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A STUDY OF PIONEER VENUS NIGHTGLOW SPECTRA

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SUMMARY

The work performed during the 12-month period of this contract involved (1) further analysis of latitudinal variations in the Venusian NO nightglow intensity from PVOUVS data, (2) corrections made to the input data for the VTGCM model, relating specifically to a factor of three increase in the three-body recombination rate coefficient of N + O, (3) consideration of limits on the rate of reaction of N-atoms with CO_2 , (4) consideration of the Venusian equivalent of the terrestrial hot N-atom reaction for NO production, and (5) successful location of video images of meteor trails from space, for the purpose of making a comparison with the meteor trail that we have hypothesized as an explanation of intense UV spectra observed on a particular PV orbit.

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INTRODUCTION

Airglow spectra provide a great deal of information about the state of the upper atmospheres of planets. The terrestrial airglow has been studied for many years, and much has been learned about atmospheric dynamics, chemistry, and energetics from ground-based measurements, rockets, and satellites. Knowledge of airglow phenomena in the atmospheres of our sister planets, Mars and Venus, is naturally much sparser, and certainly the state of our understanding is still relatively primitive.

The Pioneer Venus Orbiter had been circling the planet since 1978, before its recent demise, and one of the instruments on board was an ultraviolet spectrometer, covering the 120-350 nm spectral region. Because of the 240 earthday rotational period of Venus, any point on the planet is in darkness for ~100 days, a period of time over which one might think that the atmosphere would lose the energetic particles that could contribute to airglow. In the terrestrial atmosphere, oxygen atoms at 100 km are stable over a 12-hour dark period, but on Venus replenishment is required, presumably by circulation from the sunlit side, for there to be fuel to drive the nightglow.

This report summarizes the work done during a second year of funding on the Pioneer Venus Guest Investigator Program. During the first year, significant conclusions were reached concerning the Pioneer Venus Orbiter Ultraviolet Spectrometer (PVOUVS) data, relating to differences in spectra for high and low photon count rate scans and to the interpretation of intense emission detected on a particular orbit.

We showed that, when low and average intensity spectra are summed, the resulting NO fluorescence seems to contain features indicating some collisional relaxation, whereas for high intensity spectra, there does not seem to have been any collisional relaxation. Note that the average number of photons collected in a spectral scan is only three, and that "high intensity" refers to collection of more than ten photons in a scan. We concluded that the higher intensity scans originate from higher in the atmosphere, where two-body recombination dominates three-body recombination.

The most unusual aspect of our investigation was the conclusion that we reached concerning the very intense spectra seen in three consecutive scans on Orbit 75. As discussed further in this report and in the reprint that appears as an Appendix, we have concluded that the most consistent explanation involves the idea that a meteor trail was observed, in which N₂ and

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CO₂ dissociation by shock heating leaves a track in which N- and O-atoms recombine, giving a spectrum that looks just like the nightglow, but is of much greater intensity.

In this report, we discuss a new analysis of the latitudinal distribution of the nightglow intensity, make corrections to the input kinetic data that have been used in interpreting the PVOUVS observations, and point out the consequences of a slow but significant rate coefficient for the reaction between ground state nitrogen atoms and CO₂. We also raise the possibility that the chemistry of fast nitrogen atoms with CO₂ may be important in the Venusian atmosphere, and we present new information on meteors detected from space in the terrestrial atmosphere.

ACCOMPLISHMENTS

LOCALIZED UV EMISSION INTENSITIES

In the analysis reported during last year's study of the latitudinal variation of NO UV intensity from PVOUVS data, we claimed that we did not see any indication that more intense spectra were observed in the southern hemisphere. This claim was contrary to the conclusion reached by Stewart et al. [1980], based on a different set of data, who claimed the most intense emission originated at about 10 degrees south latitude, at 2 a.m. of the morning sector.

We have now reexamined the data that we used, and we realize that our analysis was biased by the fact that more observations were made in the northern hemisphere. A reanalysis, to determine the fraction of bright spectra seen at each latitude range, is summarized in Table 1.

		[Average = 3	pnotons/s	canj
Latitu	de	Number of High Count Scans [*]	Total Scans	Percentage
0-9.9	N S	6 5	127 114	4.7 4.4
10-19.9	N S	3 0	143 100	2.1 0
20-29.9	N S	3 5	150 63	2.0 7.9
30-39.9	N S	1 3	140 50	0.7 6.0
40-49.9	N S	1 3	123 28	0.8 10.7
>50 >50	N S	1 4	156 85	0.7 4.7

TABLE 1

Analysis of Latitudinal Location of High Count Scans (N \ge 11) [Average = 3 photons/scan]

* Percentage of high count scans, north - 1.8%

Percentage of high count scans, south - 4.5%

Looked at in this manner the fraction of bright spectra (those with 11 or more counts in a scan) are more common in the southern hemisphere than in the northern. Curiously, the only latitude range where this conclusion does not hold is at 10-19.9 degrees, just the range where Stewart et al. [1980] found their maximum. We suspect that this is only a statistical issue and that there is not an important difference between our reanalysis and the conclusions of Stewart et al.

KINETIC DATA FOR TWO- AND THREE-BODY N + O RECOMBINATION

We continued to work on the problem of understanding the differences between NO recombination spectra from high and low altitude in the Venusian atmosphere. In so doing, we looked at the relative importance of two-body and three-body atom recombination as a function of altitude, and we found some discrepancies in the recent paper by Bougher et al. [1990], which originated with the earlier study of Stewart et al. [1980].

At issue is the choice of kinetic parameters used in 1980 for the reactions

$$O + N \xrightarrow{k_1} NO$$
(1)
$$O + N + CO_2 \xrightarrow{k_2} NO + CO_2$$
(2)

$$O + N + CO_2 \xrightarrow{k_2} NO + CO_2$$
 (2)

The value given by Stewart et al. [1980] for reaction (1) is 2.5×10^{-17} cm³ s⁻¹, and for reaction (2), 1.1×10^{-32} (T/300)^{-1/2} cm⁶ s⁻¹, the source for the former being Mandelman et al. [1973], and for the latter, Baulch et al. [1973].

For reaction (2), there is clearly an error on the part of Stewart et al. [1980], the value given by them being true for N₂ as a third body, whereas the measured value for $M = CO_2$ is larger by a factor of three. For reaction (1), the issue is slightly complicated. Mandelman et al. [1973] give a value of 1.5×10^{-17} cm³ s⁻¹, which Stewart et al. [1980] interpret correctly as referring only to that part of the recombination resulting in NO(C-X) emission. For the total recombination, the rate coefficient is 2.5×10^{-17} cm³ s⁻¹, based on the assumption of 60% as a value for the C-X branching fraction. These numbers refer to 300 K.

Du and Dalgarno [1990] calculated the temperature coefficient for the recombination reaction and found a total rate coefficient of 1.9×10^{-17} cm³ s⁻¹ at 300 K. They erroneously compare this to the rate coefficient of Mandelman et al. [1973] of 1.5×10^{-17} , instead of the higher total figure. Upon determining the temperature coefficient, they obtain a value of 2.5×10^{-17} cm³ s⁻¹ at 170 K, the Venus atmospheric temperature at 100 km. This rate coefficient is the value used by Stewart et al. [1980], in the absence of temperature information, and thus is

fortuitously correct. Therefore, it is only the three-body recombination coefficient used by Stewart et al. that requires correction.

We have communicated this information to Ian Stewart and Steve Bougher, and we understand that the faster loss of N-atoms caused by the revised three-body rate coefficient will require an adjustment in parameters such as eddy diffusion coefficients and wind velocities, such that a sufficient atom flux can be conveyed between the sunlit and dark hemispheres to accommodate the observed UV intensities.

EFFECT OF CHANGED THREE-BODY RECOMBINATION COEFFICIENT

The relevance of these considerations to our study of UV spectroscopy is that three-body recombination, and thus the possibility of collisional relaxation, is confined to altitudes significantly lower than those for which emission is observed if we use the rate coefficients from Stewart et al. [1980] and Bougher et al. [1990]. With substantially enhanced three-body recombination, the altitude of the low-level background NO emission, which we claim shows evidence for collisional redistribution, is not incompatible with the emitting altitude. This subject is discussed further in the Appendix.

POSSIBILITY OF INTERACTION BETWEEN CO₂ AND GROUND STATE N-ATOMS

A point that has not been sufficiently emphasized concerns the possibility of interaction between nitrogen atoms and CO_2 . The N and O atoms whose two- and three-body recombinations cause the nightglow are generated on the sunlit side of Venus. For them to be carried around to the opposite side of the planet, there are constraints on the magnitude of collisional processes that destroy them.

It is generally accepted that the high altitude circulation pattern is such that transfer between the sunlit and dark hemispheres (over 180°) is about half a day, i.e., about 4×10^4 s. Thus, we need to know if there are two-body reactions that destroy N atoms which have rates on the order of the reciprocal of this time constant, 2.5×10^{-5} s⁻¹. The most obvious possibility is that of reaction with the majority species, CO₂,

$$N(^{4}S) + CO_{2} \xrightarrow{k_{3}} NO(X^{2}\Pi) + CO(X^{1}\Sigma^{+})$$
(3)

This is a spin-forbidden reaction, since N(4S) and CO₂ will recombine on a quartet surface, whereas the products will be formed on a doublet surface. Thus, the reaction will certainly be slow, although it is 24 kcal/mole exothermic.

If we take a standard CO₂ altitude profile, we can calculate what the necessary rate coefficient for reaction (3) must be to match the circulation rate of 2.5×10^{-5} s⁻¹. Table 2 lists this rate coefficient as a function of [CO₂] and altitude, using the concentration profile given by Fox and Dalgarno [1981].

TABLE 2

Altitude (km)	[CO ₂] (cm ⁻³)	Rate Coefficient (cm ³ s ⁻¹)
110	7 × 10 ¹³	3.5 × 10 ⁻¹⁹
120	5 × 10 ¹²	5 × 10 ⁻¹⁸
130	8×10 ¹¹	3 × 10 ⁻¹⁷
140	1 × 10 ¹¹	2.5 × 10 ⁻¹⁶
150	1.5 × 10 ¹⁰	1.7 × 10 ⁻¹⁵
160	2.5 × 10 ⁹	1 × 10 ⁻¹⁴

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Thus small rate coefficients are adequate to impede the transfer of N-atoms between hemispheres, depending on the altitude at which the process takes place. According to Fox and Dalgarno [1981], the neutral temperature over the 110-160 km range lies between 200 K and 280 K.

The measurement of such small rate coefficients is not easy, since a system impurity can lead to an overestimate and thus false conclusions. The $N(^{4}S) + CO_{2}$ rate coefficient has not been measured seriously since the work of Herron and Huie [1968]. These workers made their measurements mass spectrometrically, using a discharge flow system, and looked for a reduction in the N-atom density as CO2 was added. None was seen, from which they calculated an upper limit for the rate coefficient for reaction (3), at 550 K, of 2×10^{-16} cm³ s⁻¹. Their study was performed as a check on the work of Avramenko and Krasnen'kov [1967], who had earlier claimed a rate coefficient almost two orders of magnitude larger (at the same temperature).

The latter study was conducted by measuring the CO produced in reaction (3), which is somewhat different from measuring the loss of N-atoms. In a third study, by Campbell and Thrush [1966], O-atom densities were monitored, since any NO formed in reaction (3) would immediately react with N,

$$N(^{4}S) + NO \rightarrow N_{2} + O(^{3}P)$$
⁽⁴⁾

The chemiluminescent reaction of N and O, as in the Venus atmosphere, was then used as a measure of the O-atoms formed. Campbell and Thrush [1966] concluded that the observed increase in O-atom density with CO_2 addition was due to metastable molecular states of N₂ reacting with CO_2 ,

$$N_2(A^3\Sigma_u^+) + CO_2 \rightarrow N_2 + CO + O(^3P), \tag{5}$$

rather than a combination of reactions (3) and (4).

In these relatively early studies, there was no cognizance of the fact that, in N₂ afterglow experiments, an important discharge product is $N(^{2}D)$, the first excited state of the nitrogen atom. We have measured its relatively rapid rate coefficient with CO₂ [Black et al., 1969], and Lin and Kaufman [1971] have shown that it interacts reactively,

$$N(^{2}D) + CO_{2} \rightarrow NO + CO$$
(6)

Thus, it is not surprising that there can be considerable variation in the results of afterglow experiments. In the Russian study [Avramenko and Krasnen'kov, 1967], CO may have been detected because the discharge and flow conditions were such that a significant fraction of N(²D) was present.

From our perspective, the question of the rate coefficient for reaction (3) is not adequately settled. Although the Herron and Huie [1968] data were taken at 550 K, the rate coefficient at 300 K could be at least 1×10^{-17} cm³ s⁻¹, in which case we see from Table 1 that, at the 125-km level, half the N-atoms would be lost in crossing between the hemispheres (given that there are no other competing processes). From conversations with Ian Stewart, it seems that 135 km and above is the altitude at which the trans-hemispheric mixing of N and O takes place, so the N + CO₂ reaction is likely to be of marginal importance in that context.

However, when we consider what effect there might be lower in the atmosphere, in competition with three-body recombination of N- and O-atoms, we find that a rate coefficient of 1×10^{-17} cm³ s⁻¹ for reaction (3) is very important. For three-body N + O recombination, when

[N]/[O] is small, as is the case for the Venus atmosphere, the N-atom loss rate is k2[O][CO2]. For reaction (3), it is $k_3[CO_2]$. The ratio between these rates is $(k_2/k_3)[O]$. The three-body rate coefficient, k₂, is 3×10^{-32} cm⁶ s⁻¹ at ~300 K [Baulch et al., 1973], so the rate constant ratio is $3 \times 10^{-32}/1 \times 10^{-17} = 3 \times 10^{-15}$. Therefore, reaction (3) dominates three-body recombination for $[O] < 3 \times 10^{14}$ cm⁻³. Since this concentration is three orders of magnitude larger than the peak O-atom density [Fox and Dalgarno, 1981], k₃ can be far smaller than 1×10^{-17} cm³ s⁻¹ and still dominate the three-body recombination rate.

The two-body N + O recombination rate coefficient is 2.5×10^{-17} cm³ s⁻¹ [Du and Dalgarno, 1990], and the ratio of N-atom loss by this reaction to that by reaction (3) (for $k_3 = 1 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$) is 2.5[O]/[CO₂]. Thus, for [O]/[CO₂] < 0.4, N-atoms will be lost faster by reaction (3) than by two-body recombination. Below 140 km, [O]/[CO2] never exceeds 0.01, and thus for the assumed value of k₃, it would be the principal sink of N-atoms for all altitudes below ~160 km, converting N-atoms to NO as do the recombination processes, but also generating CO.

HOT N-ATOM REACTIONS

An interesting analogy exists with the terrestrial atmosphere. Over the last decade, we have become aware that, although the thermal reaction of N-atoms with O2 is very slow, hot N-atoms can react with O₂ to provide a significant source of NO [Solomon, 1983]. A similar process may take place between hot N-atoms and CO2. There may be some such effect on the Venusian dayside, and since there is apparently auroral activity on the nightside [Fox and Taylor, 1990], a case can be made for the importance of the process, in terms of N-atom loss and NO and CO production, on the dark side. In any case, NO can be transported between the two hemispheres, with the fast reaction between N and NO determining equilibrium concentrations.

The same source terms for fast N-atoms can be listed as has been done for the terrestrial case [Gerard et al., 1991]

$$N_2 + hv \rightarrow N(^2D) + N(^4S) \tag{7}$$

$$N_2 + hv \to N(^2D) + N(^4S)$$
(7)

$$N_2 + e \to N(^2D) + N(^2D, ^4S) + e$$
(8)

$$N(^{2}D) + O \rightarrow N(^{4}S) + O$$
⁽⁹⁾

and it is clear that the potential exists for significant $N + CO_2$ interaction. If we take the limit for the rate coefficient of 2×10^{-16} cm³ s⁻¹ at 550 K [Herron and Huie, 1968], this is larger by a factor of 5.5 than the rate coefficient for $N + O_2$ at the same temperature [Baulch et al., 1973].

There is therefore good reason to investigate the actual value of k_3 as a function of temperature, since if we concede that experiments to date have shown it to be less than 1×10^{-17} cm³ s⁻¹ at 300 K, we have demonstrated that it would still be significant in modeling the Venus (and Mars) atmospheres at a value of 1×10^{-19} cm³ s⁻¹, or even less. If the possibility of nonthermal reactions is then invoked, it seems evident that these kinetics issues need to be pursued.

From an experimental point of view, the most likely approach to studying fast N-atom reactions is to use crossed molecular beams of $N(^4S)$ and CO_2 , using laser-induced fluorescence to measure product NO and/or CO. We can also generate fast N atoms in a dissociative process, using multiphoton excitation to excite N_2 to known energies above the first dissociation limit. In either case, a critical issue would be to suppress the presence of excited N-atoms. Neither technique is easy, yet is important to get a handle on this particular reaction between nitrogen and CO_2 , the two most important species in the Venusian atmosphere.

METEORS

The publication describing the first year of our Guest Investigator studies has now appeared in the *Journal of Geophysical Research (Planets)* and is included as an Appendix to this report. Because the reviewing process was inordinately slow, much of the second year's work was added while the paper was in press, including a more complete discussion of meteor phenomena.

At the Pioneer Venus investigator presentations, doubt was expressed that the apparent long straight track of NO excitation on Orbit 75 could be explained only by a meteor passing under the satellite. The improbability of such an event seemed to be the basic criterion for this sentiment.

We agree that the event is improbable. However, the probability of a supernova explosion occurring in 1989 only 160,000 light-years from earth is also improbable; yet it did happen. Probabilities should be used with caution when considering unpredicted events. In fact, one could have stated almost with certainty that during the PV mission, one or more low probability events would be observed. Thus, only after the event is defined (meteor passing below the spacecraft) is it useful to calculate the probability for the next such occurrence.

To summarize the arguments concerning the Orbit 75 observations, we present the analysis shown in Table 3, to distinguish between the various possible explanations. None of the other possibilities so far suggested have physical characteristics as consistent with the observations as the meteor hypothesis.

TABLE 3

The O	bservation,	and	Possible	Explanations	for	Enhanced	Intensities	on	Orbit	75
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	Spectrum	Track Length	Track Width	<u>Intensity</u>
Orbit 75 Data	N+O 2-body recombination (alt. >105 km)	≥900 km (straight)	≤5 km	>>600 kR
Nightglow	N+O 2- and 3- body recomb.			3 kR, avg.
Meteor	N+O afterglow 2-body high alt. 3-body low alt. Metals and ions in fireball	Long and straight	Narrow	Variable
Lightning	Excited CO, CO ₂ + N ₂ , N ₂ + 3-body N+O in afterglow	Patches	Short	Very high
Aurora	Lightning-like	Irregular	Variable	Weak

We were curious to learn more about meteor observations and discovered considerable recent interest in the specific question of meteors in the Venus atmosphere. Chyba et al. [1993] argued that certain features seen by the Magellan spacecraft on the Venusian surface are most likely caused by shock waves. These result from large meteors entering the atmosphere and breaking up before reaching the surface because of the high (100-bar) surface pressure. A companion article [Melosh, 1993] showed a photograph of a meteor trail in the terrestrial atmosphere, taken in broad daylight from the ground. The meteor had a grazing trajectory, was estimated to be at a height of 60 km, and left a trail 1500 km long, which is comparable to the length that we stated seemed appropriate for the PV event.

Taking the question one step further, we then attempted to determine whether there were any meteor observations from satellites. It seems most likely that the same observations would be made: dissociation of N₂ and O₂ would lead to a meteor trail dominated by ultraviolet emission from recombining NO. If the altitude is high enough (>90 km), it is possible that no visible emission would be seen from a grazing collision, since the typical sodium trail results from surface heating of the meteor, rather than from shock heating of the air.

There does not seem to be any published material on meteors seen from space, unless cometary snowballs are considered [Frank et al., 1986], a subject that is still very controversial. However, we were lucky in finding the right individuals with whom to discuss this subject. With the help of Steve Mende from Lockheed Palo Alto Research Laboratory, we were directed to Steve Geller in the same laboratory, who has a set of video images taken on the Atlas 1 mission of March 1992. These images, produced by the Atmospheric Emissions Photometric Imaging Experiment, show clear evidence of meteor passages through the atmosphere.

Figure 1 shows 18 consecutive 1/30-s images, each of which shows two distinct points. The lower is a star, and the upper is a meteor, since it moves with respect to the several stars appearing in the images. This is shown in Figure 2, where the 18 images are co-added, and the track can be seen. Detection was made at 557.7 ± 1.3 nm, and thus the O($^{1}S \rightarrow ^{1}D$) nightglow emission appears prominently. It is possible that the meteor excites oxygen atoms in its passage through the atmosphere; green line emission has been seen by ground-based instruments [Bronshten, 1983]. However, it is more likely that other emissions are dominant.

The meteor is seen only faintly in the first and last images of Figure 1 and therefore is observed for 0.6 s. In this period of time, a typical meteor will travel perhaps 30 km, and thus these trajectories show, as expected, passage and destruction in the atmosphere; grazing trajectories are exceptional. The entrance angle of the meteor is of course unknown, and thus the length of the track on the image of Figure 2 does not provide useful information. Furthermore, we can ' obviously not state how intense the emission might have been in the NO ultraviolet region.

Thus, precedence exists for detecting meteor trails from space, although admittedly the PV meteor must have been rather substantial (or close). Correlating that event with a meteor shower has not been attempted; there seems to be no readily accessible data for predicting their occurrence in extraterrestrial atmospheres.

The three bright PVOUVS spectra that define the track of the meteor are not the only bright spectra. The Orbit 75 spectra have intensities of 65, 61, and 26 photons, whereas the three next most intense spectra contain 32, 26, and 25 photons. There is, however, a basic difference between the Orbit 75 spectra and the others; the former are incomplete, and have almost all their intensity in a given band, whereas the latter have photons arriving throughout the 190-250 nm region. It is this information on which we base our claim that the Orbit 75 spectra originate with a narrow line-like source, whereas other bright spectra are associated with extended regions. See the Appendix for further discussion.



Figure 1. Video images of a meteor passage viewed from space, with earth as background. Lower spot is a star; upper spot is the meteor. Viewing wavelength = 557.7 nm; 1/30 s per frame.

Courtesy of Steve Geller and Steve Mende of Lockheed Palo Alto Research Laboratory.

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Figure 2. Co-added images from Figure 1, with features identified.

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Appendix

NEW PERSPECTIVES ON THE VENUS NIGHTGLOW

New Perspectives on the Venus Nightglow

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We have reanalyzed the 190- to 250-nm nightglow spectrum of Venus recorded by the Pioneer Venus Orbiter. This spectrum is known to consist primarily of v' = 0 features of the NO & and γ -bands. However, the summed spectra, taken over many orbits, have weak and previously unidentified bands in the same spectral region, which we interpret as originating from higher vibrational levels of NO($A^2\Sigma^-$), resulting from collisional relaxation of NO($C^2\Pi | v = 0$. The intensity of the airglow is quite variable, with the average number of photon counts in a spectral scan being 3, while the maximum counts observed is 65. We divided the scans into a high-count group and a low-count group. The resulting partial-sum spectra and the wide intensity variations suggest that at least two sources of excitation are operating. The low-count spectrum looks similar to an N + O afterglow spectrum taken at relatively high pressure, containing a variety of relaxed NO states, and thus appears to have been generated at low altitude. The high-count spectrum is unrelaxed, and resembles a photoexcitation spectrum of the $C^2\Pi(v = 0)$ state, and thus would reflect N + O recombination at higher altitudes. Of particular interest is a set of three consecutive intense spectra taken on the same orbit, which suggests the presence of a long (1000 km), straight, and narrow (~5 km) track of secondary NO excitation, possibly caused by a meteor.

INTRODUCTION

The Pioneer Venus spacecraft went into orbit around Venus in December 1978, and since that time a great deal of data has been collected. The ultraviolet spectrometer took nightglow spectra over the initial 2-year period, and several papers have been written describing the observations. The most important optical result relating to the nightglow was the identification of the UV emission. At first, by analogy with the Martin dayglow, the radiation was identified as the CO(a-X) Cameron band system [Stewart et al., 1979], but subsequent analysis [Feldman et al., 1979] showed that the emission was due to NO(C-X) and NO(A-X) band systems, just as observed in the terrestrial nightglow [Tennyson et al., 1986].

The Venera 9 and 10 spacecrafts had earlier investigated the nightglow in the visible spectral region [Krasnopolsky et al., 1976] and had found a series of bands that were eventually identified [Lawrence et al., 1977; Slanger, 1978; Slanger and Black, 1978] as originating primarily from two O_2 transitions, c-X and A'-a. It was only later that the same two band systems were identified in the terrestrial nightglow [Slanger and Huestis, 1981; 1983; Stegman and Murtagh, 1988], with radically different vibrational distributions.

The appearance of NO and O_2 emission systems in the terrestrial and Venusian nightglows is a consequence of atom recombination, whereby N and O atoms that are formed by some energetic process on the dayside subsequently recombine, in a two-body or three-body process, into excited states. In the terrestrial atmosphere the loss of atoms over a 12-hour period is quite slow, so that the recombining atoms utilized in the nightglow are simply carried with the rotating planet to the dark side from the dayside where they are generated. In the Venusian atmosphere, rotation is so slow that this process cannot occur, and it is hypothesized that upper atmospheric circulation

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Paper number 93JE00997. 0148-0227/93/93JE-00997\$05.00 brings the atoms around to the dark side in 0.5-0.8 days [Stewart et al., 1980; Bougher et al., 1990].

The explanation for the appearance of the two NO band systems in the Venus nightglow is evident from the potentials shown in Figure 1. Recombination in NO takes place primarily from atoms approaching on the NO($a^{4}\Pi$) potential. Interaction between the $a^{4}\Pi$ and $C^{2}\Pi$ states occurs just at the turning point of the atomic motion, which is coincidentally the position of the C(v = 0) level. As a result, only C(0) is produced, and it radiates both to the excited $A^{2}\Sigma^{+}$ state and the $X^{2}\Pi$ ground state. Because the C and A states are Rydberg states, with similar spectroscopic parameters, radiation from C(0) to the v = 0 level of the A state is strongly favored. Thus, in the absence of multiple collisions that can lead to relaxation to other states and vibrational levels, the A-X and C-X UV systems are both expected to be simple v' = 0 progressions.

Venus does not have a magnetic field and therefore the spectacular aurorae observed in the terrestrial atmosphere should not be seen. Nevertheless, there are indications that electrons generated on the dayside are swept to the night-side, thus creating electromagnetic disturbances. Emission from O atoms at 130.4 nm has been detected [*Phillips et al.*, 1986; *Fox and Taylor*, 1990], but electron excitation of a CO_2/N_2 mixture should produce emissions of CO, CO^+ , and CO_2^+ at 190-290 nm, as observed in the Martin dayglow [*Barth et al.*, 1971]. Such radiation does not appear in the UV spectra so far analyzed. Similarly, lightning in the Venusian atmosphere has been extensively discussed [*Borucki et al.*, 1991; *Russell*, 1991], the evidence being radio wave emissions, but as presented below, there are none of the expected optical signatures in the UV.

RESULTS AND DISCUSSION

Figure 2 shows the published NO spectrum of the Venusian nightglow, using a three-point smoothing function [Stewart and Barth, 1979]. The NO A-X and C-X v' = 0progressions dominate the spectrum, with some indications of weak interspersed features. The feature at 297 nm.



Fig. 1. NO potentials.

suspiciously close to the $O({}^{1}S \rightarrow {}^{3}P)$ line, has been found to be a data artifact (A. I. F. Stewart, private communication, 1991). This point is supported by the lack of 558 nm emission from the inherently much stronger $O({}^{1}S \rightarrow {}^{1}D)$ line in the Venera 9 and 10 data [*Krasnopolsky et al.*, 1976].



Fig. 2. Venus nightglow spectrum, three-point average [Stewart and Barth, 1979].

Spectral Analysis

The Pioneer Venus Orbiter Ultraviolet Spectrometer (PVOUVS) instrument has been described by Stewart [1980]. The orbit of the spacecraft is very eccentric, with periapsis for the measurements under consideration being at approximately 150 km above the surface, while apoapsis was at 66,000 km. Two spectral regions were scanned in the UV mode, 155–258 and 258–360 nm. Each of these regions was scanned in 1 s, with the data being collected in 256 channels. Thus a single channel represents about 4 ms. The spacecraft was spin stabilized, a rotation requiring 12 s. The long- and short-wavelength regions were measured alternately, so that each was measured every 24 s. During an orbit, which typically takes 16 hours, 30–50 scans were taken during the several minutes of periapsis.

The instrumental resolution was 1.3 nm, and the data acquisition rate was quite small; very few photons were actually collected over the spacecraft mission. The sensitivity of the system was 1.68 c/kR per 32 ms. The 155- to 258-nm analysis set that we used (the same as in the initial study) is shown in Table 1, listing the total number of spectra obtained containing the indicated number of photons. It may be seen that many scans contained no photons, and the most likelý number was one. The average number was three, and the highest was 65. The total number of photons on which this analysis is based is less than 4000, collected over several months of observation. Scans taken at a solar zenith angle of less than 105° were rejected due to possible contamination with cloud-reflected sunlight.

The large dynamic range led us to make calculations concerning the expected distribution of photons from a constant brightness source. In Figure 3 are shown observed and Poisson distributions for the 190- to 258-nm spectral region. The 3.04 photons/scan average precludes excursions as high as 65 photons, and as there are a significant number of high-count spectra, there is a poor fit between observations and the Poisson distribution. We have made similar

TABLE 1. Distribution of Photons per Scan (1550-2570 Å)

Number of Photons	Number of Spectral scans	
0	188	
1	281	
2	243	
3	197	
4	127	
5	66	
6	53	
7	35	
8	21	
9	17	
10	12	
11	9	
12	3	
13	1	
14	7	
15	2	
16	4	
17	2	
18	1	
19	2	
23	1 -	
25	1	
26*	2	
32	1	
61*	1	
65*	1	

Total number of scans 1278, total number of photons 3888. *Scans 13, 15, and 17 from orbit 75.

calculations from the 258- to 360-nm data, where the average number of photons/scan is 1.28. In this case there is good agreement between the data and the Poisson distribution, suggesting that at the longer wavelength there is a constant intensity source. Since the photon collection rate is only marginally above the phototube dark count rate of 0.8 photons/scan, there seems to be little useful spectral information in the long-wavelength region.

Since the short-wavelength spectra, containing all the NO features, exhibit variable intensity, we were led to wonder what might be learned from considering the high-count and low-count spectra separately. Given that the N and O atoms that recombine are swept around to the dark side of the planet over a period of about half a day, we were surprised that there should be such a large variability in observed intensity. Stewart et al. [1980] have calculated altitude emission profiles for the NO δ bands and find only a factor of 3 variation over the 103- to 118-km range, for an eddy diffusion coefficient of 3×10^8 cm² s⁻¹ at 140 km. It therefore seems unlikely that the occasional large-intensity excursions observed by the OUVS are merely due to inhomogeneities in the ambient atom densities.

We have divided the 155- to 258-nm data into two sets, those having 5 photon counts or fewer, and those having more than 5 counts. Thus the total number is approximately equal in each. The unsmoothed summed spectra are shown in Figure 4. The high-count spectrum in Figure 4 (top), containing 176 scans and 1692 photons, is quite clean, in that there are virtually no minor peaks. Only the nine bands of the v' = 0 progressions appear. On the other hand, the low-count spectra (1102 scans, 2196 photons) show extensive weaker features. Since there are 6 times as many low-count spectra as high-count spectra appearing in the



Fig. 3. Experimental and Poisson distributions of number of photons detected per scan. Poisson distribution based on an average of 3.04 photons per scan.

summed sets of Figure 4, the overall noise level in the former is expected to be greater by that factor. The question is whether the weaker features are merely statistical noise fluctuations or are, in fact, identifiable bands. It is interesting to note that the instrumental noise is low enough that a reasonable NO spectrum can be obtained by summing the 281 one-photon spectra.

Because the high-count spectrum looks so clean, we compare it in Figure 5 to a low-pressure NO radiative recombination laboratory spectrum measured by *Kley* [1973] at a total pressure of 3×10^{14} cm⁻³. There is complete correlation between the two spectra, a suggestion that whatever the source of the high-count spectra, they are not significantly influenced by three-body recombination, and the resultant vibrational redistribution.

The appropriate comparison for the low-count spectra, where the weak features might be an indication of just such energy redistribution, is with high-pressure laboratory spectra. In Figure 6, comparison is made with two laboratory spectra of *Hack et al.* [1985]. In the argon spectrum, weak



Fig. 4. Comparison of summed high-count (>5 photons per scan) and low-count (≤5 photons per scan) spectra.



Fig. 5. Low pressure N + O recombination spectrum. (a) Laboratory spectrum, 10-mtorr N₂ [Kley, 1973]. (b) High-count Venus spectrum.

bands appear that are caused by collisional quenching of the NO(a) and NO(C) states to high levels of the NO(A) and NO(B) states. In the N₂ spectrum, all NO excitation energy is siphoned into N2, where it becomes stabilized in the $N_2(A)v = 0$, 1 levels. Transfer to NO then occurs, populating only the A state, predominantly in v = 0, but also including higher vibrational levels. Comparison with the low-count Venus spectrum shows that the correlation is fair; where there are NO(A-X) bands in the laboratory spectrum, there are typically features in the nightglow spectrum. There appear to be no laboratory spectra taken with CO₂ as a carrier gas, and thus we cannot presently say whether such a spectrum might not give a closer correlation. At any rate, there is reason to conclude, on the question of the emission altitude of the high- and low-count spectra, that the highcount spectra originate at the higher altitude. It is evident that they arise purely from radiative recombination, and thus their brightness is not a consequence of atom recombination taking place at a higher pressure than the low-count spectra. It follows that a different explanation is needed to rationalize the large dynamic intensity range of the spectra.

In their paper, Stewart et al. [1980] generated an intensity map based on detection of the 198-nm NO(C-X)0-1 band, from which they found a difference of a factor of 4-5 between the disc-averaged intensity and that in a brightpatch region. Since the spectral scans analyzed here were carried out with substantially higher spatial resolution, it to be expected that the intensity range will be greater. The maximum observed number of photon counts was 25, excluding those of orbit 75 (discussed below), whereas the average was 3. Thus the range is only twice as large as that obtained from the 198-nm study, and therefore the two data sets are compatible. The origin of this level of variability is still unclear but is discussed by *Bougher et al.* [1990] in terms of the Venus thermospheric general circulation model (VTGCM).

An interesting point arises from the hypothesis that N and O atoms originate on the dayside and are swept to the nightside. This requires that they not be lost enroute in the CO_2/N_2 atmosphere. There are large uncertainties for the rate coefficient between N(⁴S) and CO₂ [Herron and Huie, 1968],

$$N(^{4}S) + CO_{2} \rightarrow NO + CO, \qquad (1)$$

but the reaction is 14.1 kcal/mol exothermic and, although spin-forbidden, cannot be ignored as a possible N atom loss process. The flow from dayside to nightside occurs at an altitude of 130 km or greater [Bougher et al., 1990]. At this altitude the CO₂ density is $\sim 5 \times 10^{11}$ cm⁻³ [Dickinson, 1972]. A transport time of ~ 10 hours around the planet is then numerically equivalent to a rate coefficient for reaction (1) of $\sim 6 \times 10^{-17}$ cm³ s⁻¹. Such a value, or even one significantly larger, is certainly within the realm of possibility and could have some impact on the proposed mechanism of transhemispheric circulation of atoms.

Bougher et al. [1990] have presented extensive calculations on the Venus nightglow, based on the PVOUVS data set. We note, however, that there are some significant discrepancies between the rate coefficients that they have employed to model the emission intensities, and the original data. These differences are traced back to the earlier paper of Stewart et al. [1980].

For the two-body radiative recombination rate coefficient for N + O \rightarrow NO(C), they used a value of 2.5 \times 10⁻¹⁷ cm³ s^{-1} . This is derived from the study of Mandelman et al. [1973], where a value of 1.5×10^{-17} cm³ s⁻¹ is given by these authors for production of NO(C-X) radiation. Bougher et al. divide this number by a C-X branching ratio of 0.6 (literature values range from 0.62 [Groth et al., 1971] to 0.79 [Sharp and Rusch, 1981]), which gives the total rate coefficient of 2.5×10^{-17} cm³ s⁻¹. However, this value is for a temperature of 300 K, while the appropriate temperature is ~170 K. Sun and Dalgarno [1992] have recently calculated the temperature dependence of the recombination rate and find a 300 K rate coefficient of 1.9×10^{-17} cm³ s⁻¹, increasing to 2.4 \times 10⁻¹⁷ cm³ s⁻¹ at 170 K, which is coincidentally in agreement with the figure used by Bougher et al. [1990]. We note that the ratio between the partial rate coefficient of Mandelman et al. [1973] and the full rate coefficient of Sun and Dalgarno [1992] is 0.78, in agreement with the branching ratio deduced by Sharp and Rusch [1981].

It is also stated by *Bougher et al.* [1990] that three-body recombination of N + O(+ CO₂) has a rate coefficient of $1.1 \times 10^{-32} (T/300)^{-1/2}$ cm⁶ s⁻¹, from *Baulch et al.* [1973]. However, this value is for N₂ as the third body; the effectiveness of CO₂ is stated to be 3 times greater. The consequence of using the larger rate coefficient is that the flux of N and O atoms from the dayside to the nightside is significantly reduced, and within the constraints of the



Fig. 6. Comparison of low-count spectrum (dark line) with experimental spectra from Hack [1985]: (a) 100-torr and (b) 700-torr N₂.

current VTGCM, the atom concentrations become insufficient to support the observed nightglow intensities (S. W. Bougher, private communication, 1993). Adjustments in the relevant model parameters will be required in order to match the loss rates to the transhemispheric atom flux.

At 100 km the N atom loss by two-body and three-body N + O recombination is approximately equal, whereas at 110 km the ratio favoring the two-body process is about 10. The emitting region peaks at 115 \pm 2 km [Bougher et al., 1990]. Therefore it seems likely that the low-intensity relaxed emission (Figures 4 and 6) comes primarily from the 100- to 110-km region.

High-Intensity Spectra of Orbit 75

Of the four highest count spectra in Table 1, three of them appear on successive scans in orbit 75. The tracks of the 1-s sweeps superimposed on the airglow layer are shown in Figure 7, where scans 13, 15, and 17 are the scans in question. The varying track length is a result of the changing spacecraft/planet distance.

In Figure 8 are shown the photons detected on each scan for both the long-wavelength and short-wavelength regions. In the long-wavelength region there is little variation from scan to scan, and in particular, there is nothing distinctive in scans 14, 16, and 18. On the other hand, in the shortwavelength region there is an abrupt increase in scan 13, comparable intensity in scan 15, a decrease to half this intensity in scan 17, and return to a normal level in scan 19. The distance on the airglow layer between each pair of scans, 13/15 and 15/17, is 450 km, and thus the disturbed region is at least 900 km in length.

The idea that there is an enhanced airglow patch of such

dimensions is in line with the data presented by Stewart et al. [1980], but in fact, the actual spectra of the three scans present a much more restricted view. Figure 9 shows the spectra obtained on the three scans, and the most important point to notice is that they are fragmentary; only one or two bands are seen, instead of the usual nine. Moreover, different NO bands appear in the three spectra. For comparison, a 32-photon spectrum from a different orbit is shown, in which the photons are distributed throughout the whole range. This may in turn be compared to the summed highcount spectrum, showing that these latter two are quite similar.





A-5



Fig. 8. Number of photons measured on individual scans on orbit 75.

The incomplete nature of the three spectra in question indicates that the intensity varies either spatially or temporally in the course of a scan. Each scan takes 1 s, and the distance scanned by the slewing spacecraft is 20 km for scan 13, 32 km for scan 15, and 54 km for scan 17. A scan covers 100 nm, and the spacing between bands is typically 8 nm, so that for only a single band to appear in a spectrum, the temporal and/or spatial resolution must be less than 16% of the figures given above. e.g., 0.16 s and, for scan 13, 3.2 km.

Atmospheric optical emission having a temporal variability on the order of 0.16 s corresponds to a lightning flash, or a rapidly varying aurora. However, the primary signature of an electrical discharge in CO2 is a mixture of neutral and charged CO and CO₂ band systems, much like the Martian dayglow. These could certainly appear and vanish over a time scale much less than 0.16 s, but there is no indication that the three spectra are not part of the N + O recombination systems, since as pointed out below, the spectral profiles appear to be identical to those obtained from the averaged nightglow. There are no known chemical processes that can cause either N or O atoms to vanish on a 0.16-s time scale. For example, for two-body recombination, the lifetime of N atoms at $[O] = 10^{11} \text{ cm}^{-3}$ is on the order of 10^6 s , approximately the same as for three-body recombination at $[CO_2] = 10^{16} \text{ cm}^{-3}$. It thus seems that the explanation for the partial spectra in scans 13, 15, and 17 is related to spatial, not temporal, effects.

If the effect is spatial, then the glowing region observed on each scan is limited to 16% of the field of view, i.e., 3.2 km for scan 13, 5.1 km for scan 15, and 8.6 km for scan 17, although the width might be much less. Considering that these unusually bright spectra are observed on consecutive short-wavelength scans, we are compelled to say that they are correlated and do not reflect independent events. Thus we see that what must be explained is an atmospheric feature at least 900 km in horizontal length and less than 3- to 8-km wide. It is also straight, or else it could not have been detected on three consecutive scans, and it coincidentally lies along the spacecraft path, with only the angular divergence noted from the fact that different bands appear in the three spectra.

Lightning as an explanation seems unrealistic because of the spatial dimensions of the feature. It is to be expected that a residual N + O recombination glow will be seen in the aftermath of a lightning flash both on Venus and in the terrestrial atmospheres, but for it to be narrow, straight, and 900 km in length is unlikely. Furthermore, cloud-related lightning is associated with pressures (~100 torrs at 60 km) where an N + O recombination spectrum would be quite complex due to collisional relaxation, yet the spectra in Figures 4 and 5 do not show evidence for any bands with $v' \neq 0$. Similarly, NO features could appear following the passage of an auroral form, but again the geometrical characteristics seem to preclude this explanation.

A known phenomenon that would fit the facts is a highaltitude meteor trail. Not all meteors penetrate atmospheres, showing the characteristic terrestrial sodium glow at 80–100 km. A meteor on a track tangent to the atmosphere can be traveling at 15–80 km/s and leave a long, straight track of dissociated CO_2 and N_2 in its path, before exiting the atmosphere. Any meteor on a grazing trajectory will leave such a track, and in the terrestrial atmosphere the ultraviolet recombination emission cannot be seen from the ground. However, meteor tracks have been recorded by imaging systems on space shuttle missions in the visible spectral region (S. B. Mende, private communication, 1993), and the event is not as unusual as might be believed.

The meteor hypothesis has significant timing require-



Fig. 9. Various high-count spectral scans.

ments, in that if an atmospheric column is dissociated by the passage of a meteor, the rate of radial diffusion at thermospheric altitudes will cause the atom density to fall back to its quiescent value fairly quickly, while the integrated emission from the expanding column also decreases with time, even with no chemical loss of atoms.

The average nightglow count rate is about 0.2 photons per band, and from their calibrations, Bougher et al. [1990] have given an average intensity of 400 R for the C-X 0-1 band, at 198 nm. This same band in orbit 75/scan 13 has 34 photons, corresponding to an intensity of 70 kR, or more than 500 kR for the combined C-X and A-X systems. The implication is that the track must have been observed within seconds of the passage of the bolide, when it would still have been quite narrow. Alternatively, it is possible that the event took place at relatively low altitudes, in which case, diffusional losses would be slowed.

A precedent for the type of event that we are describing was captured on film in 1972, when a meteor estimated at 4-80 m in diameter grazed the terrestrial atmosphere with a velocity of 15 km s⁻¹ at an altitude as low as 58 km (the equivalent density in the Venus atmosphere occurs at 90 km [*Dickinson*, 1972]), while leaving a 1500-km track [*Melosh*, 1993]. From this daytime observation it is obvious that the track lasted for at least several seconds and was bright enough to be compatible with the intensities discussed above. Such an object on a collision course was presumabi-

responsible for the Tunguska event in 1908 [Chyba et al., 1993].

The long-wavelength scans that are interspersed with those at short wavelength, shown in Figure 8, do not show an enhanced count level. This indicates that the low photon acquisition rate, barely above the noise level, in fact does not reflect any atmospheric emission process and that therefore all the real photon counts are confined to the 190- to 258-nm region.

An interesting additional point to be noted in the spectrum of scan 13 is that, although the major feature is the NO(C-X) 0-1 band, the 0-2 band also appears. In Figure 10 is shown an expanded version of the spectrum, and it may be seen that, whereas the 0-1 band has high photon counts in five channels, the 0-2 band, which typically has the higher intensity (Figure 2), has almost all its counts in a single channel. Traces of the shape of summed spectra are also presented in Figure 10, showing that there is a reasonable fit for the case of the 0-1 band (equally true for the 0-3 band in scan 15), while the 0-2 band appears truncated. That this phenomenon might also be related to spatial effects in the supposed meteor track should not be overlooked.

Geographical Intensity Distribution

The study of Stewart et al. [1980] showed evidence of a pectrally hot area centered at approximately 15° south



Fig. 10. Comparison of 0-1 and 0-2 δ bands on orbit 75/scan 13.

latitude, at 0200 UT of the Venus morning sector, based on 198-nm NO(C-X) 0-1 band observations of the planetary disc. These observations are therefore different from the higher spatial resolution scans that we have described. Nevertheless, we thought that it was important to determine whether there was a correlation between the photon count rates and location on the nightside disc. To do this, we compare 10° north and south latitude ranges for the fraction of the total number of scans that produced high count spectra ($N \ge 11$). The results are shown in Table 2, from which it may be seen that there were almost twice as many scans taken at northern latitudes, yet there are a third more high-count scans in the southern latitude data. Curiously, there are no high-count scans out of a total of 100 scans in the 10°-19.9° south latitude set, contrary to the finding of Stewart et al. [1980]. We doubt that this is statistically significant, however, since in every other latitude range the fraction of high-count scans in the southern hemisphere is equal to or greater than that in the northern hemisphere.

Although we have, as stated earlier, excluded from our analysis any data taken at less than 105° solar zenith angle, another source of high-count spectra might be limb bright-

TABLE 2. Analysis of Latitudinal Locations of High-Count Scans $(N \ge 11)$

Latitude	Number of High-Count Scans -	Total Scans	Percentage
0-9.9°N	6	127	4.7
0-9.9°S	5	114	4.4
10°-19.9°N	3	143	2.1
10°-19.9°S	0	100	0
20°-29.9°N	3	150	2.0
20°-29.9°S	5	63	7.9
30°-39.9°N	1	140	0.7
30°-39.9°S	3	50	6.0
40°-49.9°N	1	123	0.8
40°-49.9°S	3	28	10.7
>50°N	1	156	0.7
>50°S	4	85	4.7

Percentage of high-count scans: north, 1.8%; south, 4.5%.

ening. To test this hypothesis, we have looked for a correlation between the emission angle (zero degrees is nadir viewing, 90° is limb viewing) and the intensities of the 35 high-count spectra of Table 2. The spectra were taken over a full range of emission angles, and with this limited data set, no correlation is apparent. If the emitting region were extensive, then more photons would be expected at high emission angles. That this does not apparently occur for the high-count spectra is an indication that these strong emissions originate in localized areas, which is also consistent with the fact that rarely do high-count spectra occur on more than two consecutive scans (apart from orbit 75, there is only one other example).

CONCLUSIONS

There are three principal conclusions of this study. The first conclusion is that the very wide range of intensities observed in individual scans suggests that there is more than one excitation mechanism leading to N + O atoms which subsequently recombine. We interpret this as pulsed, localized, nightside excitation, in addition to transhemispheric mixing from the dayside. The second is that summed spectra of high- and low-intensity scans are qualitatively different. The low-intensity scans may contain additional NO features that would indicate a relatively low altitude for N + O recombination, and the spectral distribution in the high-intensity scans is indicative of an emitting altitude at which there is little three-body recombination.

The third conclusion is that there were three correlated bright spectra observed on a particular orbit, the analysis of which indicates the presence of an emitting area with dimensions on the order of 900 km in length and ≤ 5 km in width. After consideration of lightning and aurora as sources, we feel that a more likely explanation is that Pioneer Venus observed the trail of an atmosphere-grazing meteor.

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