ROCKET MEASUREMENT OF NITRIC OXIDE BETWEEN 60 AND 96 KILOMETERS

by

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ABSTRACT

The height profile of the nitric oxide airglow in the gamma bands ($A\ ^2\Sigma^+ - X\ ^2\Pi$) is presented from measurements by a sounding rocket at evening twilight. The nitric oxide density profile is deduced from these measurements. The density profile is used to deduce the dominant processes controlling nitric oxide in the 60 to 96 kilometer range. Above 75 kilometers the dominant process is found to be atmospheric mixing. The chemical reaction of nitric oxide with ozone is suggested as the dominant process below 70 kilometers.

Introduction

Nitric oxide has been a subject of aeronomy since Nicolet (1945) proposed that "The essential phenomenon in Region D results from NO photo-ionization" by solar Lyman alpha radiation. Nicolet (1955) suggested additional features of the interaction of nitric oxide and the D region. The principal source of nitric oxide proposed was the three-body reaction

$$N + O + M \rightarrow NO + M \qquad (1)$$

where chemical symbols are used for atoms and molecules and M is an undesignated atmospheric constituent presumably N_2 or O_2. The principal loss reaction suggested was

$$N + NO \rightarrow N_2 + O \ (k_2) \qquad (2)$$

He also made the prophetic statement that "It is clear that atmospheric mixing, acting during the day, can play a leading role in fixing the vertical distribution of NO."

By 1960, Nicolet and Aikin (1960) found that the situation in the undisturbed D region was more complex. They found that, besides Lyman alpha radiation ionizing nitric oxide, D region ionization could be produced by cosmic rays ionizing molecular nitrogen and oxygen and by middle ultraviolet sunlight ionizing metal atoms. They also found that negative ions were important in establishing charge neutrality in the

atmosphere below 70 km. The most important process for the production of nitric oxide was stated to be the reaction

$$N + O_2 \rightarrow NO + O \qquad (k_3) \qquad (3)$$

as first suggested by Harteck (1957).

At the time of the writing of the Nicolet and Aikin paper, nitric oxide had still not been detected in the Earth's upper atmosphere. The negative results of a solar absorption experiment by Jursa, Tanaka and LeBlanc (1959) allowed them to place an upper limit upon the horizontal column density of nitric oxide of 10^{15}-10^{16} molecules cm^{-2} in the range 63-87 km.

Barth (1961) theoretically investigated the nitrogen and oxygen atomic reactions in the chemosphere at night using a computer to solve the set of coupled differential equations describing the rates of change of density of the species, N, O, NO, N_2, O_2, O_3, and NO_2. The reactions considered were the above plus

$$N + N + M \rightarrow N_2 + M \qquad (4)$$

$$O + O + M \rightarrow O_2 + M \qquad (5)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (6)$$

$$NO + O + M \rightarrow NO_2 + M \qquad (7)$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad (8)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (9)$$

The rates for reactions 2 and 3 had been measured by Kistiakowsky and Volpi (1957) and Barth had measured the rate for reactions 1 and 5. The results of Barth's analysis, which did not include the effects of vertical transport indicated that only the reaction pair 2 and 3 were important in determining the nitric oxide density. As pointed out by Nicolet and Aikin (1960) these reactions lead to the expression

$$[NO] = \frac{k_3}{k_2} [O_2] \qquad (10)$$

which is valid in any region where the nitrogen atom density is high enough such that the reactions dominate other processes such as mixing and diffusion. Barth (1961) predicted that the concentration of nitric oxide established at 90 km by equation 10 would remain constant, due to mixing, down to an altitude where nitric oxide is converted to nitrogen dioxide by reaction 7 and the reaction

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (k_{11}) \qquad (11)$$

which had been suggested by Nicolet (1955) as a possible lower D region loss mechanism for nitric oxide.

On November 17, 1963, Barth (1964) discovered the gamma bands of nitric oxide in the Earth's dayglow with a scan-

ning ultraviolet spectrometer aboard an Aerobee sounding rocket. These bands are emitted by nitric oxide molecules which are excited by the absorption of sunlight. Both the absorption and reemission take place in the 2050 to 2800 Å region. He deduced a column density of 1.7×10^{14} molecules cm^{-2} above 85 km, a value considerably in excess of that predicted by most local photochemical equilibrium theories such as those of Nicolet and Aikin (1960) and Barth (1961).

Thus Nicolet (1965b) suggested the additional source reaction

$$O_2^+ + N_2 \rightarrow NO + NO^+ \qquad (12)$$

whose rate constant was unknown at that time. This rate was then measured by Ferguson, Fehsenfeld, Goldan and Schmeltekopf (1965) and found to be less than 10^{-15} cm^3 sec^{-1} at 300 °K, a value below that necessary to explain Barth's measured densities.

When Barth (1966) reported three additional observations of nitric oxide from sounding rockets he also suggested that reaction 12, with vibrationally excited nitrogen molecules, might have a sufficiently higher rate constant than that for the unexcited molecules and would provide the necessary source

of nitric oxide. Barth's measurements were made during experiments designed to survey the middle ultraviolet dayglow up to about 190 km. As such, the techniques used were not optimized for the measurement of nitric oxide fluorescence and the rocket moved through the region near 80 km at nearly 1 km/sec. For this reason most of Barth's measurements were made in the E region and in fact only three observations of the apparent emission rate of nitric oxide are reported below 100 km.

In a systematic study of the proposed mechanisms Norton (1967) stated that the atomic nitrogen source reaction(3) would dominate the oxygen ion reaction(12) at all altitudes above 100 km and suggested that excited nitrogen atoms may increase the effective rate of reaction 3.

A recent measurement of the density of $O_2(^1\Delta)$ molecules in the atmosphere by Evans, Hunten, Llewellyn and Jones (1968) has prompted Hunten and McElroy (1968) to suggest that reaction 3 using $O_2(^1\Delta)$ oxygen molecules may also be an important source of nitric oxide in the D and E regions.

The rocket experiment which is reported here provided high accuracy, high precision measurements of the nitric oxide fluorescence at small altitude intervals from 60 to 96 km with

a scanning ultraviolet spectrometer. An evening twilight nitric oxide profile is deduced from these observations. Various processes influencing nitric oxide are considered in the light of those data.

Instrumentation

The design of the spectrometer used to make the nitric oxide fluorescence measurements in this experiment is an outgrowth of the experience gained in several other experiments both on sounding rockets and satellites. A spectrometer for sounding rocket use was described by Fastie (1963). The spectrometer used for the present measurements was of Fastie's basic design but was considerably modified in detail.

A 2160 lines per millimeter replica grating was employed in the 1/4m focal length monochromator in first order. The grating was blazed at 2000 Å and its 56 x 64 mm ruled area gave a focal ratio of f/4.2 at 2150 Å. The slits were set for 12 Å resolution at 2150 Å. The grating was rotated with an encapsulated cam and follower driven by a governed d.c. motor. The cam profile was such that the monochromator scanned from 2070 Å to 2370 Å in about 2 seconds and then rapidly returned to 2070 Å in another 0.3 seconds. During the time when the

monochromator was set near 2070 Å the scan mechanism also activated a micro switch for a wavelength fiducial. An EMR 542F photomultiplier tube with a cesium telluride photocathode was employed.

The response of the detector was compared, through an intermediate step, to the response of sodium salicylate as measure of its relative spectral sensitivity. The response of the detector head to the light from a tungsten ribbon filament as passed by an interference filter was also measured. The apparent brightness temperature of the filament was measured with an optical pyrometer. The emissivity of tungsten used was reported by de Vos (1954). The interference filter's passband was measured with a double monochromator. The peak of the filter's transmission occurs at 2660 Å. The precision of this measurement is ± 5%. There are several possible sources of systematic error. The temperature of the tungsten ribbon filament was measured both at its edge and at its center. The edges were cooler than the center by some 20°K. A weighted average value was used to estimate the effective brightness temperature. At 2357°K, the adopted value, a 10°K change in temperature changes the calculated flux at 2660 Å by 9%. The pyrometer accuracy is estimated as ± 2°K. The accuracy of the

interference filter's transmission curve is estimated as ± 3%. It was necessary to use a small diaphragm in the optical path near the photomultiplier tube. Thus the measured sensitivity does not refer to the same area of the photocathode which was illuminated by the exit slit during the flight. This effect may introduce a systematic error as large as ± 15%. The overall accuracy of the comparison with the tungsten lamp is estimated as ± 18%. Bless, Code and Schroeder (1968) have measured the emissivity of tungsten at 3400 Å and find a value lower than that of de Vos (1954) by possibly 10%. They suggest that there may be an appreciable effect on the emissivity of tungsten due to sample differences.

Observations

This spectrometer was launched aboard a Nike-Apache sounding rocket at 21:48 GMT on 12 December 1967 from Wallops Island, Virginia. The launch took place just after local ground sunset ($\chi = 92°$) into a completely clear sky. The operation of all systems both aboard the vehicle and on the ground was completely normal except that the fuse which ignited the second (Apache) stage burned longer than expected, causing the peak altitude to be lower than the predicted value.

The telemetered voltages were recovered by playing back the analog telemetry tape through a bank of discriminators. The voltages were then digitized with a multichannel analog

to digital converter and recorded on a digital computer tape. Digital methods were used to restore the converted values to the true voltages and then to apparent emission rates (Figure 1).

The spectrometer was turned on before launch. No light was detected by the spectrometer until the nose tip was ejected. Between launch and tip eject the spectrometer scanned its range 26 times under dark conditions. The observations before tip ejection were used to establish the background levels for the experiment.

When the tip was ejected from the nose cone at 49.5 km the spectrometer measured a large signal at all wavelengths during the first few scans. At this altitude the atmosphere was shadowed from light in the 2000 to 3000 Å region by stratospheric ozone. As the rocket emerged from the shadow near 56.5 km the signals in the background regions began to decrease with near atmospheric scale height.

By the time the rocket had reached 85 km the spectra consisted of the nitric oxide gamma bands and a very small background. As the rocket descended, the fins on the Apache began to affect its orientation, (which until this time had been with the thrust axis nearly vertical), and caused the

rocket to turn over. This effect was first noticed at 85 km. By 65 km the rocket was reoriented so that it was pointed in the direction of its fall.

During the time the rocket was turning over, the horizon was viewed. The signals measured during that time were greatly enhanced over those measured while observing in the zenith.

The zenith corrected nitric oxide column emission rate profile is shown in Figure 2. The observation zenith angle was obtained from an attitude reference gyro. The nitric oxide density profile was obtained from this data using a discrete point form of the following equations as suggested by Hunten (private communication, 1968). The emission rate data were smoothed using a Gaussian weight

$$\langle 4\pi\mathcal{J}(z)\rangle = \frac{1}{\sqrt{\pi}} \int 4\pi\mathcal{J}(z')\, e^{\frac{-(z'-z)^2}{\sigma}}\, dz' \qquad (13)$$

where σ was chosen as 8 km. The function $\langle 4\pi\mathcal{J}(z)\rangle$ is plotted in Figure 2 as a solid line. The density profile was then obtained using

$$n(z) = \frac{1}{g} \cdot \frac{d}{dz} \langle 4\pi\mathcal{J}\rangle = \frac{-2}{g\sqrt{\pi}} \int 4\pi\mathcal{J}\, \frac{(z'-z)}{\sigma}\, e^{\frac{-(z'-z)^2}{\sigma}}\, dz' \qquad (14)$$

where g is the emission rate factor. The emission rate factor used was 3.93×10^{-6} photons sec^{-1} $molecule^{-1}$ for the (1,0) band. This value was computed taking the rota-

tional structure of the molecule into account, (Pearce, 1968). This value is 1.93 times smaller than Barth's (1966) value. The difference is due to an improved value of the branching ratio and not due to effects of the rotational structure. The calculated nitric oxide density profile from the (1,0) band is plotted in Figure 3.

An estimated precision in the density is indicated in the figure by the shaded area. These estimates are based on the quality of the emission data. The profile is also subject to the systematic errors discussed under instrumentation. These errors do not affect the scale heights.

Ten minutes after the launch of this experiment a second rocket was launched from Wallops Island by the Goddard Space Flight Center under the direction of Dr. W. Smith. This rocket measured the atmospheric temperature profile in the 30 to 90 km region by ejecting explosive grenades. The sound from the explosives was recorded from microphones on the ground and the time delays interpreted in terms of the temperature dependent speed of sound. The temperature profile is plotted in Figure 4 (W. Smith, private communication, 1968).

Using this profile the total atmospheric density was calculated and is compared to the nitric oxide density in Figure 5. The density was normalized to 8.3×10^{14} cm^{-3} at 75 km, the value from the COSPAR International Reference Atmosphere (1965). As the figure shows, the nitric oxide distribution matches the total atmospheric distribution very accurately above 74 km. The mixing ratio for nitric oxide in this region is estimated as $(7.9 \pm 1.8) \times 10^{-7}$.

At the rocket apogee of 96 km a residual apparent emission rate of (0.9 ± .1) kR was observed. This value corresponds to an unresolved nitric oxide column density of $(2.3 \pm .3) \times 10^{14}$ cm^{-2} above 96 km. The spectrum shown in Figure 1 was taken from an altitude of 94.5 km and shows that this residual intensity is real and not scattered light. This residual is presumably due to a region of enhanced mixing ratio above 96 km, possibly an E region source of nitric oxide.

Below 69 km the density profile deviates from the total atmospheric profile. These measurements are considered reliable only down to near 60 km as the solar radiation illuminating the nitric oxide molecules, and causing them to fluoresce, was shadowed below this level. An extension

of Chapman's method for the calculation of twilight solar intensities in the atmosphere has been given by Hunten (1954), who found it necessary to include the effects of refraction, the finite size of the sun, scattering of light both out of and into the observed region and extinction by the various atmospheric constituents. Evans (1967) has adopted a high altitude ozone distribution based on experimental and theoretical studies. His distribution is appropriate for middle latitudes during the sunlight hours. Using Hunten's formulae and the ozone distribution adopted by Evans, an altitude for 1/e solar intensity of 53 km is predicted for 2150 Å. This prediction is considered only as a consistency check and does not, due to the many uncertainties in the data, allow a detailed analysis of the nitric oxide fluorescence radiation in this altitude region.

It is suggested here that there are no important sources or losses of nitric oxide operative in the 75 to 96 km region at twilight and that the distribution in this region is dominated by mixing.

Another process could dominate the nitric oxide distribution. For example, the reaction pair 2 and 3 lead to

$$[NO] = \frac{k_3}{k_2} [O_2] \qquad (15)$$

However, the rate constant k_3 is highly temperature dependent, whereas, k_2 is not (Kistiakowsky and Volpi, 1957, 1958). It is possible for the observed mixing ratio to be obtained at a single altitude by the reaction pair 2 and 3, but it will not be obtained over a range of altitudes where the temperature is changing. Since the nitric oxide mixing ratio remains constant throughout, it appears that neither sources nor losses dominate mixing in this region.

It must be stressed, however, that the above considerations only apply to an equilibrium situation. The density of nitric oxide in this region of the atmosphere is almost certainly not constant.

The horizontal column density of nitric oxide as observed from 70 km would be 3.8×10^{16} molecules cm^{-2} using the data of Figure 2. This is in conflict with the 10^{16} molecules cm^{-2} upper limit of Jursa, Tanaka and LeBlanc (1959). The difference may either be real or due to a systematic error in one (or both) of the experiments.

Barth (1966) has measured the density profile of nitric oxide with a 60° solar zenith angle. His measurements, corrected for the above reported g factor, are plotted along with the present measurements in Figure 6. Because of the small number of observations by Barth below 96 km it is probably not possible to draw detailed conclusions about the time variations of nitric oxide from this comparison. Not only are the measurements a few hours apart in solar time but they are also over four years apart in ephemeris time.

Below 69 km the nitric oxide density begins to fall below that for the constant mixing ratio of 7.9×10^{-7}. Conditions in the region are almost surely not constant with time. However, simple equilibrium methods will be used in order to explore possible sources and losses of nitric oxide.

The reduction in mixing ratio of nitric oxide below 75 km is suggestive of the following as described by Nicolet (1965b). Nitric oxide is created at an altitude above 96 km, diffuses downward through the mixing region, the scale height being necessarily very slightly greater than the atmospheric scale height, and is destroyed below 65 km. It is suggested here

that nitric oxide is converted to NO_2 by the chemical reaction 11.

The density of ozone in the 60 to 96 km region of the atmosphere is known to be variable with latitude, season and time of day. Evans (1967) has reviewed the theoretical and the experimental estimates of high altitude ozone and has adopted the distribution

$$[O_3] = 1.23 \times 10^{15} \; e^{-z/4.9} \; cm^{-3}; \; z \geq 30 \text{ km} \qquad (16)$$

The rate coefficient for reaction 11 has been measured by Johnston and Crosby (1954), Ford, Doyle and Endow (1957), and most recently by Phillips and Schiff (1962). These three sets of measurements are quite consistent with each other. Nicolet (1965a) has reviewed these measurements and adopted the expression

$$k_3 = 5 \times 10^{-14} \sqrt{T} \; e^{-1200/T} \; cm^3/sec \qquad (17)$$

The time constant for destruction of a nitric oxide molecule by reaction 11, $(k_{11} \; [O_3])^{-1}$, is plotted in Figure 7.

The time constant for eddy diffusion can be estimated as

$$\tau_{mixing} \approx H^2/K \qquad (18)$$

(See, for example, Kellogg, 1964). However, the coefficient for vertical eddy diffusion, K, is not accurately known in this region. Its value has been estimated near 100 km by Colegrove, Hanson and Johnson (1965) as 4.5×10^6 cm^2/sec. As they state, the value is expected to be altitude dependent but in an unknown way. Measurements of the eddy diffusion coefficient have been made in the upper stratosphere by observing the growth of vapor trails, but the values probably refer to horizontal eddy diffusion rather than the vertical eddy diffusion considered here. For lack of a better model, the coefficient of vertical eddy diffusion has been assumed independent of altitude and a value of 4.5×10^6 cm^2/sec adopted. The time constant computed on that basis from Equation 18 has been plotted in Figure 7.

As shown in the figure, eddy diffusion, having the smaller time constant above 65 km, should dominate in this region whereas the ozone reaction should dominate below. The curves in the figure are independent of the nitric oxide density profile and depend only on the measured temperature and the assumptions

concerning the ozone concentration, the rate constant, and the eddy diffusion coefficient. Figure 7 suggests a change in the dominant process controlling the nitric oxide distribution near 65 km. This suggestion should be compared with the nitric oxide density profile which shows a change in slope near 70 km.

A sharply defined sink region would not be expected to influence the distribution in the eddy diffusion region more than a scale height or so away from the boundary in equilibrium. In this case the boundary is not so sharply defined but extends, with decreasing effectiveness, into the eddy diffusion region.

It is necessary to consider the diurnal motion of this boundary between the mixing and loss controlled regions. A second destruction time constant curve has been plotted in Figure 7 on the basis of Hunt's (1966) theoretical estimates of the ozone density for day and night. These curves predict that in the 60 to 80 km region the measured amount of nitric oxide will not survive during the night but will be destroyed by reaction 11.

In actual fact neither the predawn high altitude ozone densities nor the vertical eddy diffusion coefficient have been adequately measured. Further measurements of the nitric oxide density at other solar zenith angles, combined with high

altitude ozone measurements could be combined in an indirect estimation of the vertical eddy diffusion coefficient. It must be stressed, however, that these processes are all time dependent and that estimates based on isolated observations using equilibrium considerations could be seriously in error.

It is suggested that a comparison of measured nitric oxide profiles during morning and evening twilight would reveal an asymmetry near 70 km, the profile in the morning having a decreased density in comparison with the evening values. This decrease would be due to the destruction by ozone, during the night. If this is in fact the case, then reaction 11 should be included in studies of the behavior of ozone.

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REFERENCES

Barth, C. A., "Nitrogen and Oxygen Atomic Reactions in the Chemosphere" in Chemical Reactions in the Lower and Upper Atmosphere, Interscience, New York, p. 303, 1961.

Barth, C. A., "Rocket Measurement of the Nitric Oxide Dayglow." J. Geophys. Res., 69, 3301, 1964.

Barth, C. A., "Nitric Oxide in the Upper Atmosphere". Ann. Geophys., 22, 198, 1966.

Bless, R. C., A. D. Code and D. J. Schroeder, "Astronomical Radiation Measurements. I. Spectrophotometric Standards for Astronomical Use". Ap. J. 153, 545, 1968.

Colegrove, F. D., W. B. Hanson and F. S. Johnson. "Eddy Diffusion and Oxygen Transport in the Lower Thermosphere". J. Geophys. Res. 70, 4931, 1965.

Cospar International Reference Atmosphere, North Holland Publishing Company, Amsterdam, 1965.

Evans, W. F. J., "An Investigation of the Temporal and Spatial Variations of the Infrared Atmospheric Bands of Molecular Oxygen in the Airglow". Thesis: University of Saskatchewan, Saskatoon, 1967.

Evans, W. F. J., D. M. Hunten, E. J. Llewellyn and A. Vallance-Jones, " Altitude Profile of the Infrared Atmospheric System of Oxygen in the Dayglow". J. Geophys. Res., 73, 2885, 1968.

Fastie, Wm. G., "Instrumentation for Far Ultraviolet Rocket Spectrophotometry." J. Quant. Spectrosc. Radiat. Transfer, 3, 507, 1963.

Ferguson, E. E., F. C. Fehsenfeld, P. D. Goldan and A. L. Schmeltekopf, "Positive Ion-neutral Reactions in the Ionosphere." J. Geophys. Res., 70, 4323, 1965.

Ford, H. W., G. J. Doyle and N. Endow, "Rate Constants at Low Concentrations. II. Reactions Between Nitric Oxide and Ozone in Air at Room Temperature." J. Chem. Phys., 26, 1337, 1957.

Harteck, P., "A Discussion on the Reactions of Nitrogen and Nitrogen Oxides in the Upper Atmosphere." The Threshold of Space, edited by M. Zelikoff, Pergamon Press, New York, P. 32, 1957.

Hunt, B. G., "Photochemistry of Ozone in a Moist Atmosphere." J. Geophys. Res., 71, 1385, 1966.

Hunten, D. M., "A Study of Sodium in Twilight: I. Theory." J. Atmospheric Terrest. Phys. 5, 44, 1954.

Hunten, D. M. and M. B. McElroy, "Metastable $O_2(^1\Delta)$ as a Major Source of Ions in the D-region." J. Geophys. Res., 73, 2421, 1968.

Johnston, H. S. and H. J. Crosby, "Kinetics of the Fast Gas Phase Reaction Between Ozone and Nitric Oxide." J. Chem. Phys., 22, 689, 1954.

Jursa, A. S., Y. Tanaka and F. LeBlanc, "Nitric Oxide and Molecular Oxygen in the Earth's Upper Atmosphere." Planet. Space Sci., 1, 161, 1959.

Kellogg, W., "Pollution of the Upper Atmosphere by Rockets." Space Sci. Rev., 3, 275, 1964.

Kistiakowsky, G. B. and G. G. Volpi, "Reactions of Nitrogen Atoms: I. Oxygen and Oxides of Nitrogen." J. Chem. Phys., 27, 1141, 1957.

Kistiakowsky, G. B. and G. G. Volpi, "Reactions of Nitrogen Atoms: II. H_2, CO, NH_3, NO and NO_2." J. Chem. Phys., 28, 665, 1958.

Nicolet, M., "Contribution a l'etude de la Structure de l'ionosphere." Mem. Inst. Meteor. Belgium, 19, 83, 1945.

Nicolet, M., "The Aeronomic Problem of Nitrogen Oxides." J. Atmospheric Terrest. Phys., 7, 152, 1955.

Nicolet, M., "Ionspheric Processes and Nitric Oxide." J. Geophys. Res., 70, 691, 1965a.

Nicolet, M., "Nitrogen Oxides in the Chemosphere." J. Geophys. Res., 70, 679, 1965b.

Nicolet, M. and A. C. Aikin, "The Formation of the D-region of the Ionsphere." J. Geophys. Res., 65, 1469, 1960.

Norton, R. B., "The Ionized Constituents in the 100 to 300 Kilometer Region of the Earth's Upper Atmosphere." Thesis: University of Colorado, Boulder, Colorado, 1967.

Pearce, J. B., to be published.

Phillips, L. F. and H. I. Schiff, "Mass Spectrometric Studies of Atom Reactions: I. Reactions in the Atomic Nitrogen-Ozone System." J. Chem. Phys. 36, 1509, 1962.

de Vos, J. C., "A New Determination of the Emissivity of Tungsten Ribbon." Physica, 20, 690, 1954.

FIGURE CAPTIONS

Figure 1. An observed dayglow spectrum showing the (1,0), (0,0) and (0,1) nitric oxide gamma bands. Also shown is a sequence from the on board telemetry voltage calibrator (2180 to 2196 Å apparent) and a wavelength fiducial, 2063 to 2078 Å. The spectrometer was at an altitude of 94.5 kilometers and viewed the atmosphere at a zenith angle of 13°.

Figure 2. The altitude profile of the nitric oxide gamma (1,0) band apparent zenith emission rate (circled dots). Also plotted is the smoothed profile of equation 13 (solid line).

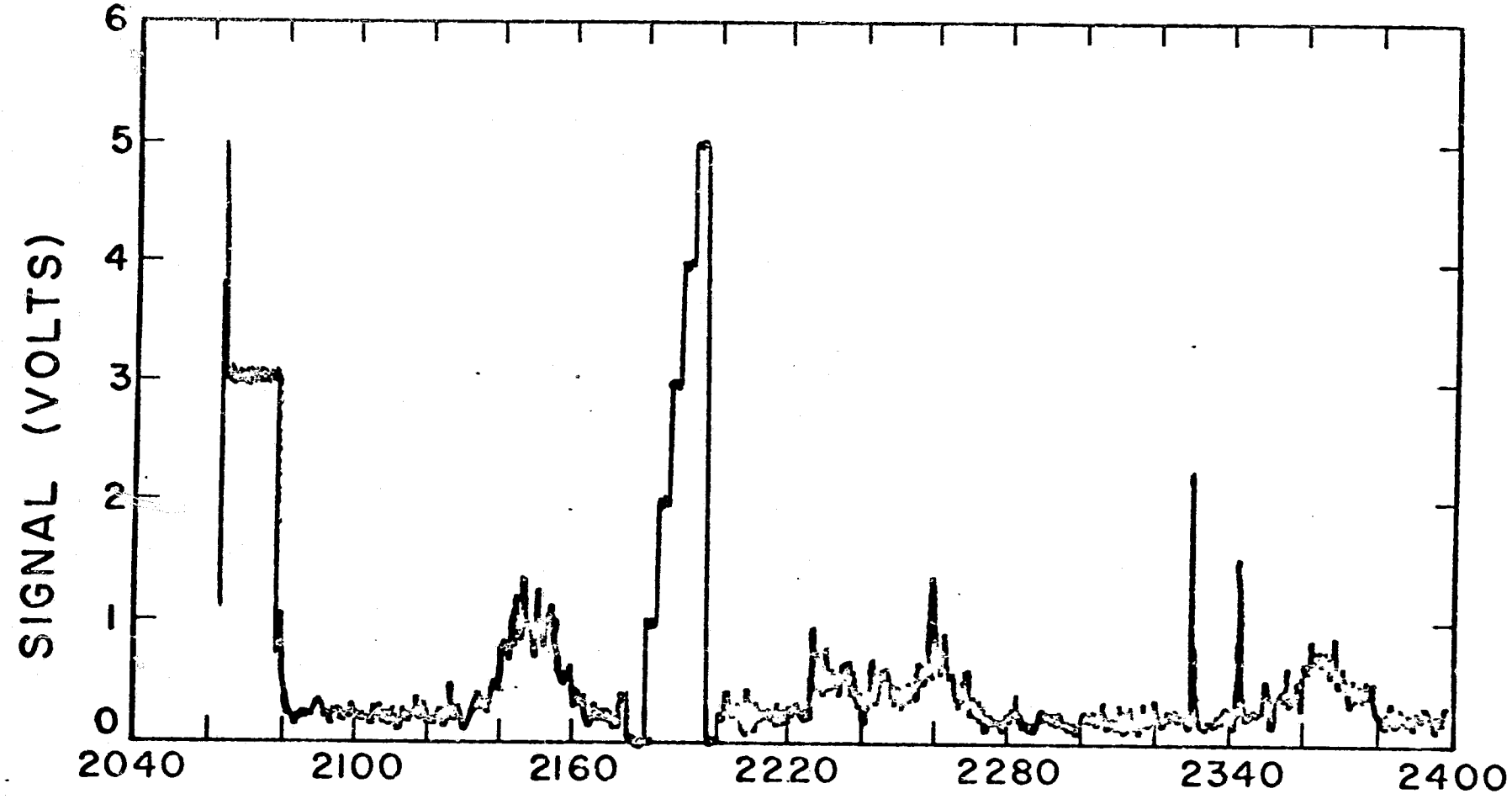
Figure 3. The derived nitric oxide density. The shaded area indicates the precision of the data.

Figure 4. The rocket grenade temperature profile for 21:58 GMT on 12 December 1967 above Wallops Island, Virginia. (W. Smith, private communication).

Figure 5. A comparison of the atmospheric (circled dots) and nitric oxide (solid line) densities.

Figure 6. Comparison of the observations of Fig. 3 with those of Barth (1966) (circled dots).

Figure 7. Diffusion and chemical removal time constants for nitric oxide molecules.


SIGNAL (VOLTS)
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3
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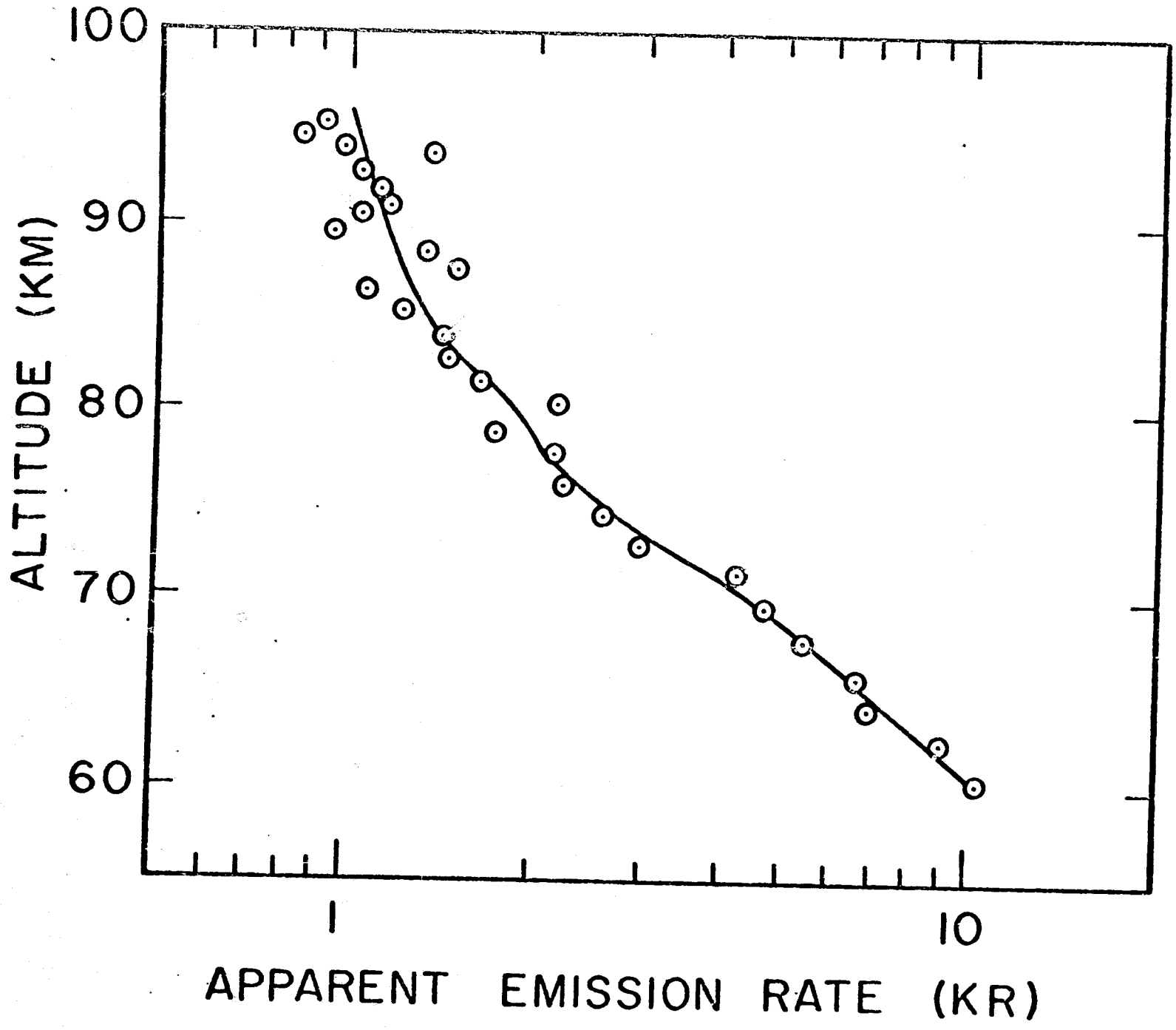
1
0
2040
2100
2160
2220
2280
2340
2400
WAVELENGTH (Å)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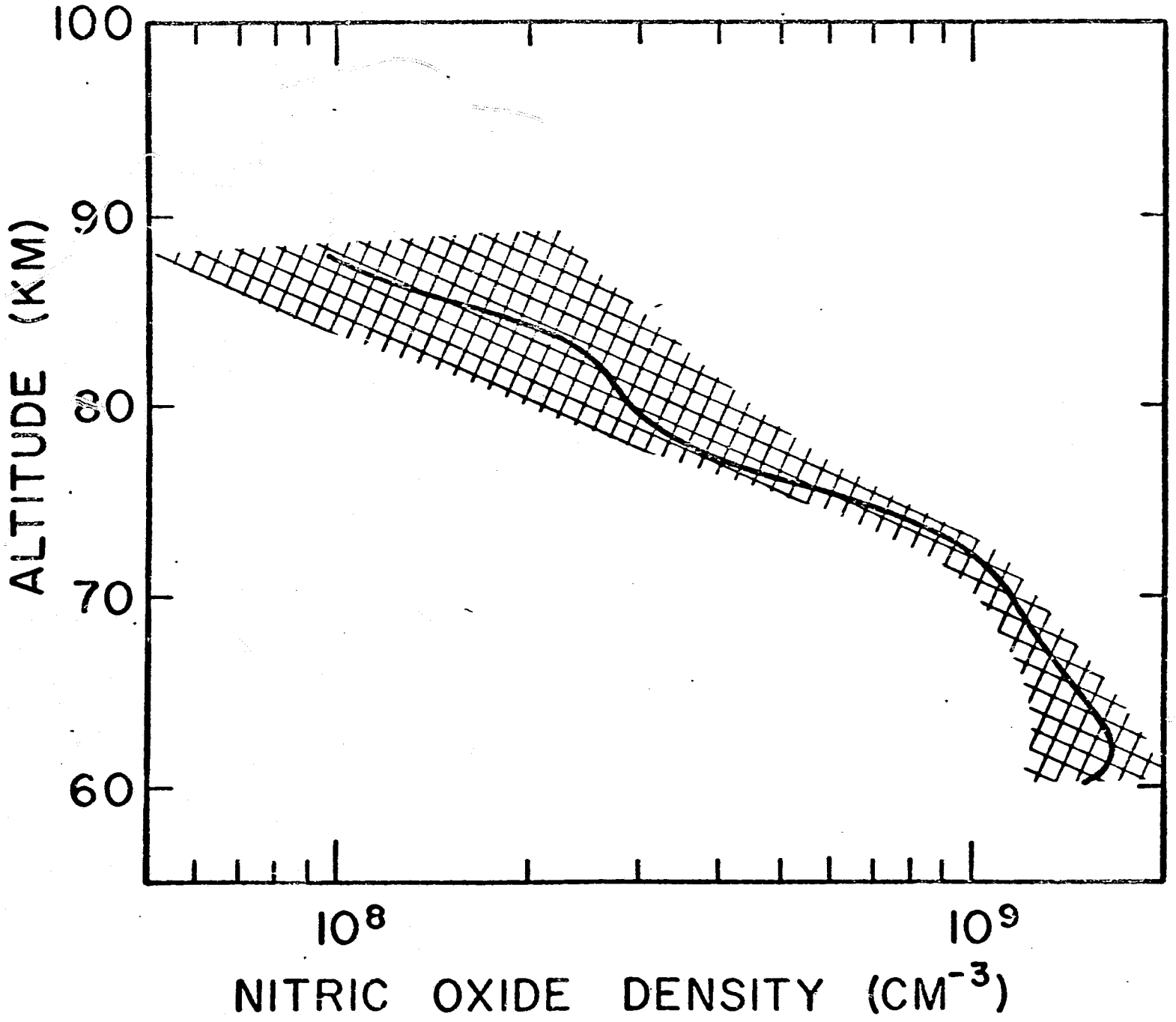
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60
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10^9
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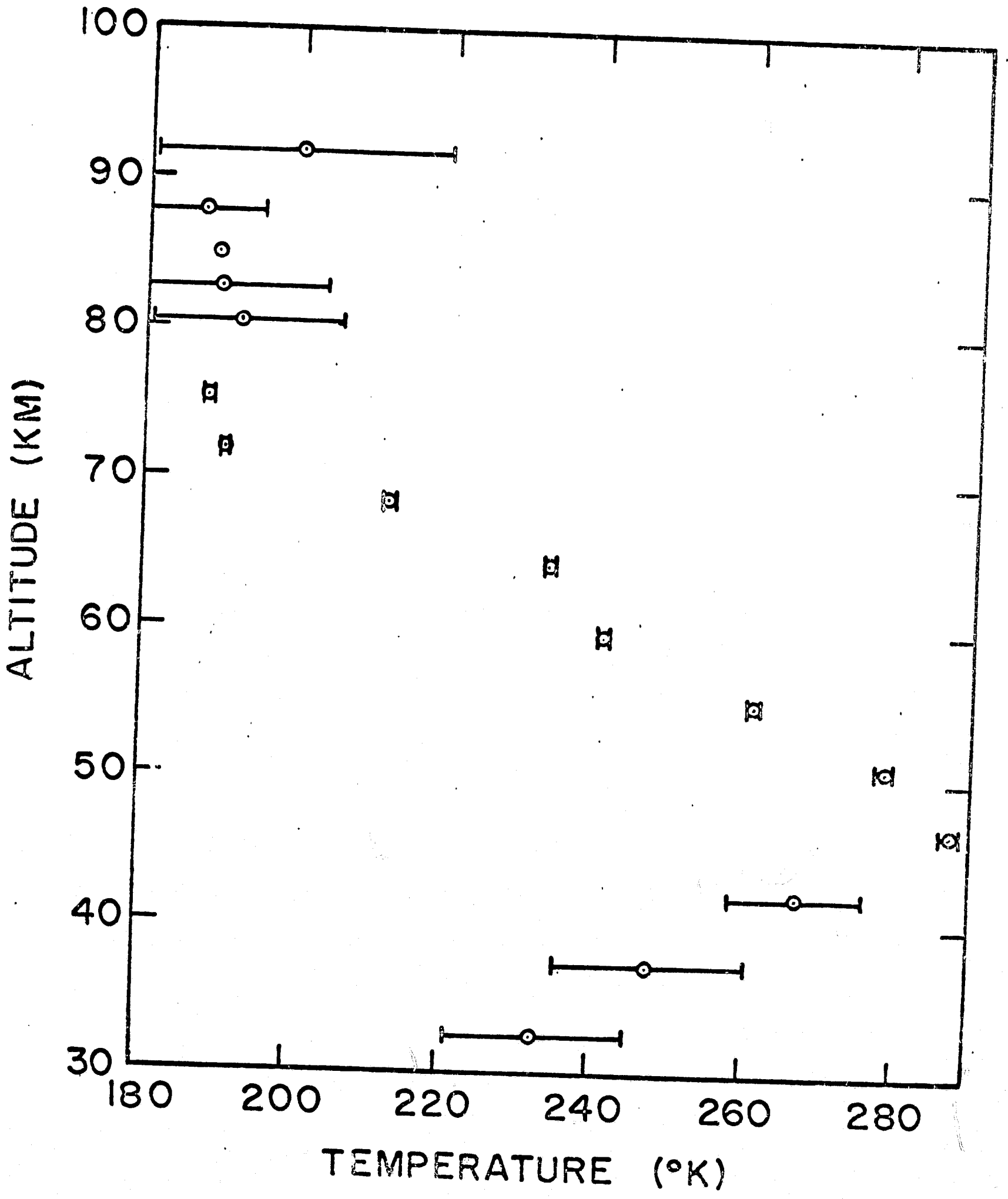
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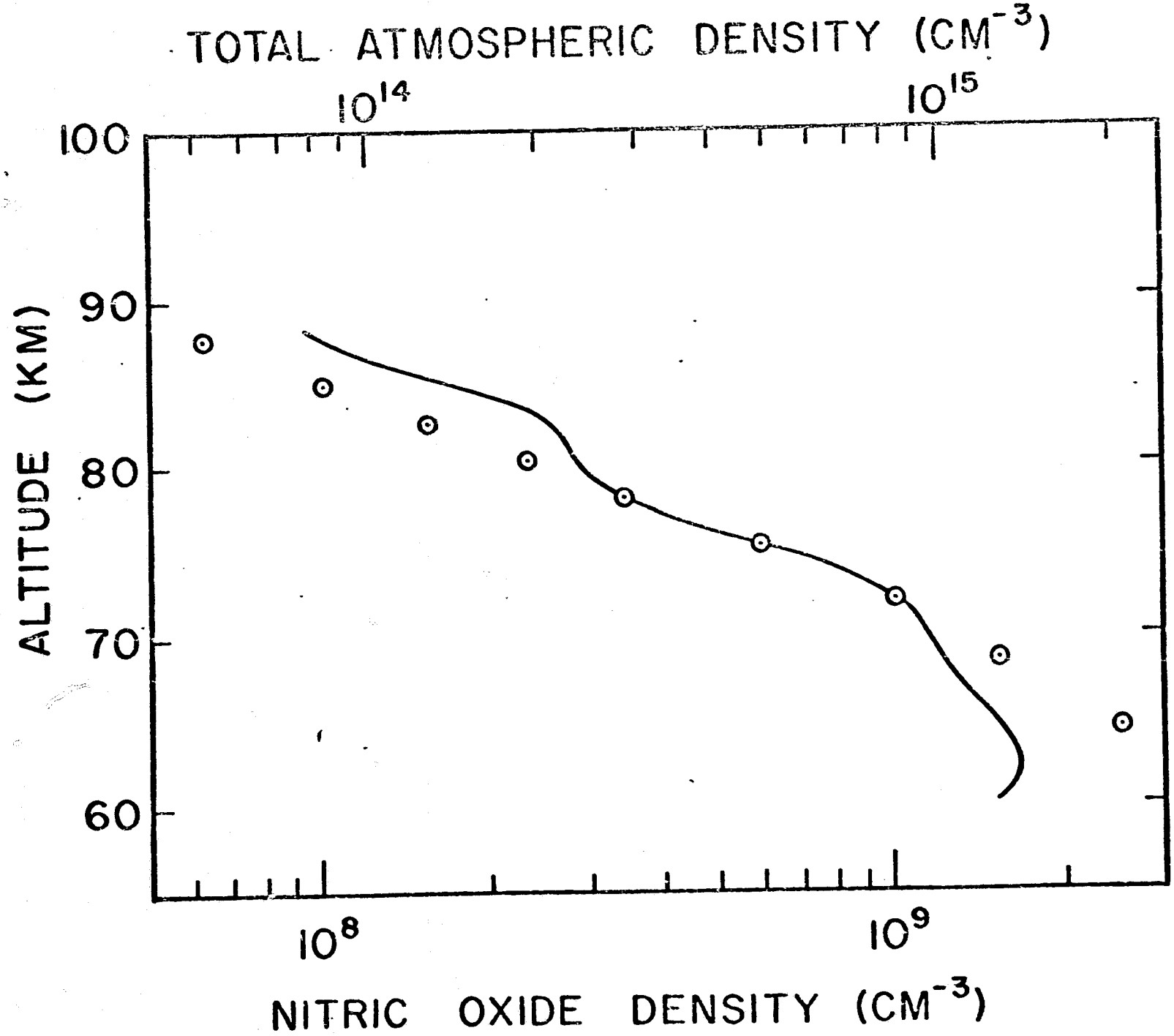
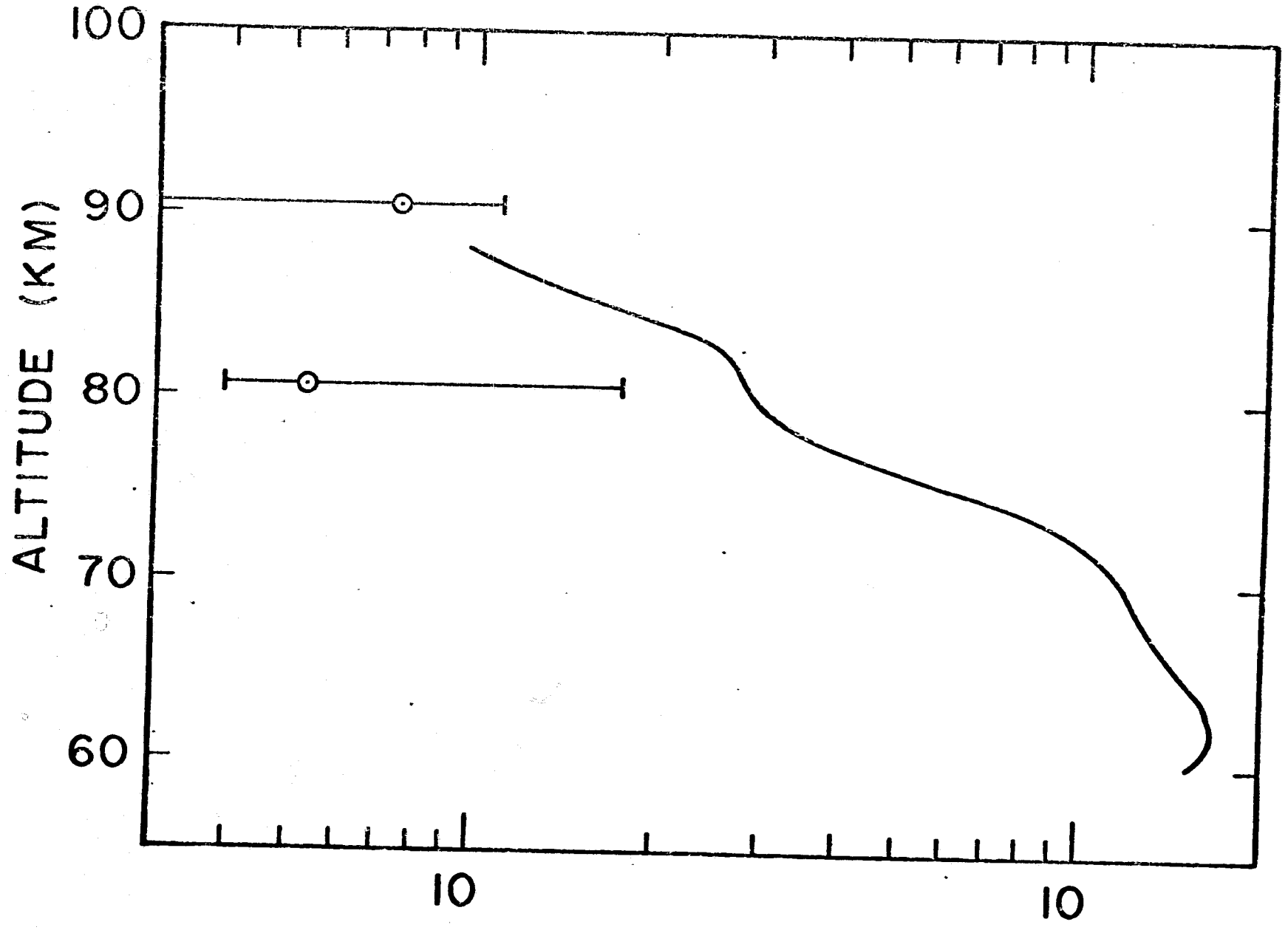
ALTITUDE (KM)
TEMPERATURE (°K)


TOTAL ATMOSPHERIC DENSITY (CM^{-3})
10^{14}
10^{15}
100
90
80
70
60
ALTITUDE (KM)
10^{8}
10^{9}
NITRIC OXIDE DENSITY (CM^{-3})


100
90
80
70
60
ALTITUDE (KM)
10
10
NITRIC OXIDE DENSITY (CM^{-3})