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A MASS SPECTROMETER OBSERVATION

OF NO IN AN AURORAL ARC

BY

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A MASS SPECTROMETER OBSERVATION OF NO IN

AN AURORAL ARC

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INTRODUCTION

On 25 March 1970 an Aerobee rocket [4.309 UA] was launched into a bright IBC II$^+$ auroral arc above Fort Churchill, Manitoba. The instrumentation on board included a quadrupole mass spectrometer that measured the local ion __and__ neutral composition in the auroral form, separate primary and secondary electron energy analyzers covering the nominal energy ranges 1 to 30 keV and 1 to 1000 eV respectively, a cylindrical electron probe and a planar total positive ion probe. These particle experiments were complemented by a 1/4-meter Ebert monochromator that scanned the VUV auroral spectrum from 1150A to 1500A and four filtered photometers that measured the overhead intensity of the (0,0) first negative band of N_2^+, the (1,0) first negative band of O_2^+, the (5,2) first positive band of N_2 and the auroral oxygen green line [$^1S \rightarrow {^1D}$; $\lambda 5577A$]. In addition, an up-down photometer (Dick and Fastie, 1969) was included to obtain information on the temporal and structural characteristics of the aurora.

In this paper we discuss the neutral and ion data obtained by our programmable mass spectrometer. The most important results are the following: The mass spectrometer observed remarkably large concentrations of NO and NO$^+$ within the auroral form. The molecular ions O_2^+ and N_2^+ were conspicuously absent and comparatively large densities of O^+ ions were detected. In the altitude range 110 km to 130 km the neutral NO concentration exceeded the ambient O_2 concentration.

In previous years we have flown similar comprehensively instrumented rockets into IBC I and II post breakup aurora (Donahue et al., 1968;

Parkinson et al., 1970a; Donahue et al., 1970; Parkinson et al., 1970b).

In these displays the primary ionization and luminosity often was

observed over a relatively wide altitude region (100 - 135 km),

the primary electron spectrum was comparatively soft (< 10 keV electrons),

and the maximum electron density observed in the aurora was modest

($\sim 2 \times 10^5$ e/cm^3). The aurora encountered on Aerobee flight 4.309 UA

was by contrast a stable arc characterized by large fluxes of 20 - 30

keV primary electrons (Doering, 1970), by large local electron densities

($\sim 10^6$ e/cm^3) and by an energy deposition confined for the most part

to a relatively narrow altitude region (95 - 115 km). This is illustrated

in Figure 1 where we show the intensity of the (0,0) first negative band

of N_2^+ measured on the upleg of the flight; similar results were obtained

for the (1,0) first nagative band of O_2^+. Using recent laboratory

measurements of the excitation cross sections for these bands (Borst

and Zipf 1970a, 1970b), the total ionization cross sections for N_2, O_2

and O (Kieffer and Dunn, 1966), and our in situ optical measurements,

we estimate that the maximum ionization rate in this arc was approximately

2×10^5 ion pairs/cm^{3}sec at 102 km.

In an earlier auroral experiment (4.217 UA; Donahue et al., 1970)

we observed an unusually large NO^+/O_2^+ ratio with a single mode ion mass

spectrometer. Similar results have been obtained by Swider et al.,

(1968). In order to explain this observation, which was made in a post-

breakup aurora, we supposed that NO^+ ions were produced by rapid charge transfer

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between ambient O_2^+ ions and neutral NO molecules within the auroral form,

$$O_2^+ + NO \xrightarrow{k_1} NO^+ + O_2 \qquad (1)$$
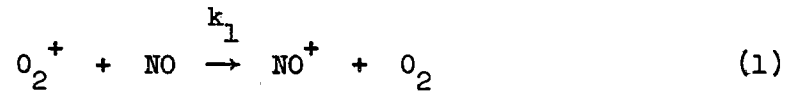
In spite of the large reaction rate coefficient for this process ($k_1 = 8 \times 10^{-10}$ cm^3/sec) a very large NO abundance ($\sim 10^9$ molecules/cm^3 at 110 km) was still required to account for the anomalous NO^+/O_2^+ ratio. Just how such a large NO concentration could be produced at auroral altitudes constitutes an intriguing geophysical problem. The ion mass spectrometer also detected comparatively large O^+ densities (more than 50 times the concentration expected on the basis of conventional ion chemistry). This result appears to demand effective ion temperatures greater than 1000°K and electron temperatures even larger unless the atomic oxygen densities are substantially larger than those assumed even in oxygen-rich model atmospheres. The present experiments were undertaken to confirm these ion observations and to search for the large NO densities [and possibly atomic oxygen densities] suggested by the analysis of our earlier observations.

INSTRUMENTATION

Table I list the design parameters for the flight quadrupole mass spectrometer. The instrument was designed to scan in the ion mode for three successive sweeps each lasting 1.5 seconds and covering a nominal ion mass range of 0 → 40 amu. On the fourth scan the potentials on the ionizer structure were changed so that the instrument became a neutral mass spectrometer. During the neutral mode ambient ions were

excluded from the ionizer by a +50 volt potential barrier.

The mass spectrometer was tuned to have a trapezoidal transmission function. By operating the mass spectrometer well into the flat-topped domain [even at some expense to the resolution] the instrument was made insensitive to any small electronic drifts that might have been expected because of a prolonged delay between the final calibration of the device and the launch date. As actually flown, the mass spectrometer had an effective resolution of 1.5 amu FWHM which was ample to distinquish between the three major neutral molecules species (N_2, NO and O_2) that were observed when the rocket passed through the arc. In the neutral mode the ionizer was emission current regulated. During the ion mode the filament was maintained at approximately the same temperature by a separate control circuit so that in switching from the ion mode to the neutral mode the emission current achieved its programmed value very rapidly (< 50 msec).

A Johnston Laboratories MM-1 mesh multiplier was used to detect the positive ions transmitted by the quadrupole lens. Pulse counting techniques, which minimized any problems caused by a change in the gain of the multiplier, were used. The mass spectrometer had a dynamic range of seven orders of magnitude.

An open ionizer design was used in this experiment in order to enhance the probability of making reliable atomic oxygen measurements. The ionizer consisted of several carefully aligned, high transparency grids and a tungsten wire filament; this is shown schematically in Figure 2. The collection mode of the mass spectrometer (ion or neutral) was determined by the potentials applied to these grids; values are given in Table II.

The ionizer had a volume of about 2 cm^3 and was liberally vented so that its effective pumping conductance was approximately 4×10^4 cm^3/sec. The mean residence time for a gas particle within the ionizer structure was about 5×10^{-5} sec so that the average molecule made only one wall collision before exiting.

The mass spectrometer was calibrated in a 200 liter multi-purpose ultra-high vacuum chamber which could reach an ultimate vacuum of about 5×10^{-11} Torr when mildly baked. The entire vacuum chamber was filled with the test gas during a calibration measurement. The absolute pressure in the collision chamber was known to within $\pm$ 5% and the pressure was held constant to within 1% during a measurement by means of a servo-controlled leak valve. The absolute calibration techniques used in this work are described in detail elsewhere (Borst and Zipf, 1970a) and will not be reviewed here.

During our calibration studies the mass spectrometer was allowed to sample undried air in order to determine whether a significant amount of NO could be created within the structure of the ionizer. No nitric oxide was detected, a result which implied that the ratio of ionizer-produced NO to O_2 was less than 10^{-7}. Tests with large concentrations of N and O atoms, which could possibly result in the production of NO within the ionizer, were not conducted. However we estimated the amount of NO produced in the ionizer by using the measured reaction rate coefficients for the following source processes

$$N + O_2 \rightarrow NO + O \qquad\qquad (2)$$

and

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

the known residence time for molecules in the ionizer and model
atmosphere estimates of the N and O densities at auroral altitudes.
Because these reactions have substantial activation energies, they
are negligible at the ambient temperatures found between 100 to
130 km for our instrument $[NO/O_2 \simeq 5 \times 10^{-10}]$. Even if we assume
an effective [but realistic] ionizer temperature of 10,000°K, the
ratio of NO to O_2 produced in the ionizer is still less than 3×10^{-6};
this is not important for the purposes of this paper. In view of these
results it is very unlikely that a significant amount of NO could be
created by the instrument itself.

The possibility always remains that the NO results from gases
venting from the rockets' motor. This appears to be unlikely for a
number of reasons: the motor was valved off following the powered flight
to minimize this potential problem; no carbon or hydrocarbon compounds
that would normally accompany NO produced as a combustion product were
detected by the neutral mass spectrometer nor was an enhanced helium abundance
observed; helium is used to pressurize the Aerobee's fuel tanks. Finally
the magnitude and altitude distribution of the N_2, O_2 and O inferred from
a preliminary review of the flight data are quite consistent with previous
measurements of the neutral atmosphere and do not indicate that the rocket
was enveloped by a unusual cloud of gas. This view is also supported
by the ion-mode data which is also conspicuously free of CO^+, hydrocarbon
and other debris ions. Both the laboratory and the flight data indicate

that there is no obvious way for the mass spectrometer to have produced

such large NO signals artifically and we conclude that the NO molecules

and the NO^+ ions observed by this instrument were important constituents

existing in the auroral arc.

RESULTS

Figure 2 shows a portion of the mass spectrometer telemetry

record when the instrument was operating in the ion mode. The positive

ions that were detected within the auroral form included H^+, O^+ and

NO^+; the molecular ions O_2^+ and N_2^+ were conspicuously absent ($< 2 \times 10^{-2}$

ions/cm^3). The dominant positive ion at all altitudes sampled by the

mass spectrometer was NO^+ which attained a maximum density of about

9×10^5 ions/cm^3 at 98 km. The mass spectrometer also detected com-

paratively large densities of O^+ ions ($\sim 1.8 \times 10^3$ at 120 km). Hence

the general features of the auroral ionosphere observed by us on flight

4.217 UA (Donahue et al., 1970) are confirmed: namely, the predominance

of NO^+, the sharply reduced O_2^+ concentration and the unusual abundance

of O^+ ions at low altitudes.

The mass spectrometer once again detected the presence of very

low mass ions within the auroral form. The density of these ions

fluctuated from scan to scan in a way reminiscent of the curious behavior

shown by the low mass ions encountered on flight 4.217 UA. The latter

ions were thought to be He^+ possibly due to helium venting from the rocket.

The present flight data were obtained with an ion mass spectrometer whose

performance at low masses was considerably better than that of the

instrument flown on 4.217 UA; this was the result of improvements in the

DC/RF tracking. The new data show quite clearly that this mass peak is

actually due to relatively slow protons (< 50 eV) and not helium ions as previously supposed. Presumably these ions are nearly thermalized primary protons. These results will be discussed in more detail in a separate note.

Figure 3 shows two portions of the mass spectrometer telemetry record when the instrument scanned in its neutral mode. Both N_2, O_2 and O were present with concentration levels close to those reported by numerous other workers (see for example Krankowsky et al., 1968). In addition to these species the mass spectrometer revealed the presence of a remarkable amount of neutral NO within the auroral form. The NO, in fact, was more abundant than O_2. The results of a preliminary reduction of the flight data at 120 km are given in Table III. The total particle at this altitude was 3.5×10^{11} cm^{-3} with a mean molecular weight of 26.4. This is in good agreement with similar measurements by Krankowsky et al. (1968).

The amount of atomic oxygen observed in somewhat larger than previously reported by most mass spectrometer workers, but it is not nearly enough to explain the enhanced O^+ densities observed in the aurora on this basis alone. A preliminary review of the neutral data obtained between 110 to 120 km indicates that the NO is probably not in diffusive or mixing equilibrium and that it is formed largely at the expense of ambient O_2 and N_2 molecules. The ratio $O/(O_2 + NO)$ [which is presumably a measure of the O/O_2 ratio in the undisturbed auroral atmosphere] has the value 0.98 at 120 km; this is also in good agreement with previous measurements at high latitude locations (u. von Zahn et al., 1970).

We also note that the absence of N_2^+ and O_2^+ ions as consistent with the large NO abundance observed by the mass spectrometer. At 120 km,

for example, the total O_2^+ production rate was approximately 10^3 ions/cm^3 sec. With the NO density given in Table II an equilibrium O_2^+ concentration of only 30 ions/cm^3 would result; this is consistent with the upper limit established by the ion mass spectrometer.

Mass spectrometer measurements by Hartman and Nier (1970) and by von Zahn et al. (1970) show that large concentrations of NO are not normally found above 120 km in the undisturbed atmosphere above Churchill. This indicates that the NO we observed was being produced actively within the form as part of a time dependent and spatially localized event. This view is supported by our mass spectrometer observations below the lower edge of the aurora (95 km). In this region the measured O_2/NO ratio was greater than 15 to 1; it was only after the rocket had penetrated into the arc that the O_2/NO ratio changed dramatically.

The mechanism producing NO in this auroral arc did so at the expense of the molecular constituents: O_2 and N_2. Ambient O atoms did not seem to be involved in any important way. Metastable $N(^2D)$ atoms probably play a significant role through the process

$$N(^2D) \; + \; O_2 \; \to \; NO \; + \; O \tag{4}$$

These metastable atoms are produced efficiently by the dissociative excitation of N_2 (Mumma and Zipf, 1970). Dissociative recombination of NO^+ is also a likely source. However, this process contributes to the NO build-up only in the early phases of the auroral event when

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$$N_2^+ + NO \rightarrow NO^+ + N_2 \tag{5}$$

and

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

are not the dominant loss processes for these ions. Ultimately NO^+ recombination serves only to recycle the existing NO.

An independent NO source outside of the $[NO^+ + e]$ loop is needed to account for the very large NO concentrations observed in this aurora. In addition to reaction (4) the following collision processes may be important.

$$N(^4S)^* + O_2 \rightarrow NO + O \tag{7}$$

and

$$O(^3P)^* + N_2 \rightarrow NO + N \tag{8}$$

where the asterisk indicates an atom with a kinetic energy considerably in excess of the activation energy for these reactions. In a recent laboratory experiment Borst and Zipf (1970c) have shown that dissociative excitation does in fact produce very energetic atoms; a substantial fraction of these atoms even have enough energy to dissociate ambient O_2

and N_2 molecules. Hence, the thermalization process itself may also serve as an effective NO source.

ACKNOWLEDGEMENTS

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Table I

Mass Spectrometer Design Parameters

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r_o	$=$	0.3 cm
ℓ	$=$	10.0 cm
f_o	$=$	3.5 mHz
$d_1^{\,a}$	$=$	5×10^{-2} cm

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[a] Entrance aperture diameter.

Table II

Ionizer Potentials

Electrode	Ion Mode[*]	Neutral Mode[*]
1	-5 volts	-5 volts
2	-10	+50
3	0	0
4	0	-25
5	0	-15
6	-15	-15

[*] The quadrupole lens was biased -15 volts with respect to the vehicle.

Table III

Particle Densities at 120 km [4.309 UA]

Species	Density (cm^{-3})
N_2	2.3×10^{11}
O_2	2.3×10^{10}
NO	3.8×10^{10}
O	6.0×10^{10}
Total	3.5×10^{11}

Mean molecules weight 26.4

Figure Captions

Figure 1 The intensity of the (0,0) first negative band of N_2^+ measured on the upleg of flight 4.309 UA.

Figure 2 Schematic cross section of ionizer through a plane containing the axis of the quadrupole lens. The filaments were about 5 mm long and consisted of 0.003" dia. tungsten wire. Filament 2 is a spare. The switching potentials V_1 through V_6 used for the ion and neutral modes are listed in Table II. Four large vent holes in the side of the plate containing the filaments are not shown.

Figure 3 Sample record of the ion mass spectrometer data obtained during flight 4.309 UA, March, 1970 at 120 km. The NO^+ signal is off-scale on the sensitivity range shown in the figure.

Figure 4 Sample records of the neutral mass spectrometer data obtained during flight 4.309 UA showing the N_2, NO and O_2 mass peaks. Mass scans A and B were obtained at an altitude of 113 km and 119 km respectively.
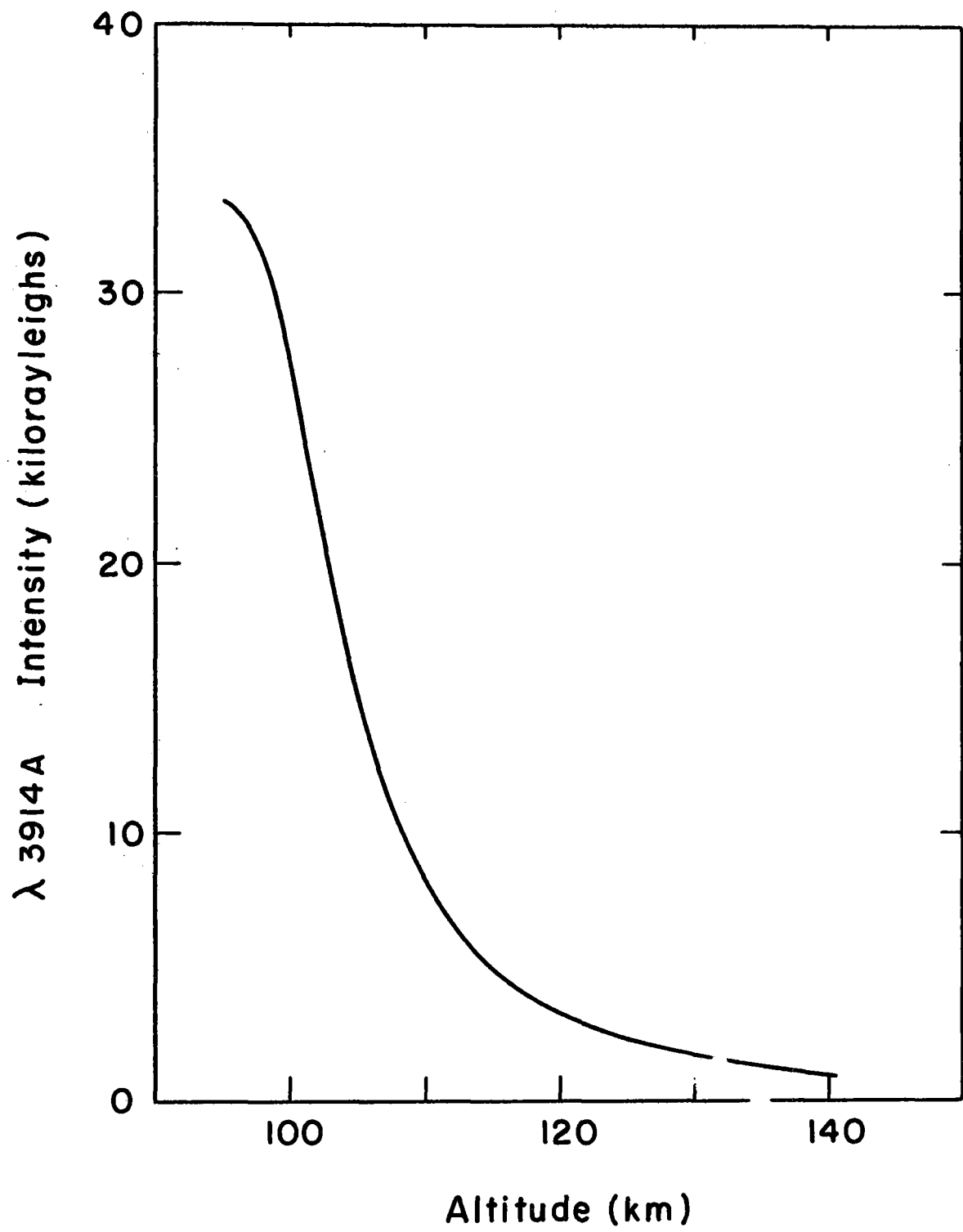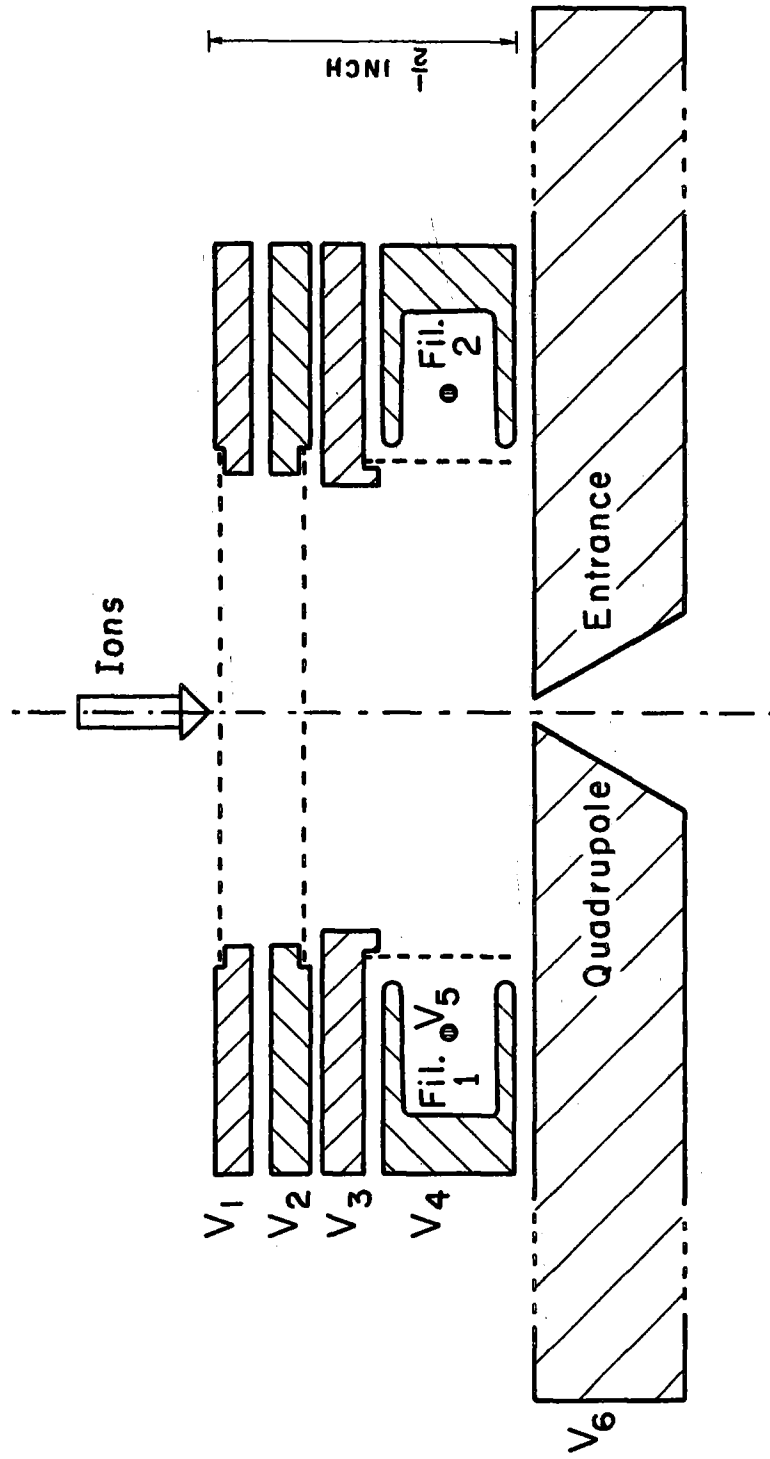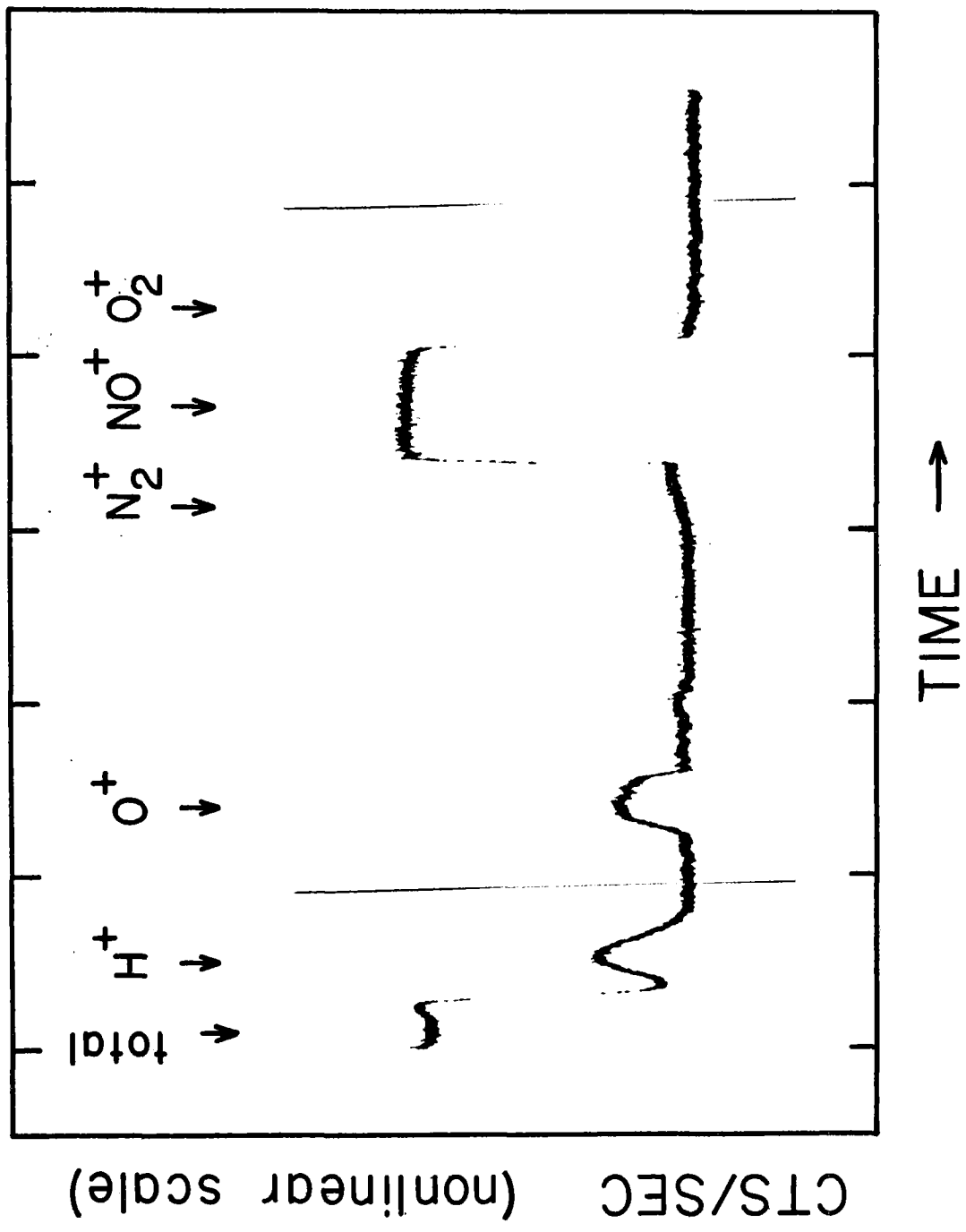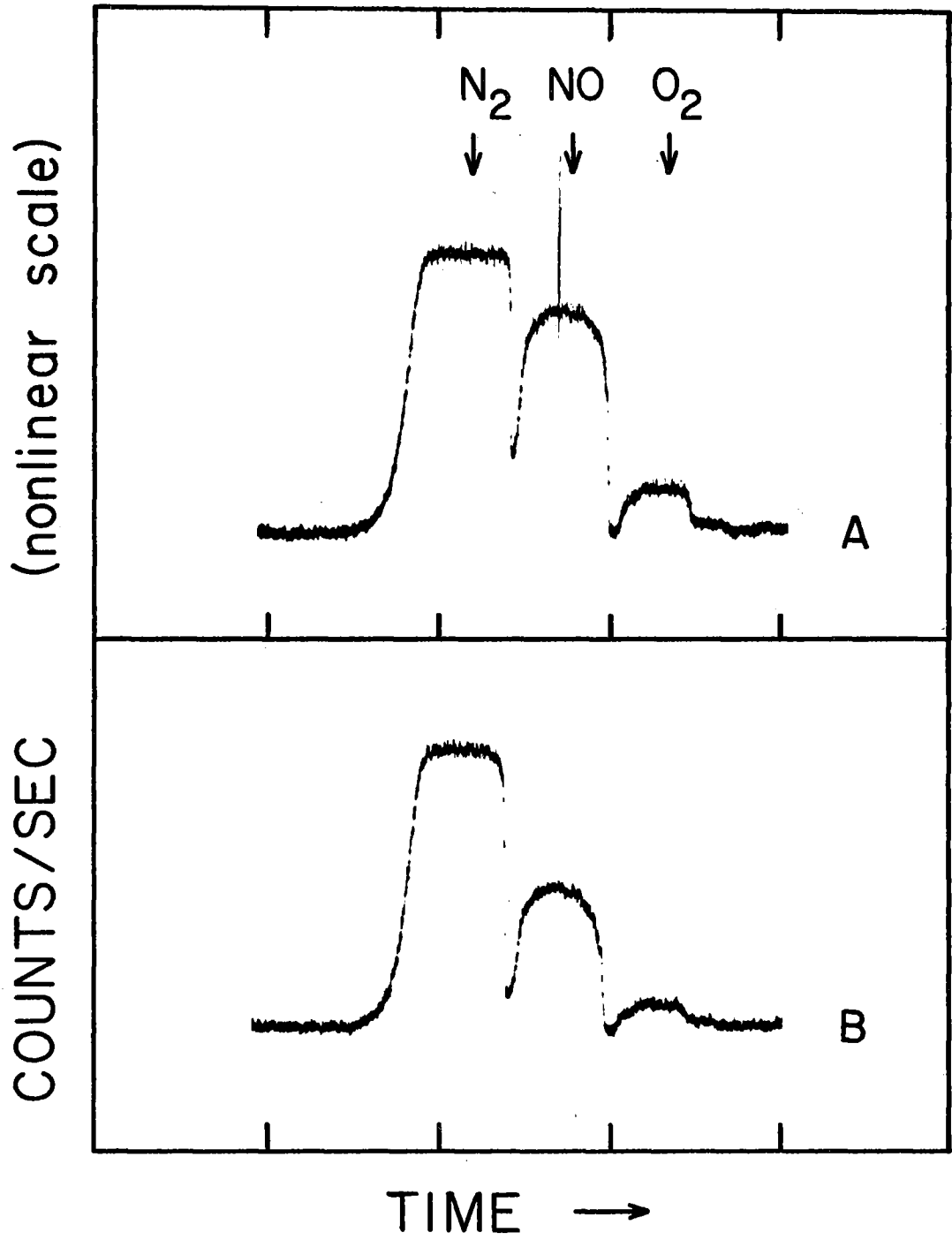
Figure 1

Figure 2

Figure 3

Figure 4