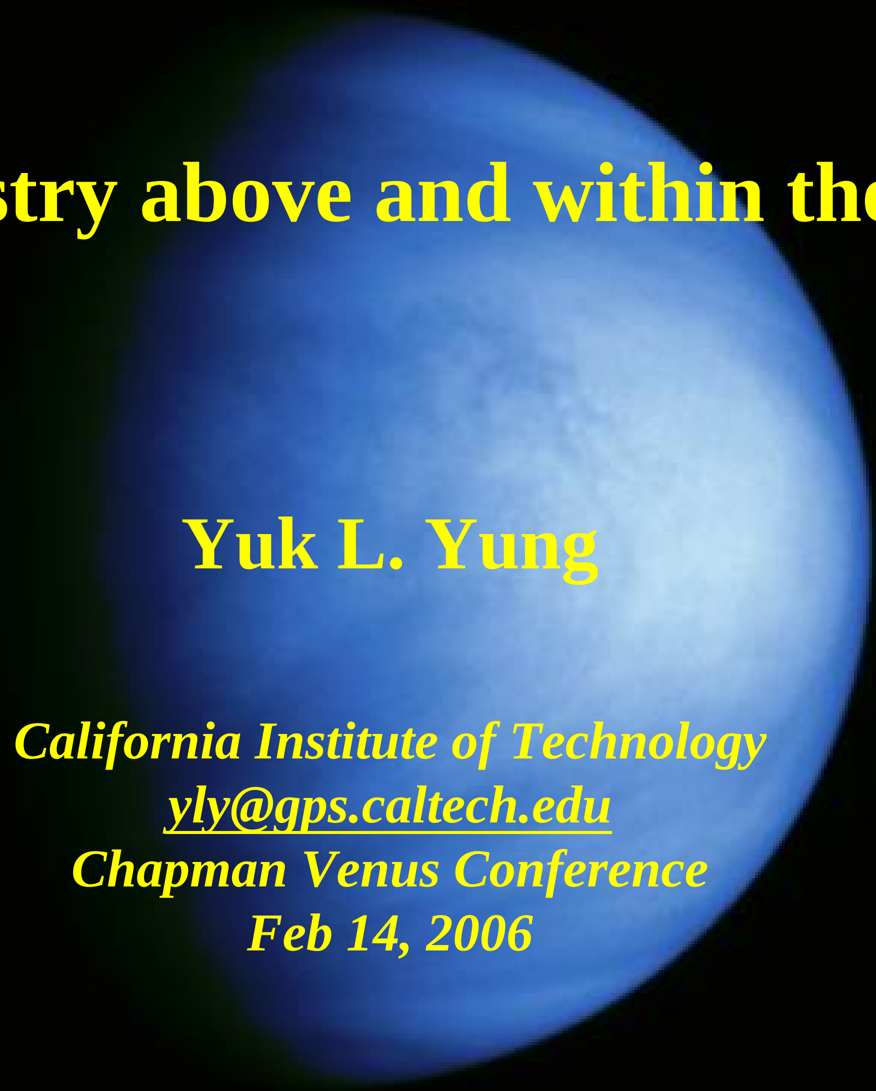
Photochemistry above and within the Clouds



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Chapman Venus Conference
Feb 14, 2006

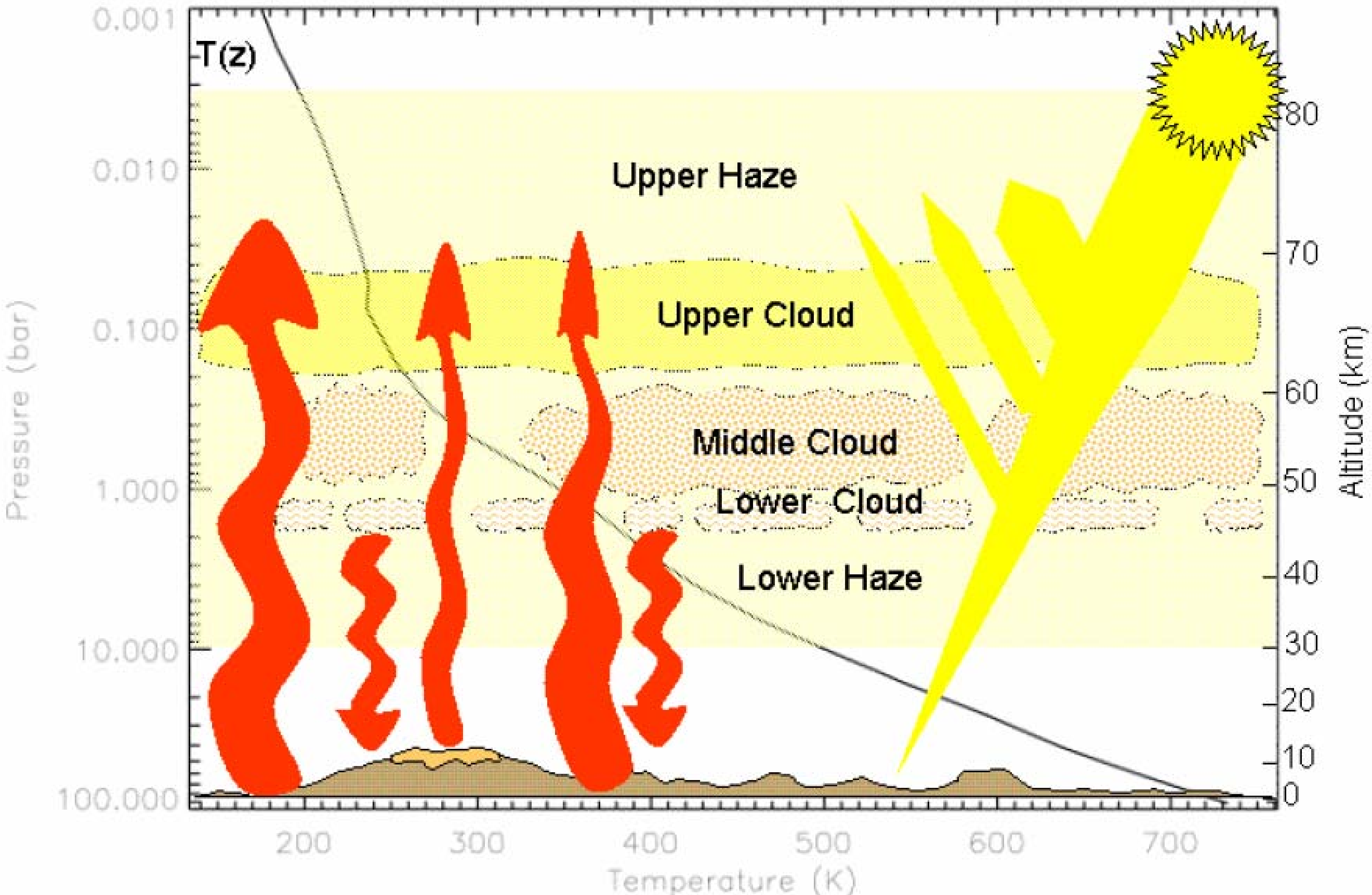
Important Processes in the Atmosphere of Venus

- Catalytic Chemical Cycles
- Heterogeneous Chemistry
- Middle Atmosphere Circulation
- Troposphere/Middle Atmosphere Exchange
- Secular Variability
- Evolution

Table 3 Chemical composition of the atmosphere of Venus

Gas	*Abundance*[a]	*Source(s)*	*Sink(s)*
CO_2	96.5±0.8%	outgassing	carbonate formation
N_2	3.5±0.8%	outgassing	—
SO_2[b]	150±30 ppm (22–42 km) 25–150 ppm (12–22 km)	outgassing & reduction of OCS, H_2S	H_2SO_4 formation & $CaSO_4$ formation
H_2O[b]	30±15 ppm (0–45 km) 30–70 ppm (0–5 km)	outgassing —	H escape & Fe^{2+} oxidation
^{40}Ar	31^{+20}_{-10} ppm	outgassing (^{40}K)	—
^{36}Ar	30^{+20}_{-10} ppm	primordial	—
CO[b]	45±10 ppm (cloud top) 30±18 ppm (42 km) 28±7 ppm (36–42 km) 20±3 ppm (22 km) 17±1 ppm (12 km)	CO_2 photolysis	photooxidation to CO_2
^4He[c]	0.6–12ppm	outgassing (U, Th)	escape
Ne	7±3 ppm	outgassing, primordial	—
^{38}Ar	5.5 ppm	outgassing, primordial	—
OCS[b]	4.4±1 ppm (33 km)	outgassing & sulfate weathering	conversion to SO_2
H_2S[b]	3±2 ppm (<20 km)	outgassing & sulfate weathering	conversion to SO_2
HDO[b]	1.3±0.2 ppm (sub-cloud)	outgassing	H escape
HCl	0.6±0.12 ppm (cloud top) 0.5 ppm (35–45 km)	outgassing	Cl-mineral formation
^{84}Kr	25^{+13}_{-18} ppb	outgassing, primordial	—
SO[b]	20±10 ppb (cloud top)	photochemistry	photochemistry
S_{1-8}[b]	20 ppb (<50 km)	sulfide weathering	conversion to SO_2
HF	$5^{+5}_{-2.5}$ ppb (cloud top) 4.5 ppb (35–45 km)	outgassing	F-mineral formation
^{132}Xe	<10 ppb	outgassing, primordial	—
^{129}Xe	<9.5 ppb	outgassing (^{129}I)	—

[Fegley, Venus, 2004]



T(z)
Upper Haze
Upper Cloud
Middle Cloud
Lower Cloud
Lower Haze
Pressure (bar)
0.001
0.010
0.100
1.000
10.000
100.000
Temperature (K)
200
300
400
500
600
700
Altitude (km)
80
70
60
50
40
30
20
10
0

$$Cl + CO + M \rightarrow ClCO + M$$

$$ClCO + O_2 + M \rightarrow ClC(O)O_2 + M$$

$$ClC(O)O_2 + Cl \rightarrow CO_2 + ClO + Cl$$

$$SO_2 + h\nu \rightarrow SO + O$$

$$SO_2 + O + M \rightarrow SO_3 + M$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$$

$$SO + ClO \rightarrow SO_2 + Cl$$

$$CO + O_2 + SO_2 + H_2O \rightarrow CO_2 + H_2SO_4$$

$$Cl + CO + M \rightarrow ClCO + M \tag{8.9}$$
$$ClCO + O_2 + M \rightarrow ClC(O)O_2 + M \tag{8.10}$$
$$ClC(O)O_2 + O \rightarrow CO_2 + O_2 + Cl \tag{8.13}$$
$$\textit{net} \quad CO + O \rightarrow CO_2 \tag{IIa}$$

$$Cl + CO + M \rightarrow ClCO + M \tag{8.9}$$
$$ClCO + O_2 + M \rightarrow ClC(O)O_2 + M \tag{8.10}$$
$$ClC(O)O_2 + Cl \rightarrow CO_2 + ClO + Cl \tag{8.14}$$
$$ClO + O \rightarrow Cl + O_2 \tag{8.15}$$
$$\textit{net} \quad CO + O \rightarrow CO_2 \tag{IIb}$$

$$Cl + CO + M \rightarrow ClCO + M \tag{8.9}$$
$$ClCO + O_2 + M \rightarrow ClC(O)O_2 + M \tag{8.10}$$
$$ClC(O)O_2 + Cl \rightarrow CO_2 + ClO + Cl \tag{8.14}$$
$$SO_2 + h\nu \rightarrow SO + O \tag{8.21}$$
$$SO_2 + O + M \rightarrow SO_3 + M \tag{8.23}$$
$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \tag{8.24}$$
$$ClO + SO \rightarrow Cl + SO_2 \tag{8.27}$$
$$\textit{net} \quad CO + SO_2 + O_2 + H_2O \rightarrow CO_2 + H_2SO_4 \tag{VI}$$

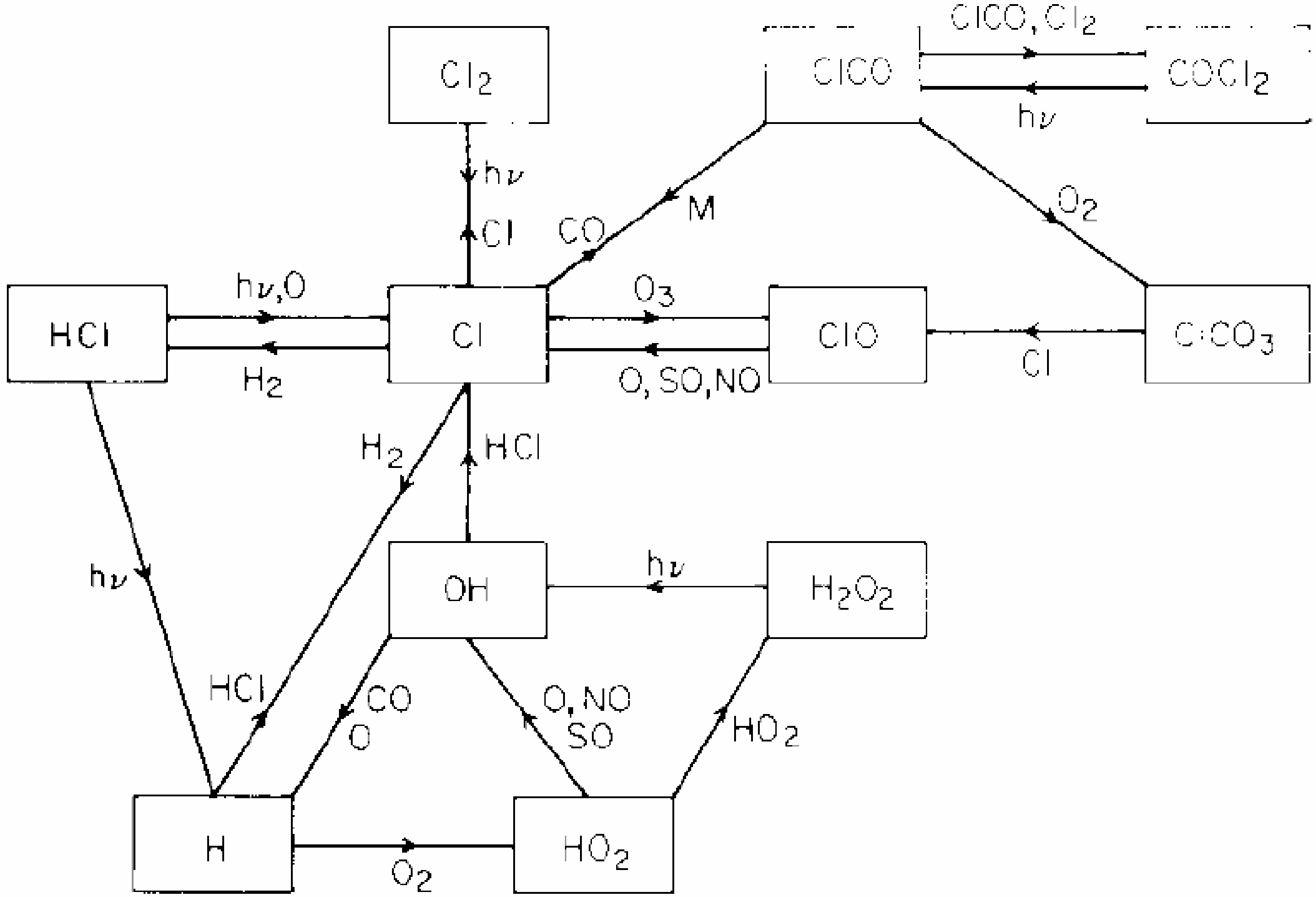
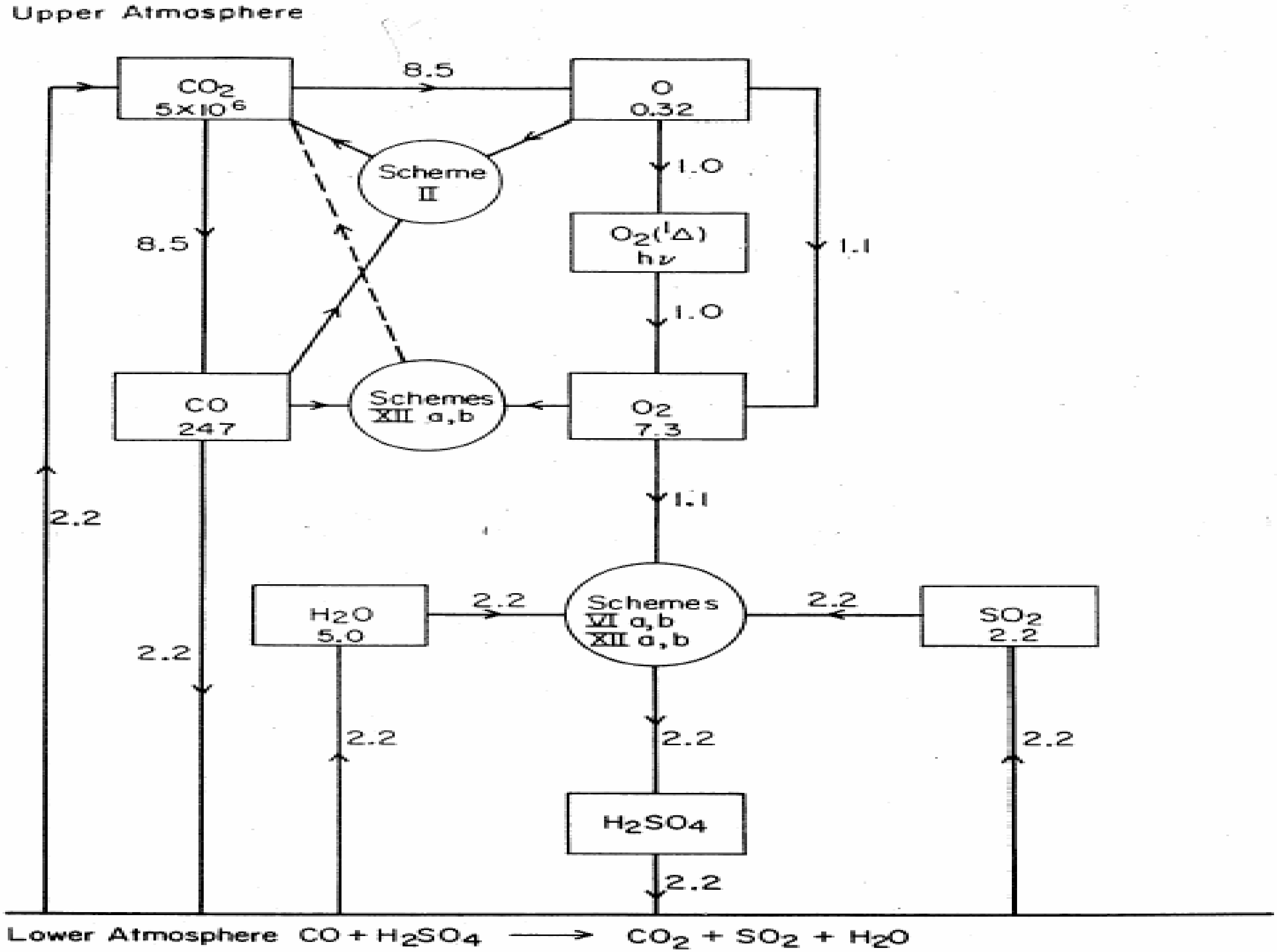
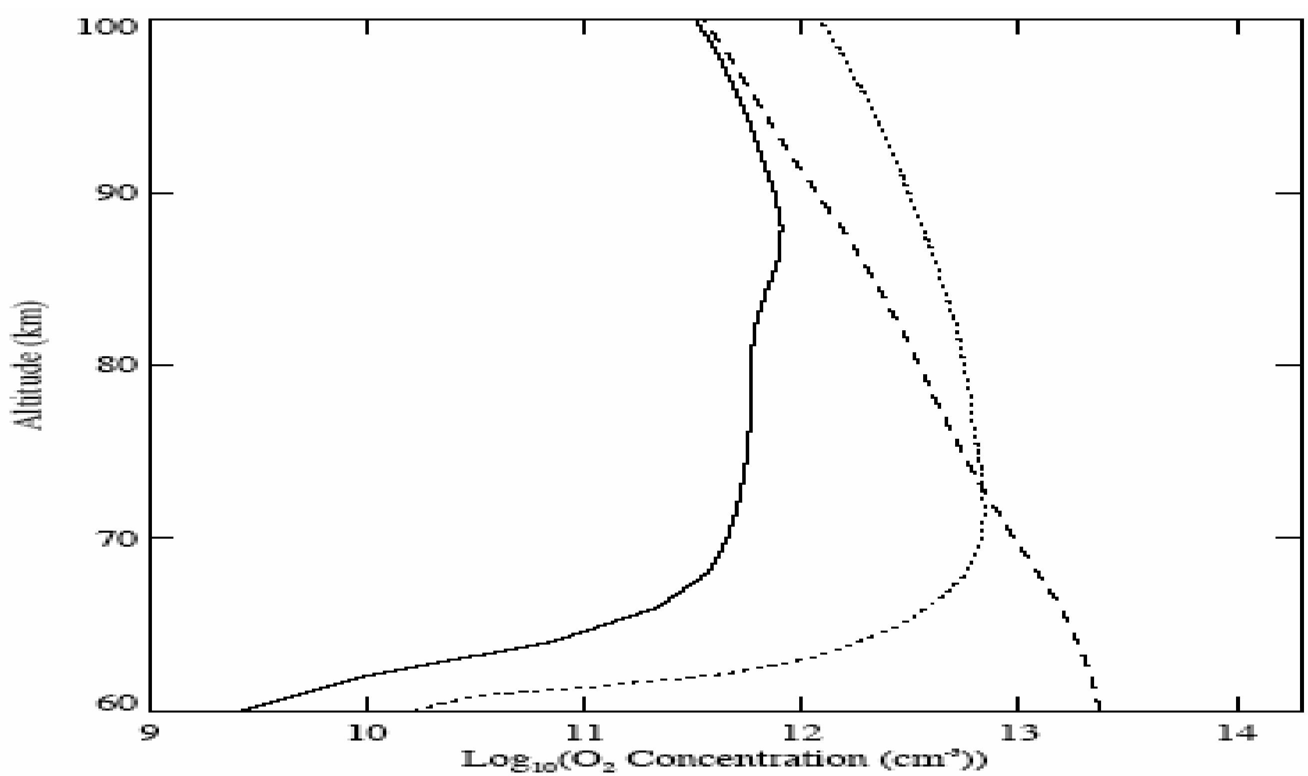


Fig. 6. Schematic diagram showing the major sources, sinks, and recycling paths for HO_x and ClO_x. Not all reactions are included in model A.

[Yung and DeMore, ICARUS, 1982]



Upper Atmosphere
CO2 5X10^6
8.5
O 0.32
Scheme II
1.0
O2(1Δ) hν
1.1
8.5
1.0
CO 247
Schemes XII a,b
O2 7.3
1.1
2.2
H2O 5.0
2.2
Schemes VI a,b XII a,b
2.2
SO2 2.2
2.2
2.2
2.2
2.2
H2SO4
2.2
Lower Atmosphere CO + H2SO4 ⟶ CO2 + SO2 + H2O



100
90
80
70
60
Altitude (km)
9
10
11
12
13
14
Log$_{10}$(O$_2$ Concentration (cm^{-3}))

Table 2: Comparison of Venus observation of column O_2 abundance with model simulations.

Result	Column O_2 (molec cm^{-2})[a]
Observation(18)	$<1.5 \times 10^{18}$
Model[b] without ClC(O)OO included	3.05×10^{19}
Model[b] with ClC(O)OO kinetic reactions	2.14×10^{18}
Model[b] with ClC(O)OO photolysis and kinetic reactions	2.13×10^{18}

[a]Integrated from 58 km altitude to top of atmosphere.

[b]Described in reference 17.

[Pernice *et al*., PNAS, 2004]

Peroxychloroformyl Radical: Spectroscopic Observation in the Laboratory and Implications for the Stability of the Atmosphere of Venus

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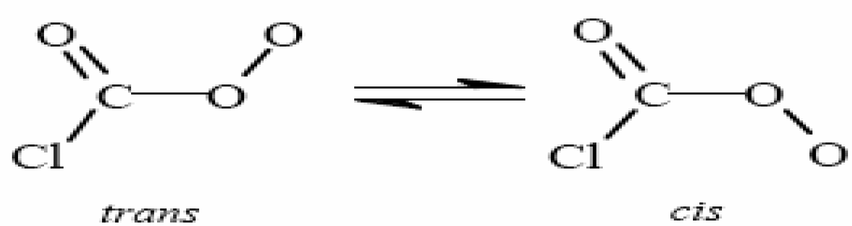
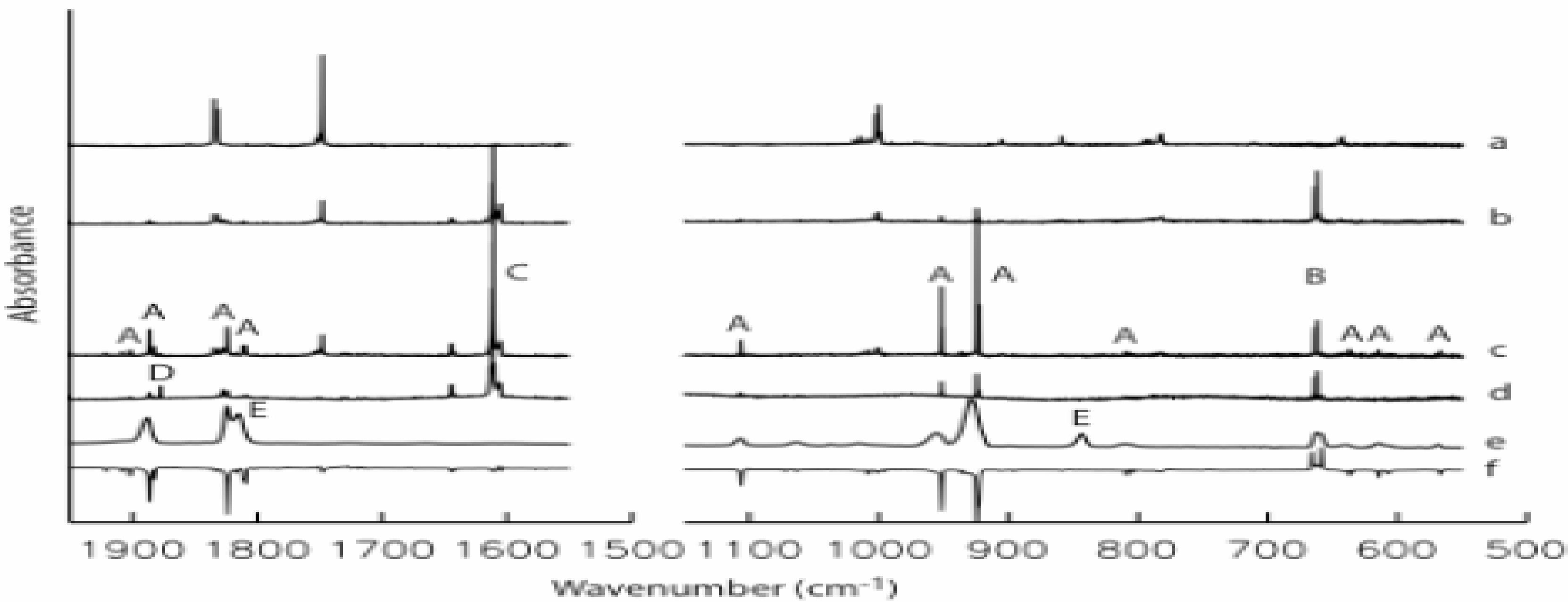


(6)



Absorbance
A
A
A
A
C
A
A
A
B
A
A
A
A
D
E
E
a
b
c
d
e
f
1900
1800
1700
1600
1500
1100
1000
900
800
700
600
500
Wavenumber (cm-1)

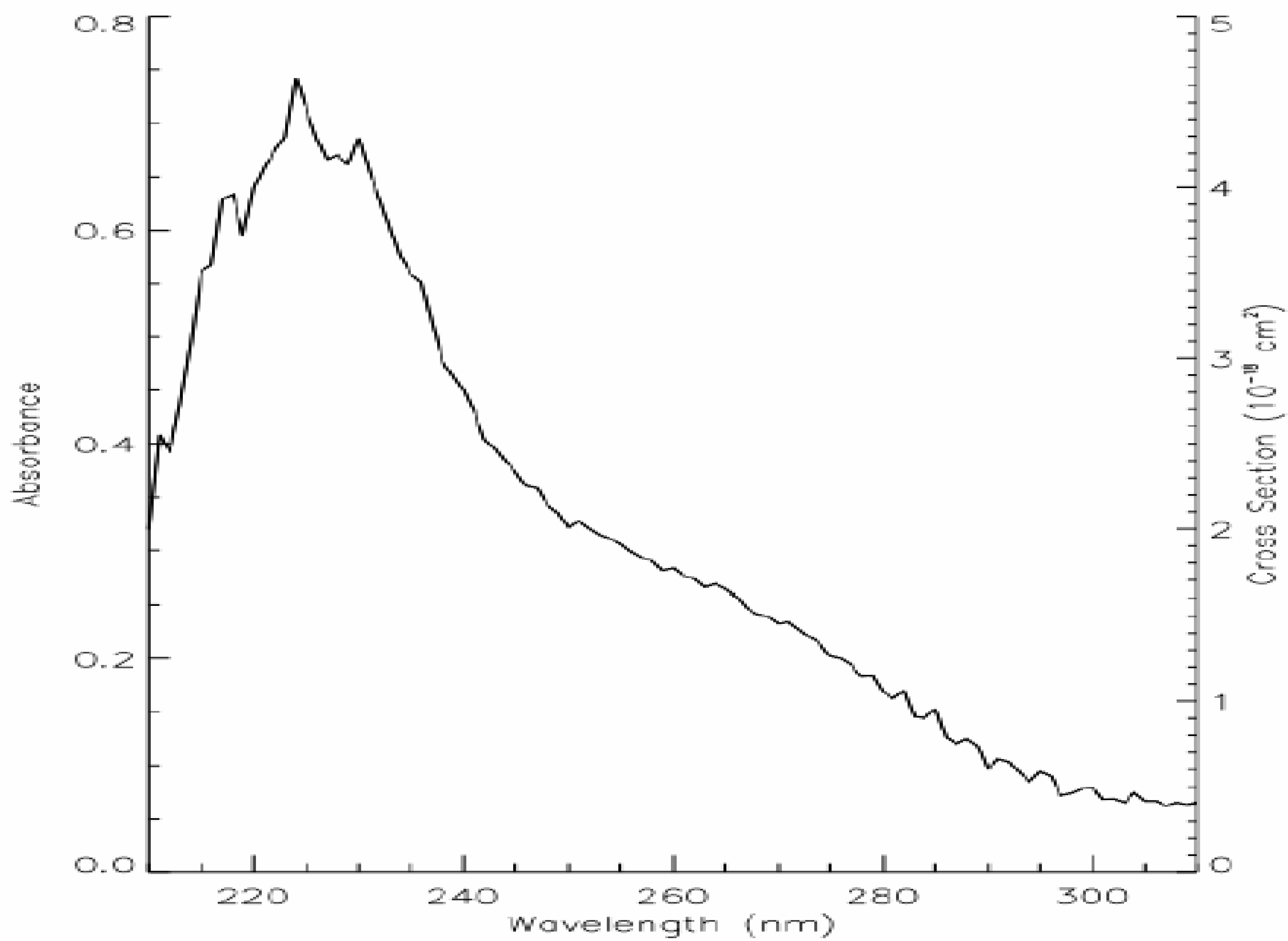
Table 1: IR band positions and intensities of $^{35}ClC(O)OO$ isolated in an argon matrix.

trans-ClC(O)OO		*cis*-ClC(O)OO			
Expt. [a]	Theor. [b]	Expt. [a]	Theor. [b]	Assign.	Mode
		1902 (8.8)		$2\nu_3$	
1886 (60)	1864 (80)	1824 (55)	1843 (87)	$\nu_1(a')$	$\nu(C{=}O)$
1811 (26)				$2\nu_3$	
1072 (2.6)	1047 (1)	1106 (17)	1093 (14)	$\nu_2(a')$	$\nu(O–O)$
1009 (12)				$2\nu_5$	
925 (100)	938 (100)	952 (37)	963 (69)	$\nu_3(a')$	$\nu(C–O)$
809 (7.4)	803 (9)	637 (5.6)	633 (6)	$\nu_4(a')$	$\nu(C–Cl)$
614 (5.7)	609 (3)	607 (3.5)	603 (4)	$\nu_8(a'')$	$\gamma(ClCOO_2)$
504 (0.9)	498 (2)	567 (6.0)	569 (7)	$\nu_5(a')$	$\delta(Cl–C{=}O)$
	401 (0.6)		462 (0.1)	$\nu_6(a')$	$\delta(O–C{=}O)$
	288 (0.3)		279 (0.5)	$\nu_7(a')$	$\delta(O–C–Cl)$
	134 (0.017)		116 (0.2)	$\nu_9(a'')$	τ

[a]Frequencies in units of cm^{-1}; relative intensities are presented in parentheses.

[b]Frequencies in units of cm^{-1} were calculated at the CCSD(T)/aug-cc-pVDZ level of theory. The relative intensities (in parentheses) were calculated at the B3LYP/aug-cc-pVDZ level of theory. The relative intensity of 100 was assigned to the absolute intensity 402.8 km mol^{-1}.

[Pernice *et al.*, PNAS, 2004]



0.8
0.6
0.4
0.2
0.0
Absorbance
220
240
260
280
300
Wavelength (nm)
5
4
3
2
1
0
Cross Section (10^-18 cm^2)

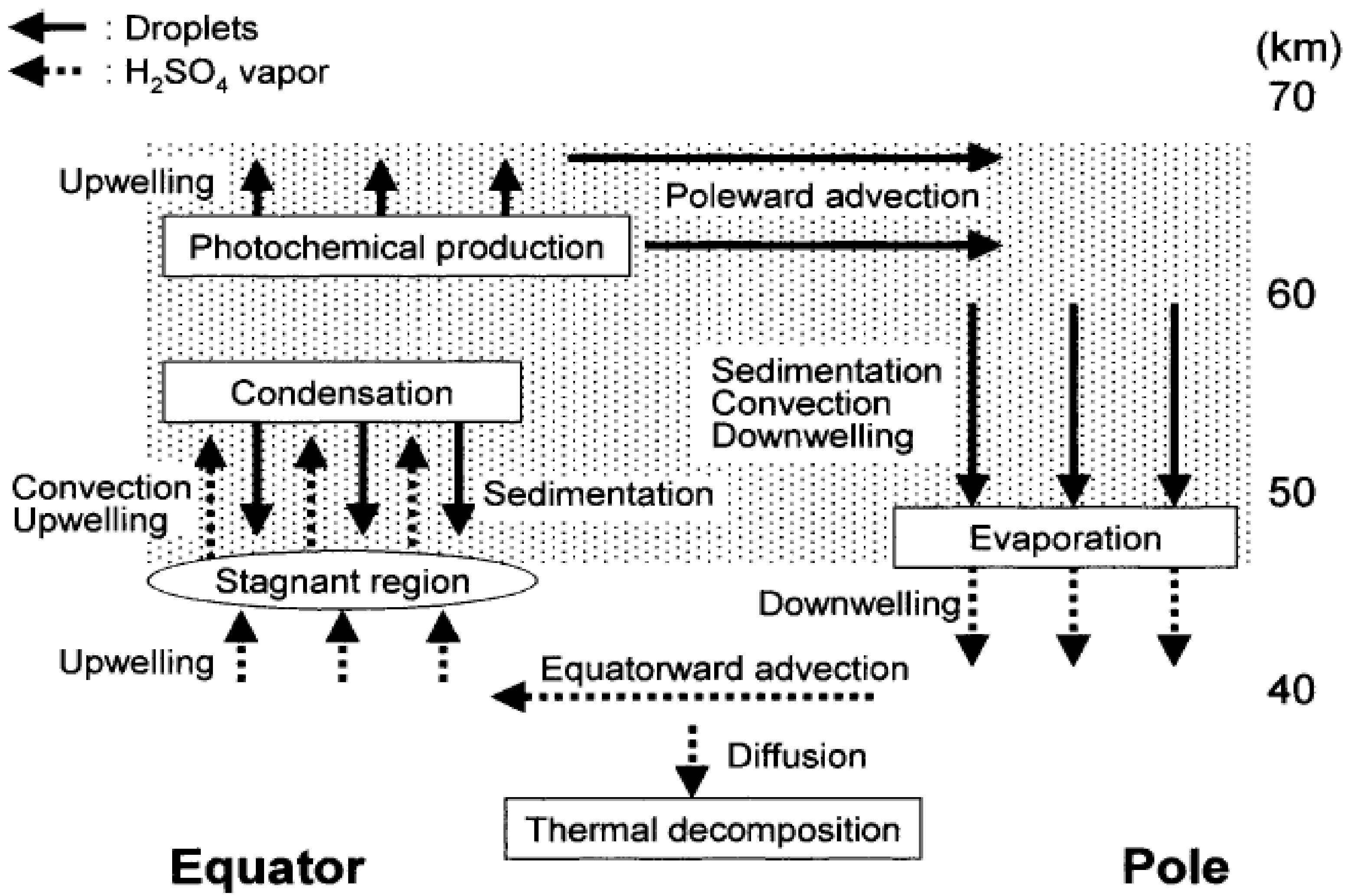


FIG. 1. Schematic view of the H_2SO_4 cycle in the Venusian atmosphere (Imamura and Hashimoto 1998). Cloud particles created photochemically near the cloud top are transported poleward by Hadley circulation, being subsequently transported downward at high latitudes and evaporating in the hot lower atmosphere. The resulting H_2SO_4 vapor is transported equatorward beneath the cloud by return flow and eventually ascends in the rising branch of Hadley circulation near the equator. Droplets that are formed in the rising air subsequently fall due to their large size and H_2SO_4 vapor accumulates near the cloud base in the equatorial region.

[Imamura and Hashimoto, JAS, 2001]

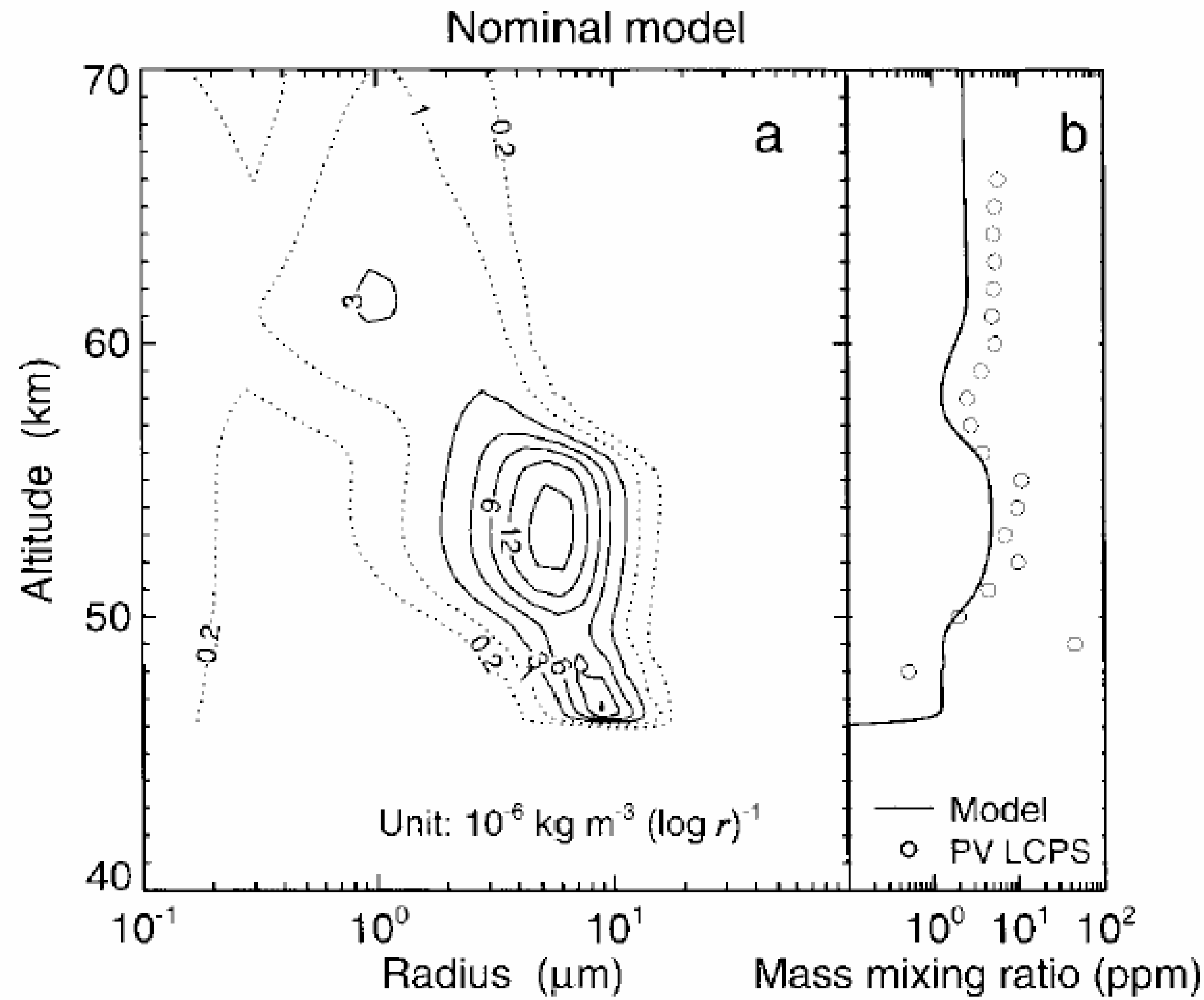
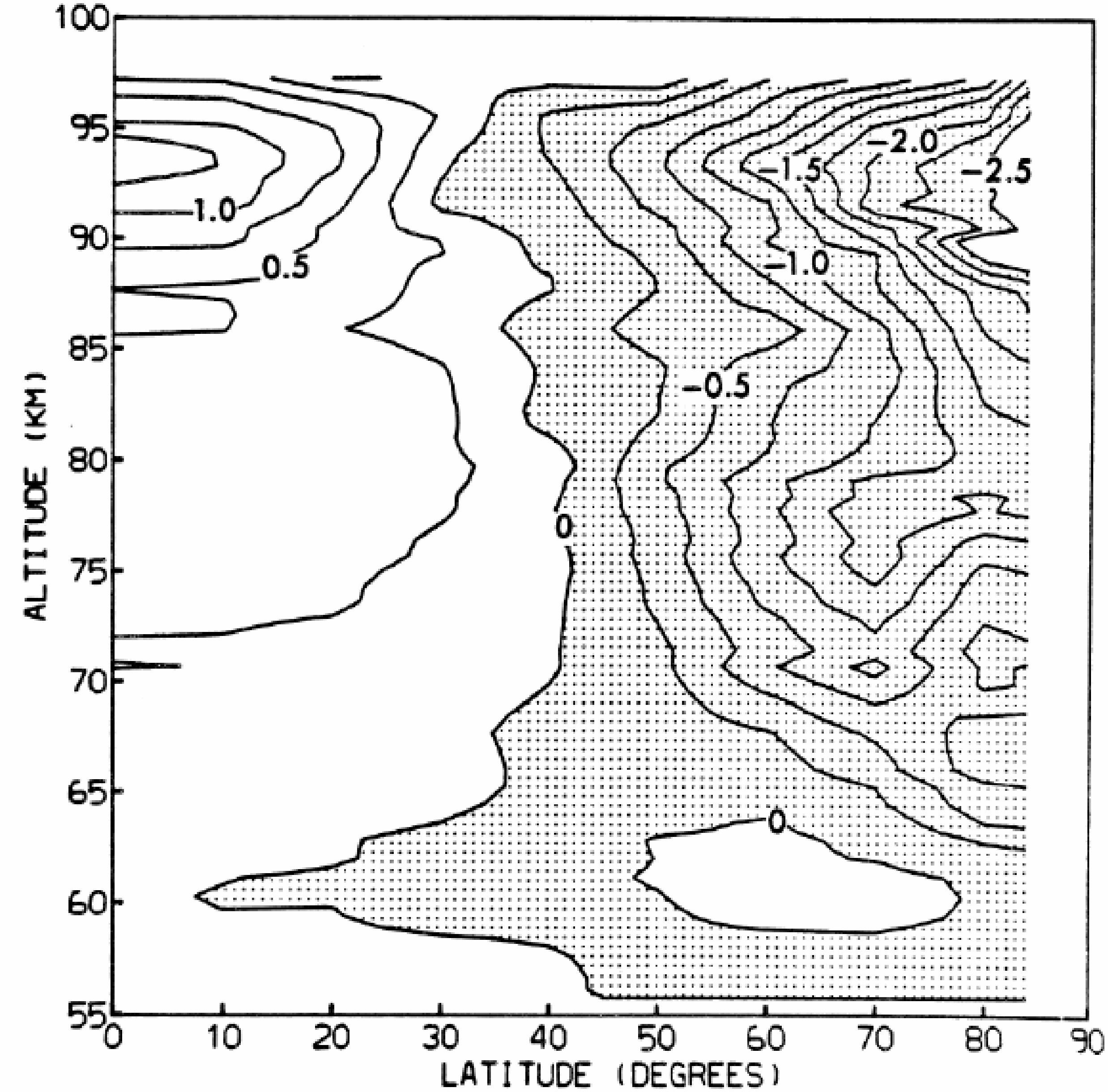
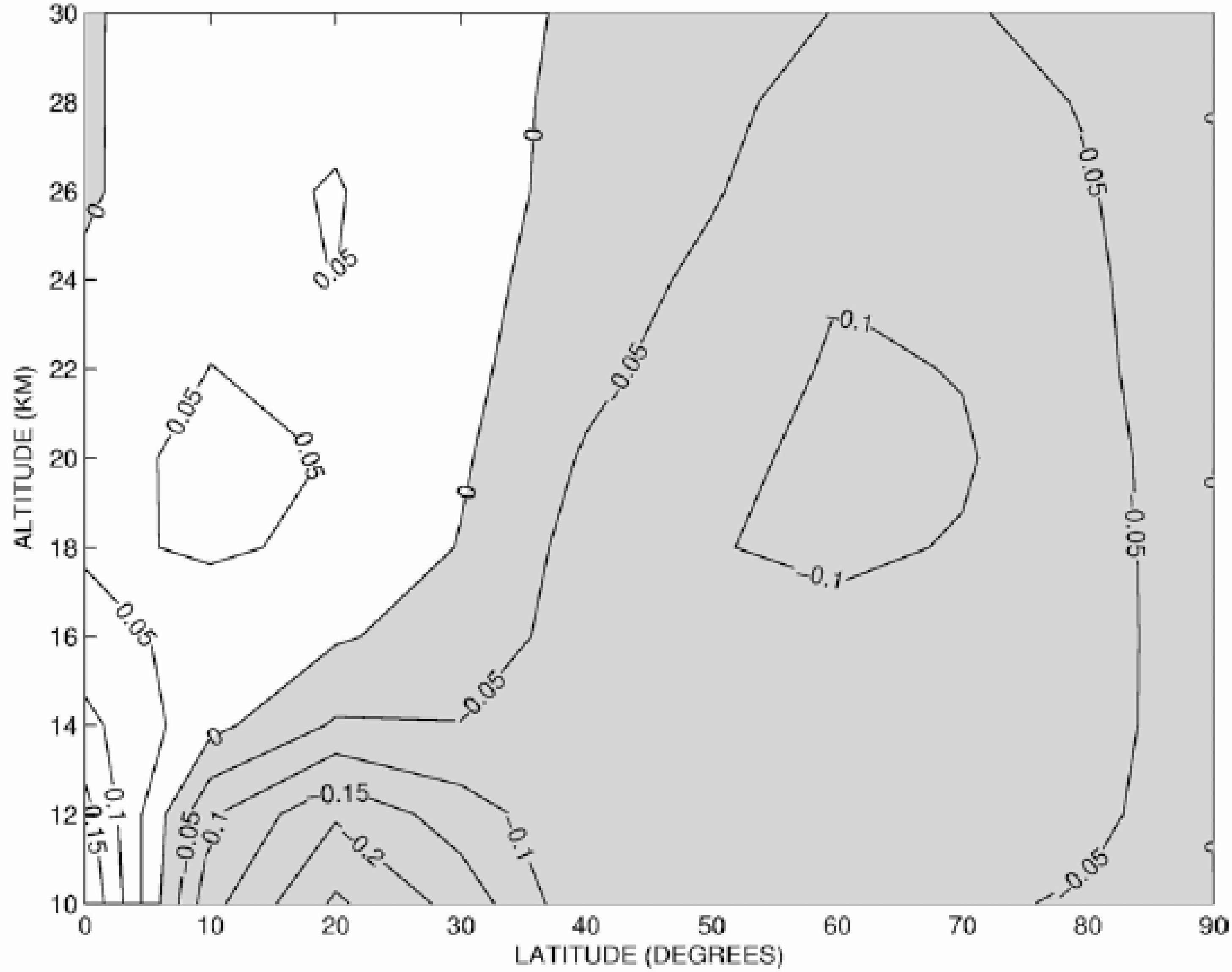


FIG. 6. (a) Mass loading distribution of cloud particles vs altitude and size in the nominal model. (b) Profile of the cloud mass mixing ratio in the nominal model compared to measurements by the Pioneer Venus LCPS.

[Imamura and Hashimoto, JAS, 2001]



Vertical velocity in $cm s^{-1}$ for diabatic circulation in the middle atmosphere of Venus (Crisp, 1983).



Vertical velocity in cms^{-1} for residual circulation in the terrestrial middle atmosphere computed using NCEP input data for January 1985 (adapted from Fig. 1a, Jiang et al. 2004).

Parameter	**Earth**	**Venus**	**Jupiter**
Orbital Distance (AU)	1	0.723	5.203
Radius (km)	6378	6052	71492
1 Day	1 day	243 days	10 hr
1 Year	365 days	225 days	11.86 yr
Atmosphere	77% N_2 21% O_2	96% CO_2 3% N_2	93% H_2 7% He
Escape Velocity (kms^{-1})	11.18	10.36	59.5
Surface Gravity (ms^{-2})	9.81	8.87	23.1
Axial Tilt (°)	23.5	177.4	3
Eccentricity of orbit	0.017	0.007	0.048

Table 4 Isotopic composition of Venus' atmosphere

Isotopic Ratio[a]	*Observed Value*	*Method*
D/H	0.016 ± 0.002	Pioneer Venus (PV) MS[b]
	0.019 ± 0.006	IR spectroscopy
$^{3}He/^{4}He$	$<3\times10^{-4}$	PV MS
$^{12}C/^{13}C$	86 ± 12	IR spectroscopy
	88.3 ± 1.6	Venera 11/12 MS
$^{14}N/^{15}N$	273 ± 56	PV MS
$^{16}O/^{18}O$	500 ± 25	PV MS
	500 ± 80	IR spectroscopy
$^{20}Ne/^{22}Ne$	11.8 ± 0.6	Venera 11/12 MS
$^{21}Ne/^{22}Ne$	<0.067	Venera 11/12 MS
$^{35}Cl/^{37}Cl$	2.9 ± 0.3	IR spectroscopy
$^{36}Ar/^{38}Ar$	5.45 ± 0.1	PV, Venera 11/12 MS
$^{40}Ar/^{36}Ar$	1.11 ± 0.02	PV, Venera 11/12 MS

Source: Lodders and Fegley (1998), Wieler (2002).
[a]No isotopic compositions are available for Kr and Xe on Venus. [b]MS = Mass Spectrometer

[Fegley, Venus, 2004]

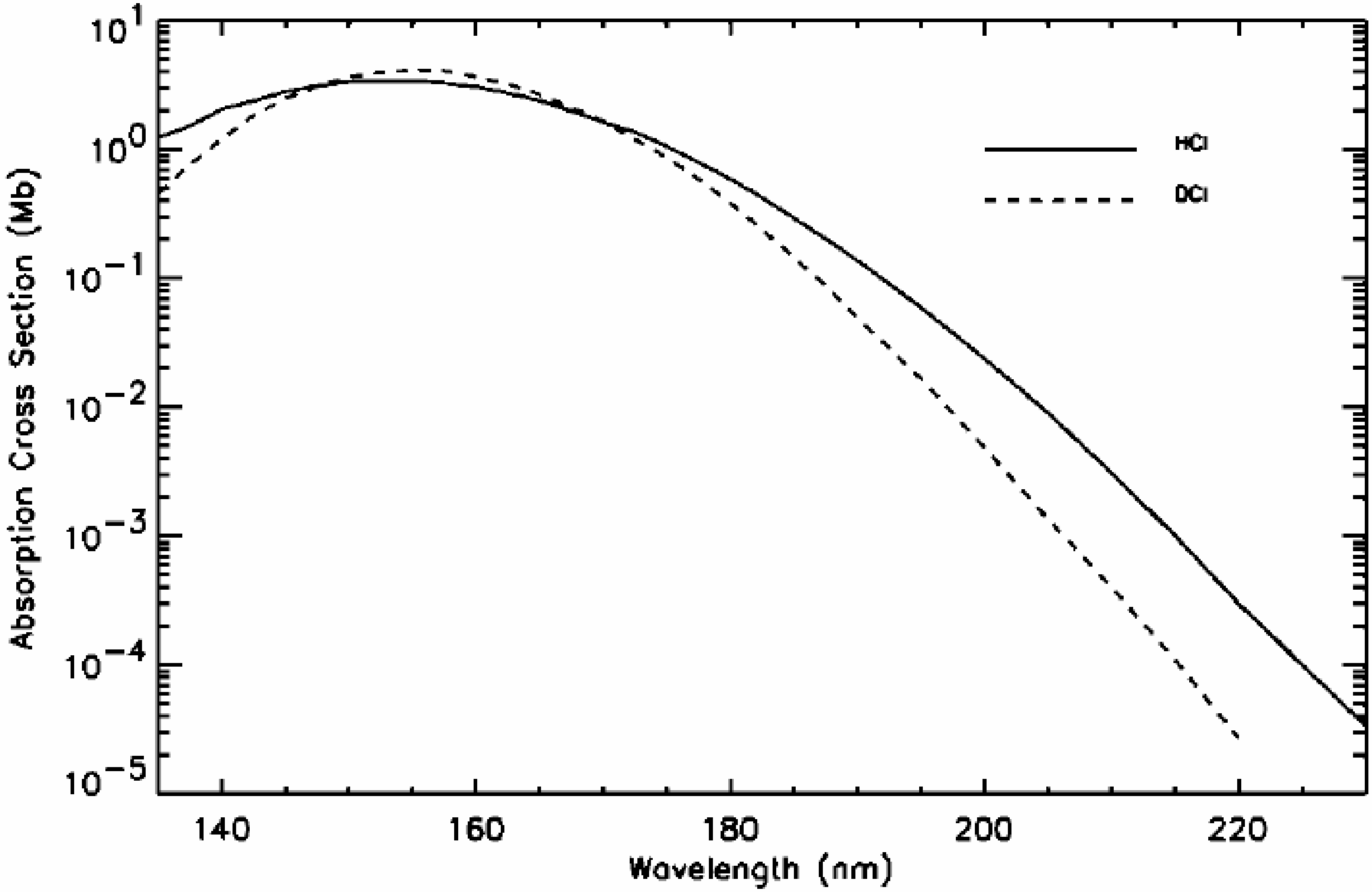


FIG. 1.—Photoabsorption cross sections of HCl and DCl in the 135–232 nm region.

[Bahou *et al*., AJ, 2001]

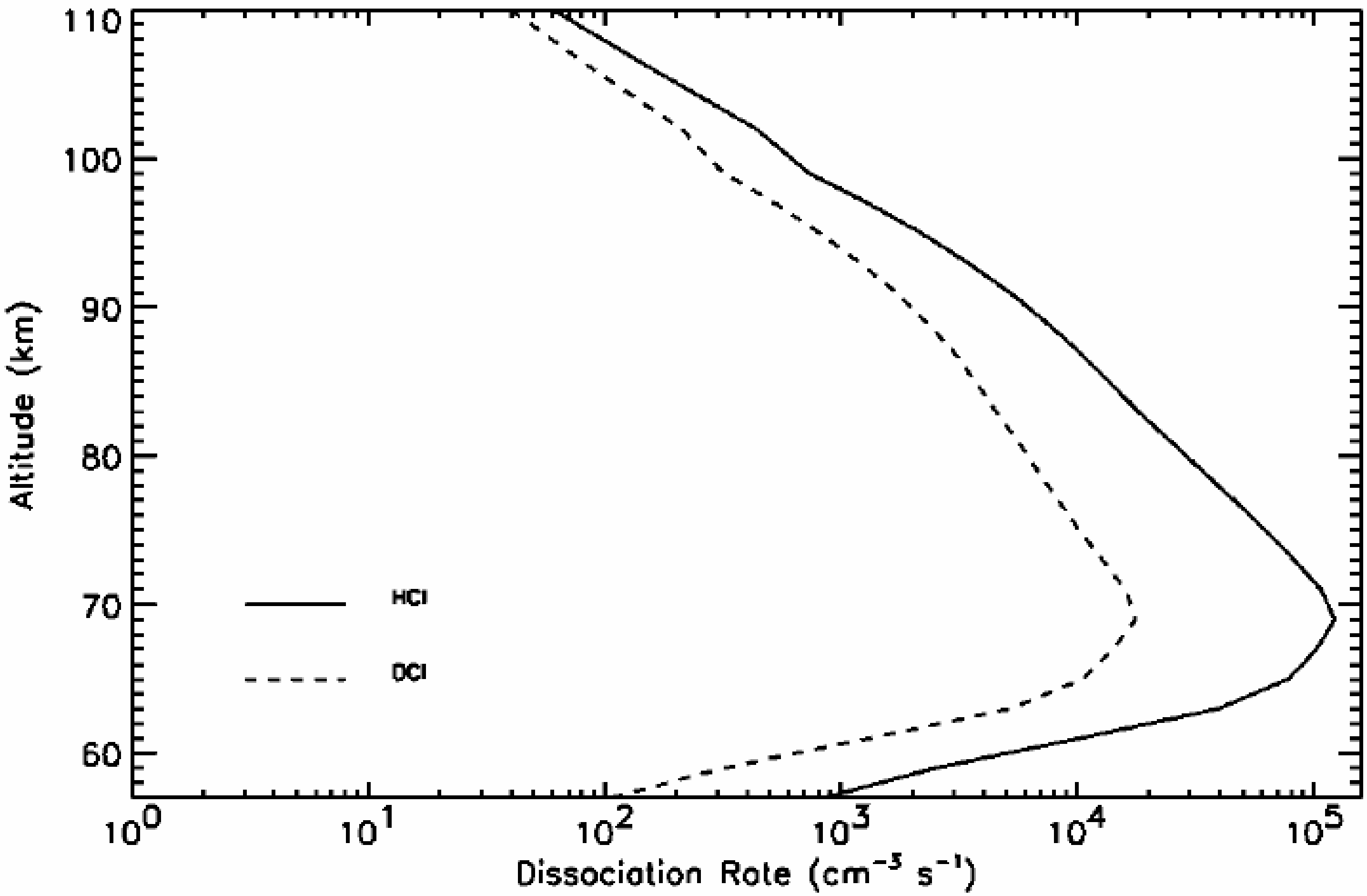


FIG. 2.—Comparison of photolysis rates (in units of cm^{-3} s^{-1}) of HCl and DCl in the atmosphere of Venus based on the model of Yung & DeMore (1982). The HCl rate is taken from their model C. The DCl rate is computed by replacing the cross sections of HCl with those of DCl as measured in Fig. 1. The integrated rates are 7.74×10^{10} and 1.27×10^{10} cm^{-2} s^{-1}.

[Bahou *et al.*, AJ, 2001]

Acknowledgements: NASA, M. Allen, F. Mills, L. Esposito, D. Crisp, V. Meadows

References:

Yung, Y. L. and W. B. DeMore (1982). "Photochemistry of the Stratosphere of Venus: Implications for Atmospheric Evolution." *Icarus* **51**(2): 199-247.

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