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ION CLUSTERS AND THE VENUS ULTRAVIOLET HAZE LAYER

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The daytime ionosphere of Venus is observed between 100- and 500-km altitude with a peak electron concentration of 5×10^5 cm^{-3} at 140 km (Ref. 1). Below 200 km, CO_2^+ is thought to be the principal ion (Refs. 2 and 3) unless oxygen is present. We suggest that at altitudes less than 130 km the ion $CO_2^+ \cdot CO_2$ is an important ionic constituent of the Venus ionosphere. Below 100 km, ion clustering processes combine with the low temperature at the mesopause to form coagulates giving rise to the ultraviolet haze layer which has frequently been observed.

For clustering of neutrals to ions, Keller and Beyer (Ref. 4) have shown the dependence of clustering rate on the polarizability of the neutral molecule and the mass of the ion. A rate of $k_1 = 5 \times 10^{-30}$ cm^6 s^{-1} and $k_{-1} = 5 \times 10^{-14}$ cm^3 s^{-1} would be predicted for the reactions

$$CO_2^+ + CO_2 + CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO_2^+ \cdot CO_2 + CO_2 \qquad (1)$$

The forward reaction has been observed in the laboratory with a rate of 3×10^{-28} cm^6 s^{-1} at 0.16 aJ (1eV) (Ref. 5). In addition, dissociative ion/electron recombination is operative in the ionosphere

$$CO_2^+ \cdot CO_2 + e \rightarrow CO_2 + CO_2 \qquad (2)$$

Based on a measured rate of 2.3×10^{-6} cm^3 s^{-1} for O_4^+/electron recombination (Ref. 6), a rate of $a_D = 2.3 \times 10^{-6}\,(300/T)$ will be assumed for equation (2) where T is the temperature. The kinetic equation is

$$\frac{[CO_2^+ . CO_2]}{[CO_2^+]} = \frac{k_1\,[CO_2]^2}{k_{-1}\,[CO_2] + a_D N_e}$$

and the concentration ratio is plotted as a function of altitude in Figure 1. The atmospheric model chosen is the Goddard Space Flight Center model (Ref. 7). At altitudes below 90 km, where cosmic rays are the dominant source of ionization, the ion ratio

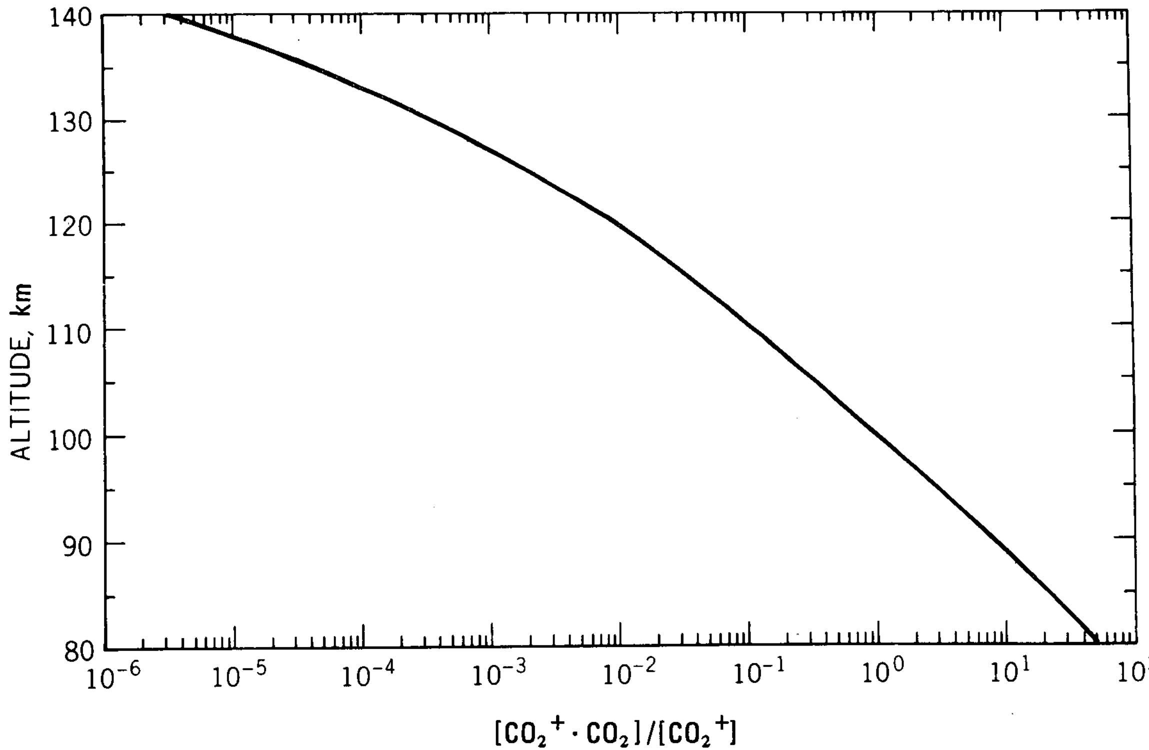

Figure 1–The ratio $[CO_2^+.CO_2]/[CO_2^+]$ as a function of altitude.

$$\frac{[CO_2^+.CO_2]}{[CO_2^+]}$$

is greater than 1. Above 100 km the ratio is less than unity.

If N_2 and O_2 are present in the Venus atmosphere, then the processes

$$CO_2^+ + N_2 + CO_2 \rightarrow CO_2^+ \cdot N_2 + CO_2 \quad (4)$$

and

$$CO_2^+ + O_2 + CO_2 \rightarrow CO_2^+ \cdot O_2 + CO_2 \quad (5)$$

as well as

$$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$$

will cause loss of CO_2^+. The formation and loss processes of $O_2^+ \cdot CO_2$ have been discussed previously for the case of the Martian atmosphere (Ref. 8).

The presence of O_2 will lead to the formation of negative ions (Ref. 9) which will modify equation (3) by the addition of a loss term for $CO_2^+ \cdot CO_2$ involving ion/ion recombination.

In the event that water vapor is present above the cloud tops, reactions occur such as

$$CO_2^+ \cdot CO_2 + H_2O + CO_2 \rightarrow CO_2^+ \cdot H_2O + CO_2 \quad (6)$$

$$CO_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ + CO_2 + OH \quad (7)$$

Coffey (Ref. 10) has shown that $H_3O^+ \cdot (H_2O)_n$ can react with NH_4 and HCl to form $NH_4Cl \cdot (H_2O)_n$ by the chain

$$H_3O^+ \cdot (H_2O)_n + NH_4 \rightarrow NH_4^+ \cdot (H_2O)_n + H_3O \quad (8)$$

$$NH_4^+ \cdot (H_2O)_n + HCl \rightarrow NH_4Cl(H_2O)_m + H_3^+O(H_2O)_{(n-m)} \quad (9)$$

It has further been observed that the compound $NH_4Cl(H_2O)_m$ coagulates easily to form micron-sized particles.

Kuiper (Ref. 11) has suggested that the Venus ultraviolet haze layer is composed of 0.1-μm-sized particles of NH_4Cl. The location of this layer at 90 km is illustrated in Figure 2, which shows the temperature distribution for the atmospheric model employed. Also indicated are the levels of the yellow haze layer and the ratio of cluster ions relative to $[CO_2^+]$.

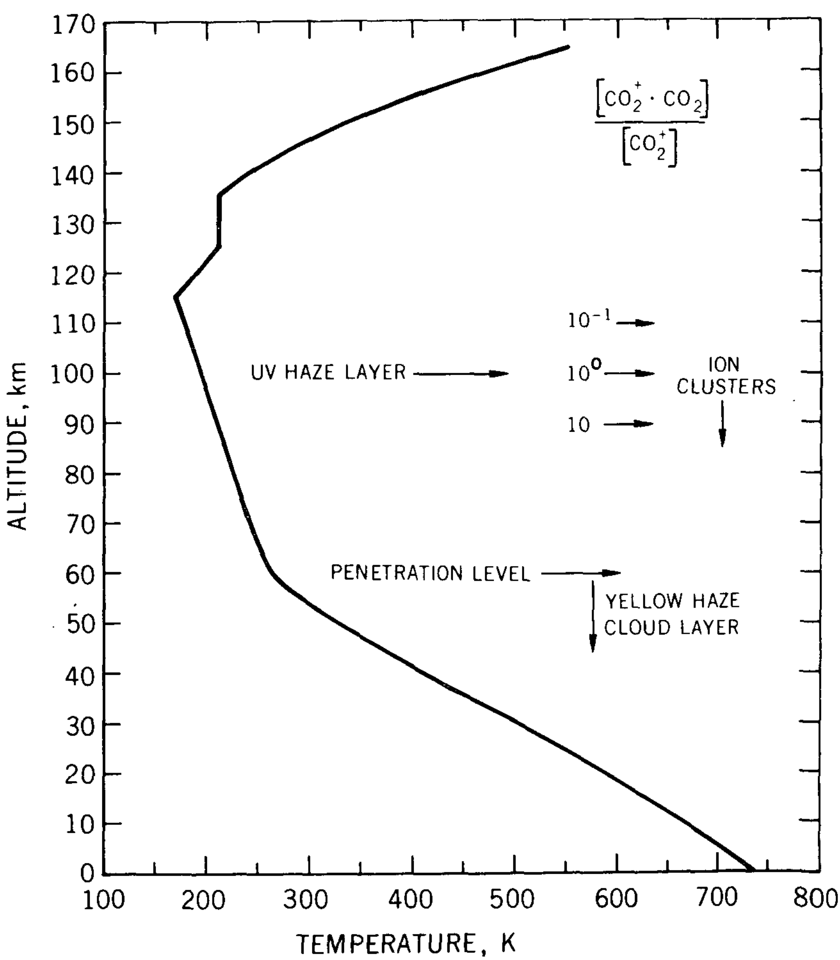

Figure 2–Altitude level of the Venus yellow cloud layer and ultraviolet haze layer in relation to the temperature distribution of the atmosphere and the ratio $[CO_2^+ \cdot CO_2]/[CO_2^+]$.

An alternate source of coagulates may be the ion $CO_2^+ \cdot H_2O$, which can attach additional water molecules as well as other neutral molecules. The complexes $CO_2^+(H_2O) \cdot XY$ can form as has been observed with NO^+, H_2O, SO_2 systems (Ref. 12). The resulting complex will further react to eliminate the ion and form coagulatable compounds. Laboratory studies at Venus atmosphere conditions will define more clearly the importance of ion clustering processes in the formation of the Venus ultraviolet haze layer.

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