The Upper Atmosphere of Venus: A Review

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ABSTRACT

The implications of recent data on Venus obtained by Mariner 5, Venera 4 and ground based observations for the aeronomy of Venus is received. The theoretical thermal structure model of McElroy based on a pure CO$_2$ atmosphere is in good agreement with the temperature deduced from the hydrogen distribution obtained by Mariner 5. No credible mechanism has been devised to recombine CO and O to CO$_2$ in the upper atmosphere. It is suggested that O$_2$ is formed but that CO and O$_2$ recombine to CO$_2$ in the dense atmosphere far enough above the cloud tops to agree with abundance measurements. Serious difficulties exist for the H$_2$ model of the upper atmosphere. It is suggested that deuterium can account for the anomalous Lyman $\alpha$ glow observed by Mariner 5 without implying a large D/H planetary ratio. Other problems such as the maintenance of the ionosphere at night and the escape of water are discussed.

1. Introduction

The atmospheric composition experiments performed on the Soviet spacecraft Venera 4 (Vinogradov et al., 1968), and the measurements of temperature, pressure and density made on Venera 4 (Avduevsky et al., 1968) and Mariner 5 (Kliore et al., 1967) indicate that the Cytherian atmosphere is composed of at least 90% CO$_2$. The implications of these results for the thermal structure of the atmosphere above the cloud tops has been examined by McElroy (1968). He has evaluated the heating by ultraviolet and infrared absorption as a function of altitude along with the cooling by thermal conduction and infrared radiation by CO$_2$ to determine the profiles of temperature and atmospheric density. His calculations show that the heat produced by ionization and photodissociation should be conducted down a temperature gradient to a mesosphere about 50 km above the tops of the clouds. Here the infrared radiation from vibrationally excited CO$_2$ molecules becomes an important source of heat loss. The thermal-pause temperature, according to his calculation, should lie between 620 and 700K.

McElroy's thermal model accords with the determination of the exospheric temperature determined from the distribution of exospheric hydrogen made by the Lyman $\alpha$ experiment (Barth et al., 1967) on Mariner 5. The variation of Lyman $\alpha$ emission rate with distance beginning about 9000 km from the center of the planet on the dayside indicates that the density of hydrogen is about 7% as large as it is at comparable distances above the earth and follows the distribution expected for a 6500K exosphere (Barth et al., 1968).

2. The recombination of CO and O

On Venus as on Mars the discovery that the atmosphere consists predominantly of CO$_2$ creates an interesting problem in aeronomy. The question arises as to why the oxygen in the atmospheres of these planets is in the form of CO$_2$ whereas it exists primarily as O$_2$ on earth. The escape of hydrogen can explain why all three planets have developed oxidizing atmospheres. Furthermore, the presence of large amounts of liquid water on earth affords a mechanism that explains the low level of CO$_2$ in the atmosphere of earth. (Why Venus and Mars should be relatively so poor in water is another problem, and I shall return to that question later.) Great amounts of CO$_2$ are locked in the oceans, in carbonates layered down as sediments or converted to O$_2$ through green plant photosynthesis on earth, and all of these processes depend on the presence of liquid water on the surface. But even in the absence of this sink for carbon on the surface of the other two planets, there remains a problem in explaining why the CO$_2$ in their atmospheres has not been converted to O$_2$ and CO.

CO$_2$ in the presence of ultraviolet below 1700Å is dissociated into CO and O in the $^1$D state. According to McElroy (1968), in the optically thin regions of Venus the rate of dissociation is given by

$$P(O, CO; z) = 2.2 \times 10^{-11} \text{cm}^3 \text{sec}^{-1} \text{cm}^{-3}$$  \hspace{1cm} (1)

The recombinantion of CO and O($^3P$) is spin forbidden and proceeds very slowly. The most reliable value for the rate coefficient of

$$CO + O(^3P) + M \rightarrow CO_2 + M \quad (k_1)$$  \hspace{1cm} (2)

has been determined by Clyne and Thrush (1963) to be given by

$$k_1 < 8 \times 10^{-35} \text{cm}^6 \text{sec}^{-1} \text{at} \ 300K.$$  

In competition with this sluggish reaction is the formation of O$_2$ through

$$O + O + M \rightarrow O_2 + M \quad (k_2)$$  \hspace{1cm} (3)
with

\[ k_z = 2.7 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \text{ at 300K}. \] (4)

On Venus as on earth, even this recombination to O\(_2\) is too slow to compete with the photoproduction \textit{in situ}. The oxygen (and the CO) must be transported downward to recombine at levels below the production region. Times long compared to the 100-sec lifetime of O(\(^{1}\)D) are required and the 40-fold faster conversion of O to O\(_2\) will surely overwhelm the recombination of O to CO\(_2\). The equation of continuity for O is

\[ \frac{d}{dz}n(O)w = 2.2 \times 10^{-6}n(\text{CO}_2) - L(z), \] (5)

where \( w \) is the flow velocity and for the loss term \( L(z) \) I contemplate for the moment only that

\[ L = k_1n(\text{CO})n(O)n(\text{CO}_2) + k_2n(O)n(O)n(\text{CO}_2). \] (6)

At the base of the production region \( z_0 \) where \( n(\text{CO}_2) \) is \( 2 \times 10^{11} \text{ cm}^{-3} \), integration of the continuity equation requires

\[ n(O)w(z_0) \geq 2.2 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}, \] (7)

where \( w \) should be of the order of 10 cm sec\(^{-1}\) at this density level and therefore both the oxygen and CO densities should be of the order of \( 2 \times 10^{10} \text{ cm}^{-3} \). Even here the recombination rate is only about 0.25 cm\(^{-2}\) sec\(^{-1}\) compared to an average production rate above of some \( 10^2 \text{ cm}^{-2} \text{ sec}^{-1} \), so the transport and density buildup must continue down to much lower altitudes before the oxygen will have recombined. There seems to be no simple way to prevent the accumulation of \( O_2 \) (and \( O_3 \)) in the upper atmosphere. The molecular oxygen in turn should be transported downward by eddy diffusion and the atmosphere gradually converted to an \( O_2 \) rich one. Although the \( O_2 \) will shield the \( \text{CO}_2 \) from photodissociation because of the longer wavelength cut-off and much larger absorption coefficient in the Schumann-Runge continuum than in the \( \text{CO}_2 \) continuum, the \( \text{CO}_2 \) will inerterably continue to be transported upward into regions where it can dissociate and the process of conversion of \( \text{CO}_2 \) to \( O_2 \) and CO should continue.

Obviously, the \( \text{CO}_2 \) atmosphere is reasonably stable. In the course of \( 4.5 \times 10^9 \) yr, half of them in sunlight, about \( 10^{28} \) molecules cm\(^{-2}\) of \( \text{CO}_2 \) would have been dissociated. The upper limit of the present \( \text{CO}_2 \) content of the atmosphere is about \( 5 \times 10^{27} \) molecules cm\(^{-2}\). Thus, \( O_2 \) and \( \text{CO}_2 \) would be about equal in abundance if the atmosphere were initially pure \( \text{CO}_2 \) and recombination had yielded principally \( O_2 \). On the other hand, Belton \textit{et al.} (1968) report that the concentration of \( O_2 < 2.5 \) parts in \( 10^4 \) above the cloud tops. Two values, both low, have been reported for the CO concentration, one of 2.2 parts in \( 10^4 \) (Benedict\(^1\)) and the other 5 in \( 10^8 \).


\(^3\) Reported by A. D. Kuzmin at the Second Arizona Conference on Planetary Atmospheres, Tucson, 11-13 March.


Unfortunately, the evidence is somewhat ambiguous with regard to atomic oxygen. The Venera 4 ultraviolet experiment of Kurt\(^3\) obtained a negative result on the night side of the terminator which is interpreted to set an upper limit to the atomic oxygen concentration at \( 10^{-8} \) times the terrestrial density at comparable altitudes. Because of the large light levels prevailing close to the bright limb, the Mariner 5 ultraviolet experiment has been analyzed for the OI resonance lines only beyond 6500 km—with negative results. There is a possibility that a weak (100 Rayleigh) 1304Å glow was detected just beyond the terminator. On the other hand, a low resolution spectrum of Venus obtained in a sounding rocket experiment by Moos \textit{et al.}\(^4\) had a bright feature near 1300Å which might imply an average dayglow emission rate of Venus of about 5 kR in the resonance triplet. Such a large emission rate would demand an optically thick atomic oxygen atmosphere irrespective of the excitation mechanism. From resonance scattering of sunlight an optical depth of \( 10^4 \) in oxygen (\( 10^{17} \) atoms cm\(^{-2}\)) would produce an average emission rate of only 2 kR. Even if it should be true that the atomic oxygen concentration in the Cytherean upper atmosphere reaches a level comparable to that on earth, the low concentration of O\(_2\) and CO together with the overall stability of the CO\(_2\) atmosphere would require that some mechanism exist to recombine the CO and O after the transport of these species downward. If the O\(_2\) concentration is to be low at all altitudes, this recombination mechanism must be fast compared to that which recombines O to O\(_2\). But if the atomic oxygen density also should be very small everywhere, a very fast recombination mechanism, presumably two-body in nature, would have to be found to recombine CO and O near the level where they are formed.

In the laboratory it has been observed repeatedly that the yield of O\(_2\) from photolysis of CO\(_2\) is not unity. Although it is not clear that wall effects are not involved, it has been suggested several times that a fast two-body like recombination of CO and O may occur at laboratory pressures involving the formation of a sufficiently long lasting complex CO\(_3\) molecule from CO\(_2\) and O(\(^{1}\)D). The scheme is

\[ \text{CO}_2 + O(\text{D}) \rightarrow \text{CO}_3^* (k_2), \] (8)

followed by

\[ \text{CO}_3^* + CO \rightarrow 2\text{CO}_2 (k_4). \] (9)

McElroy (1967, 1968) has proposed that these reactions provide the path for rapid recombination of CO\(_3\) in the Martian and Cytherean upper atmospheres.
The efficient functioning of (8) and (9) would not only explain the low concentrations of CO and O$_2$ but would also prevent an accumulation of atomic oxygen.

Since the lifetime of O($^1$D) is 100 sec, the first step must occur with a rate coefficient large enough to prevent the radiation of the red doublet in regions where the CO$_2$ density is of the order of 10$^{11}$ cm$^{-3}$. Thus, there is a condition which sets a lower limit on $k_3$, to wit,

$$\frac{1}{k_3n(CO_2)} < 10^9 \text{ sec},$$

or

$$k_3 \geq 10^{-11} \text{ cm}^3 \text{ sec}^{-1}. \quad (10)$$

McElroy (1968) obtains the same requirement on $k_3$ by placing an upper limit on the abundance of O. The difficulty with this proposal is that the unstable CO$_2^*$ must endure for hundreds of seconds before it can encounter a CO molecule to complete the recombination process. Thus, even if $k_4 = 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$,

$$\frac{1}{k_4n(CO)} = 10^9 / n(CO), \quad (11)$$

and even if we permit a hundred-fold increase in the relative CO abundance in the diffusion region above the overall planetary value of at most $5 \times 10^{-7}n(CO_2)$, the lifetime of CO$_2^*$ would need to be 20 sec.

Similarly, a three-body reaction

O($^1$D) + CO + CO$_2$ → 2CO$_2$(k$_3$) \quad (12)

would have to occur with a rate constant large enough to prevent the decay of the $^1$D term and this would demand a three-body rate coefficient satisfying

$$k_5 \geq 2 \times 10^{-22} \text{ cm}^6 \text{ sec}^{-1}. \quad (13)$$

An additional handicap for either of these schemes is that neither could tolerate competition from a large cross section for quenching of O($^1$D) in collisions with CO$_2$. There is evidence that the interaction of O($^1$D) with CO$_2$ is fast but that it results in quenching rather than reaction (Young et al., 1968).

There have been proposals also that recombination of CO to CO$_2$ can proceed via the reaction

CO + OH → CO$_2$ + H, \quad (14)

which has a measured rate constant of $2 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ at 300K (Reeves et al.). It should be remarked, however, that unless the OH is formed from the atomic oxygen partner of CO in CO$_2$, the much faster reaction

O + OH → O$_2$ + H, \quad (15)

with a rate constant of $5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ which also must occur, will result in production of one O$_2$ molecule for each CO$_2$ dissociated. Thus, while this process

\footnote{Reeves, R. R., et al. 1965. Paper presented at the 150th Meeting of the American Chemical Society, Atlantic City, N. J.}

prevents the buildup of CO it does not prevent the growth of O$_2$. A very large concentration of OH is also required. However, a much more fundamental objection to this or any recombination scheme involving the liberation of atomic hydrogen in the upper atmosphere is that they involve a production of H at least equal to the CO$_2$ photodissociation rate, or $2 \times 10^{11}$ atoms cm$^{-2}$ sec$^{-1}$. This is entirely incompatible with the hydrogen densities observed on Venus which will support a production rate of only $2 \times 10^{10}$ atoms cm$^{-2}$ sec$^{-1}$. To operate these schemes one must find channels for recombining hydrogen atoms (without liberating oxygen) at prodigious rates.

The problem of CO$_2$ recombination in the upper atmosphere is a difficult one whether it is supposed that the atomic oxygen density is very low or not. In the first case some very fast reactions are required that can effect the recombination in the region where the dissociation occurs. In the second case a process must be found which can recombine the O and CO after they are transported downward so rapidly that the mixing ratio of CO and O atoms in CO$_2$ above the cloud tops remains below $5 \times 10^{-5}$ despite the fairly fast recombination of the O atoms to form O$_2$. Since neither of these alternatives has found the support of a reasonable mechanism, it may be necessary to examine the possibility that O$_2$ is formed in the region where the atmospheric density is about $10^{14}$ cm$^{-2}$ and that the CO$_2$ mixture is carried downward by eddy mixing. In this case, somewhere above the 0.2-atm pressure level, the reaction

2CO + O$_2$ → 2CO$_2$ \quad (16)

must take place with sufficient efficiency that the spectroscopic limits on CO and O$_2$ above the cloud tops are respected.

The reaction (16) is known to be slow in a pure atmosphere of CO$_2$, CO and O$_2$, but it is catalyzed readily by small concentrations of impurity. In particular, very low admixtures of water vapor lead to the chain

OH + CO → CO$_2$ + H, \quad (17)

H + O$_2$ + M → HO$_2$ + M, \quad (18)

HO$_2$ + CO → CO$_2$ + OH, \quad (19)

which amounts to (16) without the consumption of OH and H. Admittedly, it is going well beyond laboratory experience to ask that this chain be efficient enough to convert essentially all of the CO and O$_2$ to CO$_2$ in the presence of a large excess of CO$_2$ containing only 10-40% water vapor at a temperature of 230K. On the other hand, no alternative seems acceptable to the proposal that atomic oxygen is first converted into O$_2$ and that somewhere above the clouds CO and O$_2$ undergo some kind of catalyzed recombination to CO$_2$.

To recombine the CO and O$_2$ at a rate of $2 \times 10^{11}$ cm$^{-2}$ sec$^{-1}$ above the $10^{18}$ cm$^{-2}$ level of CO$_2$, the effective three-body rate constant for (16) needs to be only $10^{-37}$
The mixture of \( \text{H}_2 \) and \( \text{CO}_2 \) is one which has received a great amount of attention from combustion chemists. In the presence of some dissociation of \( \text{H}_2 \) two reactions can occur, i.e.,

\[
\text{H} + \text{CO}_2 \rightleftharpoons \text{CO} + \text{OH} (k_6, k_6'), \quad (22)
\]

\[
\text{H}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H} (k_7, k_7'). \quad (23)
\]

These reactions use \( \text{OH} \) and \( \text{H} \) as catalysts and amount to the reactions

\[
\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}, \quad (24)
\]

which are called the water-gas reactions. The reaction rates (Schofield, 1967) are:

\[
k_6 = 5 \times 10^{-10} \exp\left[\frac{-25.7}{RT}\right] \quad 10^{-25} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 300 \text{K} \quad (25)
\]

\[
k_6' = 1 \times 10^{-12} \exp\left[\frac{-1.0}{RT}\right] \quad 2.5 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 640 \text{K} \quad (26)
\]

\[
k_7 = 10^{-10} \exp\left[\frac{-5.9}{RT}\right] \quad 4.5 \times 10^{-16} \text{ at } 300 \text{K} \quad (27)
\]

\[
k_7' = 3.0 \times 10^{-10} \exp\left[\frac{-20.6}{RT}\right] \quad 10^{-12} \text{ at } 640 \text{K} \quad (28)
\]

From these rate coefficients we have the following values for the water-gas equilibrium constant:

\[
K = \frac{n(\text{H}_2\text{O})n(\text{CO})}{n(\text{H}_2)n(\text{CO}_2)} \quad \frac{2.7 \times 10^{-9}}{3.5 \times 10^{-3}} \text{ at } 200 \text{K} \quad (29)
\]

\[
\frac{2.7 \times 10^{-9}}{3.5 \times 10^{-3}} \text{ at } 300 \text{K} \quad (30)
\]

\[
\frac{2.7 \times 10^{-9}}{3.5 \times 10^{-3}} \text{ at } 600 \text{K} \quad (31)
\]

Of course, the forward reaction (22) and the backward reaction (23) are both very slow at low temperature. Hence, in considering these reactions one must take care that the approach to equilibrium is not too slow. At the altitude where \( n(\text{CO}_2) \) is \( 10^6 \text{ cm}^{-3} \) and the temperature is 300K, a time constant of about \( 10^6 \) sec is indicated by reaction (22). Hence, since at higher altitudes both the densities and temperature are reduced, use of the equilibrium condition is safe only below the \( 10^6 \text{ cm}^{-3} \) density level.

At that altitude if we take

\[
n(\text{CO}) = 5 \times 10^{-6} n(\text{CO}_2), \quad (30)
\]

and

\[
n(\text{H}_2\text{O}) = 10^{-6} n(\text{CO}_2), \quad (31)
\]

we find that

\[
\frac{n(\text{H}_2)}{n(\text{CO}_2)} = 5 \times 10^{-6}. \quad (32)
\]

Similarly, if at the Venera 4 surface

\[
10^{-3} < n(\text{H}_2\text{O}) < 7 \times 10^{-3}, \quad (33)
\]
we find

\[ 1.4 \times 10^{-6} < \left( \frac{n(H_2)}{n(CO_2)} \right) < 10^{-4}. \]  

(34)

Hence, a mixing ratio for H_2 and CO_2 of the order of \(5 \times 10^{-6}\) is to be expected. Assume that this ratio prevails up to the "turbopause" where the H_2 density is of the order of \(10^{10}\) cm\(^{-3}\) according to the H_2 model for Lyman \(\alpha\) production. In that case the turbopause must occur where the CO_2 density is \(2 \times 10^{10}\) cm\(^{-3}\). If, as on earth, it does not occur until the \(2 \times 10^{12}\) cm\(^{-3}\) level is attained, the H_2 density could only be \(10^7\) cm\(^{-3}\), some three orders less than the model needs.

Another serious problem created by this model relates to the thermal structure of the atmosphere. The solar spectrum shorter than 804\AA\ will be absorbed in ionizing H_2 above 6500 km. The flux between 845 and 804\AA\ will be absorbed there in dissociating H_2. This leaves only a 50\AA\ band available to ionize CO_2 at lower altitudes. In contrast with McElroy's pure CO_2 model, most of the ultraviolet heating occurs above 6500 km instead of between 6200 and 6300 km. This creates a large gap between the locus of ultraviolet heat input and the CO_2 radiation region. The temperature gradient must extend over a much larger domain and the exospheric temperature must be much greater than a pure CO_2 model would produce. Furthermore, H_2 is a significantly more effective partner of CO_2 in quenching vibrational excitation than CO_2 itself. One collision in every 400 between H_2 and CO_2 in the v_2 vibrational mode results in a transfer of vibrational to translational energy, whereas 10^6 at 200K to 10^8 at 600K collisions between CO_2(v_2) and CO_2 are required (Taylor and Bitterman, 1967).

A final difficulty for this atmosphere rich in H_2 will be to explain the ionospheric electron distribution observed by Mariner 5. Most of the ionization by solar ultraviolet will occur in the H_2 above 6500 km. In the region near 6195 km where the principal ionospheric peak occurs, only the ultraviolet between 850 and 900\AA, and X rays are available to ionize CO_2. The principal ion at high altitude, where there is a negligible amount of CO_2, will be H_3^+ and at low altitude in the CO_2-H_2 mixture, it will be CO_2H^+. It is difficult to see under these circumstances how the electron density at 6195 km could even be as large as \(10^{15}\) cm\(^{-3}\) or how a pronounced layer could develop there.

The alternative explanation for the rapidly varying Lyman \(\alpha\) component between 6500 and 9000 km is that it is produced by deuterium whose density at 6500 km is about \(6 \times 10^{10}\) cm\(^{-3}\) compared to a hydrogen density of about \(5 \times 10^{10}\) cm\(^{-3}\). In this model the H and D densities are equal at about 9000 km. Although at first glance a 10:1 deuterium to hydrogen ratio above 500 km above the surface of Venus seems absurd, it is really not far from the expected ratio if the exospheric temperature is only 650K and the ratio of deuterium to hydrogen compounds in the mixing region is "normal" (a few times \(10^{-4}\)). It is the ratio of the escape fluxes near 500 km which is significant, for this must be the same as the photoproduction ratio below. In turn, this ratio will be equal to the ratio in density of deuterium and hydrogen compounds. The escape flux of deuterium is proportional to

\[ \frac{n_2(R_e)}{\sqrt{H_2}} \left( \frac{H_2}{R_e} \right) \exp \left[ -\frac{R_e}{H_2} \right], \]  

(35)

where \(R_e\) is the planetocentric distance to the base of the exosphere and \(H_2\) is the deuterium scale height. Thus,

\[ \left( \frac{n_2}{n_1} \right) = \left( \frac{n_2}{n_1} \right) \left( \frac{H_1}{H_2} \right) \exp \left[ -\frac{R_e}{H_2} \right]. \]

(36)

With \(H_1\) twice \(H_2\), this ratio becomes

\[ \left( \frac{n_2}{n_1} \right) = \left( \frac{n_2}{n_1} \right) \left( \frac{R_e}{H_2} \right) \exp \left[ -\frac{R_e}{H_2} \right]. \]

(37)

So with the deuterium to hydrogen ratio 10 at \(R_e\), the mixing ratio implied for D and H is \(5 \times 10^{-4}\). The tap water ratio on earth is \(1.4 \times 10^{-4}\).

4. Water on Venus

This brings us finally to the intriguing lack of water on Venus. In discussions of planetary hydrogen escape, attention often is focussed on the mechanism of escape from the exosphere. In a real atmosphere the escape probability per atom from the base of the exosphere has little to do with the total escape flux. This is controlled rather by the source strength in the lower atmosphere and this is determined in practice by the rate of photodissociation of hydrogen compounds each as H_2O. Thus, water vapor must be convected up from the planet's surface to the upper atmosphere with the mixing ratio determined by the value it can achieve at the temperature minimum. When the water finally reaches the altitude at which it is exposed to solar photons shorter in wavelength than 1860\AA\ it begins to dissociate. In the presence of other gases it must compete for photons below about 1800\AA\ with O_2 and below 1700\AA\ with CO_2. Some of the hydrogen atoms produced may be lost by recombination, the rest will diffuse upward. When they reach the base of the exosphere they escape. The global escape flux will equal the upward flux resulting from photodissociation and the hydrogen density between the source and escape regions will adjust itself to maintain this flux. For a given production rate, if the escape probability increases because of increased exospheric temperature or because of the sweeping effect of the solar wind, the density at the escape level will simply decrease to keep the flux constant. Thus, the fact that the hydrogen 500 km above the surface of Venus is exposed to the solar wind will have little effect
on the rate at which that planet loses hydrogen. What counts is how rapidly the hydrogen is liberated from compounds further down.

If in the course of $4.5 \times 10^9$ yr Venus has lost as much hydrogen as is stored in the form of water on the earth's surface, it has lost about $1.5 \times 10^{28}$ atoms cm$^{-2}$. This calls for an escape flux of about $10^{11}$ atoms cm$^{-2}$ sec$^{-1}$ during a large part of the planet's life. In turn, this means that the dissociation rate also must have attained that value. At present on earth the rate is about $10^8$ atoms cm$^{-2}$ sec$^{-1}$. It is interesting that there is sufficient solar flux at Venus to dissociate about $2 \times 10^{11}$ water molecules cm$^{-2}$ sec$^{-1}$ if the water did not need to compete with such gases as O$_2$ and CO$_2$ for the photons (Sagan, 1967). The threshold for CO$_2$ absorption is about 100Å beyond that for O$_2$ and the absorption coefficient almost two orders of magnitude smaller. Thus, if the O$_2$ abundance in the mesosphere of Venus is much smaller than on earth, the photodissociation rate per H$_2$O molecule is much higher there. Nevertheless, given the existence of temperatures in the neighborhood of 200K in the upper atmosphere, the water vapor content could never become high enough in the upper atmosphere for water to consume a large fraction of the solar photons below 1700Å. It is difficult to see how the photodissociation rate could approach the level of $10^{11}$ molecules cm$^{-2}$ sec$^{-1}$ unless the atmosphere was free even of CO$_2$. Only if the atmosphere were radically different in the past is it possible to understand how Venus could once have possessed as much water as the earth now has.

5. The ionosphere

It appears that there will be little difficulty in accounting for the daytime ionosphere observed on Venus by Mariner 5 (Kliore et al., 1967) in terms of an F1 model with CO$_2^+$ the major ion (McElroy, 1968). In this case we must ask why the same model runs into trouble on Mars.

The nocturnal Cytherian ionosphere with a maximum of $10^4$ electrons cm$^{-2}$ at 6200 km should present some very serious problems. The lowest layer, some 10 km wide, appears to be CO$_2^+$. If it is, the total rate of loss of these ions is given by

$$(\text{CO}_2^+)n_e n_H = 4 \times 10^7 \text{ ions cm}^{-2} \text{ sec}^{-1}. \quad (38)$$

The problem is how to account for such an ionization rate. If, for example, a mechanism involving transport of He$^+$ from the day side is involved, a daytime ionization rate for He far in excess of (38) will be required. On earth the rate is only $2 \times 10^6$ cm$^{-2}$ sec$^{-1}$.

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