mass spectrometer/incoherent scatter (MSIS) model atmospheres for low (*F*_{10.7} = 70) and high (*F*_{10.7} = 200) solar activities [Hedin, 1979]. The MSIS models give the abundance of Ar at 120 km as ~0.26%, with the mixing ratio decreasing above the turbopause. The reactions and rate coefficients used here are the same as those employed by Fox and Dalgarno [1985]. This model is a photochemical-diffusion model in which the diffusion coefficients of the ions are adjusted to reproduce measured O⁺ profiles. The solar fluxes adopted are the SC #21REF spectrum for low solar activity and the F79050N spectrum for high solar activity (Hinteregger [1976] and pri-

vate communication; see Torr *et al.* [1979]). A solar zenith angle of 45° is assumed. In the lower thermosphere, quenching limits the fraction of N₂⁺ that is vibrationally excited to less than 0.05. At altitudes above 200 km, N₂⁺ is found to be significantly vibrationally excited and at high altitudes the fraction in vibrational levels *v* > 0 asymptotically approaches 0.50. The main source of vibrational excitation is fluorescent scattering in the Meinel (*A*²Π_u → *X*²Σ_g⁺) and first-negative (*B*²Σ_u⁺ → *X*²Σ_g⁺) band systems of N₂⁺.

Vibrationally excited N₂⁺ is quenched by N₂ at near gas kinetic rates [Lindinger *et al.*, 1981; Smith and Adams, 1981; Mahan *et al.*, 1982] and slowly by O₂ [Kemper and Bowers, 1984]. The rate coefficient for quenching of N₂⁺(*v*) by atomic oxygen:



has not been measured. We have considered three different values for *k*₃, the rate coefficient for this reaction. In the standard model we adopt a rate coefficient of 1.4×10^{-10} cm³ s⁻¹. Lower and upper limits of 1.4×10^{-11} cm³ s⁻¹ and 5×10^{-10} cm³ s⁻¹ (near gas kinetic) were also investigated. The resulting vibrational distributions at 200 km are presented in Table 1 for the three values of *k*₃, for both low and high solar activities. The fraction that is vibrationally excited varies from 13% for *k*₃ = 5×10^{-10} cm³ s⁻¹ to 20% for *k*₃ = 1.4×10^{-11} cm³ s⁻¹ in the low solar activity case. The variation for high solar activity is less, from 17% to 21%, largely because of the increased importance of collisional excitation:



at the higher temperatures which characterize the high solar activity model atmosphere. The vibrational distribution at 200 km is in neither case sensitive to the rate coefficient assumed for *k*₃ because quenching by N₂ is somewhat more important as a loss process for N₂⁺(*v* = 1) at that altitude.

Ar⁺ DENSITIES

We have computed the densities of Ar⁺ for the two standard models of Fox and Dalgarno [1985]. Figure 1 shows altitude profiles of the sources of Ar⁺ for the low solar activity case. In the lower ionosphere, electron impact is the major source. The source due to electron impact shows a large peak in the lower ionosphere for two reasons: First, the absorption of soft X rays in the lower thermosphere produces more energetic primary photoelectrons and therefore more ionizing secondary electrons. The photon fluxes in this wavelength region are, however, very uncertain. Second, the electron impact ionization cross sections for Ar are large in comparison with the photoionization cross sections [cf. Fox and Dalgarno, 1977, 1979].

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TABLE 1. Vibrational Distributions of $N_2^+ X^2\Sigma_g^+$ at 200 km in the Terrestrial Ionosphere for Low and High Solar Activities

v	Low Solar Activity			High Solar Activity		
	1.4×10^{-11}	1.4×10^{-10}	5×10^{-10}	1.4×10^{-11}	1.4×10^{-10}	5.0×10^{-10}
0	0.80	0.83	0.87	0.79	0.81	0.83
1	0.072	0.071	0.063	0.098	0.10	0.10
2	0.053	0.045	0.032	0.045	0.040	0.03
3	0.030	0.027	0.019	0.025	0.023	0.017
4	0.022	0.019	0.012	0.018	0.016	0.011
5	0.019	0.013	0.007	0.016	0.012	0.0065

The columns are labeled by the value assumed for k_3 in $\text{cm}^3 \text{s}^{-1}$.

Above 150 km, photoionization dominates. Between 150 and 250 km, the charge transfer reaction from vibrationally excited N_2^+ (reaction (R2)) is nearly as important as photoionization. The fraction of the total production due to (R2) maximizes near 200 km in both the low and high solar activity models at 38% and 49%, respectively. It then decreases with increasing altitude to 18% and 28%, respectively, at 300 km.

The rate coefficient we have adopted for the charge transfer of Ar^+ to N_2 (reaction (R1)) is

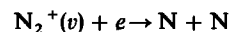
$$k_1 = 1 \times 10^{-11} (T/280)^{0.86} \text{ cm}^3 \text{ s}^{-1}$$

an interpolation between the thermal SIFT results of Smith and Adams [1981] and the drift tube results of Lindinger *et al.* [1981]. The reaction with N_2 is the major loss process for Ar^+ at all altitudes considered. Ar^+ also charge transfers to O_2 and NO [Laudenslager *et al.*, 1974; Rakshit *et al.*, 1978], but these processes are important only below about 125 km where they constitute about 20% of the total loss. The fraction of the total loss attributable to reactions with O_2 and NO decreases toward higher altitudes to about 8% at 200 km.

In Figure 2 we present altitude profiles of the densities of Ar^+ from 120 to 260 km for the standard models, at low and high solar activities. The dashed lines show the Ar^+ densities computed including only photoionization and electron impact ionization of Ar as sources. The maximum densities are about 7 and 11 cm^{-3} for the low and high solar activity cases, respectively. The solid lines show the densities which result when charge transfer from vibrationally excited N_2^+ (reaction (R2)) is included. The corresponding maximum densities are about 11 cm^{-3} and 22 cm^{-3} when (R2) is included. The

charge transfer source of Ar^+ is therefore significant even though only about 20% of the N_2^+ ions are vibrationally excited near 200 km.

Table 2 shows the maximum densities of Ar^+ for three values of the quenching coefficient k_3 . These densities show little dependence on the value of k_3 . As the fraction of vibrationally excited N_2^+ increases, so that the effective rate coefficient for (R2) increases, the density of N_2^+ declines. This is because the rate coefficient for loss of N_2^+ by dissociative recombination:



increases with increasing vibrational quantum number [Zipf, 1980; cf. Fox and Dalgarno, 1985]. Thus the total rate for (R2) does not increase proportionately.

The density of Ar^+ between 200 and 300 km is given approximately by

$$[\text{Ar}^+] = \frac{(J_{\text{Ar}}(z) + k_2[N_2^+(v > 0)])[\text{Ar}]}{k_1[N_2]}$$

where $J_{\text{Ar}}(z)$ is the photoionization rate coefficient of argon at altitude z . A simultaneous measurement of the densities of Ar^+ , Ar, and N_2 and the solar fluxes theoretically provides a measurement of the density of vibrationally excited N_2^+ , although experimental verification may be difficult. The peak densities of Ar^+ are within, albeit near, the lower limits of the sensitivity of rocket-borne mass spectrometers. Zbinden *et al.* [1975] have measured number densities of mass-40 ions, presumably Ca^+ , as low as 2–3 cm^{-3} in the D region. We can,

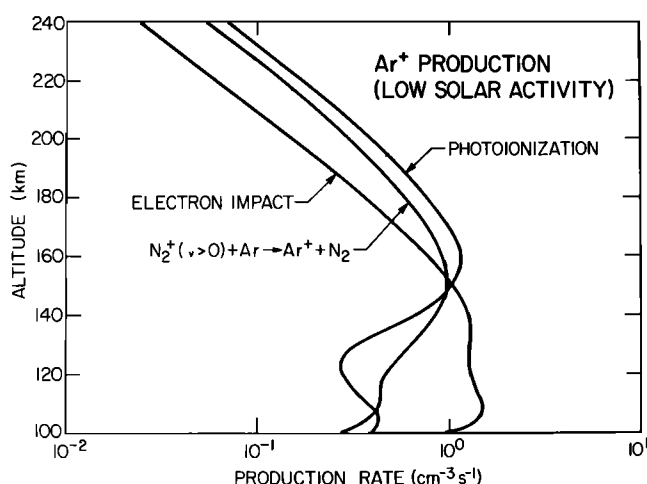


Fig. 1. Altitude profiles of the major sources of Ar^+ in the low solar activity model.

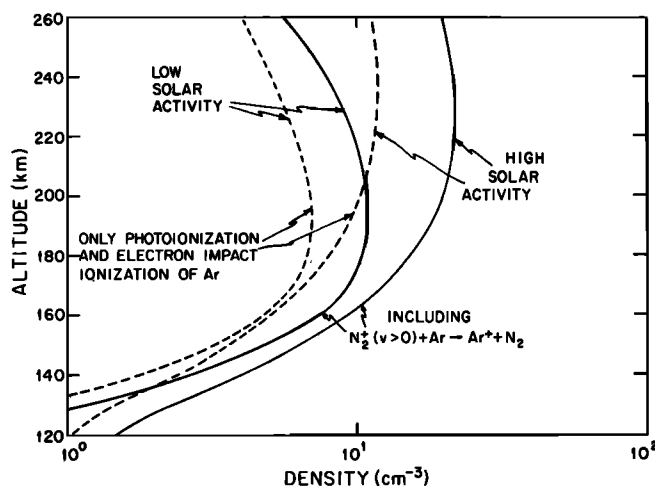


Fig. 2. Altitude profiles of the computed densities of Ar^+ excluding and including the effect of (R2): $N_2^+(v > 0) + \text{Ar} \rightarrow \text{Ar}^+ + N_2$. Both the low and high solar activity models are shown.

TABLE 2. Maximum Values of Ar^+ for Three Values of the Quenching Coefficient of $\text{N}_2^+(v > 0)$ by O (Reaction (R3)) for the Low and High Solar Activity Models

$k_3, \text{cm}^3 \text{s}^{-1}$	Maximum Density, cm^{-3}	
	Low Solar Activity (190 km)	High Solar Activity (220 km)
1.4×10^{-11}	11.7	22.4
1.4×10^{-10}	11.3	21.8
5×10^{-10}	10.3	20.2

The solar zenith angle is 45° .

nonetheless, conclude that charge transfer from vibrationally excited N_2^+ is a major source of Ar^+ in the terrestrial ionosphere comparable to direct photoionization and electron impact ionization of Ar.

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