Introduction

In order to understand the evolution of water on Venus, we must know the hydrogen escape flux as a function of the tropospheric water abundance. We have studied the connection between total stratospheric hydrogen and exobase hydrogen available to non-thermal escape processes and examined the details of the photochemical trap for water at the Venus cloud tops. Our immediate goal is to calculate the stratospheric water abundance as a function of the tropospheric water abundance.

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The ratio of stratospheric water to tropospheric water is of order 10^{-2} (von Zahn and Moroz, 1984), while the ratio of stratospheric SO_2 to tropospheric SO_2 apparently varies from 10^{-4} to 10^{-2} (Esposito, 1984; von Zahn and Moroz, 1984). Photochemical production of H_2SO_4 acts as a sink for both water and sulfur and is capable of keeping stratospheric abundances low if a proper balance exists between the tropospheric abundances. If production of H_2SO_4 were the only sink for H_2O and SO_2, the excess in tropospheric abundance of one over the other would reach the stratosphere, and the functional dependence of stratospheric H_2O on tropospheric H_2O would be linear near the present state. On Venus, however, sulfuric acid condenses at cloud top temperatures and the resulting aerosols can absorb additional water of hydration. This complicates the water budget, increasing the efficiency of sulfur as a sink for water. We have investigated the balance between tropospheric H_2O and SO_2 and how delicate the balance is.

Procedure

For this investigation we have used a one dimensional photochemical model to investigate the atmosphere of Venus between the cloud tops and the exobase (Yatteau, 1983). Results from the upper atmosphere model are

used as upper boundary conditions for the cloud model, which calculates composition between 47 km and 70 km. Chemistry of carbon-, oxygen-, hydrogen-, chlorine-, and sulfur-bearing species is calculated following the work of Yung and Demore (1983) and Yatteau (1983). The list of reactions considered in the photochemical model, together with their rate coefficients, is given in Table 1. Settling of H_2SO_4 aerosols is modelled using a constant settling velocity appropriate for mode 2 aerosols (Knollenberg and Hunten, 1980). Hydration of H_2SO_4 aerosols is calculated using equilibrium at local temperature and humidity. Lower boundary densities of H_2O and SO_2 are treated as adjustable parameters whose range is constrained by observation. Lower boundary densities for radical species are set to zero, since photochemical production is negligible at the cloud base, and lower boundary mixing ratios for long-lived species are set to spectroscopically determined values. Eddy diffusivity is assumed to follow a downward extrapolation of von Zahn et al. (1980) profile with a lower bound as an adjustable parameter.

Results

Figure 1 shows typical dayside mixing ratio profiles of important hydrogen-bearing species between the cloud top region and the exobase. HCl and H_2O are efficiently converted to atomic H above 100 km, which establishes a direct relationship between total stratospheric hydrogen and exobase H.

Supply of H_2O to the stratosphere is controlled by the photochemical trap near the cloud tops. We have performed a series of calculations for 2 sets of tropospheric SO_2 and H_2O abundances which yield stratospheric mixing ratios consistent with observation. The SO_2 mixing ratio at 47 km is set to 10 ppm and 40 ppm in the two sets of calculations. The mode 2

particles identified by Knollenberg and Hunten (1980) from the particle size spectrometer data are most likely to be sulfuric acid droplets and they dominate the mass loading in the upper cloud.

Our model calculates more H_2SO_4 in the upper cloud than is consistent with simple settling of mode 2 particles at their most likely settling velocity of 0.03 cms^{-1}. Figure 2 shows mixing ratio profiles for H_2SO_4 corresponding to settling velocities of 0.03 cms^{-1} and 0.06 cms^{-1} for an SO_2 mixing ratio of 10 ppm at 47 km; it also shows the mixing ratio profile of H_2SO_4 corresponding to the inferred mass loading of mode 2 particles from Knollenberg and Hunten (1980). Figure 3 shows the same profile for an SO_2 mixing ratio of 40 ppm at 47 km. The discrepancy between the model and observations probably reflects oversimplification in the aerosol model, although the sounder probe may have entered a subsiding region.

Our model calculates aerosol hydration states at the low end of the range inferred from observed indices of refraction, suggesting that the model contains too little water. But higher water abundances are not consistent with low SO_2 in the cloud region. Figure 4 shows altitude profiles of aerosol hydration state for 2 values of tropospheric SO_2.

We have calculated the dependence of stratospheric H_2O mixing ratio on tropospheric H_2O mixing ratio for 40 ppm SO_2. Figure 5 shows the H_2O mixing ratio at 70 km as a function of the H_2O mixing ratio at 47 km. The effect of aerosol hydration is to delay penetration of the photochemical trap by H_2O.

Recent reports of variations in stratospheric SO_2 at 70 km (Esposito, 1984) have prompted us to investigate controls on stratospheric SO_2 with our model. Since sulfur and hydrogen are so intimately linked, we have also considered associated changes in hydrogen.

We have calculated profiles of SO_2 and H_2O for different values of eddy diffusivity. We find that SO_2 varies dramatically, but that H_2O varies less or not at all. Figure 5 shows SO_2 mixing ratio profiles for 2 values of minimum eddy diffusivity such that the SO_2 mixing ratios at 70 km are 1 ppb and 100 ppb, the range reported by Esposito (1984). Corresponding profiles for H_2O are shown in Figure 7. These results show that a factor of 3 change in eddy diffusivity can produce a 2 order of magnitude change in SO_2 at 70 km while lowering H_2O by only a factor of 4. The same calculations for 10 ppm SO_2 at 47 km are depicted in Figure 8. There is negligible change in H_2O in the case of 10 ppm SO_2 at 47 km. Since HCl probably supplies at least half the stratosphere's hydrogen (Yatteau, 1983), we conclude that modest changes in the turbulent mixing rate near the cloud tops can account for the reported changes in stratospheric SO_2 without substantially altering the hydrogen budget. We expect changes of less than a factor of 2 in upper atmospheric hydrogen associated with reported changes in stratospheric SO_2.

Discussion

We have used our model to examine timescales for changes in stratospheric H_2O and SO_2 associated with disturbances to the cloud regions. The photochemical timescale for conversion of SO_2 to H_2SO_4 is of order 10^8 sec at 70 km and of order $2x10^5$ sec at 62 km. The diffusive timescale at 70 km is about $1-2x10^7$ sec depending on the eddy diffusivity, but in the case of low eddy diffusivity, the diffusive timescale at 62 km is about $3-5x10^7$ sec. We conclude that both SO_2 and H_2O at 70 km are diffusively controlled, responding to changes lower down.

Our results show that changes in sulfur at 70 km may be associated with changes in H_2O, but the magnitude of the changes in H_2O depends on

the tropospheric SO_2 abundance. It may be possible to use observations of SO_2, H_2SO_4 haze and upper atmospheric H to distinguish between different processes which could be responsible for observed variation, such as direct injection and enhanced mixing. If higher levels of SO_2 result from enhanced mixing, SO_2 and H_2O should change on a timescale of order 10^7 sec. In situ production of aerosols at 70 km takes about 10^8 sec; upward mixing of aerosols produced at 62 km could occur in 10^7 sec. Mixing would initiate H_2SO_4 production immediately; direct injection would result in less total haze located at different altitudes occurring at later times if the injected material had an H_2O/SO_2 ratio substantially different from the tropospheric ratio. Associated changes in upper atmospheric H may not be dramatic enough to detect. HCl may supply more than half the stratospheric hydrogen budget, and diffusion would prevent even direct injection of pure SO_2 at 70 km from eliminating water from the stratosphere.

Our major conclusions from this work are the following: 1) H_2O and SO_2 are mutually limiting if proper tropospheric balance is maintained; 2) changes in tropospheric abundances on the order of 5 ppm are significant; 3) changes in mixing rates near the cloud tops can cause dramatic changes in SO_2 without causing dramatic changes in H_2O.

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Table 1

$CO_2 + h\nu \rightarrow CO + O(^1D)$	$J_1 = 8.8 \times 10^{-7}$ calculated
$O(^1D) + M \rightarrow O + M$	$k_2 = 7.4 \times 10^{-11} e^{\frac{117}{T}}$ DeMore et al. (1982)
$CO + O + M \rightarrow CO_2 + M$	$k_3 = 6.5 \times 10^{-33} e^{\frac{-2180}{T}}$ Baulch et al. (1976)
$O + O + M \rightarrow O_2 + M$	$k_4 = 4.8 \times 10^{-33} (\frac{T}{300})^{-2}$ Campbell and Gray (1973)
$O_2 + h\nu \rightarrow O + O$	$J_5 = 2.2 \times 10^{-6}$ calculated
$H_2O + h\nu \rightarrow OH + H$	$J_6 = 6.8 \times 10^{-6}$ calculated
$H + O_2 + M \rightarrow HO_2 + M$	$k_7 = 5.5 \times 10^{-32} (\frac{T}{300})^{-1.4}$ DeMore et al. (1982)
$OH + HO_2 \rightarrow H_2O + O_2$	$k_8 = 7.0 \times 10^{-11}$ DeMore et al. (1982)
$H + HO_2 \rightarrow H_2 + O_2$	$k_9 = 7.0 \times 10^{-12}$ DeMore et al. (1982)
$H + H + M \rightarrow H_2 + M$	$k_{10} = 9.2 \times 10^{-33} (\frac{T}{300})^{0.802}$ fit to Trainor et al. (1973)
$OH + H_2 \rightarrow H_2O + H$	$k_{11} = 6.1 \times 10^{-12} e^{\frac{-2030}{T}}$ DeMore et al. (1982)

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{12} = 2.5 \times 10^{12}$
	DeMore et al. (1982)
$O + HO_2 \rightarrow OH + O_2$	$k_{13} = 3.0 \times 10^{-11} e^{\frac{200}{T}}$
	DeMore et al. (1982)
$H + HO_2 \rightarrow OH + OH$	$k_{14} = 6.4 \times 10^{-11}$
	DeMore et al. (1982)
$H_2O_2 + h\nu \rightarrow OH + OH$	$J_{15} = 1.1 \times 10^{-4}$
	calculated
$CO + OH \rightarrow CO_2 + H$	$k_{16} = 1.5 \times 10^{-13}$
	DeMore et al. (1982)
$O + OH \rightarrow H + O_2$	$k_{17} = 2.2 \times 10^{-11} e^{\frac{117}{T}}$
	DeMore et al. (1982)
$O + H_2 \rightarrow OH + H$	$k_{18} = 1.6 \times 10^{-11} e^{\frac{-4570}{T}}$
	Dubinsky and McKenney (1975)
$H + HCl \rightarrow H_2 + Cl$	$k_{19} = 1.0 \times 10^{-11} e^{\frac{1605}{T}}$
	Westenberg and deHaas (1968)
$Cl + HO_2 \rightarrow HCl + O_2$	$k_{20} = 1.8 \times 10^{-11} e^{\frac{170}{T}}$
	DeMore et al. (1982)
$HCl + h\nu \rightarrow H + Cl$	$J_{21} = 2.4 \times 10^{-6}$
	calculated
$Cl + H_2 \rightarrow HCl + H$	$k_{22} = 3.7 \times 10^{-11} e^{\frac{-2300}{T}}$
	DeMore et al. (1982)

$OH + HCl \rightarrow H_2O + Cl$	$k_{23} = 2.8 \times 10^{-12} e^{\frac{-425}{T}}$
	DeMore et al. (1982)
$O + HCl \rightarrow OH + Cl$	$k_{24} = 1.0 \times 10^{-11} e^{\frac{-3340}{T}}$
	DeMore et al. (1982)
$CO_2^+ + H_2 \rightarrow H + H$	$k_{25} = 1.0 \times 10^{-9}$
	Sze and McElroy (1975)
$Cl_2 + h\nu \rightarrow Cl + Cl$	$J_{26} = 2.4 \times 10^{-3}$
	calculated
$Cl + Cl + M \rightarrow Cl_2 + M$	$k_{27} = 6.3 \times 10^{-34} e^{\frac{900}{T}}$
	Watson (1977)
$Cl + O_2 + M \rightarrow ClO_2 + M$	$k_{28} = 2.0 \times 10^{-33} (\frac{T}{300})^{-1.3}$
	DeMore et al. (1982)
$Cl + ClO_2 \rightarrow Cl_2 + O_2$	$k_{29} = 1.4 \times 10^{-10}$
	DeMore et al. (1982)
$Cl + ClO_2 \rightarrow ClO + ClO$	$k_{30} = 8.0 \times 10^{-12}$
	DeMore et al. (1982)
$O + ClO \rightarrow O_2 + Cl$	$k_{31} = 7.7 \times 10^{-11} e^{\frac{-130}{T}}$
	DeMore et al. (1982)
$ClO + ClO \rightarrow Cl_2 + O_2$	$k_{32} = 5.0 \times 10^{-13} e^{\frac{-1238}{T}}$
	Hudson (1977)
$ClO + ClO \rightarrow Cl + ClO_2$	$k_{33} = 1.0 \times 10^{-12} e^{\frac{-1238}{T}}$
	Hudson (1977)

$ClO + ClO + M \rightarrow Cl_2 + O_2 + M$	$k_{34} = 1.0 \times 10^{-31}$
	Johnston et al. (1969)
$O + Cl_2 \rightarrow ClO + Cl$	$k_{35} = 4.2 \times 10^{-12} e^{\frac{-1370}{T}}$
	Clyne et al. (1976)
$ClO_2 + M \rightarrow Cl + O_2 + M$	$k_{36} = 2.7 \times 10^{-9} e^{\frac{-2650}{T}}$
	DeMore et al. (1982)
$ClO + CO \rightarrow Cl + CO_2$	$k_{37} = 4.0 \times 10^{-18}$
	DeMore et al. (1982)
$ClO_2 + CO \rightarrow ClO + CO_2$	$k_{38} = 1.0 \times 10^{-15}$
	Sze and McElroy (1975)
$Cl + HO_2 \rightarrow ClO + OH$	$k_{39} = 4.1 \times 10^{-11} e^{\frac{-450}{T}}$
	DeMore et al. (1982)
$O_3 + h\nu \rightarrow O_2 + O1D$	$J_{40} = 8.2 \times 10^{-3}$
	calculated
$O1D + H_2O \rightarrow OH + OH$	$k_{41} = 2.2 \times 10^{-10}$
	DeMore et al. (1982)
$O1D + H_2 \rightarrow OH + H$	$k_{42} = 1.0 \times 10^{-10}$
	DeMore et al. (1982)
$O + O_2 + M \rightarrow O_3 + M$	$k_{43} = 6.0 \times 10^{-34} (\frac{T}{300})^{-2.3}$
	DeMore et al. (1982)
$O + O_3 \rightarrow O_2 + O_2$	$k_{44} = 1.5 \times 10^{-11} e^{\frac{-2218}{T}}$
	DeMore et al. (1982)
$O_3 + H \rightarrow OH + O_2$	$k_{45} = 1.4 \times 10^{-10} e^{\frac{-470}{T}}$

	DeMore et al. (1982)
$O_3 + OH \rightarrow HO_2 + O_2$	$k_{46} = 1.6 \times 10^{-12} e^{\frac{-940}{T}}$
	DeMore et al. (1982)
$O_3 + HO_2 \rightarrow OH + O_2 + O_2$	$k_{47} = 1.4 \times 10^{-14} e^{\frac{-580}{T}}$
	DeMore et al. (1982)
$O_3 + Cl \rightarrow ClO + O_2$	$k_{48} = 2.8 \times 10^{-11} e^{\frac{-257}{T}}$
	DeMore et al. (1982)
$O_3 + ClO \rightarrow ClO_2 + O_2$	$k_{49} = 1.0 \times 10^{-12} e^{\frac{-4000}{T}}$
	DeMore et al. (1982)
$OH + OH \rightarrow H_2O + O$	$k_{50} = 4.2 \times 10^{-12} e^{\frac{-242}{T}}$
	DeMore et al. (1982)
$SO + h\nu \rightarrow S + O$	$J_{51} = 6.7 \times 10^{-4}$
	calculated
$SO_2 + h\nu \rightarrow SO + O$	$J_{52} = 1.9 \times 10^{-4}$
	calculated
$S + O_2 \rightarrow SO + O$	$k_{53} = 2.3 \times 10^{-12}$
	DeMore et al. (1982)
$S + CO_2 \rightarrow SO + CO$	$k_{54} = 1.0 \times 10^{-20}$
	Yung and DeMore (1982)
$S + O_3 \rightarrow SO + O_2$	$k_{55} = 1.2 \times 10^{-11}$
	Yung and DeMore (1982)
$S + OH \rightarrow SO + H$	$k_{56} = 6.6 \times 10^{-11}$
	DeMore et al. (1982)

$S + HO_2 \rightarrow SO + OH$	$k_{57} = 2.3 \times 10^{-11}$
	Yung and DeMore (1982)
$SO + O + M \rightarrow SO_2 + M$	$k_{58} = 6.0 \times 10^{-31}$
	Yung and DeMore (1982)
$SO + O_2 \rightarrow SO_2 + O$	$k_{59} = 9.0 \times 10^{-18}$
	DeMore et al. (1982)
$SO + O_3 \rightarrow SO_2 + O_2$	$k_{60} = 3.2 \times 10^{-12} e^{\frac{-1100}{T}}$
	DeMore et al. (1982)
$SO + OH \rightarrow SO_2 + H$	$k_{61} = 8.6 \times 10^{-11}$
	DeMore et al. (1982)
$SO + HO_2 \rightarrow SO_2 + OH$	$k_{62} = 1.0 \times 10^{-19}$
	DeMore et al. (1982)
$SO + ClO \rightarrow SO_2 + Cl$	$k_{63} = 2.3 \times 10^{-11}$
	Clyne and MacRobert (1981)
$SO + SO \rightarrow SO_2 + S$	$k_{64} = 8.3 \times 10^{-15}$
	Herron and Huie (1980)
$SO_2 + O + M \rightarrow SO_3 + M$	$k_{65} = 8.0 \times 10^{-32} e^{\frac{-1000}{T}}$
	Yung and DeMore (1982)
$SO_2 + HO_2 \rightarrow SO_3 + OH$	$k_{66} = 1.0 \times 10^{-18}$
	Sander and Watson (1981)
$SO_2 + ClO \rightarrow SO_3 + Cl$	$k_{67} = 1.0 \times 10^{-18}$
	Yung and DeMore (1982)
$SO_3 + SO \rightarrow SO_2 + SO_2$	$k_{68} = 2.0 \times 10^{-15}$
	Yung and DeMore (1982)

$SO_3 + O + M \rightarrow SO_2 + O_2 + M$	$k_{69} = 1.4 \times 10^{-31} e^{\frac{785}{T}}$
	Westenberg and deHaas (1968)
$SO_2 + OH + M \rightarrow HSO_3 + M$	$k_{70} = 3.0 \times 10^{-31} (\frac{T}{300})^{-2.9}$
	DeMore et al. (1982)
$SO_3 + H_2O \rightarrow H_2SO_4$	$k_{71} = 9.0 \times 10^{-13}$
	Yung and DeMore (1982)
$Cl + H_2O_2 \rightarrow HCl + HO_2$	$k_{72} = 1.1 \times 10^{-11} e^{\frac{-980}{T}}$
	DeMore et al. (1982)
$COCl_2 \rightarrow ClCO + Cl$	$k_{73} = 5.0 \times 10^{-5}$
	Yung and DeMore (1982)
$Cl + CO + M \rightarrow ClCO + M$	$k_{74} = 1.3 \times 10^{-34} e^{\frac{1000}{T}}$
	Yung and DeMore (1982)
$ClCO + M \rightarrow Cl + CO + M$	$k_{75} = 6.0 \times 10^{-11} e^{\frac{-2250}{T}}$
	Yung and DeMore (1982)
$ClCO + O_2 + M \rightarrow ClCO_3 + M$	$k_{76} = 5.7 \times 10^{-32} e^{\frac{500}{T}}$
	Yung and DeMore (1982)
$ClCO + O \rightarrow CO_2 + Cl$	$k_{77} = 3.0 \times 10^{-11}$
	Yung and DeMore (1982)
$ClCO + O \rightarrow CO + ClO$	$k_{78} = 3.0 \times 10^{-12}$
	Yung and DeMore (1982)
$ClCO + H \rightarrow HCl + CO$	$k_{79} = 1.0 \times 10^{-11}$
	Yung and DeMore (1982)
$ClCO + Cl \rightarrow CO + Cl_2$	$k_{80} = 1.0 \times 10^{-11}$

	Yung and DeMore (1982)
$ClCO + Cl_2 \rightarrow COCl_2 + Cl$	$k_{81} = 6.0 \times 10^{-13} e^{\frac{-1400}{T}}$
	Yung and DeMore (1982)
$ClCO + ClCO \rightarrow COCl_2 + CO$	$k_{82} = 1.0 \times 10^{-11}$
	Yung and DeMore (1982)
$ClCO_3 + O \rightarrow CO_2 + Cl + O_2$	$k_{83} = 1.0 \times 10^{-11}$
	Yung and DeMore (1982)
$ClCO_3 + Cl \rightarrow CO_2 + Cl + ClO$	$k_{84} = 1.0 \times 10^{-11}$
	Yung and DeMore (1982)
$ClCO_3 + H \rightarrow CO_2 + Cl + OH$	$k_{85} = 1.0 \times 10^{-11}$
	Yung and DeMore (1982)
$H_2SO_4 \rightarrow$ Aerosol	
	condensation
$HSO_3 \rightarrow$ Aerosol	
	condensation
$H_2O \rightarrow$ Aerosol	
	hydration
	see text

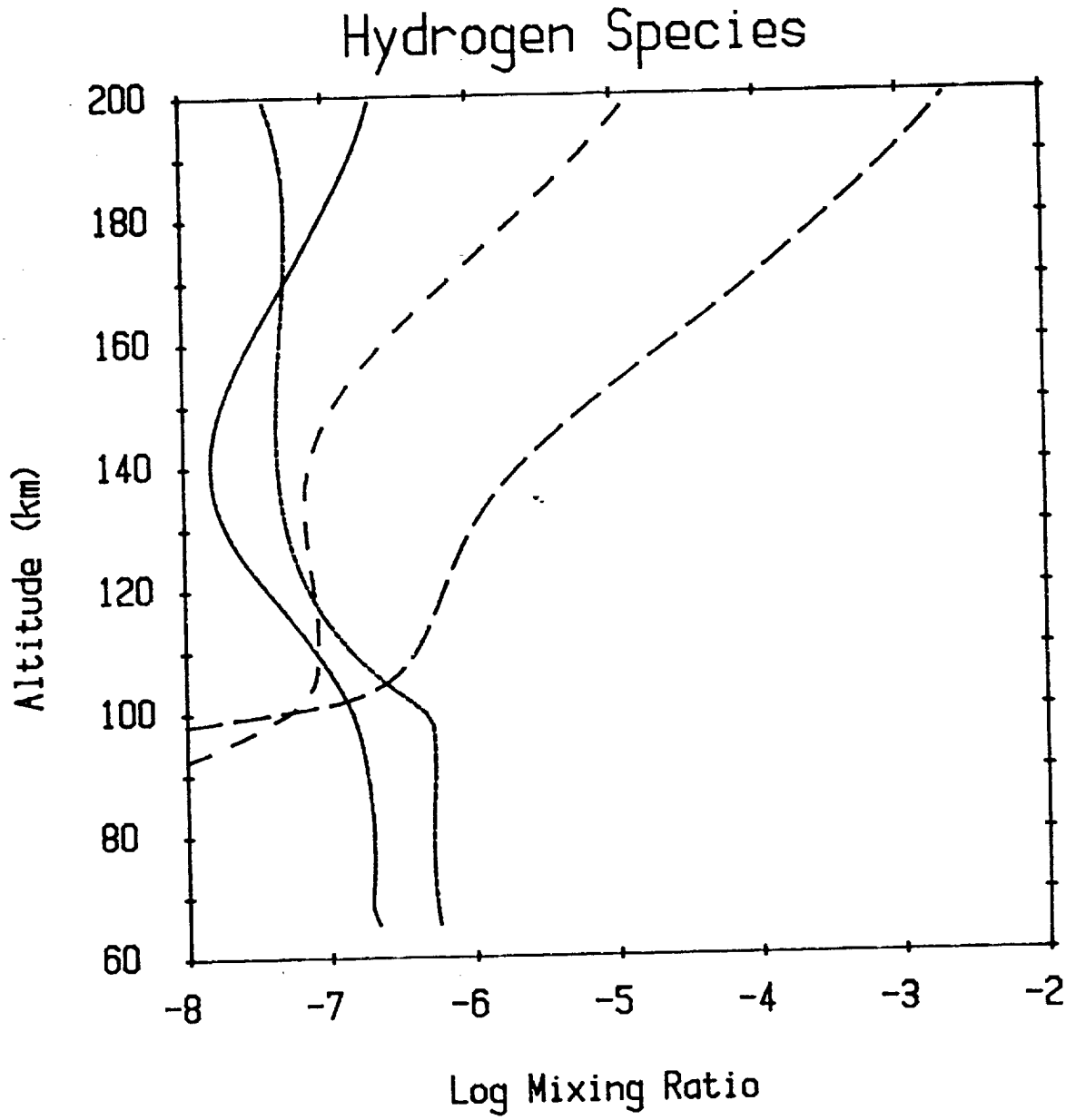

Figure 1

H2O (solid line), H2 (short dashes), H (long dashes), HCl (dash-dot), clouds to exobase.

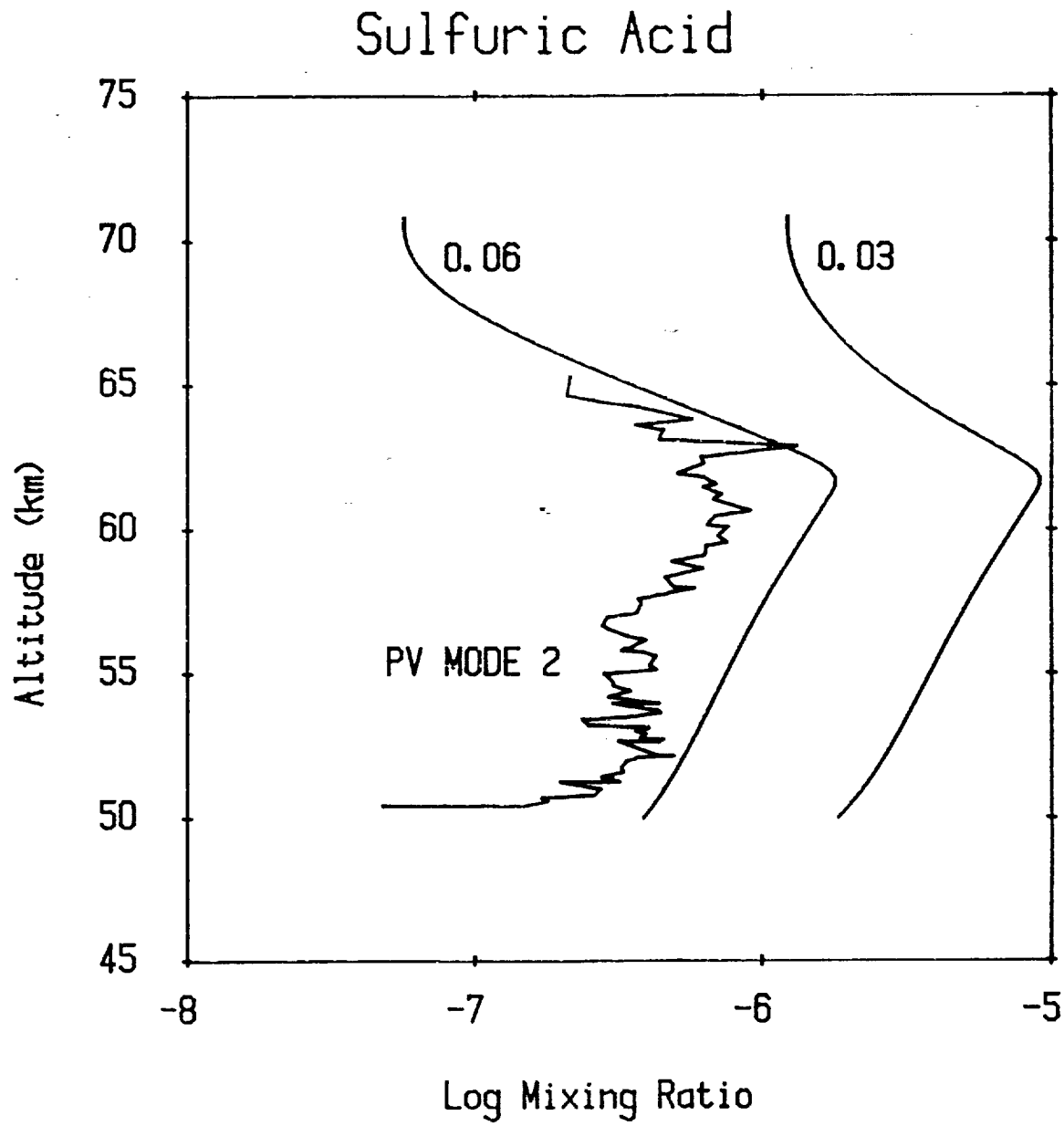

Figure 2

SO2 = 10 ppm. Settling velocities of 0.03 cm/s and 0.06 cm/s. PV mode 2 also shown.

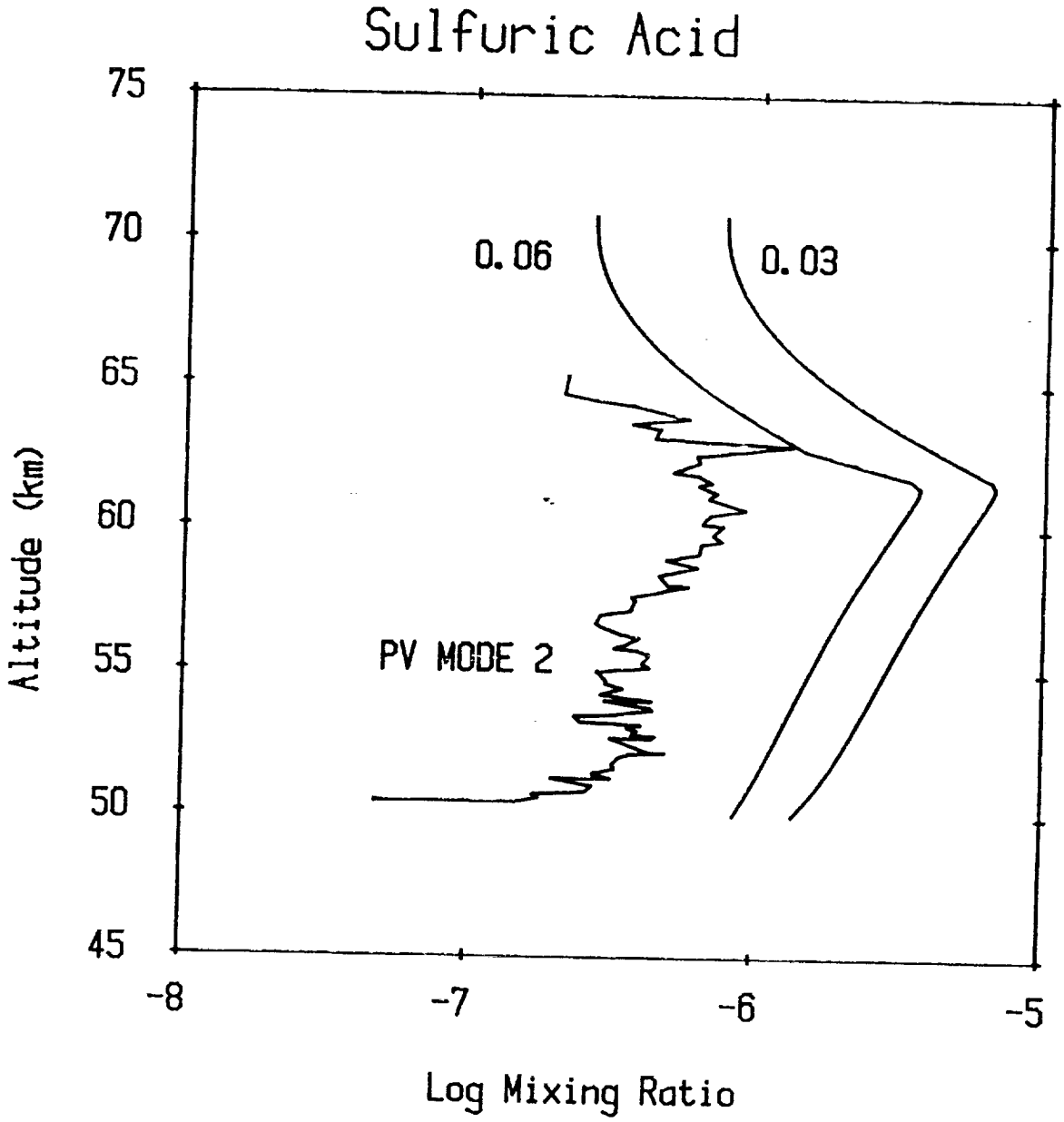

Figure 3

SO2 = 39 ppm. Settling velocities of 0.03 cm/s and 0.06 cm/s. PV mode 2 also shown.

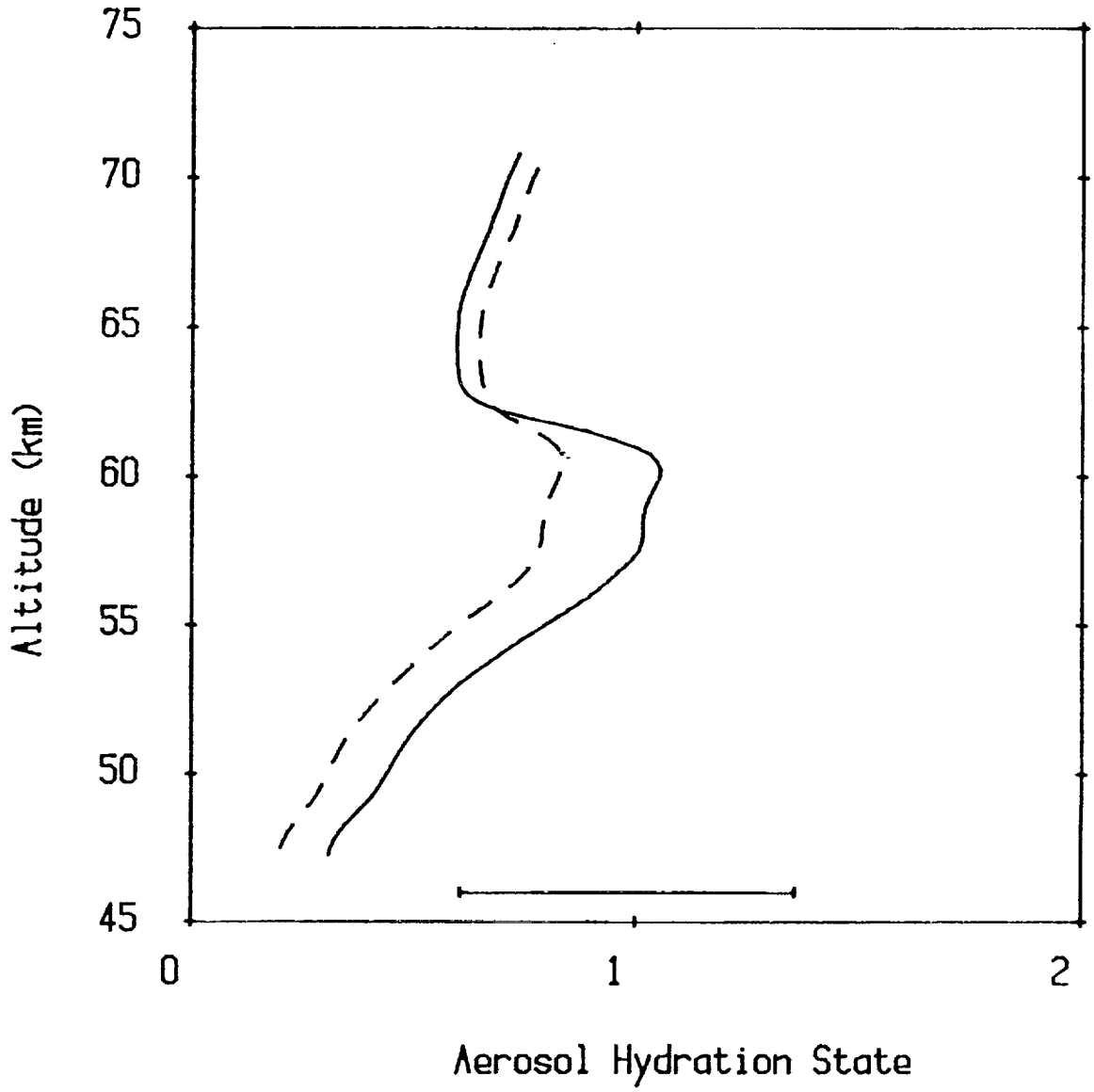

Figure 4

SO2 = 10 ppm (dashed), SO2 = 39 ppm (solid).
Range inferred from observation also shown.

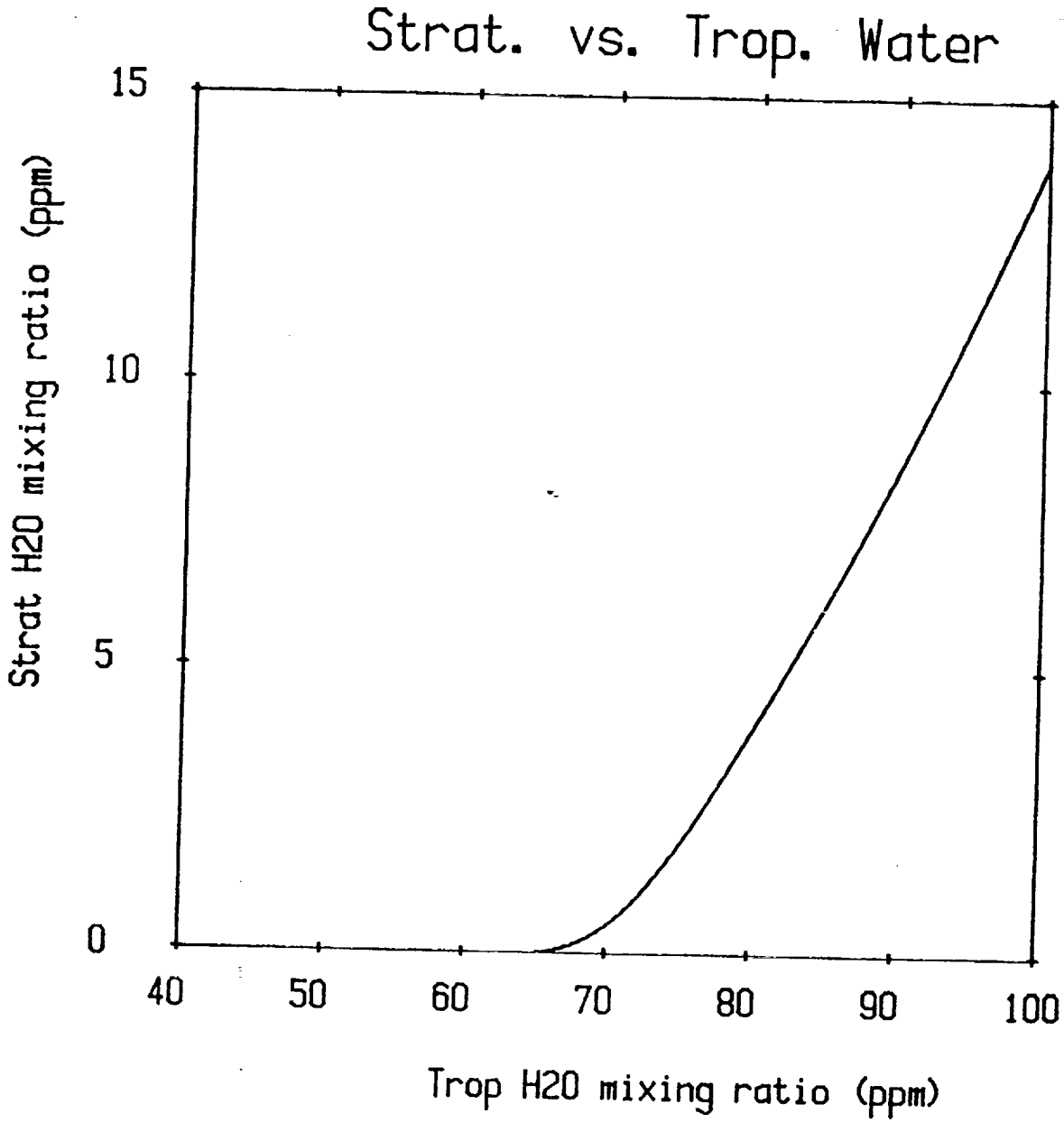

Figure 5

Water vapor mixing ratio at 70 km as a function of water vapor mixing ratio at 47 km.

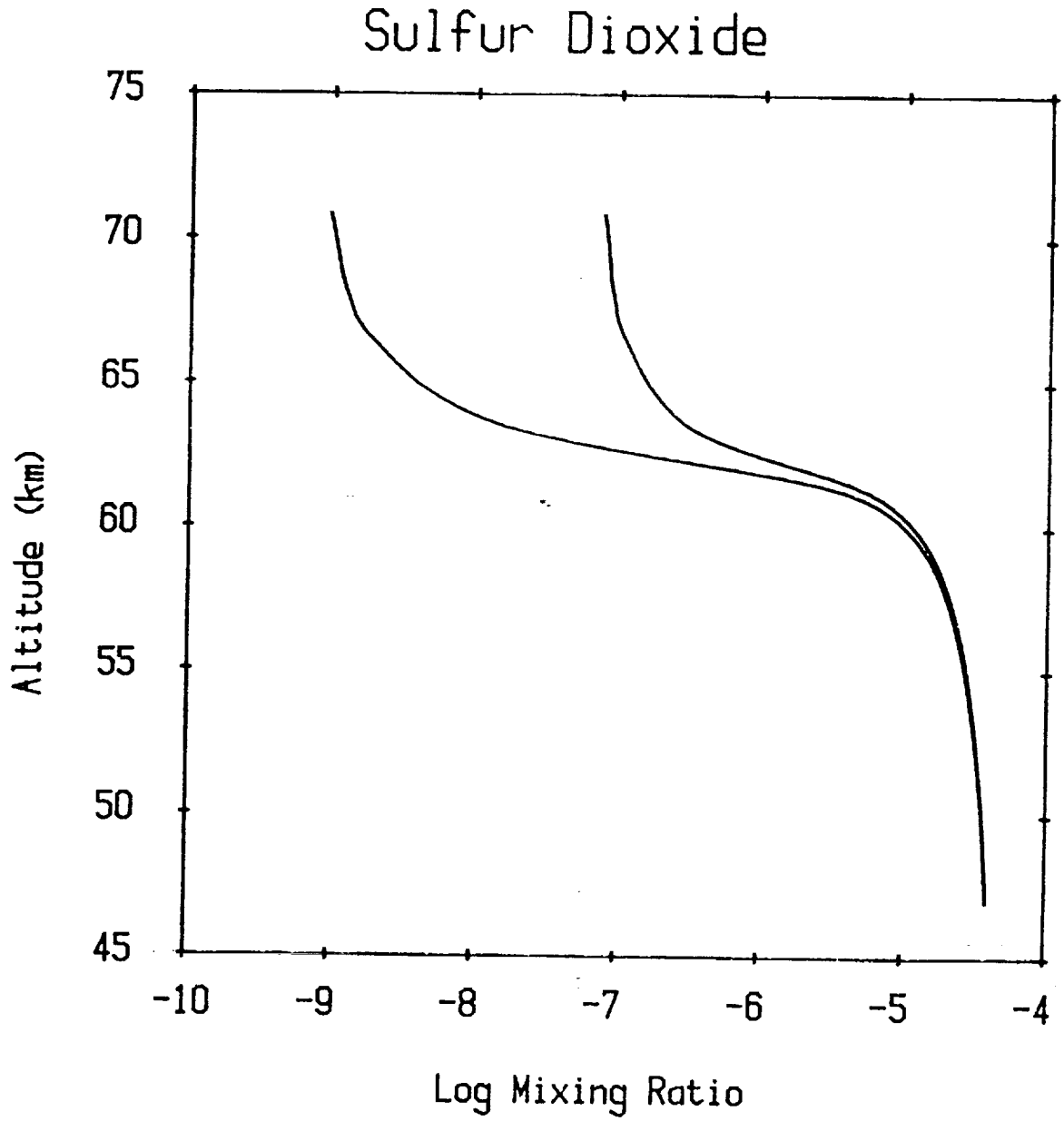

Figure 6

SO2 for eddy diffusivity = 6.0E+03 cm2/s and 2.0E+04 cm2/s.

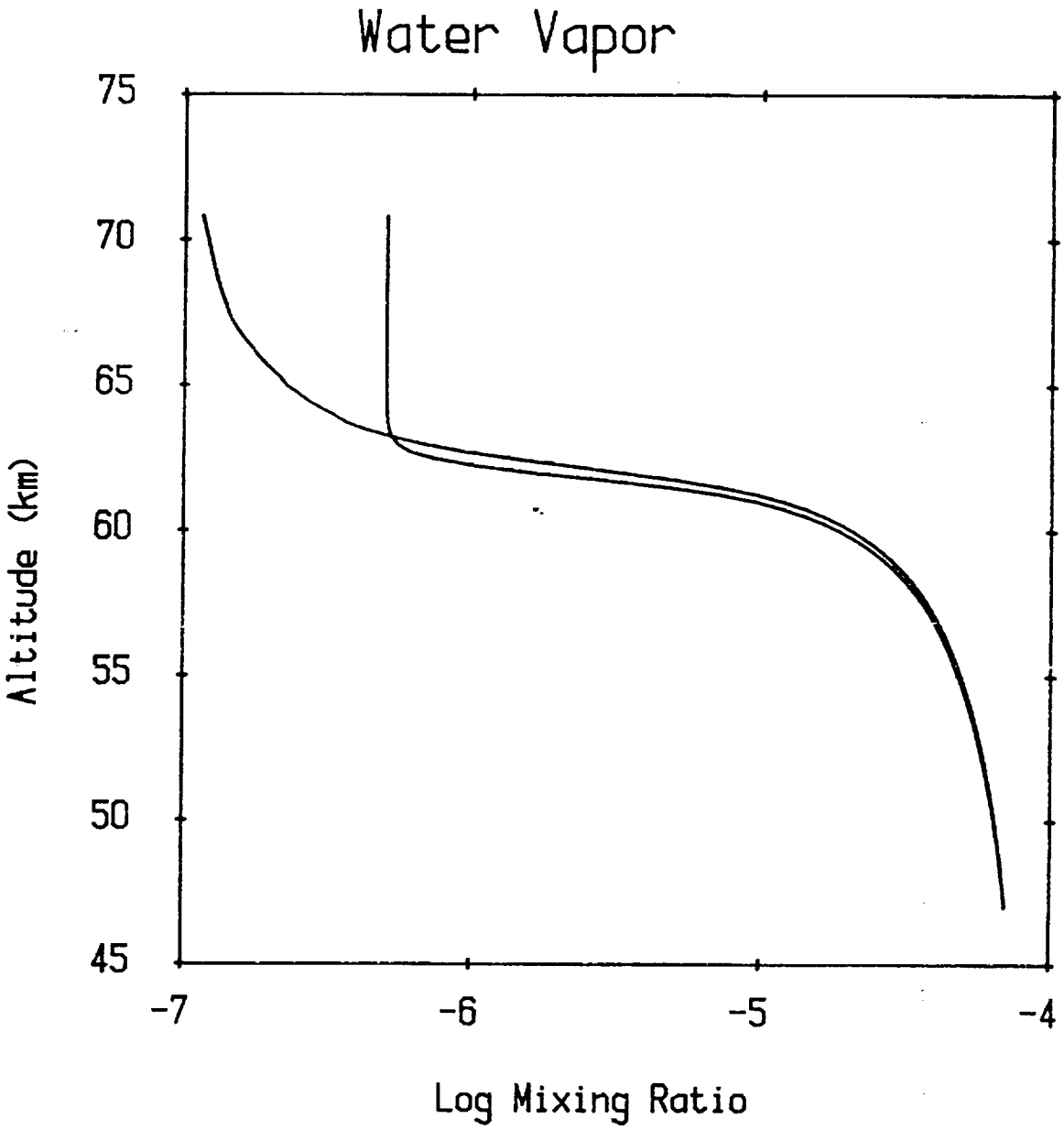

Figure 7

H20 for eddy diffusivity = 6.0E+03 cm2/s and 2.0E+04 cm2/s

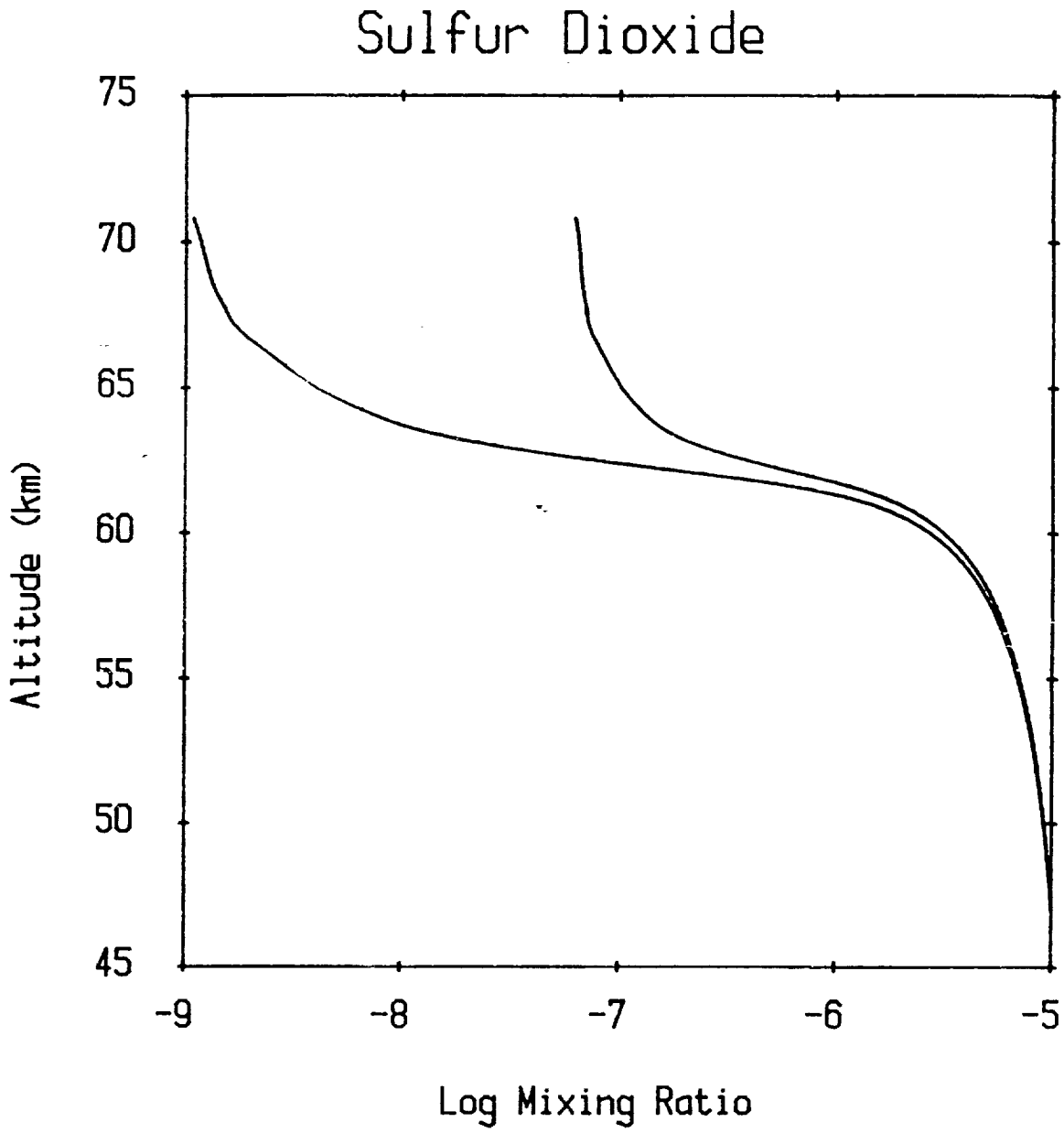

Figure 8

SO2 for eddy diffusivity = 9.0E+03 and 3.0E+04. Water vapor is unchanged.