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Mariner 6 and 7 Ultraviolet Spectrometer Experiment: Upper Atmosphere Data.

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Mariner 6 and 7 observations of the Mars upper atmosphere show the ultraviolet emission spectrum to consist of the CO_2^+ A-X and B-X bands, the CO α -X and A-X bands, the CO^+ B-X bands, the C I 1561- and 1657-A lines, the O I 1304-, 1356-, and 2972-A lines, and the H I 1216-A line. Laboratory measurements and theoretical calculations show that the CO_2^+ band systems are produced by the combination of photoionization excitation of CO_2 and fluorescent scattering of CO_2^+ . An analysis of the vibrational populations of the CO Cameron bands shows that they may be produced from photon or electron dissociative excitation of CO_2 . The vibrational distribution of the CO fourth positive bands is the same in the Mars spectrum as in a laboratory CO_2 dissociative excitation spectrum, except for the bands that are self-absorbed by CO in the Mars atmosphere. Since the C I 1561- and 1657-A lines and the O I 1356- and 2972-A lines may be produced in the laboratory by CO_2 dissociative excitation processes, these are the most likely sources in the Mars atmosphere. The altitude distribution of all the emissions is the same, except for the H I 1216-A and O I 1304-A lines and part of the CO_2^+ A-X bands. The scale heights indicate a cold, predominantly CO_2 atmosphere. The O I 1304-A line emission extends to much higher altitudes than the CO_2 emissions showing that atomic oxygen is present. Its profile suggests that it is excited by more than one mechanism. Fluorescent scattering of the CO_2^+ A-X and B-X bands indicates the presence of CO_2^+ , but CO_2^+ is not necessarily an abundant ion. Lyman α radiation with a single scale height extending several radii from the planet establishes the presence of atomic hydrogen in the Mars exosphere.

On July 31 and August 5, 1969, the first observations of the ultraviolet spectrum of the Mars upper atmosphere were made with ultraviolet spectrometers on board the Mariner 6 and 7 spacecraft. The principal emission features were quickly identified and reported in the literature [Barth *et al.*, 1969]. A continued examination of these ultraviolet observations has revealed that they are rich in spectral detail and contain sufficient altitude information to

make possible the determination of the composition and structure of the Mars upper atmosphere.

The purpose of the present report is twofold: (1) to give the results of a detailed spectroscopic analysis of the data that lead to the identification of the principal mechanisms producing the upper atmosphere emissions, and (2) to present the intensities of individual spectral features as a function of altitude so that models of the Mars upper atmosphere may be constructed. A review of the techniques and

theory of the ultraviolet spectroscopy of planets [Barth, 1969] shows a number of the spectral emissions that were being sought in the Mariner 6 and 7 experiment.

INSTRUMENT

The Mariner 6 and 7 ultraviolet spectrometer consists of a 250-mm focal length Ebert-Fastie scanning monochromator, a 250-mm focal length off-axis telescope, and a two-photomultiplier tube detector system [Pearce *et al.*, 1971]. The spectral range 1900–4300 Å was measured in the first order at 20-Å resolution with a bialkali photomultiplier tube, and the spectral range 1100–2100 Å was measured in the second order at 10-Å resolution with a cesium iodide photomultiplier tube. A complete spectral scan including both orders was completed every 3 sec. Extensive light baffling was used to reject light from the bright disc of the planet while observing the upper atmosphere.

OBSERVATIONAL GEOMETRY

The spectral emissions from the upper atmosphere of Mars were observed by having the ultraviolet spectrometer look tangentially through the atmosphere as the spacecraft flew

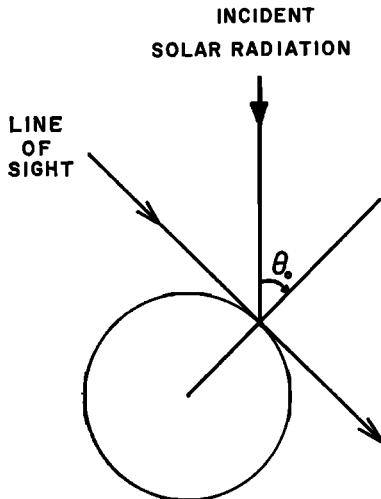


Fig. 1. Geometry of atmospheric limb observations. In all four limb crossings, the line of sight was perpendicular to a radius vector making the instrument zenith angle $\theta = 90^\circ$. The solar zenith angle θ_0 was 27° and 44° for the first limb crossings of Mariner 6 and 7, respectively, and 0° for both second limb crossings.

by the planet. Since the relative velocity of the spacecraft with respect to the planet was 7 km/sec, a complete spectral scan was obtained every 21 km as the effective observation point, i.e., the closest point of the tangential line of sight, moved deeper into the atmosphere. The ultraviolet spectrometers on each Mariner had the opportunity to view the atmosphere twice, once looking ahead and once looking sideways, as each spacecraft flew by Mars making a total of four probes of the upper atmosphere. The geometry of the observations is shown in Figure 1. In the case of Mariner 6, the solar zenith angle of the effective observation point was 27° for the first limb crossing and 0° for the second. For Mariner 7, the first limb crossing had a solar zenith angle of 44° and the second had a 0° angle. In all cases, the observations were made at an instrument zenith angle of 90° .

SPECTRUM

The ultraviolet spectrum of the upper atmosphere of Mars consists of the $\text{CO}_2^+ A^2\Pi_u-X^2\Pi_g$ and $B^2\Sigma_u^+-X^2\Pi_g$ bands, the $\text{CO } a^3\Pi-X^1\Sigma$ Cameron and $A^1\Pi-X^1\Sigma^+$ fourth positive bands, the $\text{CO}^+ B^2\Sigma^+-X^2\Sigma^+$ first negative bands, the C I 1561- and 1657-Å lines, the O I 1304-, 1356-, and 2972-Å lines, and the H I 1216-Å Lyman α line. These spectral emission features are shown in the spectra in Figures 2 and 3. Figure 2 displays the Mars spectrum between 1900 and 4000 Å at 20-Å resolution, which was obtained while the instrument was observing the Mars atmosphere at an altitude between 160 and 180 km above the surface. Figure 3 shows the spectral interval between 1100 and 1800 Å at 10-Å resolution. This spectrum originated from the 140- to 160-km level of the Mars upper atmosphere. Both the long and short wavelength spectra displayed here are the result of summing four individual 3-sec spectral scans.

EMISSION MECHANISMS

The $B-X$ and $A-X$ CO_2^+ bands may be produced in the Mars upper atmosphere by one or more of three mechanisms: (1) fluorescent scattering of solar radiation by carbon dioxide ions; (2) photoionization excitation of neutral carbon dioxide by extreme ultraviolet solar radiation; and (3) electron impact excitation of neutral carbon dioxide by the photoelectrons produced in the photoionization of the major

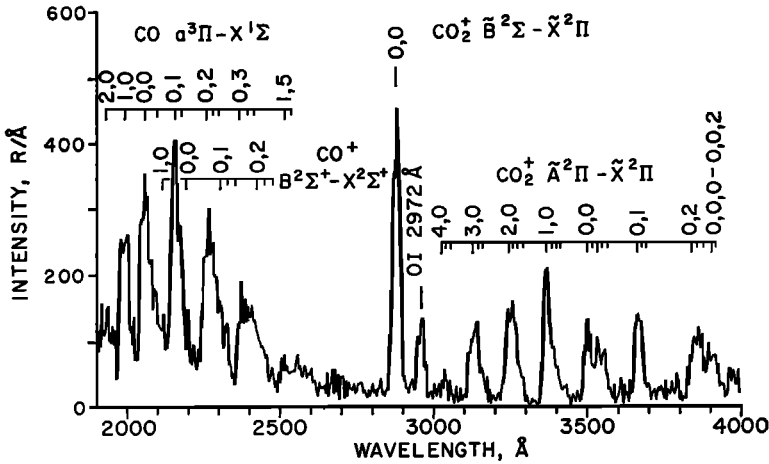


Fig. 2. Ultraviolet spectrum of the upper atmosphere of Mars, 1900-4000 Å, 20-Å resolution. Spectrum was obtained by observing the atmosphere tangentially at an altitude between 160 and 180 km. This spectrum was obtained from the sum of four individual observations.

constituents in the Mars atmosphere. These processes may be represented by the following set of equations, which also lists the wavelength of the solar radiation or the energy of the electrons responsible for the excitation.

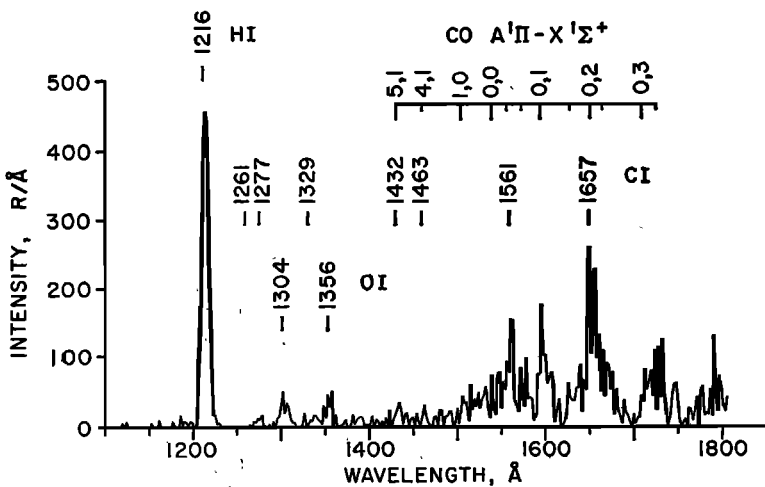
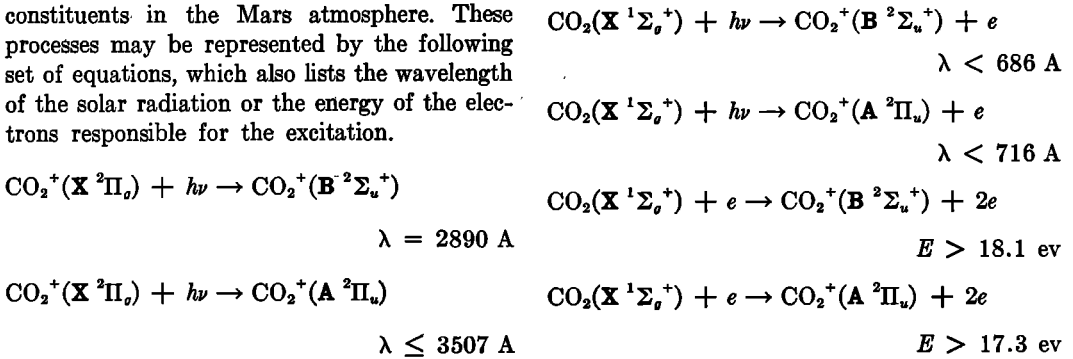


Fig. 3. Ultraviolet spectrum of the upper atmosphere of Mars, 1100-1800 Å, 10-Å resolution. Spectrum was obtained by observing the atmosphere tangentially at an altitude between 140 and 160 km. This spectrum was obtained from the sum of four individual observations.

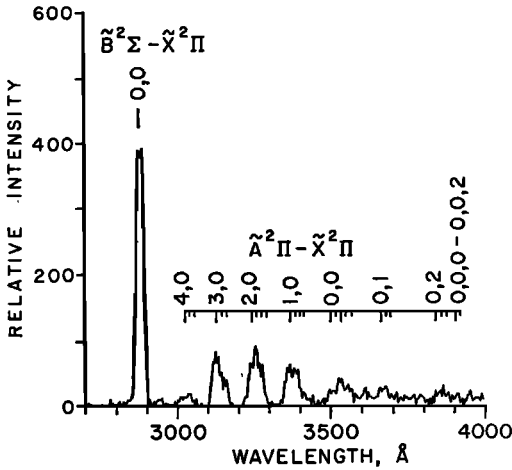


Fig. 4. Laboratory photoionization excitation spectrum of CO_2 produced with 584-Å photons.

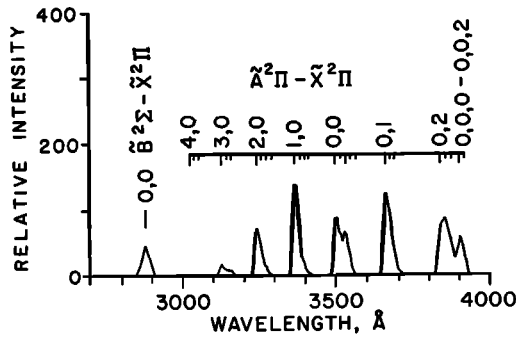


Fig. 5. Theoretical fluorescent scattering spectrum for CO_2^+ .

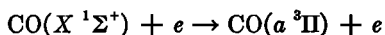
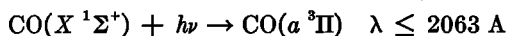
Since the relative intensities between the two electronic transitions and among the extensive vibrational development in the $A-X$ system contain information about the excitation mechanism, laboratory and theoretical studies were conducted for each of the three mechanisms. The spectra produced by the impact of 20-ev electrons on neutral carbon dioxide were found to be similar but not identical to the spectra produced by the impact of 584-Å photons on CO_2 . At equivalent energies, the cross sections for the two processes were found to be nearly equal [Wauchope and Broida, 1971; Ajello, 1971]. In analogy to the production of the N_2^+ 3914-Å band in the earth's atmosphere, photoionization excitation is a more likely source of excitation of the CO_2^+ bands in the Mars spec-

trum than photoelectron excitation, because a large number of photons are available for the photoionization excitation and because the threshold for electron impact excitation lies above the energy of most of the photoelectrons. A dayglow model calculation for a pure $\text{CO}_2-\text{CO}_2^+$ atmosphere illustrates the dominance of the photoionization excitation and because the [1970]. The photoionization excitation spectrum produced by 584-Å photons that was recorded in the laboratory by a Mariner ultraviolet spectrometer is shown in Figure 4. A comparison between it and the Mars spectrum in Figure 2 shows that the vibrational distribution in the $A-X$ bands is not the same in the two spectra. For example, in the Mars spectrum the 0, 0 band is more intense than the 2, 2, whereas in the laboratory spectrum the reverse is true. When the laboratory spectrum was subtracted from the Mars spectrum, the bands at longer wavelengths that arise from the lowest vibrational levels were the most intense in the spectrum that remained. The emphasis on the lower vibrational levels is indicative of a spectrum produced by fluorescent scattering, since the higher vibrational levels require shorter wavelength photons for excitation, and the solar spectrum falls off with decreasing wavelength in this part of the spectrum. A synthetic spectrum that shows the relative intensities expected from fluorescent scattering is plotted in Figure 5. This spectrum was calculated from the transition probabilities measured by Hesser [1968] and the branching ratios derived by Dalgarno and Degges [1970] from the work of Poulizac and Dufay [1967]. The relative intensity of the (0, 0, 0 to 0, 0, 2) band was determined from the laboratory measurements of Wauchope and Broida [1971].

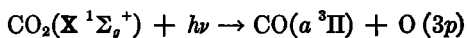
The two spectra, the photoionization excitation spectrum in Figure 4 and the fluorescent scattering spectrum in Figure 5, add up quantitatively to match the intensity distribution of the CO_2^+ $B-X$ and $A-X$ bands in the Mars spectrum. At the particular altitude where this Mars spectrum was observed, the $B-X$ (0, 0) band is produced 90% by photoionization excitation and 10% by fluorescent scattering. Photoionization excitation is the stronger source of the $A-X$ band system, but individual bands such as the (0, 0) are produced more strongly by fluorescent scattering. Thus this analysis

shows how the Mars ultraviolet spectrum between 2800 and 4000 Å may be used to measure quantitatively the number of CO_2^+ ions in the Martian ionosphere, the number of CO_2 molecules at the same altitude, and the rate of photoionization occurring in the Martian upper atmosphere.

The CO a -X Cameron bands are the most intense emission in the Mars ultraviolet spectrum. They may be excited by: (1) the fluorescent scattering of solar radiation by CO molecules in the Mars upper atmosphere; (2) the photoelectron excitation of carbon monoxide; (3) the photodissociation excitation of CO_2 molecules in the Mars upper atmosphere; (4) the photoelectron excitation of carbon dioxide molecules to produce excited carbon monoxide molecules; and (5) the dissociative recombination of ionized carbon dioxide molecules. These excitation mechanisms are described by the following set of equations, where the energy of the photoelectrons or the wavelength of radiation responsible for the excitation is also listed.



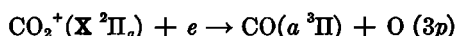
$$E > 6.01 \text{ eV}$$



$$\lambda < 1082 \text{ \AA}$$



$$E > 11.5 \text{ eV}$$



Since the vibrational distribution of the CO Cameron bands is not the same for all five mechanisms, the relative populations of the upper vibrational levels give a clue to the actual mechanism operating in the upper atmosphere of Mars. The vibrational distributions for fluorescent scattering and photoelectron excitation of carbon monoxide were calculated previously [Barth, 1966, 1969]. Both predicted spectra differ from the vibrational distribution of the Cameron bands in the Mars spectrum. In the fluorescent scattering spectrum, the vibrational population of the upper level falls off more rapidly than in the Mars spectrum. In the photoelectron excitation spectrum, the (1, 0)

band is more intense than the (0, 0) band, while in the Mars spectrum the reverse is true. These two mechanisms are also inadequate to account for the intensity of the Cameron bands quantitatively. The upper state of the Cameron bands, the $a^3\Pi$, is metastable; its lifetime has been measured to be 7.5 ± 2 msec [Lawrence, 1971]. Because of the small oscillator strength associated with this transition, an amount of carbon monoxide far in excess of the total number of molecules in the Mars upper atmosphere would be required to produce the intensity of the Cameron bands observed in the Mars spectrum from fluorescent scattering. A similar quantitative argument may be made against production of these bands by the photoelectron excitation of carbon monoxide.

The vibrational distribution produced by the remaining three processes is less well known. In fact, there is not yet experimental evidence that the Cameron bands are produced by photodissociation excitation or dissociative recombination while they have been produced by electron impact excitation. To investigate the vibrational populations further, the Cameron bands were produced in the laboratory by bombarding carbon dioxide at a pressure of 10^{-3} torr with 20-eV electrons. The electron-excited spectrum recorded by a Mariner-type ultraviolet spectrometer is shown in Figure 6. The vibrational distribution of the Cameron bands in this laboratory source and the Mars ultraviolet spectrum is nearly the same. By using Franck-Condon factors calculated by Nicholls [1962], it was determined that the lowest vibrational level of the upper state was the most populated. Levels up through $v' = 6$ were observed with their populations dropping off relatively slowly with increasing vibrational number. When the identified Cameron bands were subtracted from the Mars ultraviolet spectrum with the aid of the Franck-Condon factors, some spectral features remained. These are identified as the $\text{CO}^+ B^2\Sigma-X^2\Sigma$ first negative bands. They are also produced in the laboratory by the impact of electrons on carbon dioxide. A laboratory spectrum that emphasizes these bands is shown in Figure 7 as recorded by a Mariner-type spectrometer. In the figure the amplitude of the first negative bands has been adjusted to match the intensity present in the Mars spectrum in Figure 2. First negative bands

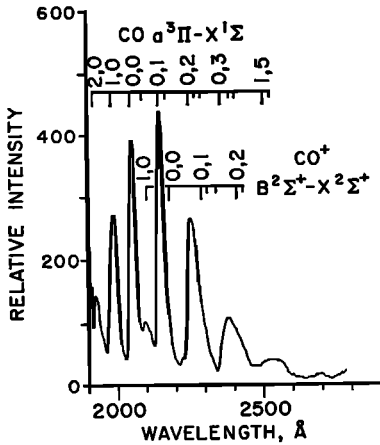


Fig. 6. Laboratory electron excitation spectrum of CO_2 produced with 20-eV electrons.

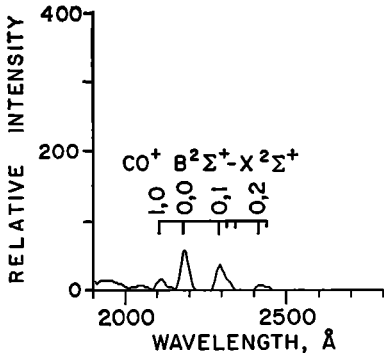


Fig. 7. Laboratory electron excitation spectrum of CO_2 produced with 50-eV electrons.

are also present in the laboratory spectrum in Figure 6. The relative populations of the vibrational levels of the $\text{CO } a^3\Pi$ state and the $\text{CO}^+ B^2\Sigma$ state in the Mars spectrum are given in Table 1.

On the basis of the laboratory experience with the CO_2^+ band systems where similar spectra are produced with similar cross sections by electrons and photons of equal energy, it may be expected that photodissociation excitation of carbon dioxide by extreme ultraviolet radiation will produce the Cameron bands with a vibrational distribution similar to that produced by electrons. If the cross sections for photon and electron impact are similar, then an argument analogous to the one used with the CO_2^+ bands would suggest that photodissociative excitation of carbon dioxide would be

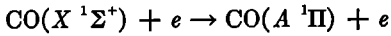
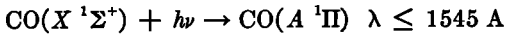
TABLE 1. Vibrational Populations of the Upper States of the Cameron Bands $a^3\Pi-X^1\Sigma$, the First Negative Bands $B^2\Sigma-X^2\Sigma$, and the Fourth Positive Bands $A^1\Pi-X^1\Sigma^+$ in the Mars Spectrum.

| Excited State | Relative Population |
|---------------------|---------------------|
| $a^3\Pi, v' = 0$ | 1.00 |
| 1 | 0.67 |
| 2 | 0.36 |
| 3 | 0.29 |
| 4 | 0.18 |
| 5 | 0.10 |
| 6 | 0.10 |
| $B^2\Sigma, v' = 0$ | 1.00 |
| 1 | 0.90 |
| 2 | 0.21 |
| $A^1\Pi, v' = 0$ | 1.00 |
| 1 | 0.77 |
| 2 | 0.46 |
| 3 | 0.32 |
| 4 | 0.17 |
| 5 | 0.15 |
| 6 | 0.14 |

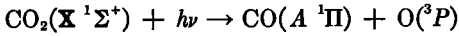
the dominant mechanism in the Mars upper atmosphere. If the electron impact dissociative excitation cross section is much larger than the photodissociative excitation cross section, then photoelectron excitation may be the dominant source of the Cameron bands.

The dissociative recombination of CO_2^+ is energetically capable of producing the Cameron bands with an extensive number of vibrational levels populated, but the laboratory experiment to measure radiation from this reaction has not been performed. However, with the CO_2^+ densities from the Mars ionosphere that are derived from the $\text{CO}_2^+ A-X$ bands, and the recombination rate measured in the laboratory [Weller and Biondi, 1967], it does not appear that sufficient recombinations can take place to produce the observed intensity even if all recombinations produce the Cameron bands.

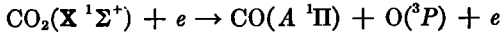
The $\text{CO } A-X$ fourth positive bands may be produced in the Mars upper atmosphere by the same five processes that are potential sources of the Cameron bands: (1) fluorescent scattering by CO , (2) photoelectron excitation of CO , (3) photodissociation excitation of CO_2 , (4) photoelectron dissociative excitation of CO_2 , and (5) dissociative recombination of CO_2^+ . The following equations describe these mechanisms and the wavelengths of the solar radiation responsible for their excitation.



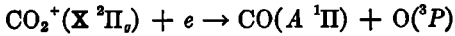
$$E > 8.02 \text{ eV}$$



$$\lambda < 920 \text{ \AA}$$



$$E > 13.5 \text{ eV}$$



In contrast to the Cameron bands, the first mechanism, the fluorescent scattering of solar radiation by carbon monoxide molecules, cannot be eliminated on a quantitative basis. In fact, because of the large oscillator strength of the $A-X$ transition, this band system is ideally suited to be a measure of the amount of carbon monoxide in the Mars upper atmosphere [Barth, 1969]. As will be seen from the analysis of the vibrational distribution, however, the bulk of the excitation of the fourth positive band in the Mars spectrum cannot come from fluorescent scattering by CO molecules. A similar argument can be made against photoelectron excitation of CO being a strong contributor.

How the vibrational distribution of the fourth positive bands may be used to identify the source of excitation was explored by using the techniques developed for the previous band systems; namely, the production of this band system in the laboratory by bombarding CO_2 with 20-ev electrons. The spectrum in Figure 8,

which was obtained in the laboratory with a Mariner-type spectrometer, shows bands arising from vibrational levels from $v' = 0$ up to $v' = 6$. The lowest level has the greatest population, but all levels up through 6 are populated as well. When the laboratory spectrum is compared with the Mars spectrum in Figure 3, an analysis shows that the vibrational populations in the two sources are nearly the same, although the spectra themselves have differences. What are missing in the Mars spectrum, as compared with the laboratory spectrum, are fourth positive bands whose lower vibrational level is the lowest vibrational level of the ground electronic state, the $v'' = 0$ level. The reason why they are missing must be that sufficient CO molecules are present in the Mars upper atmosphere so that self-absorption is taking place in transitions connected to the ground vibrational level.

The measured vibrational populations of the upper state of the fourth positive bands are also given in Table 1. The population distribution in the Mars spectrum is different from the distribution that would be produced by mechanisms 1 and 2 (fluorescent scattering and photoelectron excitation of CO) and these data thus may be used to eliminate these mechanisms as principal contributors. Dissociative recombination of CO_2^+ (mechanism 5) is also eliminated by these measured vibrational populations, since this mechanism is energetically only able to excite the $v' = 0$ and 1 levels, and the observed Mars spectra show substantial populations up through the $v' = 3$ level. This

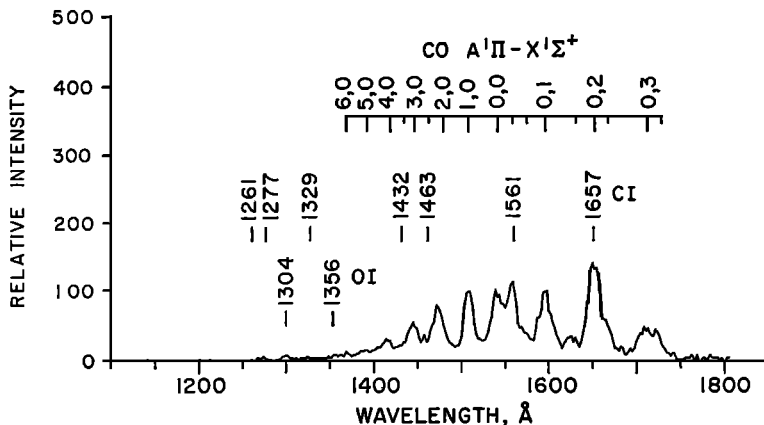


Fig. 8. Laboratory electron excitation spectrum of CO_2 produced with 20-ev electrons.

leaves only mechanisms 3 and 4 (photodissociative excitation and photoelectron dissociative excitation of CO₂) as sources of the Mars fourth positive bands. No doubt both mechanisms are operating, but, following the arguments given previously for the Cameron bands (that in dissociative excitation processes, the excitation cross sections are approximately the same for photons or electrons of equal energy), the major source of fourth positive band excitation should be photodissociative excitation because the number of photons available is greater than the number of photoelectrons.

When a synthetic spectrum of the fourth positive bands was subtracted from the Mars spectrum, emission lines from atomic carbon remained. From the positions of a number of the ultraviolet lines of C I marked in the figure, it may be seen that there is a clear cut identification of the 1561- and 1657-A lines. Carbon lines also appear in the laboratory spectrum produced by the impact of 20-ev electrons on CO₂ as can be seen in Figure 8. The most likely source of excitation of the carbon lines in the Mars spectrum is photodissociative excitation or photoelectron dissociative excitation of carbon dioxide. If there were free carbon atoms in the Martian atmosphere, the 1561- and 1657-A lines could be produced by resonant scattering [Barth, 1969]. In any case, the measured intensity of the carbon lines may be used to determine an upper limit to the number of carbon atoms present in the upper atmosphere.

The atomic oxygen lines at 1304, 1356, and 2972 Å may be produced in the Mars upper atmosphere by (1) resonant scattering of solar radiation by atomic oxygen, (2) photoelectron excitation of atomic oxygen, (3) photodissociative excitation of carbon dioxide, and (4) photoelectron dissociative excitation of carbon dioxide. Only the ³P-³S transition that produces the 1302-, 1304-, and 1306-Å triplet is an allowed transition and thus is the only serious candidate for the resonant scattering mechanism. The ³P-⁵S transition that produces the 1356-, 1358-Å doublet and the ³P-¹S transition that produces the 2972-Å lines are forbidden transitions but may be produced by the photoelectron and photodissociation mechanisms. The atomic hydrogen 1216-Å Lyman α line may be excited by (1) resonant scattering of solar radiation by atomic hydrogen, or (2) photodissociative

excitation of molecular hydrogen [Barth et al., 1968]. Photoelectron excitation of either the atom or molecule is not significant because of the small fractional abundance of either form of hydrogen in the Mars ionosphere. The most plausible first choice of excitation for the 1216-Å line is resonant scattering of solar Lyman α radiation.

ALTITUDE DETERMINATION

While the distance from the earth to the Mariner spacecraft flying by Mars could be measured to a fraction of a kilometer [Anderson et al., 1970], it was not possible to determine the height above the surface of Mars of the tangential line of sight of the ultraviolet spectrometer to better than tens of kilometers from the spacecraft orientation. However, the distance between successive ultraviolet spectrometer measurements was determined to better than a kilometer, since those measurements were dependent on the motion of the spacecraft. Thus scale heights of particular emission features could be determined with sufficient accuracy to be useful in formulating atmospheric models.

It is possible, however, to determine a nominal altitude scale by assuming a simple atmospheric model and by using the ultraviolet data themselves to determine the altitude scale [Stewart, 1971]. The radio occultation experiment that measured the electron density in the Mars ionosphere determined that the maximum electron concentration occurred at an altitude of 135 km at a location where the solar zenith angle was 57° [Fjeldbo et al., 1970]. Since this height measurement directly depended on the tracking of the spacecraft, it was possible to achieve an accuracy to within 1 km. By assuming that the upper atmosphere is nearly pure CO₂ and that the maximum electron density occurs at the same altitude as the maximum rate of photoionization, it is possible to calculate that the total column density of CO₂ above 135 km is 4.2×10^{20} molecules cm⁻². As will be seen in the next section, the Cameron bands, besides being the most intense emission, were observed over the most extensive altitude range of any of the ultraviolet emissions. By using CO₂ absorption coefficients and the model atmosphere, the location of a maximum in the Cameron band emission was calculated to be at

135 km, assuming that photodissociation was the excitation mechanism. Since the observations were made edge-on through a spherical atmosphere, the maximum in the intensity distribution occurs 10 km lower at 125 km. The altitude variations of the Cameron bands for each of the four limb crossings were then fitted to a calculation appropriate to an overhead sun even in the cases where the solar zenith angle was 27° and 44° . This procedure then established the altitude scale for all the upper atmosphere emissions.

ALTITUDE VARIATION

Observations made on each of the two limb crossings on Mariners 6 and 7 yielded the variation with altitude of the spectral emissions from the 100-km level of the upper atmosphere to as far up as the particular constituent could be detected. For the airglow that originates with the carbon dioxide molecule, the emissions extend upward to 220 km, near the top of the thermosphere. Atomic oxygen and atomic hydrogen emissions are present in the exosphere as well, extending outward to an altitude of 700 km for atomic oxygen and to a planetocentric distance of 25,000 km for atomic hydrogen.

The intensity of the CO_2 $B-X$ and $A-X$ bands as viewed tangentially through the atmosphere is shown in Figure 9. The scale height of the $A-X$ bands is greater than that of the $B-X$ bands, since, as the spectroscopic analysis has shown, fluorescent scattering by CO_2^+ makes a major contribution to the $A-X$ emissions, whereas the photoionization excitation of CO_2 is the major source of the $B-X$ bands. The scale height of the ion is usually greater than that of the neutral species for either photochemical or diffusive equilibrium. The two different scale heights for the two mechanisms may be seen more clearly in Figure 10, where the intensity of two bands of the $A-X$ transition that originate from different upper vibrational levels are plotted. The (2, 0) band originating principally from photoionization excitation has a smaller scale height than the (0, 1) band, which originates predominantly from fluorescent scattering.

The most intense emission in the ultraviolet portion of the spectrum, the $\text{CO } a-X$ Cameron bands, is plotted as a function of altitude in Figure 11. Since this emission originates from photodissociation or photoelectron dissociative

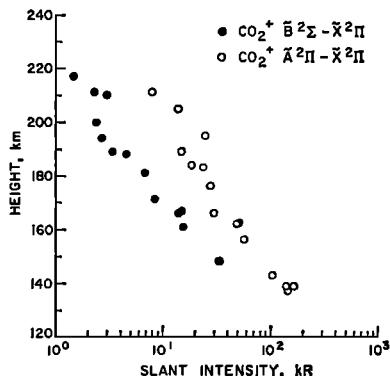


Fig. 9. Slant intensity of the CO_2^+ $B-X$ and $A-X$ band systems as a function of altitude.

excitation of CO_2 , the altitude profile of the emission is proportional at high altitudes to the density distribution of neutral carbon dioxide. The maximum intensity that is measured near 125 km is over 600 kR, or 6×10^{11} photons $\text{cm}^{-2} \text{sec}^{-1}$, of airglow between 1903 and 2843 Å consisting principally of the Cameron bands, although there is a small contribution from the CO^+ first negative bands. When this emission rate is adjusted to give the zenith rate for this emission, the value obtained is 20 kR or 2×10^{10} photons $\text{cm}^{-2} \text{sec}^{-1}$. This is equal to a sizeable fraction of the total number of photons $\text{cm}^{-2} \text{sec}^{-1}$ in the solar flux at wavelengths shorter than 1082 Å, the photodissociative threshold for the Cameron bands.

The altitude variation of the $\text{CO } A-X$ fourth positive bands was determined by fitting a syn-

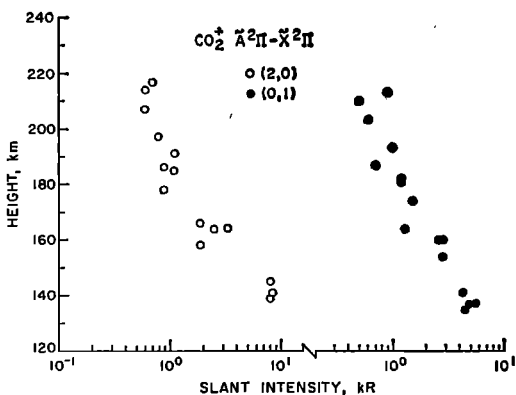


Fig. 10. Slant intensity of the CO_2^+ $A-X$ (2, 0) and (0, 1) bands as a function of altitude. Note discontinuity in the intensity scale.

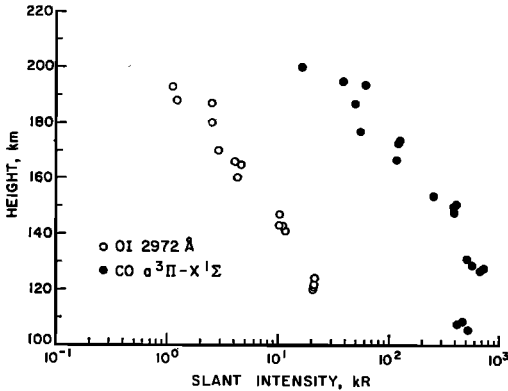


Fig. 11. Slant intensity of the CO α -X Cameron bands and the O I 2972-A line as a function of altitude.

thetic spectrum including the (ν' , 0) bands to the Mars spectra normalizing on the ν' , $\nu'' \neq 0$) bands. The emission rate of the atomic carbon lines was determined by subtracting the synthetic spectra from the Mars spectra. The slant intensities as a function of altitude of the fourth positive bands and the C I 1657-A line are plotted as a function of altitude in Figure 12. These emissions reach a maximum near 145 km, because below that altitude the airglow at this wavelength is absorbed by CO₂. At higher altitudes, the fourth positive bands also follow the same scale height as the Cameron bands, which is the neutral carbon dioxide scale height. The altitude profile of the atomic carbon line also follows this scale height with the exception

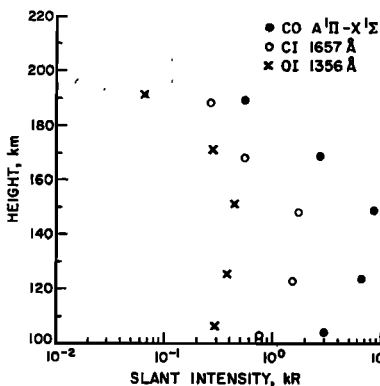


Fig. 12. Slant intensity of the CO A-X fourth positive bands, the C I 1657-A line, and the O I 1356-A line as a function of altitude.

of the point at the highest altitude measured whose deviation may or may not be real. The most likely altitude dependence of this line is the same as that of the other emissions arising from dissociative excitation processes on CO₂.

The slant intensity of the 2972-A atomic oxygen line is shown in Figure 11 as a function of altitude. Since its altitude dependence clearly follows that of the CO α -X Cameron bands plotted in the same figure, the excitation mechanism for the line most probably is the same as for the Cameron bands; namely, the dissociation of CO₂ by photons or electrons. Above the altitude where the maximum intensity occurs, about 125 km, the 2972-A intensity follows the carbon dioxide altitude distribution. In Figure 12, the 1356-A atomic oxygen has the same altitude dependence as the carbon monoxide bands, thus suggesting that this line also is produced from CO₂ in a dissociative excitation process.

The altitude distribution of the atomic oxygen 1304-A line is quite different from that of the other atomic oxygen emissions, thus indicating that its excitation process is different from those producing the 1356- and 2972-A lines. In Figures 13 and 14, the slant intensity of the 1304-A emission is plotted as a function of altitude for the two limb crossings for each of the two spacecraft. This atomic oxygen line was detectable all the way up to 700 km in contrast to the altitude range of all of the other spectral emissions described so far, which terminate at approximately 240 km. Such an altitude distribution indicates that the 1304-A emission originates from a process that excites atomic oxygen itself. This is true certainly above 240 km and may be true over the entire observed altitude range. Examination of the data indicates that there is not a single well-defined scale height, but instead there is an altitude variation that suggests that there are two excitation processes, one with a maximum at very high altitudes in the range 500 to 700 km and the other with a maximum in the range 100 to 300 km. In analogy with the excitation processes producing the 1304-A line in the earth's airglow, the high-altitude excitation process on Mars must be the resonant scattering of solar radiation by atomic oxygen and the low-altitude source, the photoelectron excitation of atomic oxygen. Photon or electron impact dissociative

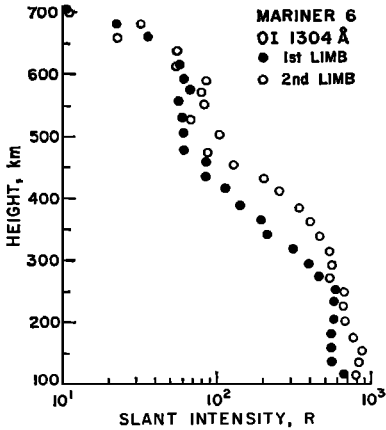


Fig. 13. Slant intensity of the O I 1304-A line as a function of altitude for the two limb crossings of Mariner 6.

excitation of carbon dioxide may also contribute to the low-altitude source.

Lyman α radiation was observed all the way out to more than 20,000 km above the surface of Mars. The slant intensity as a function of the distance from the center of the planet is shown in Figure 15 for Mariner 6 and Figure 16 for Mariner 7. A value of 300 R for the Lyman α sky background has been subtracted from the observed intensity in preparing these figures [Barth, 1970]. The existence of a single scale height in this altitude distribution suggests the most plausible excitation mechanism to be the

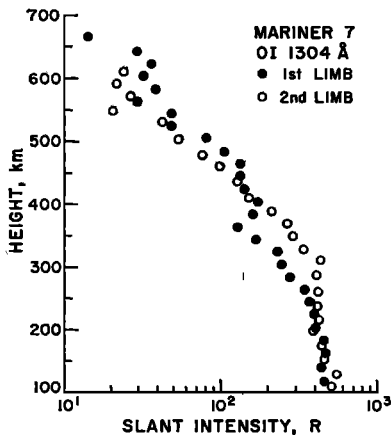


Fig. 14. Slant intensity of the O I 1304-A line as a function of altitude for the two limb crossings of Mariner 7.

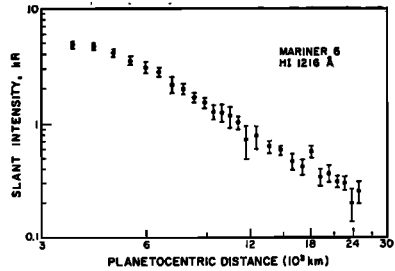


Fig. 15. Slant intensity of the H I 1216-A Lyman α line as a function of planetocentric distance for Mariner 6. A value of 300 R for the Lyman α sky background has been subtracted.

resonant scattering of solar radiation by atomic hydrogen in the Mars exosphere.

DISCUSSION

While the data that have been presented contain sufficient information to determine the structure and composition of the upper atmosphere of Mars, quantitative interpretation of the spectral emissions and the construction of model atmospheres is left for future publications. However, a qualitative examination of these ultraviolet observations allows several important conclusions to be drawn concerning the Mars upper atmosphere. First, with the exception of the H I 1216-A, O I 1304-A lines and a portion of the CO₂⁺ A-X bands, all the emissions may be and probably are produced by action of solar photons and photoelectrons on carbon dioxide. Second, with these same exceptions, all the scale heights are the same and are small. These two conclusions mean that the upper atmosphere is essentially undissociated and cold. Third, since atomic oxygen emissions

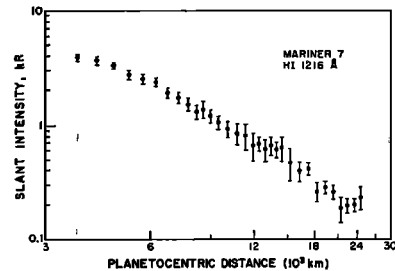


Fig. 16. Slant intensity of the H I 1216-A Lyman α line as a function of planetocentric distance for Mariner 7. A value of 300 R for the Lyman α sky background has been subtracted.

TABLE 2. Slant Intensities of the CO_2^+ $B-X$ Band, the CO_2^+ $A-X$ Band System, the $A-X$ (2,0) Band, and the $A-X$ (0,1) Band as a Function of Altitude for the Four Limb Crossings.

| Crossing | CO_2^+ | | CO_2^+ | | $A-X$ | | $A-X$ | |
|--------------------------|-----------------|------------|-----------------|------------|--------------|------------|--------------|------------|
| | Altitude, km | $B-X$, kR | Altitude, km | $A-X$, kR | Altitude, km | $2,0$, kR | Altitude, km | $0,1$, kR |
| Mariner 6 | 217 | 1.5 | 211 | 8. | 214 | 0.6 | 210 | 0.5 |
| First Limb | 194 | 2.7 | 189 | 15. | 191 | 1.1 | 187 | 0.7 |
| | 171 | 8.5 | 166 | 30. | 168 | 1.9 | 164 | 1.3 |
| | 148 | >33.8 | 143 | 104. | 145 | 8.1 | 141 | 4.3 |
| | 211 | 2.3 | 184 | 19. | 186 | 0.9 | 182 | 1.2 |
| Second Limb | 189 | 3.4 | 162 | 51. | 164 | 3.3 | 160 | 2.8 |
| | 167 | 15.4 | 139 | >142. | 141 | 8.4 | 137 | 4.8 |
| | — | — | — | — | 217 | 0.7 | 213 | 0.9 |
| Mariner 7 First Limb | 200 | 2.4 | 195 | 25. | 197 | 0.8 | 193 | 1.0 |
| | 181 | 6.9 | 176 | 28. | 178 | 0.9 | 174 | 1.5 |
| | 161 | 15.5 | 156 | 57. | 158 | 1.9 | 154 | 2.8 |
| | — | — | 137 | >146. | 139 | 8.0 | 135 | 4.5 |
| Mariner 7 Second Limb | 210 | 3.0 | 205 | 14. | 207 | 0.6 | 203 | 0.6 |
| | 188 | 4.6 | 183 | 24. | 185 | 1.1 | 181 | 1.2 |
| | 166 | 14.3 | 162 | 49. | 164 | 2.5 | 160 | 2.6 |
| | | | 139 | >165. | | | 137 | 5.5 |

are observed above 250 km, some dissociation of the CO_2 has occurred. Fourth, because part of the CO_2^+ $A-X$ emission is attributed to fluorescent scattering, ionized carbon dioxide is a constituent of Mars' ionosphere, but not necessarily the major constituent. Last, the presence of atomic hydrogen in the exosphere of a planet with such a comparatively low gravitational field means that there must be a source of dissociation of a hydrogen-bearing molecule such

as water that is currently operating in the Mars atmosphere.

APPENDIX

The slant intensities of the various emission features as a function of altitude are given in tabular form in this appendix. Table 2 lists the intensities for the CO_2^+ bands, the $B-X$ band, the $A-X$ band system, the $A-X$ (2, 0) band, and the $A-X$ (0, 1) band; Table 3 lists the CO

TABLE 3. Slant Intensities of the CO $\alpha-X$ Band System and the O I 2972-A Line as a Function of Altitude for the Four Limb Crossings.

| | CO | | O I | |
|-----------------------------------|--------------|-----------------|--------------|------------|
| | Altitude, km | $\alpha-X$, kR | Altitude, km | 2972-A, kR |
| Mariner 6 | 200 | 16. | 193 | 1.1 |
| First Limb Crossing | 177 | 55. | 170 | 2.9 |
| | 154 | 251. | 147 | 10.2 |
| | 131 | 511. | 124 | 21.0 |
| | 108 | 420. | — | — |
| | 195 | 38. | 188 | 1.2 |
| Mariner 6 Second Limb Crossing | 173 | 111. | 166 | 4.0 |
| | 150 | 380. | 143 | 10.3 |
| | 127 | 673. | 120 | >20.0 |
| | 187 | 48. | 180 | 2.5 |
| Mariner 7 First Limb Crossing | 167 | 116. | 160 | 4.3 |
| | 148 | 388. | 141 | 11.6 |
| | 129 | 567. | 122 | 21.5 |
| | 109 | 465. | — | — |
| | 194 | 60. | 187 | 2.5 |
| Mariner 7 Second Limb Crossing | 173 | 123. | 165 | 4.6 |
| | 151 | 409. | 143 | 11.0 |
| | 128 | 712. | 121 | 20.6 |
| | 106 | 526. | — | — |

TABLE 4. Slant Intensities of the CO A-X Band System, the O I 1356-A Line and the C I 1657-A Line as a Function of Altitude.*

| Altitude, km | CO | O I | C I |
|--------------|---------|------------|------------|
| | A-X, kR | 1356 A, kR | 1657 A, kR |
| 200 | 0.6 | 0.1 | 0.3 |
| 175 | 2.7 | 0.3 | 0.5 |
| 150 | 8.6 | 0.4 | 1.7 |
| 125 | 6.9 | 0.4 | 1.5 |
| 100 | 3.0 | 0.3 | 0.8 |

* The intensities for the four limb crossings have been averaged and are given as a function of the average altitude.

α -X band system and the O I 2972-A line; Table 4 the CO A-X band system, the O I 1356-A line, and the C I 1657-A line; and Table 5 the O I 1304-A line. In all instances, the slant intensity, which is given in kilorayleighs, is the apparent column emission rate that is observed by viewing the spherical atmosphere from the outside, perpendicular to a radius vector. A kilorayleigh is 10^6 photons sec from a square centimeter column. It is equal to 4π times the apparent surface brightness of the atmosphere in 10^6 photons $\text{sec}^{-1} \text{cm}^{-2} \text{ster}^{-1}$.

For emissions at wavelengths longer than 2800 Å, a substantial background has been subtracted from the spectral data. The origin of this background is the off-axis response of the instrument to the light from the bright disc of the planet. The spectral character of the disc is known from Mariner measurements made subsequent to the atmospheric limb observations and it consists of the Fraunhofer spectrum of reflected sunlight. The intensities listed assume that the emission is uniform over the $0.23^\circ \times 2.3^\circ$ field of view of the instrument and that the slit is aligned tangentially with the spherical atmosphere. Corrections for these assumptions can be made by using the analytic formalism given in a discussion of the geometry of planetary spacecraft observations [Hord *et al.*, 1970]. For the two limb crossings each for Mariners 6 and 7, the slant range to the point where the line of sight was perpendicular to the radius vector was 7600, 6000, 8900, and 6200 km, respectively, and in all cases the slit was aligned tangentially within 3° .

For the spectral range above 1900 Å, the slant intensity of the emission features is given for each individual limb crossing, whereas for

those emission features below 1900 Å, with the exception of the 1304-Å line, the slant intensities for the four limb crossings are averaged and the altitude given is the average altitude for the four observations. Because of the large number of data points, the Lyman α 1216-Å data are not given in tabular form but are available, along with the rest of these data, from the National Space Science Data Center.

Possible errors in the measured intensity of the Mars upper atmosphere spectral emissions may result from four causes: (1) the absolute calibration of the spectral response of the instrument, (2) the subtraction of the background produced by the off-axis response of the instrument, (3) the elimination of impulsive noise generated by the photomultiplier tubes, and (4) the subtraction of the electronic off-set produced by imbalance in the amplifier circuits. The method of calibration and the estimate of the calibration errors are given in the instrument paper [Pearce *et al.*, 1971]. Because of a lack of photometric standards for wavelengths less than 3000 Å, systematic errors in the calibration may be discovered in the future as standards are developed and adopted. For this same reason, the measured values of solar flux, which are used in conjunction with the planetary airglow data to determine upper atmosphere densities, may also be revised. However, the relative change in intensity with altitude, which is used to determine scale heights, will not be affected by changes in the absolute standards.

The three remaining causes, the subtraction of off-axis response, photomultiplier noise, and electronic off-set, are susceptible to subjective judgement in the reduction process. The subtraction process has the largest effect on the data at high altitudes where the intensity is small and at low altitudes where the background is large. The errors involved in the subtraction process do affect the variation of intensity with altitude. These errors may best be evaluated by a repetition of the reduction process, which is possible by using the data available through the National Space Science Data Center.

For all of the emissions with the exception of the 1216-Å Lyman α line, there were relatively few measurements made over the critical altitude region and an evaluation of the statistical variation of the measurements was not possible.

TABLE 5. Slant Intensities of the 1304-A Line as a Function of Altitude for the Four Limb Crossings.*

| Mariner 6 | | | | Mariner 7 | | | |
|--------------|----------------|--------------|----------------|--------------|----------------|--------------|----------------|
| First | | Second | | First | | Second | |
| Altitude, km | O I, 1304 A, R | Altitude, km | O I, 1304 A, R | Altitude, km | O I, 1304 A, R | Altitude, km | O I, 1304 A, R |
| 704 | 11. | 700 | 11. | 684 | 3. | 682 | 3. |
| 681 | 23. | 677 | 3. | 664 | 15. | 660 | 8. |
| 659 | 37. | 655 | 23. | 644 | 28. | 638 | 3. |
| 636 | 54. | 632 | 56. | 624 | 36. | 616 | 24. |
| 614 | 59. | 610 | 55. | 604 | 32. | 594 | 21. |
| 591 | 63. | 587 | 87. | 585 | 39. | 572 | 27. |
| 568 | 68. | 564 | 80. | 565 | 29. | 550 | 20. |
| 545 | 58. | 542 | 86. | 545 | 48. | 528 | 43. |
| 523 | 61. | 519 | 69. | 525 | 48. | 505 | 52. |
| 500 | 62. | 496 | 103. | 505 | 81. | 484 | 76. |
| 477 | 63. | 473 | 89. | 486 | 104. | 462 | 99. |
| 454 | 88. | 450 | 130. | 466 | 132. | 440 | 130. |
| 432 | 86. | 428 | 205. | 446 | 132. | 418 | 152. |
| 409 | 116. | 405 | 254. | 426 | 142. | 395 | 211. |
| 387 | 142. | 383 | 344. | 406 | 175. | 373 | 259. |
| 364 | 200. | 360 | 410. | 387 | 162. | 351 | 292. |
| 341 | 212. | 337 | 473. | 367 | 127. | 329 | 331. |
| 319 | 328. | 315 | 540. | 347 | 168. | 307 | 438. |
| 296 | 395. | 292 | 561. | 327 | 232. | 285 | 403. |
| 274 | 460. | 270 | 558. | 307 | 247. | 263 | 414. |
| 251 | 588. | 247 | 679. | 287 | 278. | 241 | 410. |
| 228 | 582. | 224 | 676. | 267 | 344. | 219 | 421. |
| 205 | 579. | 202 | 693. | 248 | 370. | 197 | 382. |
| 183 | 570. | 179 | 781. | 229 | 399. | 175 | 439. |
| 160 | 574. | 156 | 897. | 209 | 410. | 153 | 455. |
| 137 | 562. | 133 | 830. | 190 | 453. | 131 | 558. |
| 114 | 650. | 110 | 800. | 170 | 469. | 109 | 507. |
| | | | | 151 | 427. | | |
| | | | | 131 | 460. | | |
| | | | | 111 | 427. | | |

* The intensities have been derived from a running five-point average where the altitude is that of the central point.

However, for the Lyman α measurements, where the scale height is very large compared to the altitude interval between measurements, the root mean square variation, which was determined for groups of 50 measurements, is given in Figures 15 and 16.

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