

Atmospheric Composition, Chemistry, and Clouds

Franklin P. Mills

*Research School of Physical Sciences and Engineering and Centre for Resource and Environmental Studies,
Australian National University, Canberra, Australia*

Larry W. Esposito

Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, Colorado

Yuk L. Yung

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California

Venus' atmosphere has a rich chemistry involving interactions among sulfur, chlorine, nitrogen, hydrogen and oxygen radicals. The chemical regimes in the atmosphere range from ion-neutral reactions in the ionosphere to photochemistry in the middle atmosphere to thermal equilibrium chemistry and surface-atmosphere reactions in the lower atmosphere. This variety makes Venus an important planet to understand within the context of terrestrial-like planets, both in our own solar system and outside it. The primary chemical cycles are believed to be known but surprisingly few details about these cycles have been fully verified by concurrence among observations, experiments, and modelling. Good models have been developed that account for many properties of the cloud layers, but the size distribution, shape, and composition of the majority of the aerosol mass are still open issues. This chapter reviews the state of knowledge prior to the Venus Express mission for the composition, chemistry, and clouds of the neutral atmosphere on Venus. Observations by instruments on Venus Express, in combination with ground-based observations, laboratory experiments, and numerical modelling, should answer some of the major open questions regarding the composition, chemistry, and clouds of Venus' atmosphere.

1 INTRODUCTION

Interest in the composition of the Venus atmosphere began as early as Lomonosov's report from observations of the 1761 transit that Venus had an atmosphere and the proposal that there were clouds in the atmosphere [*Huggins and Miller*, 1864]. In the latter half of the 20th century, numerous space missions and extensive ground-based telescopic observations provided significant insight into the composition and chemistry of the Venus atmosphere. The most intense study of Venus' photochemistry was in the decade from the early 1970's to the mid-1980's when the modern understanding of Earth's stratospheric chemistry also was being derived. Indeed, much of the chlorine and sulfur chemistry identified in Earth's stratosphere was first proposed in early models of Venus photochemistry [*Prinn*, 1985]. Photochemical modeling has had a renewed burst of interest since 2000. Throughout the 1980's and 1990's, and continuing to the present, ground-based observations showed that the abundances of trace species, intensity of airglow emission, temperatures, and wind velocities could vary markedly on timescales from hours to years. This variability has introduced a new dimension, time, into our understanding of chemistry in Venus' atmosphere, but few modeling studies have tackled this aspect and major uncertainties still surround the basic chemical state of the atmosphere. Observational advances in the last 20 years enabled retrieval of cloud characteristics and trace species abundances, many for the first time, from the base of the upper cloud layer to the lowest scale height above the surface. Since 2000, there has been a resurgence in interest in the chemistry of the Venus atmosphere that has brought together advances from experimental measurements,

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ground-based observations, and numerical modeling. This chapter reviews the current state of knowledge of the chemistry of Venus' atmosphere (prior to the Venus Express mission), outlines current uncertainties, provides recommendations of future directions for research, and compares Venus' atmospheric chemistry to that of other terrestrial-like planets.

The Venus atmosphere can be divided into regions based on its composition, chemistry, and clouds. The upper atmosphere, above ~ 110 km, has low densities and overlaps with the ionosphere so that photodissociation, ion-neutral, and ion-ion reactions are increasingly dominant as one goes to higher altitudes. The middle atmosphere, ~ 60-110 km, receives sufficiently intense ultraviolet (UV) radiation from the sun that its chemistry is dominated by photon-driven processes, termed "photochemistry." The lower atmosphere, below ~ 60 km, receives little UV radiation from the sun, and due to the high atmospheric temperatures the chemistry is controlled by thermal processes, termed thermodynamic equilibrium chemistry or "thermochemistry." Bridging across the boundary between the lower and middle atmospheres are the cloud and haze layers which extend from ~ 30 – 90 km with the main cloud deck lying at ~ 45 – 70 km. The clouds define a transition region that reflects the competition between the middle atmosphere, dominated by photochemistry, and the lower atmosphere, dominated by thermochemistry [Esposito *et al.*, 1997]. This region is also where lightning could occur and produce NO [Krasnopolsky, 2006] and where heterogeneous chemistry on aerosol and cloud particle surfaces may be important [Mills *et al.*, 2006]. Finally, the lowest scale height of the atmosphere is the region where surface-atmosphere interactions may dominate.

Three dominant processes have been identified in the Venus atmosphere, which we will term the CO₂ cycle, the sulfur oxidation cycle, and the polysulfur cycle. The CO₂ cycle includes the photodissociation of CO₂ on the day side, transport of a significant fraction of the CO and O to the night side, production of O₂, emission of highly variable oxygen airglow on both the day and night sides, and conversion of CO and O₂ into CO₂ via catalytic processes. The sulfur oxidation cycle involves the upward transport of SO₂, oxidation of a significant fraction of the SO₂ to form H₂SO₄, condensation of H₂SO₄ and H₂O to form a majority of the mass comprising the cloud and haze layers, downward transport of sulfuric acid in the form of cloud droplets, evaporation of the cloud droplets, and decomposition of H₂SO₄ to produce SO₂. There is solid observational evidence for both the CO₂ and the sulfur oxidation cycles. The polysulfur cycle is more speculative but plausible based on existing laboratory data. It involves the upward transport of sulfur as either SO₂ or OCS, photodissociation to produce S, formation of polysulfur (S_x) via a series of association reactions, downward transport of S_x, thermal decomposition of S_x, and reactions with oxygen and CO to produce SO₂ and OCS, respectively. Each of the cycles involves a number of trace species, such as ClO_x, HO_x, NO_x, and SO_x. The three cycles may (and probably do) interact through these trace species; see Figure 1. The strength of these links between the cycles in existing models depends on parameters that have significant uncertainties and few constraints from direct observational evidence. In the model of Figure 1, the net impact of the thermodynamic equilibrium chemistry is shown by the dashed arrows in Figure 1 while the net impact of the disequilibrium (photochemical) reactions is shown by solid lines.

The first part of this chapter summarizes observations of the composition of the Venus atmosphere. The second and third parts discuss sulfur chemistry and the cloud layers, including the sulfur oxidation and polysulfur cycles. The fourth part discusses the chlorine chemistry that is believed to control the CO₂ cycle. The final sections discuss linkages among the chemical cycles and offer recommendations for future research.

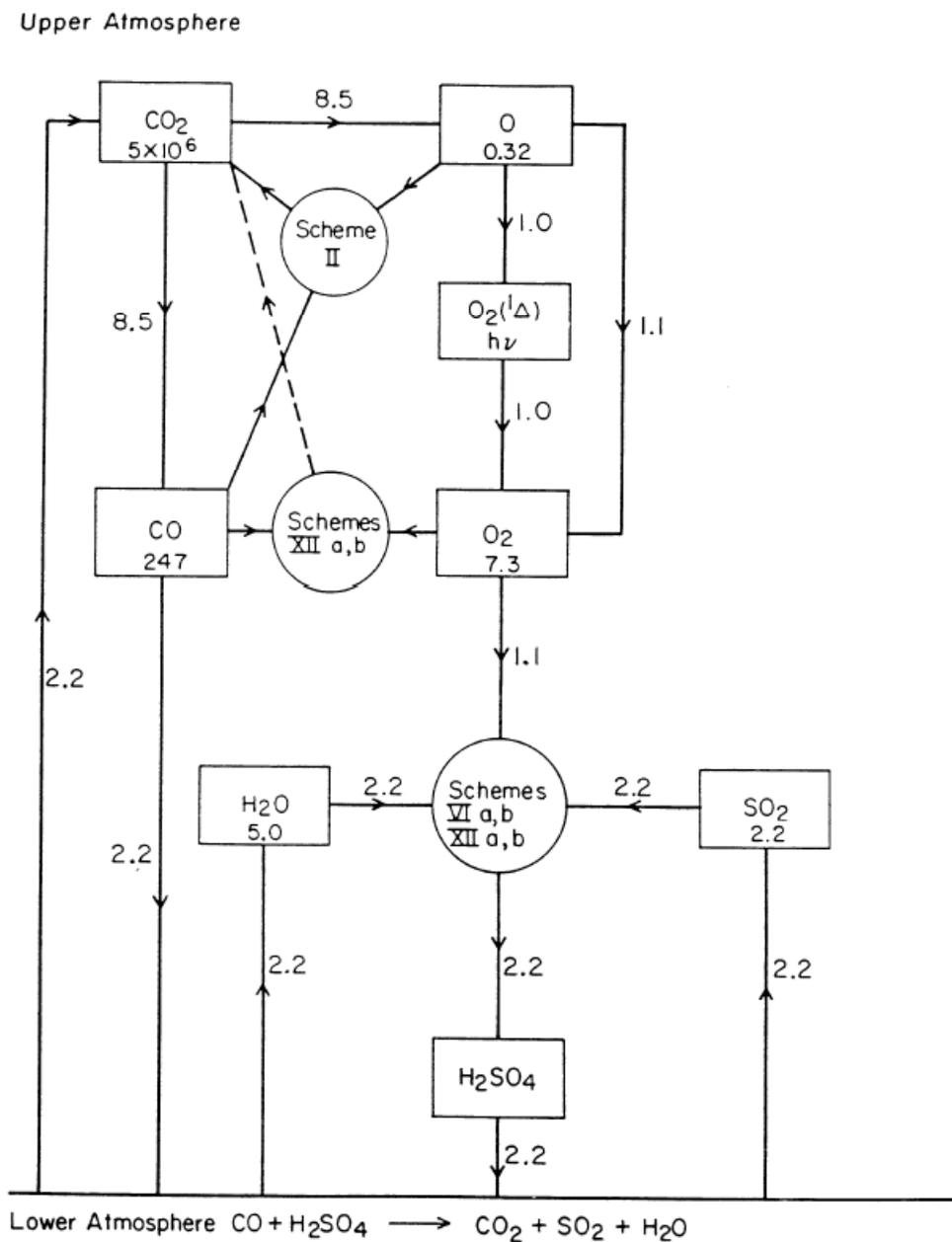


Figure 1. Schematic diagram for the column abundances above the cloud tops (1×10^{18} molecules cm^{-2}) and fluxes (10^{12} molecules $\text{cm}^{-2} \text{ s}^{-1}$) of major oxygen bearing species in the atmosphere of Venus. Taken from Fig 4b of Yung and DeMore (1982).

2 SUMMARY OF OBSERVATIONS AND RECENT DEVELOPMENTS

Species	Mixing Ratio (v/v)	Altitude	Year/Location	Notes
Cloud-top H ₂ O	10 – 90 ppm		1978 – 1979	<i>Koukouli et al.</i> [2005]
Cloud-top H ₂ O	~ 12 ± 5 ppm		1983	<i>Koukouli et al.</i> [2005]
H ₂ O (from HDO)	(0.0 ± 0.06) – (3.5 ± 0.3) ppm	65 – 100 km	1998 – 2004	<i>Sander and Clancy</i> [2005]
SO ₂	10 - 430 ppb	40 mbar	1968 – 1995	See Figure 3
SO ₂	≤ (50-100) ppm	35 - 55	1996	<i>Jenkins et al.</i> [2002]
SO ₂	≤ 50 ppm	Below lower cloud	1996, 1999	<i>Butler et al.</i> [2001]
H ₂ SO ₄ (g)	0 - 9 ppm	35 - 55	1996	<i>Jenkins et al.</i> [2002]
H ₂ SO ₄ (g)	1-30 ppm	47-58 km	1983-1984, mid to high latitudes	<i>Gubenko et al.</i> [2001]
H ₂ SO ₄ (g)	1 - 2.5 ppm	At and below lower cloud	1996, 1999	<i>Butler et al.</i> [2001]
HCl	< 0.4 – 1 ppm	5 - 70 km		<i>Dalton et al.</i> [2000]
NO	5.5 ± 1.5 ppb	≤ 60 km	2004	<i>Krasnopolsky</i> [2006]
NO flux	(6 ± 2) × 10 ⁷ cm ⁻² s ⁻¹		2004	<i>Krasnopolsky</i> [2006]
S ₃	0.03 – 0.1 ppb	3 – 19 km	1978	<i>Maiorov et al.</i> [2005]
CO	2 × 10 ⁻⁶ – 2 × 10 ⁻⁴	10 – 90 km	2003 – 2004	<i>Marcq et al.</i> [2005]
OCS	2 × 10 ⁻⁷ – 10 ⁻⁵	20 – 48 km	2003 – 2004	<i>Marcq et al.</i> [2005]

Table 1. Gas-phase species abundance observations published since 2000.

Airglow Band	Intensity	Altitude	Year/Location	Notes
O (¹ S – ¹ D) 557.7 nm	(≤ 10) - 167 R	~ 100 km	1999, 2001, 2002	<i>Slanger et al.</i> [2006]
O (¹ D – 3P) 630 nm	< 20 R		1999	<i>Slanger et al.</i> [2001]
O ₂ (c ¹ Σ – X ³ Σ) Herzberg II	5.1 kR	mesosphere	1999	<i>Slanger et al.</i> [2001]
O ₂ (c ¹ Σ – X ³ Σ) Herzberg II	3.1 kR	mesosphere	2001	<i>Slanger et al.</i> [2006]
O ₂ (A ³ Δ – a ¹ Δ) Chamberlain	120 R	mesosphere	1999	<i>Slanger et al.</i> [2001]

Table 2. Airglow observations published since 2000.

Observation	Value	Altitude	Year/Location	Notes
Cloud top pressure	5 – 30 mbar		1978 - 1991	<i>Braak et al.</i> [2002]
Cloud-top unit optical depth	110 – 160 mbar		1978 – 1979	<i>Koukouli et al.</i> [2005]
Cloud-top unit optical depth	120 – 200 mbar		1983	<i>Koukouli et al.</i> [2005]
Upper haze column abundance	1.5 μm ⁻²	> cloud top	1978-1991	<i>Braak et al.</i> [2002]
H ₂ SO ₄ Droplet column abundance	15 cm ⁻²	> cloud top	1999 - 2004	<i>Mallama et al.</i> [2006]
H ₂ SO ₄ Droplet diameter	2.1 μm	> cloud top	1999 - 2004	<i>Mallama et al.</i> [2006]

Table 3. Cloud and haze observations published since 2000.

Predicted Species	Maximum Abundance	Altitude	Column Abundance	Notes
ClO	4 x 10 ⁷ cm ⁻³	70 km	1 x 10 ¹⁴ cm ⁻²	<i>Pernice et al.</i> [2004]
Cl ₂	6 x 10 ¹⁰ cm ⁻³	60 km	6 x 10 ¹⁶ cm ⁻²	<i>Pernice et al.</i> [2004]

CIC(O)OO	$1 \times 10^8 \text{ cm}^{-3}$	84 km	$7 \times 10^{13} \text{ cm}^{-2}$	<i>Pernice et al.</i> [2004]
COCl ₂	$4 \times 10^8 \text{ cm}^{-3}$	66 km	$7 \times 10^{14} \text{ cm}^{-2}$	<i>Pernice et al.</i> [2004]
CISO ₂	$3 \times 10^{10} \text{ cm}^{-3}$	58 km	$6 \times 10^{15} \text{ cm}^{-2}$	<i>Pernice et al.</i> [2004]
S ₂ O	$1 \times 10^{10} \text{ cm}^{-3}$	64 km		<i>Na and Esposito</i> [1997]

Table 4. Predicted gas-phase species in the middle atmosphere which have not been observed.

2.1 VENERA 15 INFRARED SPECTRA: OBSERVATIONAL RESULTS AND INTERPRETATION

VENERA 15 observed mainly the northern hemisphere, except for one orbital session when the spacecraft's orientation was changed to obtain a few tens of spectra in the equatorial region and southern midlatitudes. Absorption bands of three atmospheric gases (CO₂, H₂O and SO₂) and also H₂SO₄ aerosols are clearly visible. The very strong 15 micrometer CO₂ band has different morphology at different locations, mostly owing to variability of the temperature profiles. Band center emission arises from atmospheric layers at about 90 km altitude. Differences appearing in the continuum likely reflect variability in the vertical structure of the upper clouds and haze.

Interpretation of Fourier Spectrometer (FS) data [*Moroz et al.*, 1985, 1986, 1990; *Spankuch et al.*, 1985, 1990; *Zasova et al.*, 1985, 1989, 1993; *Schaefer et al.*, 1987, 1990; *Linkin et al.*, 1985) gives the following results:

- (1) Upper cloud and upper haze particles consist of sulfuric acid water solutions, confirmed by the good agreement of synthetic and observed spectra.
- (2) The particle size distribution corresponds to the measured "mode 2" from the Pioneer Venus Lander Cloud Particle Spectrometer? (LCPS), with parameters as proposed by *Pollack et al.* [1980]. That is, a log-normal distribution with mean cross-section weighted size $r = 1.05$ micrometers and variance $\sigma = 1.21$. Possibly some other size distributions could also successfully match the data.
- (3) CO₂ pure gas transmission functions for a set of channels within the 15 micrometer band and computed aerosol transmission functions allow an iterative procedure, (e.g., using relaxation as by *Zasova et al.* [1989]) to simultaneously retrieve the temperature and aerosol profiles.
- (4) The retrieved temperature and aerosol profiles from step (3) yield synthetic spectra for the SO₂ and H₂O bands, which allow derivation of their abundances. These abundances are in good agreement with SO₂ measured in the UV [*Zasova et al.*, 1993].

2.2 SULFUR DIOXIDE MEASUREMENTS

SO₂ was first detected in the atmosphere of Venus by *Barker* [1979] from the ground, and it was subsequently confirmed by *Stewart et al.* [1979] and *Conway et al.* [1979]. These observations indicated that the abundances of SO₂ in 1978-1979 period were larger than the previously established upper limits [*Owen and Sagan*, 1972] by orders of magnitude. Continuous observations by Pioneer Venus from 1978 to 1986 show a steady decline in the cloud top SO₂ abundance toward values consistent with previous upper limits [*Esposito et al.*, 1988]. This decline has been confirmed by International Ultraviolet Explorer (IUE) observations [*Na et al.*, 1990] and by Hubble [*Na and Esposito*, 1995], see Figure 2 and Figure 3. Analysis of UV spectra from the Hubble Space Telescope (HST) Goddard High Resolution Spectrometer (GHRS) give an SO₂ abundance of less than 25 ppb at the cloud tops [*Na and Esposito*, 1996]. See Figure 3 for the time history of SO₂ cloud top measurements. Explanations that have been advanced for the likely rapid increase and observed slow decline of SO₂ include active volcanism [*Esposito*, 1984] and changes in atmospheric dynamics [*Clancy and Muhleman*, 1991]. It is important to note that the volcano hypothesis uses the volcanic eruption as a source of buoyancy that allows the abundant SO₂ below the Venus clouds to break through the stable upper cloud layer. The entrained SO₂ is then observable remotely at the cloud top in the UV. The SO₂ abundance below the clouds varies much more slowly, related to the amount of volcanic activity over geologic time scales of millions of years. See *Fegley et al.*, 1997.

The changes in SO₂ above and within the clouds of Venus may have a significant effect on the photochemistry of the clouds of Venus. Pioneer Venus observations have shown that the clouds of Venus are created by the photochemical processes that oxidize upwelling SO₂ [*Winick and Stewart*, 1980; *Yung*

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and DeMore, 1982]. Thus any significant changes in SO₂ may have an effect on the chemistry and dynamics of the clouds.

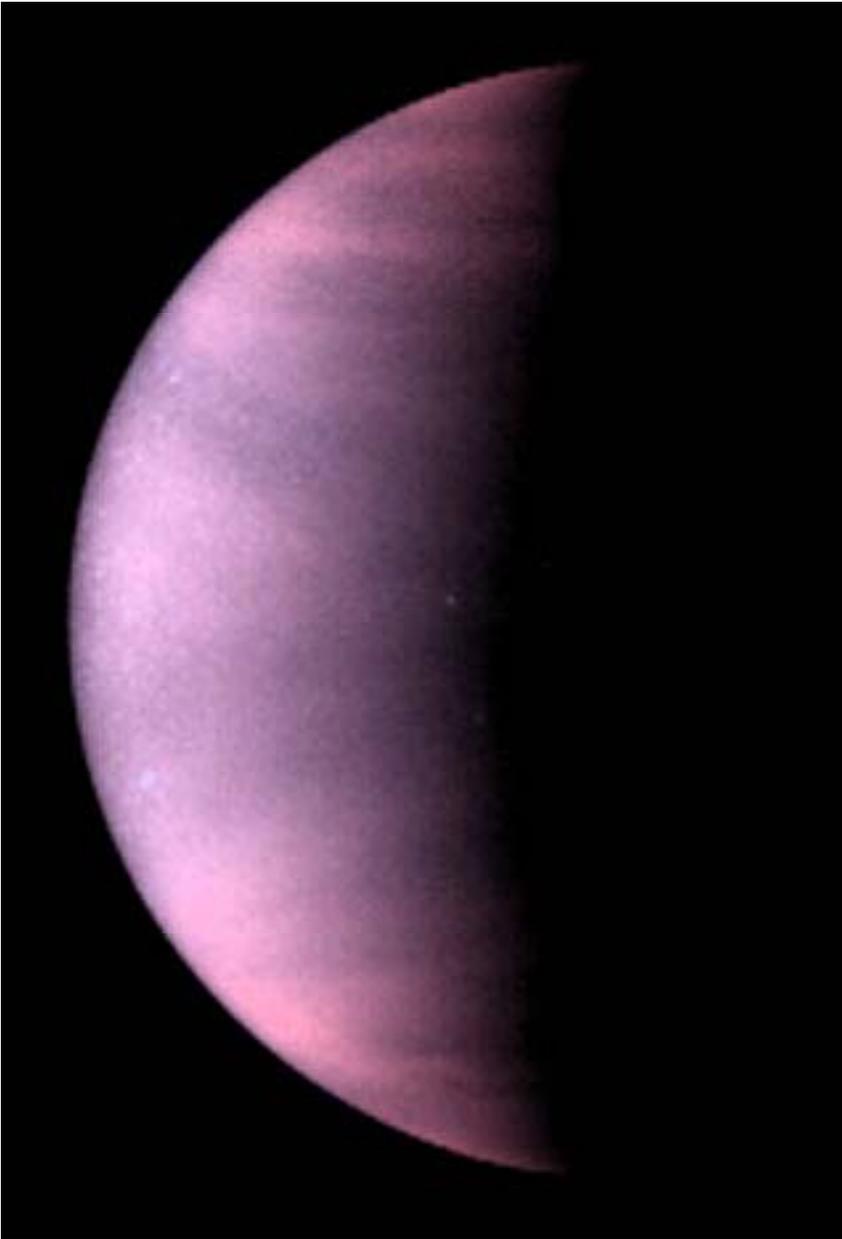


Figure 2. Venus image from HST at 218 nm. (From Esposito et al., 1997)

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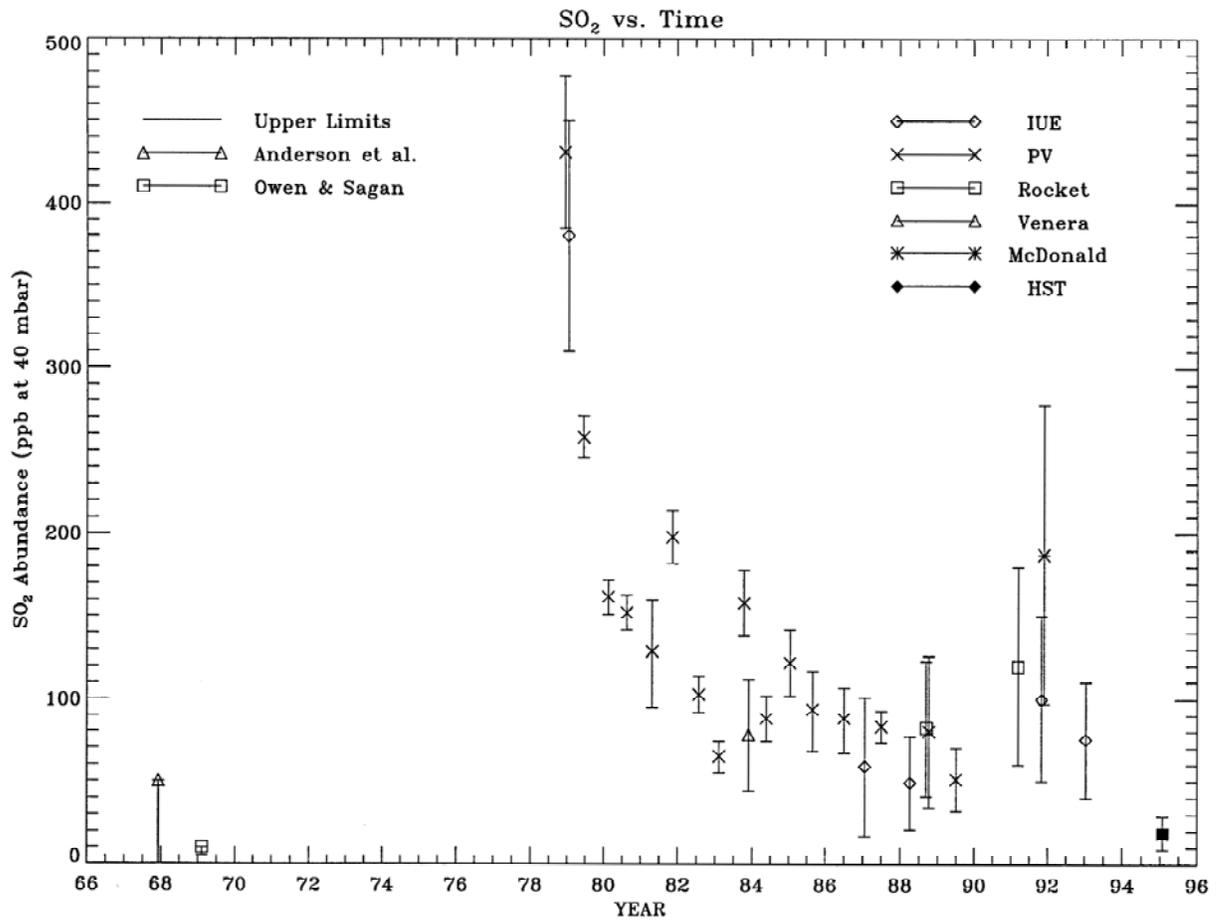


Figure 3. SO₂ abundance near the Venus cloud tops. (From Esposito et al., 1997)

2.3 CLOUDS AND HAZES

VENERA-15 FS spectra provided a strong confirmation of aqueous solution (75-85%) of sulfuric acid as the particulate material in the upper clouds. Otherwise, such good coincidence of synthetic and observed spectra would be impossible. The first *in situ* detection of sulfuric acid was made in experiments SIGMA-3 and MALAHIT. The analysis of SIGMA-3 results yields the average mass loading of sulfuric acid about 1 mg/m^3 , estimated for heights 48-54 km and “much lower” at about 54 km [Porshnev *et al.*, 1987]. Conclusions from MALAHIT analysis are even less definite and not in a good agreement with SIGMA-3 results; they give an average mass loading between 2 and 10 mg/m^3 [Surkov *et al.*, 1987]. Both experiments can say nothing about the upper clouds.

Very interesting, but puzzling, results were obtained by elemental X-ray analysis of the thin layers collected by the IPF experiment [Andreichikov *et al.*, 1987], which was an aerosol analyzer on VEGA. Three elements were identified: sulfur, chlorine and phosphorus. Sulfur and chlorine in cloud particles had been detected previously by similar measurements, but not phosphorus. It is clear that some P-bearing substance can be important as a particulate in lower clouds. Phosphoric acid H_3PO_4 is a likely candidate for this substance and phosphorous anhydride P_4O_6 may be the gas responsible for its production [Andreichikov, 1987]. A critical review of these data was given by Krasnopolsky [1989]. The key conclusion in the paper is that the lower subcloud boundary at the level about 33 km registered on VENERA 8 and later on some other missions can be explained by phosphoric acid particles dominating in the subclouds. The refractive index 1.7 estimated for some of the particles registered in ISAV-A experiment can be understood if they consist of free condensed sulfur. Some evidence for the presence of free sulfur in clouds is also found in the analysis of the SIGMA-3 and IPF results.

2.4 GROUND-BASED OBSERVATIONS OF THE LOWER ATMOSPHERE

Important new information from near IR measurements of the Venus nightside probes the deeper Venus atmosphere through windows in the CO_2 absorption spectrum. Discovery of nightside emissions at 1.7 and $2.3 \mu\text{m}$ on Venus by Allen and Crawford [1984] has been extremely important for further progress in study of the chemical composition. These emissions were readily identified [e.g., Krasnopolsky, 1986, p. 181] as spectral windows to the lower atmosphere. Later, windows at 1.31, 1.27, 1.18, and $1.01 \mu\text{m}$ were found, and lines of CO_2 , H_2O , HDO, SO_2 , CO, OCS, HCl, and HF have been identified. Radiation in each window is formed at a particular altitude range, and by comparing data for the same species at different windows, it becomes possible to obtain vertical profiles. Furthermore, lines of different strengths were observed in the $2.3 \mu\text{m}$ window, and this allowed Pollack *et al.* [1993] to derive both the mixing ratio and its gradient.

These measurements show that HCl and HF are constant throughout the atmosphere, H_2O is constant and equal to 20-45 ppm from an altitude of 10 km up to the lower cloud boundary. The mixing ratio close to the surface is harder to constrain [deBergh *et al.*, 2006]. CO and OCS are equal to 23 ± 5 and 4.4 ± 1 ppm at 36 and 33 km, respectively, with gradients of 1.2 ± 0.45 and -1.58 ± 0.3 ppm/km, respectively [Taylor *et al.*, 1997; Crisp and Titov, 1997; Marcq *et al.*, 2006].

Sulfur chemistry is critical to the composition of the Venus atmosphere, and four sulfur species have been firmly identified: SO₂, SO, OCS, and H₂SO₄ (vapor and in aerosols). Recent measurements of their abundances are summarized in Table 1 and Table 3. H₂S was reported by Pioneer Venus [Hoffman *et al.*, 1980], but it was never confirmed by an independent measurement. Strong absorption in spectrophotometer data from VENERA 11 and 12 at 450–600 nm between 10 and 30 km has been attributed variously to gaseous elemental sulfur [Moroz *et al.*, 1979], polysulfur (S_x) [Sanko, 1980], or SO₂ [Pollack *et al.*, 1980]. No independent measurement has been reported. The presence of thiozone (S₃) and polysulfur (S_x) in the clouds has been inferred but has not been proved.

The chemical scheme proposed by Prinn [1975, 1978, 1979] is based on a prediction by Lewis [1970] of sulfur species with mixing ratios of 60 ppm for OCS, 6 ppm for H₂S, and 0.3 ppm for SO₂. In the seventies, sulfuric acid was clearly identified in the clouds, while a search for gaseous sulfur components was not successful until 1979 (see Sec. (2.2)). Prinn [1975] suggested a scheme of photochemical formation of sulfuric acid from carbonyl sulfide OCS and later [Prinn, 1978] proposed the inverse processes leading to OCS and elemental sulfur from H₂SO₄. The predicted SO₂ mixing ratio was of a few ppm above 30 km and much larger than that near the surface. Prinn [1979] supposed that dissociation of S₃ and S₄ by the near ultraviolet ($\lambda \approx 350$ nm) might produce hot sulfur atoms which could drive the chemistry.

As noted above, there are two parts to the chemistry of sulfur species in the atmosphere of Venus. In the lower atmosphere and on the surface, the chemistry is dominated by thermodynamic equilibrium chemistry. Above the cloud tops, the chemistry is driven by photochemistry. Thus, the partitioning of sulfur among the different species represents a competition between thermodynamic equilibrium chemistry in the lower atmosphere and photochemistry above the cloud tops. We first discuss the photochemistry of sulfur in the middle atmosphere and then the thermal equilibrium chemistry of sulfur in the lower atmosphere.

3.1 SULFUR PHOTOCHEMISTRY

The most reducing species of sulfur that has been observed is OCS. In the upper atmosphere it readily undergoes photolysis:



where S(¹D) is the first electronically excited state of the S atom. The most likely fate of S(¹D) is quenching:



The S atom gets oxidized to SO by reacting with O and O₂



Further oxidation to SO₂ can proceed via the three-body reaction



Catalytic oxidation by ClO is also possible



Note that the net result is the oxidation of S to SO₂, and eventually to H₂SO₄. Figure 1 summarizes the concentrations of major oxygen bearing species and the fluxes computed by Yung and DeMore [1982]. This figure illustrates the central themes of the chemistry of Venus for the oxidation of CO and SO₂.

The ultimate fate for SO₂ in the middle atmosphere is oxidation to H₂SO₄. The spectroscopic limit on OCS above 60 km is 10 ppb while the observed SO₂ mixing ratio at 40 mb (~70 km) is ~20-400 ppb, so oxidation of SO₂ that has been transported upward from the lower atmosphere is the primary source for H₂SO₄. Photochemical models by *Krasnopolsky and Parshev* [1980, 1983] and *Yung and DeMore* [1982] show that sulfuric acid is produced mostly in a thin layer of 2 km depth centered at 62 km. The H₂SO₄ eventually forms aerosols [*Yung and DeMore*, 1982; *Esposito et al.*, 1988] that are transported by the meridional circulation to the polar region where they descend into the lower atmosphere [*Imamura and Hashimoto*, 1998]. Thermodynamic equilibrium reactions in the lower atmosphere decompose the sulfuric acid and turn the H₂SO₄ back to SO₂. This cycle of oxidation of SO₂ to H₂SO₄ followed by condensation, subsidence, evaporation, and decomposition has been termed the “fast atmospheric sulfur cycle” [*von Zahn et al.*, 1983], Figure 4.

In addition to oxidation to SO₂ and eventually to H₂SO₄, there is another possible fate for sulfur compounds in the atmosphere of Venus: formation of polysulfur (Figure 4). S atoms generated by the photolysis of OCS can react via



Production of S₃ is possible through successive addition reactions such as



S₃ is the sulfur analog of ozone, known as thiozone. As the number of sulfur atoms increases, the polyatomic sulfur compounds tend to have lower saturation vapor pressures. It is convenient to name all sulfur species beyond S₃ “polysulfur” or S_x. The production of S_x is part of what has been termed the “slow atmospheric sulfur cycle” [*von Zahn et al.*, 1983], which is completed by decomposition reactions in the lower atmosphere (Sec. (3.2)). In the UV region S_x absorbs strongly, and it may be the principal constituent of the unidentified UV absorber in the upper atmosphere of Venus.

Whether the ultimate fate of sulfur in the middle atmosphere is H₂SO₄ or S_x depends crucially on the branching for the S atom in the following two reactions.



The H₂SO₄ path would be preferred if

$$[\text{O}_2] > k_b / k_a [\text{OCS}] \quad (11)$$

Thus when the O₂ abundance exceeds this value, production of oxidized sulfur species is favored, and ultimately H₂SO₄ is produced. When the O₂ abundance is below this value, production of polysulfur becomes possible. Since the source of O₂ is photolysis of CO₂ in the upper atmosphere and the source of OCS is thermodynamic equilibrium chemistry in the lower atmosphere and the surface, we can imagine that the oxygen content of the subsiding and upwelling air parcels could be quite different. This may indeed be the explanation for the patchiness and the transience of the UV markers in the cloud tops of Venus.

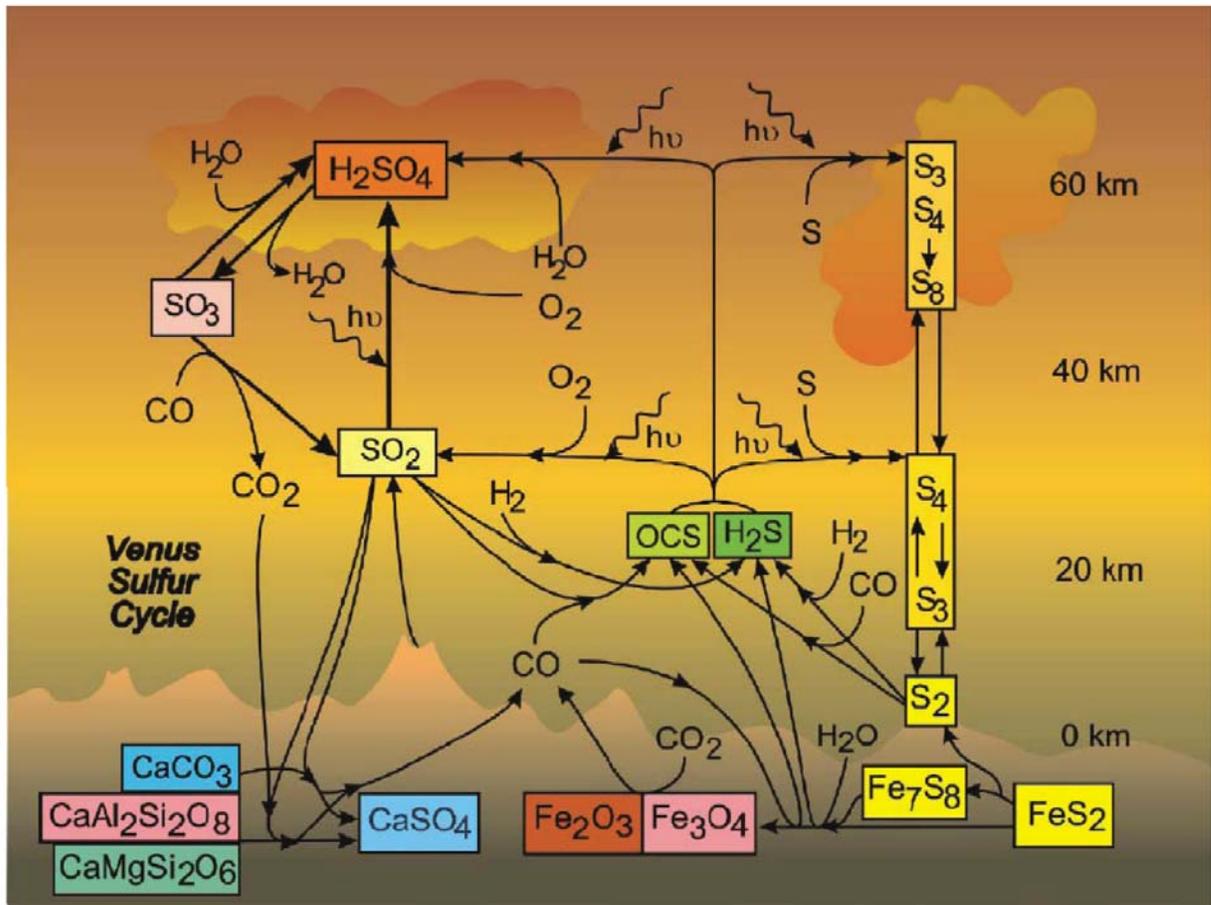
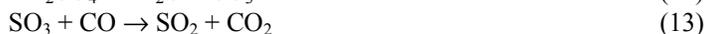


Figure 4. Sulfur chemical cycles on Venus. [From Fegley et al., 1997]

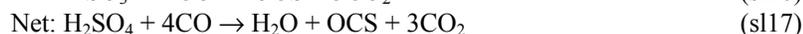
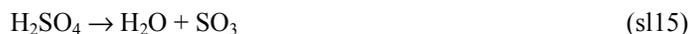
3.2 SULFUR THERMAL EQUILIBRIUM CHEMISTRY

Pioneer Venus, VENERA, and ground-based observations showed that the main sulfur species in the lower atmosphere (< 60 km) is SO₂ with a mixing ratio close to 150 ppm below the upper cloud [Bertaux *et al.*, 1996; Bezard *et al.*, 1993; Oyama *et al.*, 1980]. At these heights, photons with $\lambda > 450\text{-}500$ nm are the only ones available, and the energy of sulfur atoms released by photolysis of S₃ and S₄ is too low to drive exothermic reactions, so the chemistry is controlled by thermodynamic equilibrium chemistry. The sulfur chemistry in the lower atmosphere has been summarized in terms of three cycles, Figure 4. The middle atmosphere portions of the fast and slow atmospheric sulfur cycles were described in Sec. (3.1). The lower atmosphere portions of these cycles and of the geological cycle are described here. The coupled photochemical and thermodynamic equilibrium chemistry is shown in Figure 5.

Decomposition of H₂SO₄ in the lower atmosphere initially produces H₂O and SO₃. SO₃ can then oxidize CO to produce CO₂ and complete the fast atmospheric sulfuric cycle.



One version of the slow atmospheric sulfur cycle [von Zahn *et al.*, 1983] balanced the oxidation of OCS in the middle atmosphere via



The net result from this version of the slow atmospheric sulfur cycle was a null reaction as the lower atmosphere portion exactly balanced the upper atmosphere portion. However, Krasnopolsky and Pollack [1994] re-examined the oxidized portion of the slow atmospheric sulfur cycle following observations of profiles of OCS and CO between 20 and 45 km [Pollack *et al.*, 1993]. They concluded that the lower atmosphere portion of it proceeded via a different pathway.



Computed vertical profiles from the two models developed by Krasnopolsky and Pollack [1994] are shown in Figure 6. There is a significant difference between these “closures” for the slow atmospheric sulfur cycle. The first gives a net null cycle, so an external source of OCS is not required and the atmosphere is not evolving. Krasnopolsky and Pollack’s scheme results in net destruction of OCS, which implies either the slow atmospheric sulfur cycle is completed below 20 km or the atmosphere is evolving or both. Krasnopolsky and Pollack emphasize that this is only a partial solution to the problem of explaining the processes which govern profiles of OCS, CO, H₂SO₄, and SO₃, and their study does not cover some aspects of sulfur chemistry below 25 km.

The polysulfur branch of the slow atmospheric sulfur cycle is balanced by



The net result of the fast atmospheric sulfur cycle and both branches of the slow atmospheric sulfur cycle is that there must be a significant flux of CO from the middle atmosphere to the lower atmosphere which is balanced by an upward flux of CO₂.

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The geological cycle involves reactions between atmospheric gases and surface minerals. These chemical weathering reactions proceed slowly compared to those comprising the atmospheric cycles, so significant disequilibria may exist between the surface and the atmosphere. There have been no measurements of the surface mineralogy and the only geochemical data for the surface are abundances of Mg and heavier elements from x-ray fluorescence spectrometers on the VENERA 13 and 14 and Vega 2 landers [Surkov *et al.*, 1984, 1986]. The absence of definitive data has led to speculation about what surface minerals may exist, how they may buffer the atmosphere, and how the surface-atmosphere system may have interacted over the course of Venus' evolution. The general form of the proposed reactions is [Johnson and Fegley, 2002]



Surface rocks that have been proposed include carbonate (CaCO_3), wollastonite (CaSiO_3), anhydrite (CaSO_4), pyrite (FeS_2), pyrrhotite (Fe_7S_8), magnetite (Fe_3O_4), and tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$). A number of good laboratory experiments have provided information on how rapidly chemical weathering would occur for minerals that may (or could have) existed on the surface of Venus. The experiments show that the rates for many of the posited reactions can be sensitive functions of temperature, oxygen fugacity, and/or the gaseous sulfur abundance [See Chapter 2 by Treiman *et al.*].

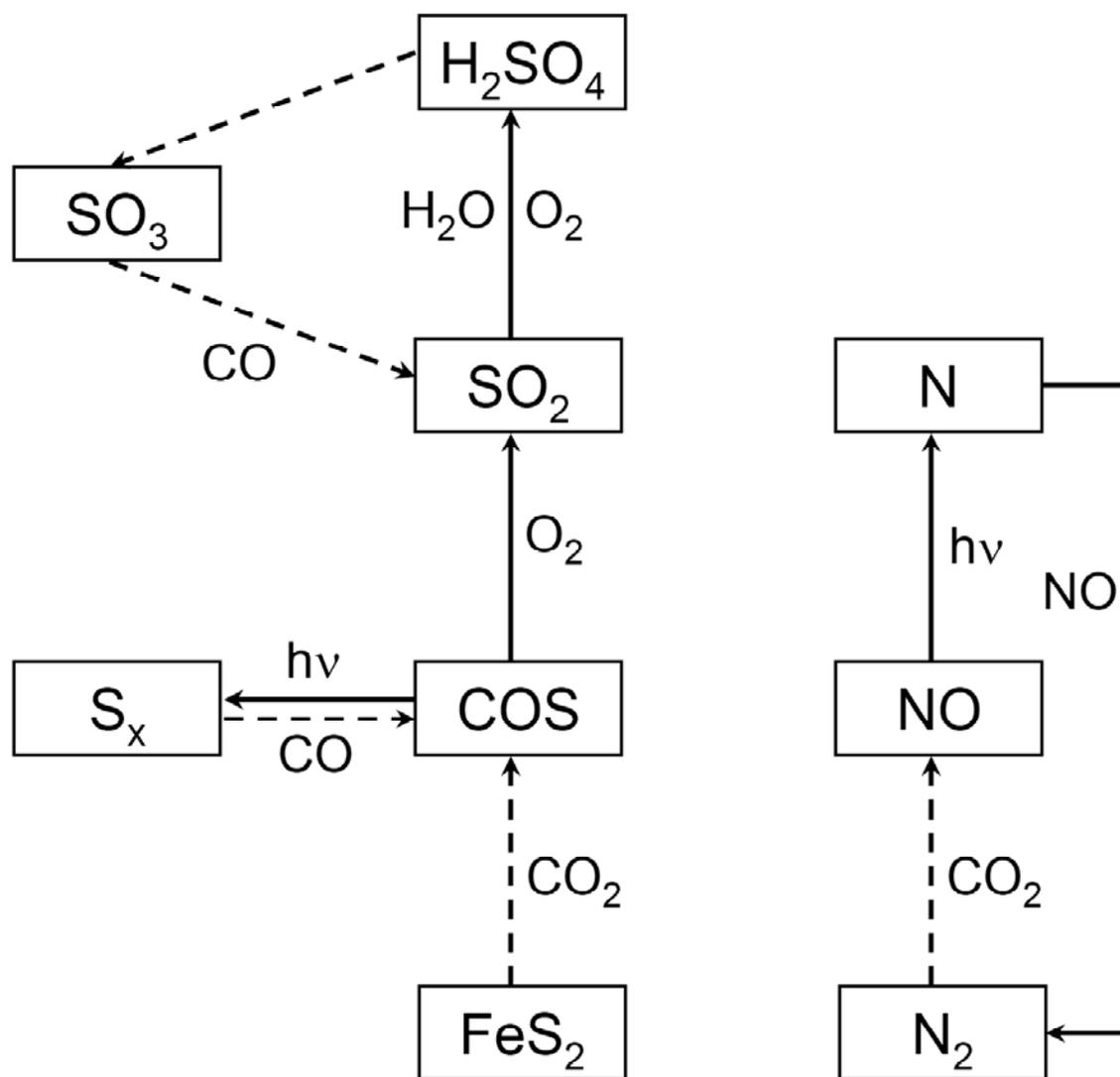


Figure 5. Schematic of the transformation of sulfur and nitrogen compounds in the atmosphere of Venus. The disequilibrium (photochemical) and thermodynamic equilibrium reactions are shown by solid and dashed arrows, respectively.

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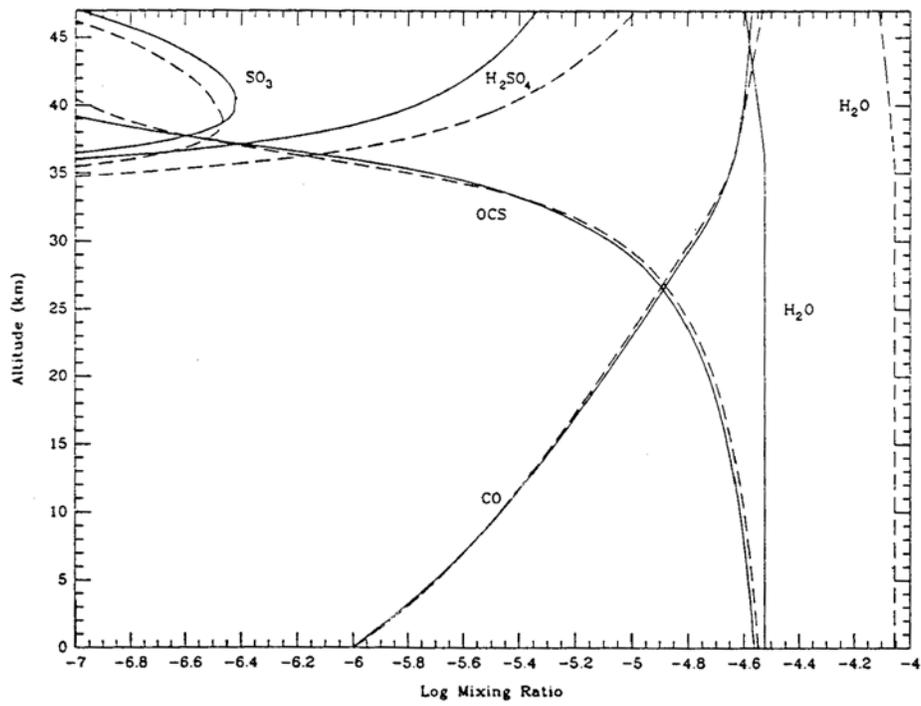


Figure 6. Predicted composition of lower atmosphere [Krasnopolsky and Pollack, 1994].

4 CLOUDS

The Venus clouds and hazes have enormous vertical extent, with a lower haze down to ~30 km and an upper thick haze up to 90 km altitude; the entire system covers a vertical depth of ~60 km, with an average visibility in the Venus clouds better than several km. The main cloud deck extends from ~70 km (the level of unit optical depth in the ultraviolet) down to altitudes between 45 and 50 km.

4.1 CLOUD STRUCTURE, PROPERTIES, AND FORMATION

Spacecraft *in situ* measurements allow us to divide the cloud system into upper, middle and lower clouds [see the review by *Esposito et al.*, 1983], Figure 7. Based on the Pioneer Venus and VENERA nephelometer results and the LCPS (Pioneer Venus Cloud Particle Size Spectrometer) measurements, it appears that the middle and upper cloud structure are planetwide features. In all cases the opacity is higher in the middle than upper cloud, typically by a factor of 2. The lower cloud is well defined and highly variable from location to location. Sharp layers are evident at the Pioneer Venus Large and Night probe sites.

The clouds within the main deck would all be thin stratoform in terrestrial classification. Instabilities are slight and latent convection potential is negligible [see *Knollenberg et al.*, 1980]. Only the middle cloud region appears to have any potential for convective overturning.

Considering the downward flux of sulfuric acid droplets, it is possible to understand why the clouds divide into three layers. Due to the photochemical formation of sulfuric acid (mostly in a thin layer of 2 km depth centered at 62 km based on models [*Krasnopolsky and Parshev*, 1980, 1983; *Yung and DeMore*, 1982]), its flux increases steeply with decreasing altitude in the upper cloud layer which ends near 59 km (the measurements give 57 km). This increase correlates with the increasing H₂O mixing ratio while the concentration of sulfuric acid is relatively constant.

The flux of liquid sulfuric acid is constant in the middle cloud layer (57-50 km according to the measurements).

In the model, the lower cloud layer forms at 52-48 km, where the predicted flux of liquid sulfuric acid exceeds that in the middle cloud layer by a factor of 4-7. The H₂O mixing ratio is rather constant, and thus the water fraction continues to decrease by a factor of 3 until the lower cloud boundary is reached. This corresponds to the acid concentration increasing to 97-98% at the lower cloud boundary. A strong gradient of gaseous sulfuric acid drives an upward flux which condenses and forms a strong downward flux of liquid sulfuric acid with the sum of both fluxes being constant in the lower and middle cloud layers. According to *Krasnopolsky and Pollack* [1994], this is the mechanism of the formation of the lower cloud layer. Thus, the upper cloud is created by photochemical production, the middle cloud by droplet growth and sedimentation, and the lower cloud by condensation enhancing the downward flux.

Krasnopolsky and Pollack [1994] developed a method to calculate the lower cloud boundary, with results between 48.4 km and 46.6 km. This is in good agreement with the PV radio occultation observations [*Cimino*, 1982], which show the boundary varying from 47-48 km at the low and middle latitudes and 47-43 km at high and subpolar latitudes.

The location of the lower boundary varies due to variations of the H₂SO₄ vapor mixing ratio, the water vapor mixing ratio below the clouds, and temperature and pressure. *Krasnopolsky and Pollack* [1994] found the boundary variations are produced mostly by variations of the sulfuric acid abundance and temperature. Variations of density of the lower cloud layer reflect variations of gaseous sulfuric acid, because water contributes only slightly to the sulfuric acid aerosol in the lower cloud layer.

ATMOSPHERIC COMPOSITION, CHEMISTRY, AND CLOUDS

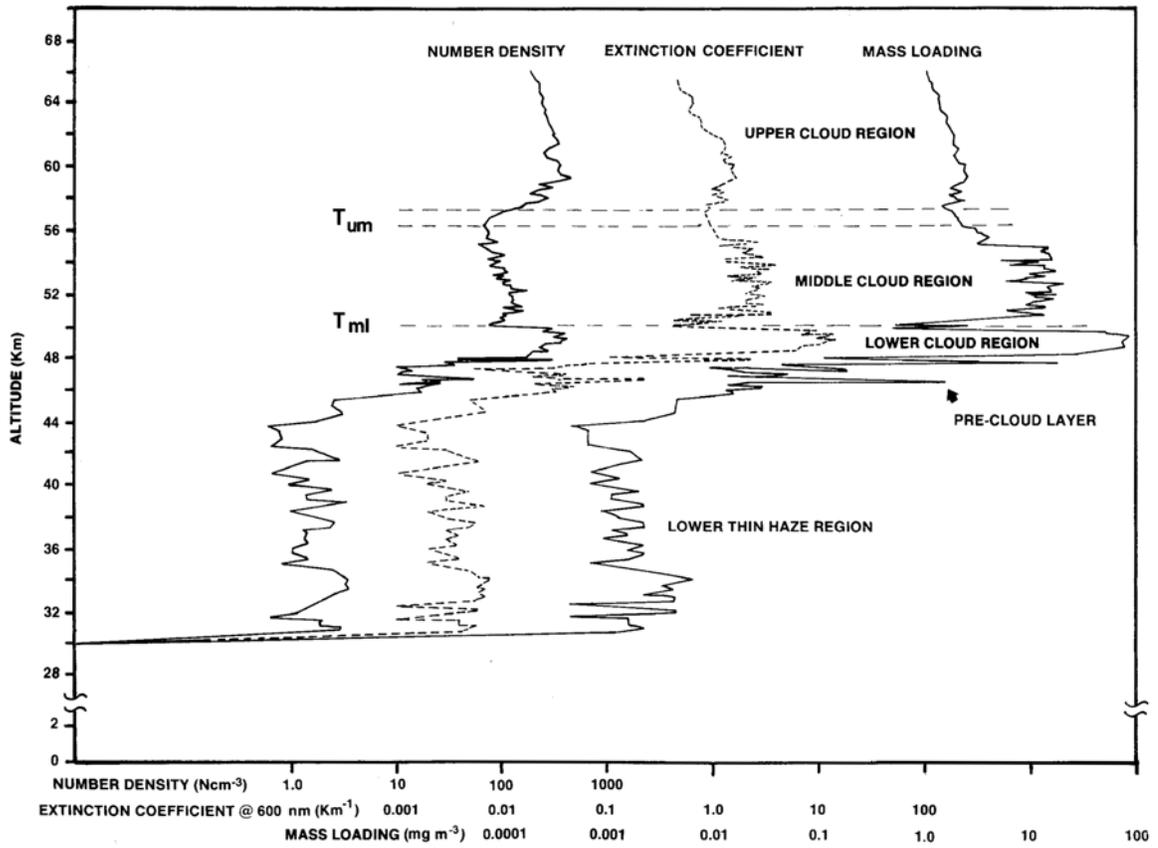


Figure 7. Cloud property vertical profiles. T_{ml} is the middle-lower cloud transition. T_{um} is the upper-middle cloud transition. [From Knollenberg *et al.*, 1980]

4.2 THE MODE 3 PARTICLE CONTROVERSY

The Pioneer Venus LCPS measurement of larger, so called “Mode 3” particles has provided a controversy that is still unresolved; see *Esposito et al.* [1983]. The starting point for the Mode 3 controversy comes from direct evidence for asymmetric (possible crystalline) particles provided by *Knollenberg and Hunten* [1980]. *Knollenberg et al.* [1980] further state that only such crystals of high aspect ratio could satisfy the Pioneer Venus LCPS, LSFR, and LN results simultaneously. However, since the largest amount of mass (~80% according to *Knollenberg and Hunten* [1980]) is within the Mode 3 particles, it is extremely important to verify their existence and determine their composition.

The LCPS undoubtedly detected large particles, but the evidence for solid particles is indirect. There were internal inconsistencies in the LCPS measurements as well as inconsistencies between the LCPS measurements and the measurements made by other instruments. Some of these inconsistencies were:

1. Calculations employing LCPS size distributions do not give the backscatter observed by the PV nephelometer in the lower clouds if reasonable refractive indices are used.
2. The LCPS size distributions do not yield the optical depths derived by the LSFR, assuming spherical particles.
3. Overlapping size ranges of the LCPS give conflicting measurements in the lower clouds.

In addition, independent VENERA results show some oddities at the same altitudes:

1. VENERA nephelometer phase function measurements are inconsistent with spherical particles having reasonable refractive indices in the lower cloud.
2. X-ray fluorescence measurements [*Surkov*, 1979] show about ten times as much chlorine as sulfur in the Venus clouds.

The various inconsistencies can be explained by the simple hypotheses that Mode 3 is composed of solid, nonspherical particles. However this explanation requires an abundant gas-phase chemical in the clouds as the source for these particles. No such gas has yet been discovered.

Toon et al. [1982] reexamined the evidence that solid particles form a distinctive size mode. They find that Mode 3 is defined by a discontinuity located between two size ranges of the LCPS. Although this could be real, it could also be the result of a small calibration shift of the PV instrument. A shift in the calibration removes the discontinuity, along with the internal inconsistency of the LCPS. The revised size spectrum is consistent with the VENERA and Pioneer Venus optical data in the lower clouds; all the modes can be composed of sulfuric acid droplets without any solid particles. The only unexplained data are those showing large amounts of chlorine compared to sulfur in the clouds. We note, though, that the more recent Soviet measurements from VENERAs 13 and 14 show a large sulfur to chlorine ratio, the opposite of *Surkov's* [1981] findings. The VEGA landers detected no large particles.

From the data in hand, it seems impossible to disprove the existence of Mode 3. Two self-consistent, alternative interpretations of the data exist. Accepting the spacecraft observation at face value, we are led to the existence of a mode of large solid particles whose composition is unknown and whose source vapor has escaped detection. On the other hand, we may conclude that the large particle mode is merely the (mis-measured) tail end of the Mode 2 sulfuric acid droplets. This allows a simple understanding of the source of all the cloud particles, but at the cost of disbelieving some of the measurements.

5 CHLORINE CHEMISTRY

The most important consequence of photochemistry in the Venus atmosphere is the breaking of the strong O-CO bond, yielding O₂,



The central problem of Venus photochemistry, thus, is the very low observational limit on the abundance of O₂. The observed large production rate of O₂ [*Connes et al.*, 1979; *Crisp et al.*, 1996] combined with the low upper limit on its abundance implies either a large reservoir in which oxygen is sequestered or fast

ATMOSPHERIC COMPOSITION, CHEMISTRY, AND CLOUDS

oxidation of CO and/or SO₂, or all three. The abundance of O₂ is determined by the sulfur oxidation cycle, as described in Sec. (3.1), and the CO₂ cycle, which is the dominant chemical cycle above the cloud layers (>~ 70 km altitude). Hydrogen, chlorine, and sulfur chemistries are all linked to the CO₂ cycle, but chlorine chemistry is believed to provide the critical pathway for catalyzing oxidation of CO to CO₂ [Yung and DeMore, 1982; Pernice et al., 2004].

Observations in 1966 [Connes et al., 1967] detected a substantial (0.4–0.6 ppm at 67–70 km altitude [Young, 1972]) abundance of HCl. HCl should be the dominant source of hydrogen and chlorine radicals at ~ 75–95 km because (1) the water vapor abundance should be suppressed by condensation onto the concentrated sulfuric acid particles in the upper haze layer [Mills, 1999a] and (2) photodissociation of H₂O is strongly attenuated below 100 km by CO₂ photoabsorption while photodissociation of HCl is still significant at 75 km.

Detection of HCl led to the proposal that CO oxidation occurs via Reactions (27) and (28) [Prinn, 1971].



Subsequent laboratory studies, however, showed these reactions proceed too slowly to be significant. The next advances in understanding chlorine chemistry in the Venus atmosphere came in the early 1980s after VENERA 11 and 12 and near the beginning of the Pioneer Venus mission. Three modeling studies of increasing complexity and accuracy were published. Winick and Stewart [1980] introduced the first model with both sulfur and chlorine chemistry, including the now classic chlorine cycle for converting odd oxygen to molecular oxygen, Reactions (30) and (31).



This cycle was so efficient it completely balanced the new sulfur cycles involving Reaction (4) that Winick and Stewart had introduced to break the O-O bond. Consequently, the predicted O₂ column abundance was a factor of 50 larger than the then extant upper limit (and a factor of 150 larger than the current upper limit).

The next two modeling studies developed independently the chemistry of the chloroformyl radical (ClCO) and identified it as a potentially significant intermediary in the production of CO₂. These schemes involving ClCO are the only ones proposed to date that operate efficiently in the 75–90 km altitude region where CO₂ photodissociation is largest. Krasnopolsky and Parshev [1981; 1983] introduced Reactions (32) and (33) and calculated a much smaller O₂ abundance than any other model developed in the 1980's.

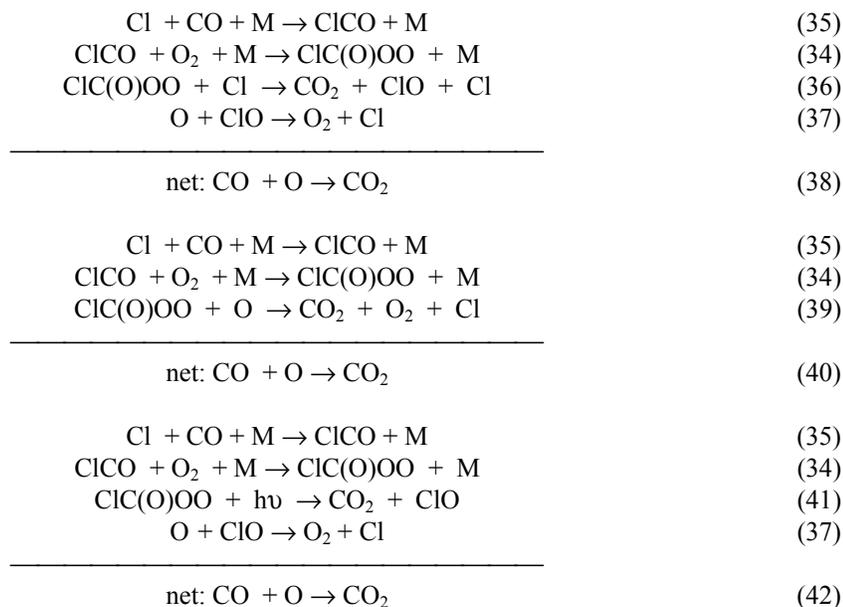


There are two major problems with the Krasnopolsky and Parshev model. First, the equilibrium constant for ClCO in the compilation from which they drew their laboratory data [Kondratiev, 1971] was incorrect due to a typographical error and implied ClCO was two orders of magnitude more stable than laboratory studies had found. Second, laboratory studies [Yung and DeMore, 1982] found the mechanism postulated for Reaction (33) was incorrect. Production of CO₂ instead proceeds via the peroxychloroformyl radical (ClC(O)OO or ClCO₃), which is produced by Reaction (34).



Reaction (34), introduced by Yung and DeMore [1982], is the key step in what are believed to be the dominant gas-phase pathways for production of CO₂ in the Venus atmosphere, Figure 8. Production of CO₂ via pathways that include Reaction (34) account for 80% of the column total CO₂ production in the Yung and DeMore [1982] model C. Neither reaction directly breaks the O-O bond in O₂. Subsequent modeling [Mills, 1998; Pernice et al., 2004] has shown that a model using these gas-phase pathways can be

brought into agreement with the extant upper limit on O₂ [Trauger and Lunine, 1983; Mills, 1999b] by enhancing the stability of ClCO within its experimental uncertainty. Three important pathways included in *Pernice et al.* [2004] for oxidation of CO are Reactions (38), (40), and (42). Reaction (38) accounts for just over 50% of the column total CO₂ production in the *Pernice et al.* [2004] model and the +2.0σ model from Table 5 while Reactions (40) and (42) account for 10 and 12%, respectively, of the column total CO₂ production in these two models. The improvement in the agreement with the O₂ observations may create a disagreement with the CO vertical profile but the observational constraints for CO from ground-based studies are not definitive, particularly on the day side and in the upper cloud.



There are three critical steps in the primary pathway for production of CO₂, Figure 8: formation of ClCO; association of ClCO with O₂ to form ClCO₃ before ClCO thermally decomposes; and formation of CO₂ from ClCO₃. All three critical steps now have been observed in laboratory studies, so the reaction mechanism initially proposed by *Yung and DeMore* [1982] may be considered validated. The formation of ClCO and its thermal stability were studied most recently by *Nicovich et al.* [1990]. The assessed uncertainties in their results for heat of formation and reaction enthalpy are ~ 1.5 kcal/mol and in the reaction entropy is ~ 5 cal/mol/K [Sander et al., 2002]. Formation of ClCO₃ via Reaction (34) was demonstrated in cryogenic matrix experiments [Pernice et al., 2004]. Other experiments reported in *Pernice et al.* [2004] demonstrated the formation of CO₂ from photodissociation of ClCO₃, derived the UV absorption spectrum for ClCO₃, and determined that ClCO₃ is thermally stable at temperatures below 350 C. However, substantial uncertainties remain in the rates at which each of the three critical steps occur in Venus' atmosphere. The experimental uncertainty in the equilibrium constant for ClCO, although small by experimental standards, translates into a large uncertainty in the predicted O₂ profile and the calculated O₂ column abundance, as illustrated in Table 5. No experimental uncertainty has been reported for Reaction (34) and only one laboratory study of this reaction rate is published, [Yung and DeMore, 1982]. No experimental measurements exist for the rates at which ClCO₃ reacts with any of the important radicals in the Venus atmosphere (e.g., O, SO, Cl). Further, none of the chlorine radicals has yet been observed in the Venus atmosphere. Their detection would provide a major confirmation of this proposed model.

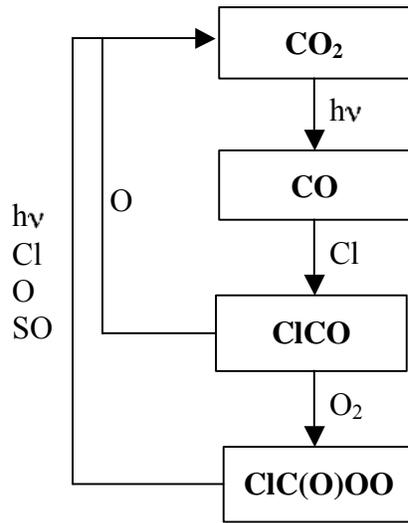


Figure 8. Schematic showing primary pathways for production of CO_2 via chlorine chemistry. The reaction $\text{ClCO} + \text{O} \rightarrow \text{CO}_2 + \text{Cl}$ accounts for 15 and 20% of the column total CO_2 production in the $+0.5\sigma$ and $+2.0\sigma$ models from Table 5, respectively.

Table 5. Sensitivity of modeled O₂ column abundance to thermal stability of ClCO in baseline chlorine chemistry model [*Pernice et al.*, 2004].

ClCO stability	+2 σ ^a	+1 σ	+0.5 σ	Nomin al	-0.5 σ	-1 σ	-2 σ ^b
O ₂ column abundance (10 ¹⁸ cm ⁻²)	2.0	2.4	3.1	8.6	27	39	49

^a Increased the thermal stability of ClCO by twice the assessed uncertainty in its equilibrium constant [*Sander et al.*, 2002].

^b Decreased the thermal stability of ClCO by twice the assessed uncertainty in its equilibrium constant [*Sander et al.*, 2002].

6 UNIDENTIFIED UV AND BLUE ABSORPTION

Currently, the only positively identified species in the visible atmosphere that absorb in the near UV are SO₂ and SO. However, they do not absorb longward of 3200Å. Thus, other absorbers must explain the absorption in Venus' spectrum and the dark markings which extend to 5000Å. [Esposito, 1980; Pollack *et al.*, 1980]. In addition, these other absorbers must explain the phase angle dependence of the UV dark markings [Barker *et al.*, 1975] as well as their short lifetime above the clouds (from hours to days, see Esposito *et al.*, [1983]). This must also be consistent with the solar flux observations of Tomasko *et al.* [1980] which show absorption at 58-62 km, and little absorption below. Similar solar flux absorption results from VENERA 14 [Ekonomov *et al.*, 1983, 1984] provide an additional constraint. Esposito and Travis [1982] noted the correlation between dark markings seen longward of 3200Å and SO₂ enhancements seen at 2070Å. This means that in addition to the absorption spectrum, a good candidate must also match the vertical distribution, lifetime and correlation with SO₂ enhancement. This last correlation could be either chemical or dynamical because the SO₂ observable in the far UV is likely the result of local upwelling [Esposito and Travis, 1982]. We briefly review the suggested candidates below.

S₈. S₈ was proposed by Hapke and Nelson [1975] and Young [1977, 1983] as the second absorber since it absorbs strongly in the UV. However, Pollack *et al.* [1980] showed that the spectral characteristics of S₈ were inconsistent with those of the second absorber. Another shortcoming of S₈ as the second absorber is its vertical profile. S₈ is not expected to disappear rapidly below the upper cloud layer since it precipitates as a solid, and the idea of these particles hiding inside sulfuric acid aerosols has been discounted by Young [1983]. Thus, the vertical profile of S₈ does not match that of the second absorber. Furthermore, the chemical lifetime of S₈ above the clouds is much longer than the timescale of the dark markings, thus it is difficult to explain the rapid disappearance (lifetime <3 hours) of small scale dark markings [e.g., Rossow *et al.*, 1980].

S₃ and S₄. Toon *et al.* [1982] suggested metastable sulfur allotropes, S₃ and S₄, as the most likely candidate for the second absorber. The absorption cross sections of S₃ and S₄ peak around 400 and 520 nm, respectively. The combination of these two sulfur gases with SO₂ provides a very close match to the albedo of Venus. The peak in the absorption cross sections of S₃ around 400 nm lines up with a kink in the albedo spectrum of Venus. S₃ and S₄ are metastable, and once produced they quickly relax to S₈ which exists as particulates. In this model, the S₈ would therefore contribute less. It is not clear if this contradicts Young's assertion (above). S₈ particles could then become incorporated into the sulfuric acid aerosols and fall out of the cloud region. This scenario thus explains the short lifetime of the dark features and the absence of the second absorber below the upper clouds. Furthermore, these sulfur allotropes can account for the high real refractive index of the upper cloud material, and the bimodal size distribution observed in the Venus clouds. When there is little oxygen in the atmosphere, sulfur allotropes can be produced from SO₂ photolysis instead of sulfuric acid [Prinn, 1975, 1985], so S₃ and S₄ may be produced in areas where sulfur vapor is enriched. However, there has been no positive detection of S₃ or S₄ to date. Further, these allotropes are rapidly photo-dissociated, giving lifetimes close to 1 second in the upper cloud. One further problem with the above scenario is that sulfur particles would still absorb UV photons below the upper clouds.

Cl₂. Pollack *et al.* [1980] proposed Cl₂ as a candidate for the second absorber. Pollack *et al.* showed that about 1 ppm of Cl₂ in the upper cloud could produce the brightness contrast seen in the UV images of the clouds. Cl₂ may exist in the atmosphere of Venus since it is produced from photodissociation of HCl which was detected in the atmosphere of Venus by Connes *et al.* [1967]. Some of the difficulties of Cl₂ being the second absorber include the relative scarcity of HCl in the atmosphere. The photochemical calculations of Winick and Stewart [1980] and Yung and DeMore [1982] showed that the amount of Cl₂ produced from HCl photolysis is two orders of magnitude smaller than 1 ppm. Furthermore, the vertical profile shows no maximum around 60 km, or rapid decline below 58 km. Finally, there is no obvious chemical or dynamical connection between Cl₂ and SO₂.

FeCl₃. Ferric Chloride is a possible candidate to explain absorption in the cloud layer. Krasnopolsky [1985, 1986] showed that many properties of the clouds can be explained if condensation of Fe₂Cl₆ vapor occurs at 47.5 km at the PV sounder probe site. This means that this species' mixing ratio is equal to 15

ppbv below 47.5 km. The calculated profile of the FeCl₃ condensate coincides with that of the mode 1 particles in the lower and middle cloud layer. The mode 1 FeCl₃ particles can then be transported by eddy diffusion to the upper cloud layer where they serve as condensation centers for the mode 2 H₂SO₄ particles. These particles are liquid below 62-63 km, and the ratio of the FeCl₃ flux to the H₂SO₄ production rate corresponds to a solution with concentration of FeCl₃ close to 1%. It is this solution which can explain the 320-500 nm absorption [Zasova *et al.*, 1981]. The reaction between FeCl₃ and concentrated H₂SO₄ is rather slow at temperatures 250-280 K at 62-58 km, and the lifetime of the solution is close to the precipitation time of one month. Colorless ferric sulfate, Fe₂(SO₄)₃, replaces FeCl₃ near 58 km. In thermochemical equilibrium:



it is favorable to form Fe₂Cl₆ vapor throughout the atmosphere. FeCl₃ in aerosol particles was observed by X-ray fluorescent spectroscopy from the VENERA 14 and VEGA landers [Petryanov *et al.*, 1981; Andreychikov *et al.*, 1987; Krasnopolsky, 1989]. The transition from FeCl₃ to colorless ferric sulfate predicted to occur at 58 km is close to the lower boundary of absorption observed by Ekonomov *et al.* [1983, 1984] on VENERA 14.

SCl₂. Krasnopolsky [1986] found a mixture of sulfur aerosol and SCl₂ fits well the absorption, but the required mixing ratio for SCl₂ of 10⁻⁷ exceeds his estimate of its mixing ratio by at least an order of magnitude. The SCl₂ mixing ratio in the models whose results are shown in Table 5 and in Pernice *et al.* [2004] is less than 10⁻⁹ with the maximum in the lowest layer at 58 km altitude.

Croconic acid. Hartley *et al.* [1989] proposed croconic acid (C₅O₅H₂) as a candidate for the second absorber based on their measurement of its absorption spectrum. They carried out radiative transfer calculations to show that sulfuric acid aerosols mixed with 2.5% of croconic acid can produce the observed UV contrast in the clouds of Venus. According to Hartley *et al.*, croconic acid can be produced by reactions involving CO and HO_x, for example, in the equilibrium



Its production is proportional to [CO]⁶ and should be maximum near 40 km, because this acid decomposes at 40 km (T = 150°C). All these facts reduce the possibility of C₅O₅H₂. Widemann *et al.* [1993] reported a negative detection of croconic acid in the spectra of Venus' atmosphere taken with the VEGA probe.

Ammonium pyrosulfite. Titov [1983] studied the formation of aerosol in a mixture of SO₂, NH₃, and H₂O, and found that ammonium pyrosulfite, (NH₄)₂S₂O₅, resulted from the mixture. He studied the absorption spectrum of (NH₄)₂S₂O₅ and found that the mixture of NH₃ with H₂SO₄ has spectral characteristics similar to that of the second absorber. Krasnopolsky [1985] points out that formation of ammonium pyrosulfate is enhanced at low temperatures. This would predict an anti-correlation between the albedo at 365 nm and the radiance at 11.5 μm (this latter wavelength is sensing the upper cloud temperature), which is not seen in PV observations.

Nitrosylsulfuric acid. NOHSO₄ [Watson *et al.*, 1979; Sill, 1983]. Unfortunately, it only has weak blue absorption and requires the presence of NO and NO₂ with abundances that seem incompatible with the upper limit of 6 ppb for NO₂ and with the expected production of NO by lightning if it really occurs on Venus. These negative comments are still true, although Krasnopolsky [2006] has observed 5.5 ppb of NO below 60 km.

S₂O. Hapke and Graham [1985, 1989] proposed that disulfur monoxide (S₂O) and polysulfur oxides (PSO) may be responsible for the UV markings in the clouds of Venus. They measured the relative reflectance of S₂O frost at 77K, and found that it has a low reflectivity in the wavelength region from 200 to 500 nm. Na and Esposito [1997] estimated the chemical lifetime and vertical distribution of S₂O, both of which match the second absorber. Its obvious chemical connection with SO₂ could explain the correlations of the dark markings with SO₂ enhancements. Unfortunately, we do not have a good spectrum measured for the gas phase. In addition, recent ab-initio calculations [Groves and Lewars, 2000] suggest (SO)₂, the precursor to S₂O, may not be as stable as has been assumed but there are no experimental data.

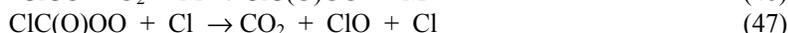
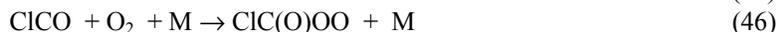
Of the candidates discussed above, elemental sulfur, S₂O, and ferric chloride solution in sulfuric acid are good candidate species for being responsible for the observed absorption at 320-500 nm, perhaps even in combination. Venus Express images and spectra will allow real progress on this topic!

7 EMERGING DEVELOPMENTS: COUPLING AMONG CYCLES AND NITRIC OXIDE

7.1 COUPLING AMONG CHEMICAL CYCLES

The three chemical cycles couple at a number of key points. First, as discussed in Section 3, the middle and lower atmosphere portions of the two sulfur cycles are believed to balance each other, on the assumption that the atmosphere is near a long-term equilibrium point. However, little modeling has been done across the boundary between photochemistry and thermochemistry and there appear to be inconsistencies between the best fit solutions derived for each altitude region. *Esposito et al.* [1997] provide an excellent discussion of these issues, so only a summary is provided here. Model 1 from *Krasnopolsky and Pollack* [1994] assumes a lower production rate for H₂SO₄ ($2.2 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$), places the lower cloud boundary at 48.4 km (agrees with *in-situ* data), and predicts the H₂O mixing ratio is 30 ppm at 30 km (agrees with *Pollack et al.* [1993]). Model 1 can be roughly correlated with Yung and DeMore's Model C which has good kinetic data for the middle atmosphere. Model 2 from *Krasnopolsky and Pollack* [1994] assumes a higher production rate for H₂SO₄ ($6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$), places the lower cloud boundary at 46.5 km (agrees with radio occultations), and predicts the H₂O mixing ratio is 90 ppm at 30 km (close to *Moroz et al.* [1983]). Model 2 can be roughly correlated with *Krasnopolsky and Parshev's* [1981] photochemical model. *Yung and DeMore's* [1982] Model C has much firmer photochemical data but the predicted O₂ column abundance exceeds the spectroscopic upper limit by an order of magnitude. *Krasnopolsky and Parshev's* [1981] model overpredicts the O₂ column abundance by only a factor of two but key kinetic data underlying the calculations were not correct (Section 5). Modeling and data over the depth of the cloud layers are needed to resolve these apparent conflicts.

The CO₂ and sulfur oxidation cycles are also linked near the cloud tops in a manner that can efficiently break the O-O bond in O₂ [*Yung and DeMore*, 1982]. The essence of the chemical scheme may be summarized as



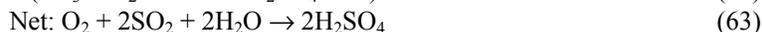
where ClC(O)OO is the peroxychloroformyl radical and M is a third body (ambient atmosphere). Note that this scheme oxidizes SO₂ to H₂SO₄ while oxidizing CO to CO₂. The relative importance of Reaction (52), when compared to Reactions (38), (40), and (42), determines the efficiency with which the O-O bond in O₂ is broken. Reaction (52) likely requires vertical transport of ClC(O)OO or SO because photodissociation of CO₂ occurs predominantly above 75 km altitude while photodissociation of SO₂ occurs predominately below 70 km altitude, vertical transport of significant amounts of O₂ would likely require violating the observational upper limit on its abundance, and the lifetime of ClO should be short.

Cl-SO₂ interaction can lead to formation of sulfuryl chloride, SO₂Cl₂, [*DeMore et al.*, 1985] via



The inclusion of Reaction (53) but not Reaction (54) in the models whose results are presented in Table 5 increases the SO₂ scale height near 70 km altitude from ~ 2.5 km [Yung and DeMore, 1982] to ~ 3.0-3.5 km, both of which are within the 2-4 km observational constraint [Na et al., 1994]. This buffering of SO₂ also contributes to decreasing the H₂SO₄ production rate from 1.4 x 10¹² cm⁻² s⁻¹ [Yung and DeMore, 1982] to ~ 5 x 10¹¹ cm⁻² s⁻¹, which is closer to an early observational estimate of the H₂SO₄ production rate, ~ 2 x 10¹¹ cm⁻² s⁻¹ [Winick and Stewart, 1980]. All of these production rates for H₂SO₄ from photochemical models are smaller than those required to match Models 1 and 2 [Krasnopolsky and Pollack, 1994] and suggest either there may be a constraint that was not considered by Krasnopolsky and Pollack [1994] or a critical process is missing from these photochemical models. Krasnopolsky and Pollack [1994] assumed the upper limit on the H₂SO₄ production rate was the photodissociation rate of SO₂. However, production of SO₂ via Reactions (5) and (6) is rapid, so the upper limit on the H₂SO₄ production rate should be the net production rate of O which may be much smaller than the photodissociation rate of SO₂. Alternatively, the large H₂SO₄ production rates required for Models 1 and 2 may indicate production of H₂SO₄ is much faster than current photochemical models predict.

One way the rate of formation of sulfuric acid might be enhanced is via Cl-SO₂ interactions



DeMore et al. [1985] proposed these processes could be quite important in the Venus atmosphere but they have not been developed further. The interaction of chlorine and sulfur chemistry in the Venus cloud layers merits further study as it provides key links among the primary chemical cycles and may provide a mechanism for sequestering oxygen for transport to the lower atmosphere.

7.2 NITRIC OXIDE (NO)

Lightning is equivalent to thermodynamic equilibrium chemistry at high temperatures, initially in excess of 30,000 K in the fireball, but as temperature decreases rapidly due to adiabatic expansion, the constituents are quenched at about 2000 K. The net result may be summarized by the chemical scheme [Yung and McElroy, 1979],



This scheme is analogous to that operating in the present terrestrial atmosphere [Price et al., 1997], where NO is made via the chemical scheme,



On Venus, as it was on prebiotic Earth, CO₂ replaces O₂ as the oxidant for N₂. The NO is eventually removed by reactions above the cloud tops,



8 COMPARISONS TO OTHER PLANETS

8.1 COMPARISONS AMONG VENUS, THE EARTH, AND MARS

Catalytic chemistry plays fundamental roles in the atmospheres of all three planets [see, *e.g.*, *Yung and DeMore*, 1999]. This means trace abundances of highly reactive radicals govern the primary chemical cycles on each planet. On Venus, a small amount of Cl has a major impact on the production of CO₂ from CO and O₂. On the Earth, hydrogen, nitrogen, and halogen radicals play an analogous role. The most prominent example is the regulation of the stratospheric ozone layer. A large number of the catalytic cycles are of the form



where X = H, OH, NO, Cl and Br. The net result of these catalytic cycles is the destruction of O₃. On Mars the key catalytic cycle that recombines CO and O to form CO₂ involves hydrogen radicals [*McElroy and Donahue*, 1972].



A similar scheme by *Parkinson and Hunten* [1972] is also important.

The greatest difference between Venus and Earth concerns the amount of water on these two planets [see, *e.g.*, *Yung and DeMore*, 1999]. The mixing ratio of water vapor in the lower atmosphere of Venus is variable, with a maximum value of 1.5×10^{-4} . This is equivalent to a layer of 2-10 cm of water, uniformly spread over the surface of the planet. For comparison, Earth contains an average layer of 2.7 km of water, residing mostly in the oceans. The lack of an ocean on Venus has at least three dramatic consequences for the atmosphere. First, most of the planet's CO₂ remains in the atmosphere, in contrast to Earth, where most of the 50 bars of CO₂ are sequestered as carbonate rock in the sediments. Second, the atmosphere of Venus contains large quantities of SO₂. On Earth, most of the volatile sulfur resides in the ocean as sulfate ions. The presence of this large amount of SO₂ in the atmosphere is responsible for the production of a dense H₂SO₄ cloud on Venus. Third, the atmosphere of Venus contains large amounts of HCl. On Earth, the bulk of chlorine is in the form of salt (NaCl) in the oceans.

8.2 ATMOSPHERIC CHEMISTRY AND ATMOSPHERIC EVOLUTION

It is now generally accepted that the origin of water in the planets is dehydration of hydrous minerals during formation. The bulk of infalling material has composition similar to that of CI chondrites, which contain up to 3 wt% H₂O. Once the accreting planetary body exceeds a critical size, impact velocities become sufficiently high that devolatilization can start. The critical radii, R₁, for Earth, Venus, and Mars are about 20%, 20%, and 40% of their present radii, respectively. Complete devolatilization (total loss of H₂O to space) can occur when the planets grow to another critical radius, R₂. The values for R₂ are roughly 50% of the present radii for the Earth and Venus; Mars never reached R₂. This implies that the terrestrial planets all should have acquired massive amounts of water of the order of terrestrial oceans. Why, then, is the ocean of water absent from Venus?

In a seminal paper, *Ingersoll* [1969] showed that water vapor could have been a major constituent in the atmosphere of Venus, and that photolysis of H₂O, followed by hydrogen escape could approach the UV

photon limit of about $10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. Under such conditions, an amount of water equivalent to the terrestrial ocean could be lost in 100 Myr.

Evidence that the atmosphere of Venus has lost most of its water (assuming it had acquired a large quantity) came from the Pioneer Venus measurements of the D/H ratio, which is about 100 times the terrestrial value [McElroy *et al.*, 1982; Donahue *et al.*, 1982] and has been confirmed by Earth-based spectroscopy [deBergh *et al.*, 1991]. This implies that Venus has likely lost at least the equivalent of 100 times more water than its present reservoir. The loss of hydrogen from Venus is determined by the efficiency of the escape processes and the rate at which hydrogen is transferred from the lower atmosphere to the upper atmosphere where the escape processes operate [Gurwell and Yung, 1993]. Kasting and Pollack [1983] suggested the early escape of hydrogen from Venus could have been a hydrodynamic process rather than kinetic evaporation from the exosphere. However, there was no evidence for hydrodynamic escape from a planetary atmosphere until the recent observation of H atoms escaping from the extrasolar planet HD209458b [Vidal-Madjar *et al.*, 2003]. Liang *et al.* [2003] showed that the source of the H atoms that fuel the hydrodynamic escape on this planet is photolysis of H₂O. This process could have been the same as the one postulated by Ingersoll [1969] for the atmosphere of Venus.

The D/H ratio in water vapor on Mars also is enhanced, but by a factor of 6 [Owen *et al.*, 1988], which implies that Mars also may have lost large amounts of water in the past [Yung *et al.*, 1988; Kass and Yung, 1995; 1999; Cheng *et al.*, 1999; Miller and Yung, 2000]. This enrichment of D over H is largely the result of photochemical processes that preferentially dissociate H₂O relative to HDO and the lower efficiency for the escape of D relative to H at the exobase (where the atmosphere merges into space). In addition, Bertaux and Montmessin [2001] point out that there is a trap for deuterium on Mars due to water vapor condensation. The authors name this the “deuteropause”, by analogy with the tropopause in the terrestrial atmosphere [Moyer *et al.*, 1996; Kuang *et al.*, 2003]. One implication of these theories about Mars’ evolution theory is that Mars must have been warmer in the past, which implies it was more likely to have been habitable.

It is a remarkable fact that the Earth has remained habitable throughout its planetary history even though the solar luminosity has increased substantially. The major energy source for the solar system is the sun. The sun's luminosity has gradually increased by about 40% since the origin of the solar system. The reduced solar constant during the nascent period of the Earth would imply that the planet was completely frozen, a result in conflict with known geological evidence (e.g., sedimentary rocks). A resolution of this paradox is to postulate that the CO₂ content of the atmosphere has been changing with time to compensate for the changing solar constant. According to the Gaia hypothesis, the biosphere may indeed have evolved since its origin to counteract the problem of the increasing luminosity of the sun. However, there is a finite limit to the power of Gaia. The abundance of CO₂ is now very low, while the luminosity of the sun continues to increase. Further decrease of CO₂ by biological activity may be difficult because photosynthesis itself stops when the CO₂ mixing ratio falls below a threshold level of about 150 ppmv. Thus, there is a point beyond which the Gaian control of the global environment would fail and the Earth would become Venus-like in 30-300 Myr [Lovelock and Whitfield, 1982]. Venus may be the ultimate graveyard of all terrestrial planets above a certain critical size (see Chapter 11 by Bullock *et al.*).

8.3 IMPLICATIONS OF VENUS CLOUDS AND CHEMISTRY FOR STUDIES OF EXTRA-SOLAR PLANETS

NASA is undertaking a major effort to find terrestrial planets around other stars. A hope is that they may resemble Earth. A likely possibility from the present state of the solar system, and from the increasing luminosity of the Sun, is that some significant fraction of these terrestrial planets will resemble Venus. Many of the observable characteristics of a terrestrial planet resembling Venus are determined by its atmospheric chemistry and clouds. The first observations will not resolve an extra-solar planet: its global brightness, variability and spectrum will be the first measurements. The mass, radius and albedo can also be inferred from the observations. It is important to remember that the observed temperature may differ from

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the effective temperature and also from the surface temperature. Venus provides an excellent example in our own solar system.

The distinctive characteristics of Venus would be clear to the first observations from another solar system:

1. High albedo with blue and UV broadband absorption.
2. CO₂ atmosphere, detectable from CO₂ absorption bands and CO emissions.
3. Lack of water, from absence of H₂O absorption bands and OH emission.
4. Clouds of H₂SO₄, inferred from SO₂ absorption bands.
5. In the UV, Venus' brightness will vary over the 4-day super-rotation of the cloud-top markings.

Thus, Venus-like planets could be clearly distinguished from potentially habitable Earth-like planets. The models we have developed for Venus' clouds and chemistry (along with the coupled radiation and dynamics) provide a starting point for understanding those planets. Since our evolutionary models of Venus may encompass Earth's future evolution, this may allow inferences about whether Venus-like planets around other stars ever *were* habitable, and thus to examine the effects of the runaway greenhouse in other solar systems.

9 RECOMMENDATIONS AND FUTURE DIRECTIONS

Better observations of atmospheric composition, including vertical, horizontal, and temporal variations are required to advance our understanding of Venus' clouds and chemistry.

1. The most critical observation required for understanding the chemistry of the middle atmosphere is a determination of the ground-state O₂ abundance. Venus Express will not provide this, but high resolution (resolving power $\sim 400,000$) ground-based spectra might determine its column abundance.
2. Vertical profiles of the time-varying O₂(¹Δ) airglow emission and O₃ abundances from Venus Express will constrain models of the oxygen chemistry and limit the range of acceptable models.
3. The most direct observational test of the proposed chlorine chemistry would be detection of ClCO₃, which may be possible now that its structure and spectroscopy are known [Pernice *et al.*, 2004]. Observing COCl₂, ClO, or Cl₂ from Venus Express would provide important indirect tests.
4. Direct observational tests of sulfur chemistry will be provided by three-dimensional maps of SO₂, SO, H₂S (if present and observable), and OCS derived from Venus Express spectroscopy and VMC images.

Better observations of cloud particle properties and their variation also are required. The size distribution, shape, and composition of the majority of the aerosol mass are still open, despite our assurance that "mode 2" (the aerosols visible at the cloud tops) are spherical droplets of concentrated sulfuric acid. Venus Express will make remote measurements of the clouds. Multiple observations will be combined to improve our understanding. Key tasks are to compare, reconcile and consolidate these measurements.

The information expected from Venus Express also should justify more detailed studies of the interactions among radiation, clouds, chemistry and dynamics. For example,

1. Simultaneous three-dimensional maps of time-varying temperatures and the abundances of CO and other species will permit development of multi-dimensional chemical transport models.
2. Spatially-resolved observations of H₂O are needed to understand the large temporal variations reported in ground-based studies [Sandor and Clancy, 2005] and to refine our understanding of the cloud layers.

Determination of the mineralogy on the surface of Venus is needed for significant progress on understanding the chemical interaction between the atmosphere and surface and how this interaction may have changed over the course of Venus' evolution.

The most important laboratory measurement needed for understanding the chemistry in the Venus middle atmosphere is a more accurate determination of the equilibrium constant for ClCO and any temperature dependence. Verification of the rate for Reaction (34) which forms ClCO₃ and an assessment of its uncertainties is also needed. Laboratory measurements are also required to assess whether more speculative schemes for oxidizing CO, such as heterogeneous reactions, are sufficiently rapid. Finally, laboratory spectra will be the only means by which the unknown UV absorber can be identified. Spectra do not exist for many of the proposed candidates, so it is not possible to compare model calculations with observations.

The discovery of NO presents the exciting possibility that heterogeneous chemistry on the surface of sulfate aerosols may convert the reservoir species of chlorine into active species, which can then participate in catalytic chemistry. The reservoir species (HCl, ClONO₂) are chemically unreactive, but the labile species can readily participate in catalysis. These reactions have been shown to play a major role in the destruction of ozone in the Earth's atmosphere [Solomon *et al.*, 1997].

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11 REFERENCES

- Allen, D. A., and J. W. Crawford (1984), Cloud structure on the dark side of Venus. *Nature*, *307*, 222-224.
- Andreichikov, B.M. (1987), Chemical composition and structure of the clouds of Venus inferred from the results of X-ray fluorescent analysis on descent probes VEGA 1 and 2, *Kosmich. Issled.*, *25*, 737-743 (in Russian).
- Andreichikov *et al.* (1987),
- Andreychikov, B.M., *et al.* (1987), X-ray radiometric analysis of the cloud amount of Venus by the Vega 1 and 2 probes, *Kosmich. Issled.*, *25*, 721-736 (in Russian).
- Barker, E. S. (1979), Detection of SO₂ in the UV spectrum of Venus, *Geophys. Res. Lett.*, *6*, 117-120.
- Barker, E.S., *et al.* (1975) Relative spectrophotometry of Venus from 3067 to 5960 Å, *J. Atmos. Sci.*, *32*, 1205.
- Bertaux, J.L., and F. Montmessin (2001), Isotopic Fractionation through Water Vapor Condensation: The Deuteropause, a Cold Trap for Deuterium in the Atmosphere of Mars., *J. Geophys. Res.*, *106* (E12), 32879-32884.
- Bertaux, J-L, T. Widemann, A. Hauchecorne, V.I. Moroz, and A.P. Ekonomov (1996), VEGA 1 and VEGA 2 entry probes: An investigation of local UV absorption (220-400 nm) in the atmosphere of Venus (SO₂, aerosols, cloud structure), *J. Geophys. Res.*, *101*, 12709-12745.
- Bezard, B., C. deBergh, B. Fegley, J-P Maillard, D. Crisp, T. Owen, J.B. Pollack, and D. Grinspoon (1993), The abundance of sulfur-dioxide below the clouds of Venus, *Geophys. Res. Lett.*, *20*, 1587-1590.
- Braak, C.J., J.F. de Haan, J.W. Hovenier, and L.D. Travis (2002), Spatial and temporal variations of Venus haze properties obtained from Pioneer Venus Orbiter polarimetry, *J. Geophys. Res.*, *107* (E5), 5029.
- Butler, B.J., P.G. Steffes, S.H. Suleiman, and J.M. Jenkins (2001), Accurate and consistent microwave observations of Venus and their implications, *Icarus*, *154*, 226-238.
- Cheng, B.M., E. P. Chew, C. P. Liu, M. Bahou, Y. P. Lee, Y. L. Yung and M. F. Gerstell (1999), Photo-induced fractionation of water isotopomers in the Martian atmosphere, *Geophys. Res. Lett.*, *26*, 3657-3660.
- Cimino, J. (1982), The composition and vertical structure of the lower cloud deck on Venus, *Icarus*, *51*, 334-357.
- Clancy, R.T., and Muhleman, D.O. (1991), Long-term (1979-1990) changes in the thermal dynamical, and compositional structure of the Venus mesosphere as inferred from microwave spectral observations of ¹²CO, ¹³CO and C¹⁸O, *Icarus*, *89*, 129-146.
- Connes, P., Connes, J., Kaplan, L., and Benedict, W. (1967), Traces of HCl and HF in the atmosphere of Venus, *Ap. J.*, *147*, 1230-1237.
- Connes, P., Noxon, J.F., Traub, W.A., and Carleton, N.P. (1979), O₂(¹Δ) emission in the day and night airglow of Venus, *Astrophys. J. Lett.*, *233*, 29-32.
- Conway, R.R., McCoy, R.P., Barth, C.A., and Lane, A.L. (1979), IUE detection of sulfur dioxide in the atmosphere of Venus, *Geophys. Res. Lett.*, *6*, 629-631.
- Crisp, D., D. Titov. (1997), The thermal balance of the Venus atmosphere, in *Venus II* edited by S. W. Bougher, D. M. Hunten, and R. J. Phillips, pp. 353-384, Univ. of Arizona Press, Tucson.
- Crisp, D., Meadows, V.S., Bezard, B., de Bergh, C., Maillard, J-P., and Mills, F.P. (1996), Ground-based Near-Infrared Observations of the Venus Night Side: Near-Infrared O₂(¹Δ) Airglow from the Upper Atmosphere, *J. Geophys. Res.*, *101*, 4577-4593.
- Dalton, J.B., J.B. Pollack, D.H. Grinspoon, B. Bezard, and C. de Bergh (2000), Distribution of chlorine in the lower atmosphere of Venus, *Bull. Am. Astron. Soc.*, *32*, 1120. Presented at the 32nd Annual Meeting of the Division of Planetary Sciences of the American Astronomical Society, Pasadena, CA, October 27, 2000.
- deBergh, C., B. Bezard, T. Owen, D. Crisp, J-P Maillard, and B.L. Lutz (1991), Deuterium on Venus – Observations from Earth, *Science*, *251*, 547-549.
- deBergh, *et al.* (2006),
- DeMore, W.B., M-T. Leu, R.H. Smith, and Y.L. Yung (1985), Laboratory studies on the reactions between chlorine, sulfur dioxide, and oxygen: Implications for the Venus stratosphere, *Icarus*, *63*, 347-353.

ATMOSPHERIC COMPOSITION, CHEMISTRY, AND CLOUDS

- Donahue, T. M., *et al.* (1982), Venus was wet - a measurement of the ratio of deuterium to hydrogen, *Science*, *216*, 630-633.
- Ekonomov, A.P., *et al.* (1983), UV photometry at the VENERA 13 and 14 landing probes, *Cosmic Res.*, *21*, 194-206.
- Ekonomov, *et al.* (1984),
- Esposito, L. W. (1980), Ultraviolet contrasts and the absorbers near the Venus cloud tops. *J. Geophys. Res.*, *85*, 8151-8157.
- Esposito, L. W. (1984), Sulfur dioxide: Episodic injection shows evidence for active Venus volcanism. *Science*, *223*, 1072-1074.
- Esposito, L. W., and L. D. Travis (1982), Polarization studies of the Venus UV contrasts: Cloud height and haze variability. *Icarus*, *51*, 374-390.
- Esposito, L. W., R. G. Knollenberg, M. Y. Marov, O. B. Toon, and R. P. Turco (1983), The clouds and hazes of Venus. in *Venus*, edited by D. M. Hunten, L. Colin, T. M. Donahue, and V. I. Moroz, pp. 484-564, Univ. of Arizona Press, Tucson.
- Esposito, L. W., M. Copley, R. Eckert, L. Gates, A. I. F. Stewart, and H. Worden (1988), Sulfur dioxide at the Venus cloud tops, 1978-1986. *J. Geophys. Res.*, *93*, 5267-5276.
- Esposito, L.W., J.L. Bertaux, V. Krasnopolsky, V.I. Moroz, and L.V. Zasova (1997), Chemistry of lower atmosphere and clouds, in *Venus II*, edited by S.W. Bougher, D.M. Hunten, and R.J. Phillips, pp. 415-458, Univ. of Arizona Press, Tucson.
- Fegley, B., Jr., G. Klingelhofer, K. Lodders, and T. Widemann (1997), Geochemistry of surface-atmosphere interactions on Venus. in *Venus II*, edited by S.W. Bougher, D.M. Hunten, and R.J. Phillips, pp. 591-636, Univ. of Arizona Press, Tucson.
- Groves, C., and E. Lewars (2000), Dimers, trimers, and oligomers of sulfur oxides: An ab initio and density functional study, *J. Molec. Structure*, *530*, 265-279.
- Gubenko, V.N., O.I. Yakovlev, and S.S. Matyugov (2001) Radio occultation measurements of the radio wave absorption and the sulfuric acid content in the atmosphere of Venus, *Cosmic Res.*, *39*, 439-445.
- Gurwell, M. A., and Y. L. Yung (1993), Fractionation of hydrogen and deuterium on venus due to collisional ejection, *Planet. Space Sci.*, *41*, 91-104.
- Hapke, B., and F. Graham (1985), Disulfur monoxide and the spectra of Io and Venus. *Lunar Planet. Sci.*, *XV*, 316-317 (abstract).
- Hapke, B. and F. Graham (1989), Spectral Properties of Condensed Phases of Disulfur Monoxide, Polysulfur Oxide, and Irradiated Sulfur. *Icarus*, *79*, 47-55.
- Hapke, B., and R. Nelson (1975), Evidence for an Elemental Sulfur Component of Clouds from Venus Spectrophotometry, *J. Atmos. Sci.*, *32*, 1212-1218.
- Hartley, K.K., A.R. Wolf, and L.D. Travis (1989), Croconic acid: An absorber in the Venus clouds? *Icarus*, *77*, 382-390.
- Hoffman, J.H., R.R. Hodges, Jr., T.M. Donahue, and M.B. McElroy (1980), Composition of the Venus lower atmosphere from the Pioneer Venus mass spectrometer. *J. Geophys. Res.*, *85*, 7882-7890.
- Huggins, W., and W.A. Miller (1864), On the spectra of some of the fixed stars. *Phil. Trans. Royal Soc. London*, *154*, 413-435.
- Imamura, T., and G.L. Hashimoto (1998), Venus cloud formation in the meridional circulation, *J. Geophys. Res.*, *103*, 31349-31366.
- Ingersoll, A. P. (1969), Runaway greenhouse: A history of water on Venus, *J. Atmos. Sci.*, *26*(6), 1191-1198.
- Jenkins, J.M., M.A. Kolodner, B.J. Butler, S.H. Suleiman, and P.G. Steffes (2002), Microwave remote sensing of the temperature and distribution of sulfur compounds in the lower atmosphere of Venus, *Icarus*, *158*, 312-328.
- Johnson, N.M., and B. Fegley, Jr. (2002), Experimental studies of atmosphere-surface interactions on Venus. *Adv. Space Res.*, *29*(2), 233-241.
- Kass, D.M., and Y.L. Yung (1995), Loss of Atmosphere from Mars Due to Solar Wind-Induced Sputtering, *Science*, *268* (5211), 697-699.
- Kass, D.M., and Y.L. Yung (1999), Water on Mars: Isotopic Constraints on Exchange Between the Atmosphere and Surface, *Geophys. Res. Lett.*, *26* (24), 3653-3656.
- Kasting, J. F., and J. B. Pollack (1983), Loss of water from venus .1. hydrodynamic escape of hydrogen, *Icarus*, *53*, 479-508.
- Knollenberg, R.G., and D.M. Hunten (1980), Results of the Pioneer Venus particles and size spectrometer experiment. *J. Geophys. Res.*, *85*, 8039-8058.
- Knollenberg, R., L. Travis, M. Tomasko, P. Smith, B. Ragent, L. Esposito, D. McCleese, J. Martonchik, and R. Beer. (1980), The clouds of Venus: A synthesis report, *J. Geophys. Res.*, *85*, 8059-8081.
- Kondratiev, V.N. (1971), *Rate Coefficients of Gas Phase Reactions*, Nauka Press, Moscow.

- Koukouli, M.E., P.G.J. Irwin, and F.W. Taylor (2006), Water vapor abundance in Venus' middle atmosphere from Pioneer Venus OIR and Venera 15 FTS measurements, *Icarus*, 173, 84-99.
- Krasnopolsky, V.A. (1985), Chemical composition of Venus' clouds. *Planet. Space Sci.*, 33, 109-117.
- Krasnopolsky, V.A. (1986), *Photochemistry of the atmosphere of Mars and Venus*, Springer-Verlag, Berlin.
- Krasnopolsky, V.A. (1989), Vega mission results and chemical composition of Venusian clouds. *Icarus*, 80, 202-210.
- Krasnopolsky, V.A. (2006), A sensitive search for nitric oxide in the lower atmospheres of Venus and Mars: Detection on Venus and upper limit for Mars, *Icarus*, in press.
- Krasnopolsky V.A., and V.A. Parshev (1980),
- Krasnopolsky, V.A., and V.A. Parshev (1981), Chemical-Composition of the Atmosphere of Venus, *Nature*, 292, 610-613.
- Krasnopolsky, V. A., and V. A. Parshev (1983), Photochemistry of the Venus atmosphere. in *Venus*, edited by D. M. Hunten, L. Colin, T. M. Donahue, and V. I. Moroz, pp.431-458, Univ. Arizona Press, Tucson.
- Krasnopolsky, V. A., and J. B. Pollack (1994), H₂O-H₂SO₄ system in Venus' clouds and OCS, CO, and H₂SO₄ profiles in Venus' troposphere. *Icarus*, 109, 58-78.
- Kuang, Z.M., G.C. Toon, P.O. Wennberg, and Y.L. Yung (2003), Measured HDO/H₂O ratios across the tropical tropopause, *Geophys. Res. Lett.*, 30(7), 1372, doi:10.1029/2003GL017023.
- Lewis, J.S. (1970), Venus: atmospheric and lithospheric composition. *Earth Planet. Sci. Lett.*, 10, 73-80.
- Liang, M. C., et al. (2003), Source of atomic hydrogen in the atmosphere of HD209458b, *Astrophys. J. Lett.*, 596, 247-250.
- Linkin, V.M., et al. (1985),
- Lovelock, J. E., and M. Whitfield (1982), Life-span of the biosphere, *Nature*, 296, 561-563.
- Maierov, B.S., et al. (2005), A new analysis of the spectra obtained by the VENERA missions in the Venusian atmosphere. I. The analysis of the data received from the VENERA-11 Probe at altitudes below 37 km in the 0.44 – 0.66 μm wavelength range, *Solar System Research*, 39, 267-282.
- Mallama, A., D. Wang, and R.A. Howard (2006), Venus phase function and forward scattering from H₂SO₄, *Icarus*, in press.
- Marcq, E., Bruno, B., Encrenaz, Th., and Birlan, M. (2005), Latitudinal variations of CO and OCS in the lower atmosphere of Venus from near-infrared nightside spectro-imaging. *Icarus*, 179, 375-386.
- Marcq, E., T. Encrenaz, B. Bezard, M. Birlan. (2006), Remote sensing of Venus' lower atmosphere from ground-based IR spectroscopy: latitudinal and vertical distribution of minor species. Submitted to *Elsevier Science*.
- McElroy, M.B., and T.M. Donahue (1972), Stability of the Martian atmosphere, *Science*, 177, 986-988.
- McElroy, M.B., et al. (1982), Escape of Hydrogen from Venus, *Science*, 215, 1614-1615.
- Miller, C.E., and Y.L. Yung (2000), Photo-induced Isotopic Fractionation, *J. Geophys. Res.* 105, 29039-29051.
- Mills, F.P. (1998), I. Observations and Photochemical Modeling of the Venus Middle Atmosphere. II. Thermal Infrared Spectroscopy of Europa and Callisto, Ph.D. dissertation, 366 pp., California Institute of Technology, Pasadena, Calif.
- Mills, F.P. (1999a), Water vapor in the Venus middle atmosphere, *Adv. Space Res.*, 23(9), 1573-1576.
- Mills, F.P. (1999b), A spectroscopic search for molecular oxygen in the Venus middle atmosphere, *J. Geophys. Res.*, 104, 30757-30763.
- Mills, F.P., M. Sundaram, T.G. Slanger, M. Allen, and Y.L. Yung (2006), Oxygen chemistry in the Venus middle atmosphere, in *Advances in Geoscience Volume 3: Planetary Science (PS)*, edited by W-H Ip and A. Bhardwaj, pp. 109-117, World Scientific Publishing, Singapore.
- Moroz, V.I., et al. (1979),
- Moroz, V.I., et al. (1983), The VENERA 13 and 14 spectrophotometric experiment. II. Preliminary analysis of H₂O absorption bands in spectra, *Cosmic Res.*, 21, 187-194.
- Moroz, V. I., W. Dohler, E. A. Ustinov, K. Schafer, L. V. Zasova, D. Spankuch, A. A. Dyachkov, R. Dubois, V. M. Linkin, D. Oertel, V. V. Kerzhanovich, I. Nopirakovskii, I. A. Matsygorin, H. Becker-Ross, A. A. Shurupov, W. Stadthaus, and A. N. Lipatov (1985), VENERA 15 and VENERA 16 infrared experiment. 4. Preliminary results of spectral analyses in the region of H₂O and SO₂ absorption bands, *Cosmic Res.*, 23, N2, 202-211.
- Moroz, V. I., D. Spankuch, V. M. Linkin, W. Dohler, I. A. Matsygorin, K. Schafer, L. V. Zasova, D. Oertel, A. V. Dyachkov, R. Schuster, V. V. Kerzhanovich, H. Becker-Ross, E. A. Ustinov, and W. Stadthaus (1986), Venus spacecraft infrared radiance spectra. Some aspects of their interpretation, *Applied Optics*, 25, N10.
- Moroz, V. I., D. Spankuch, D. V. Titov, K. Schafer, A. V. Dyachkov, W. Dohler, L. V. Zasova, D. Oertel, V. M. Linkin, and J. Nopirakowski (1990), Water vapor and sulfur dioxide abundances at the Venus cloud tops from the VENERA 15 infrared spectrometry data, *Adv. Space Res.*, 10, N5, 77.
- Moyer, E. J., F. W. Irion, Y. L. Yung, and M. R. Gunson. (1996). ATMOS Stratospheric Deuterated Water and Implications for Troposphere-Stratosphere Transport, *Geophys. Res. Lett.*, 23, 2385-2388.
- Na, C.Y., and L.W. Esposito, L.W (1995), UV observations of Venus with HST, *Bull. Amer. Astron. Soc.*, 27, 1071 (abstract).

ATMOSPHERIC COMPOSITION, CHEMISTRY, AND CLOUDS

- Na, C.Y., and L.W. Esposito (1996),
 Na, C. Y., and L. W. Esposito (1997), Is disulfur monoxide the second absorber on Venus? *Icarus*, *125*, 361–368.
 Na, C. Y., L. W. Esposito, and T. E. Skinner (1990), International Ultraviolet Explorer observation of Venus SO₂ and SO, *J. Geophys. Res.*, *95*, 7485–7491.
 Na, C. Y., L. W. Esposito, W. E. McClintock, and C. A. Barth (1994), Sulfur dioxide in the atmosphere of Venus, II. Modeling results. *Icarus*, *112*, 389–395.
 Nicovich, J., K. Kreutter and P. Wine (1990), Kinetics and thermochemistry of ClCO formation from the Cl+CO association reaction, *J. Chem. Phys.*, *92*, 3539-3544.
 Owen, T., and C. Sagan (1972), Minor constituents in planetary atmospheres: Ultraviolet spectroscopy from the Orbiting Astronomical Observatory, *Icarus*, *16*, 557-568.
 Owen, T., J-P. Maillard, C. de Bergh, and B.L. Lutz (1988), Deuterium on Mars: The Abundance of HDO and the Value of D/H, *Science*, *240* (4860), 1767-1770.
 Oyama, V.I., G.C. Carle, F. Woeller (1980), Corrections in the Pioneer Venus Sounder probe gas-chromatographic analysis of the lower Venus atmosphere, *Science*, *208*, 399-401.
 Parkinson, T.D., and D.M. Hunten (1972), Spectroscopy and aeronomy of O₂ on Mars, *J. Atmos. Sci.*, *29*(7), 1380-1390.
 Pernice, H., *et al.* (2004), Laboratory evidence for a key intermediate in the Venus atmosphere: Peroxychloroformyl radical, *Proc. Natl. Acad. Sci. U. S. A.*, *101*, 14007-14010.
 Petryanov, I.V., *et al.* (1981), Iron in the Venus clouds. *Dokl. AN SSSR*, *260*, 834.
 Pollack, J.B., *et al.* (1980), Distribution and source of the UV absorption in Venus atmosphere, *J. Geophys. Res.*, *85*, 8141-8150.
 Pollack, J. B., J. B. Dalton, D. Grinspoon, R. B. Wattson, R. Freedman, D. Crisp, D. A. Allen, B. Bezard, C. deBergh, L. P. Giver, Q. Ma, and R. Tipping (1993), Near-infrared light from Venus' nightside: A spectroscopic analysis, *Icarus*, *103*, 1-42.
 Porshnev, N. V., L. M. Mukhin, B. G. Gelman, D. F. Nenarokov, V. A. Rotin, A. V. Dyachkov, and V. B. Bondarev (1987), Gas chromatographic analysis of products of thermal reactions of the cloud aerosol of Venus by the Vega 1 and 2 probes, *Cosmic Res.*, *25*, 715.
 Price C, Penner J, Prather M. (1997), NO_x from lightning. 1. Global distribution based on lightning physics, *J. Geophys. Res.*, *102*, 5929-5941.
 Prinn, R.G. (1971), Photochemistry of HCL and Other Minor Constituents in Atmosphere of Venus, *J. Atmos. Sci.*, *28* (6), 1058-1068.
 Prinn, R. G. (1975), Venus: chemical and dynamical processes in the stratosphere and mesosphere, *J. Atmos. Sci.*, *32*, 1237-1247.
 Prinn, R. G. (1978), Venus: chemistry of the lower atmosphere prior to the Pioneer Venus mission, *Geophys. Res. Lett.*, *5*, 973-976.
 Prinn, R. G. (1979), On the possible roles of gaseous sulfur and sulfanes in the atmosphere of Venus, *Geophys. Res. Lett.*, *6*, 807-810.
 Prinn, R.G. (1985), The photochemistry of the atmosphere of Venus, in *The Photochemistry of Atmospheres*, edited by J.S. Levine, pp. 281-336, Academic Press, Orlando.
 Rossow, W.B., *et al.* (1980), Cloud morphology and motions from Pioneer Venus images, *J. Geophys. Res.*, *85*, 8107-8128.
 Sander, S.P., *et al.* (2002), Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling Evaluation Number 14, Jet Propul. Lab. Pub. 02-25, Pasadena, Calif. (<http://jpldataeval.jpl.nasa.gov/>).
 Sandor, B.J., and R.T. Clancy (2005), Water vapor variations in the Venus mesosphere from microwave spectra, *Icarus*, *177*, 129-143.
 Sanko, (1980),
 Schaefer, *et al.* (1987),
 Schaefer, *et al.* (1990),
 Sill, G. T. (1983), The clouds of Venus: sulfuric acid by the lead chamber process. *Icarus*, *53*, 10.
 Slanger, T.G., P.C. Cosby, D.L. Huestis, and T.A. Bida (2001), Discovery of the atomic oxygen green line in the Venus night airglow, *Science*, *291*, 463-465.
 Slanger, T.G., D.L. Huestis, P.C. Cosby, N.J. Chanover, and T.A. Bida (2006), The Venus nightglow: Ground-based observations and chemical mechanisms, *Icarus*, in press.
 Solomon, S., *et al.* (1997), Heterogeneous chlorine chemistry in the tropopause region, *J. Geophys. Res.*, *102*, 21411-21429.
 Spankuch, D., L. V. Zasova, K. Schafer, E. A. Ustinov, J. Guldner, V. I. Moroz, W. Dohler, V. M. Linkin, R. Dubois, A. A. Dyachkov, H. Becker-Ross, A. A. Lipatov, W. Stadthaus, I. A. Matsygorin, D. Oertel, V. V. Kerzhanovich, I.

- Nopirokovskii, H. Jahn, G. Fellberg, W. Schuster, and A. A. Shurupov (1985), VENERA-15 and VENERA-16 infrared experiment. 2. Preliminary results of temperature profile retrieval, *Cosmic Res.*, 23, N2, 176-188.
- Spankuch, D., I. A. Matsygorin, R. Dubois, and L. V. Zasova (1990), Venus middle-atmosphere temperature from VENERA-15, *Adv. Space Res.*, 10, N5, 67.
- Stewart, A. I., D. E. Anderson, L. W. Esposito, and C. A. Barth (1979), Ultraviolet spectroscopy of Venus: Initial results from the Pioneer Venus orbiter. *Science*, 203, 777-779.
- Surkov, Yu. A. (1979),
- Surkov, Yu. A. (1981),
- Surkov, Yu. A., et al. (1984),
- Surkov, Yu. A., et al. (1986),
- Surkov, Yu. A., V. F. Ivanova, A. N. Pudov, and D. Caramel (1987), Determination of the aerosols chemical composition in the Venusian clouds by means of the mass-spectrometer MALAHIT on the VEGA-1 probe, *Kosmich. Issled.*, 15, 744-750 (in Russian).
- Taylor, F.W., D. Crisp, B. Bezdard (1997), Near-infrared sounding of the lower atmosphere of Venus, in *Venus II*, edited by S. W. Bougher, D. M. Hunten, and R. J. Phillips, pp. 325-351, Univ. of Arizona Press, Tucson.
- Tomasko, M.G., Doose, L.R., Smith, P.H., and Odell, A.P. (1980), Measurements of the flux of sunlight in the atmosphere of Venus, *J. Geophys. Res.*, 85, 8167-8186.
- Toon, O. B., R. P. Turco, J. B. Pollack (1982), The ultraviolet absorber on Venus: amorphous sulfur, *Icarus*, 51, 358.
- Trauger, J.T., and J.I. Lunine (1983), Spectroscopy of Molecular-Oxygen in the Atmospheres of Venus and Mars, *Icarus*, 55, 272-281.
- Titov, D. V. (1983), On the possibility of aerosol formation by the reaction between SO₂ and NH₃ in Venus' atmosphere, *Cosmic Res.*, 21, 401.
- Vidal-Madjar A., et al. (2003), An extended upper atmosphere around the extrasolar planet HD209458b, *Nature*, 422, 143-146.
- von Zahn, U., S. Kumar, H. Niemann, and R.G. Prinn (1983), Composition of the Venus atmosphere, in *Venus*, edited by D.M. Hunten, L. Colin, T.M. Donahue and V.I. Moroz, pp. 299-430, Univ. of Arizona Press, Tucson.
- Watson, A.J., et al. (1979), Oxides of nitrogen and the clouds of Venus, *Geophys. Res. Lett.*, 6, 743-746.
- Widemann, T., J-L. Bertaux, V.I. Moroz, and A.P. Ekonomov (1993), VEGA-1 and VEGA-2 descent modules: In-situ measurements of ultraviolet absorption and relationship with present active volcanism on Venus, *Bull. Amer. Astron. Soc.*, 25, 1094 (abstract).
- Winick, J.R., and A.I. Stewart (1980), Photochemistry of SO₂ in Venus' upper cloud layers, *J. Geophys. Res.*, 85, 7849-7860.
- Young, A.T. (1977), An improved Venus cloud model, *Icarus*, 32, 1-26.
- Young, A. T. (1983), Venus cloud microphysics. *Icarus* 56, 568.
- Young, L.D.G. (1972), High resolution spectrum of Venus – A review, *Icarus*, 17, 632-658.
- Yung, Y.L., and W.B. Demore (1982), Photochemistry of the Stratosphere of Venus - Implications for Atmospheric Evolution, *Icarus*, 51 (2), 199-247.
- Yung, Y.L., and W.B. DeMore (1999), *Photochemistry of Planetary Atmospheres*, Oxford University Press, New York.
- Yung, Y. L. and M. B. McElroy (1979) Fixation of Nitrogen in the Prebiotic Atmosphere. *Science*, 203(4384), 1002-1004.
- Yung, Y.L., J.S. Wen, J.P. Pinto, M. Allen, K.K. Pierce, and S. Paulson (1988), HDO in the Martian Atmosphere - Implications for the Abundance of Crustal Water, *Icarus*, 76 (1), 146-159.
- Zasova, L.V., V.A. Krasnopolsky and V.I. Moroz (1981), Vertical distribution of SO₂ in the upper cloud layer of Venus and origin of UV absorption, *Adv. Space Res.*, 1(9), 13-16.
- Zasova, L.V., et al. (1985),
- Zasova, L.V., et al. (1989), Venusian clouds from VENERA-15 data, *Veroffentlichungen Forschungsbereichs Geo-Kosmoswissenschaften*, 18, Akademie-Verlag, Berlin.
- Zasova, L. V., V. I. Moroz, L. W. Esposito, and C. Y. Na (1993), SO₂ in the middle atmosphere of Venus: IR measurements from Venera-15 and comparison to UV data, *Icarus*, 105, 92-109.