

Global Cloud Properties on Venus from Orbital Infrared Spectroscopy

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This thesis describes the derivation of Venusian global cloud properties from infrared remote sensing data obtained by the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) on the European Space Agency Venus Express satellite. A computationally-efficient retrieval method is designed to exploit the dataset, which provides coverage of the entire nightside southern hemisphere of Venus. Spatially-resolved near-infrared spectra have been used to derive improved models of the vertical structure and global distribution of cloud properties in the southern hemisphere. Wavelengths within transparency windows in the 1.0—2.6 μm range covered by VIRTIS are sensitive on the nightside to absorption by the lower and middle sulphuric acid cloud layers, which are back-lit by thermally-emitted radiation from the hot lower atmosphere (Taylor et al. 1997).

The cloud model used to interpret the spectra builds on work by Crisp (1986), Pollack et al. (1993) and Grinspoon et al. (1993). Retrieved parameters are the acid concentration in the cloud droplets, the average size of the particles in the lower cloud and the altitude of the cloud base in the model. Values are estimated initially using wavelength pairs selected for their unique sensitivity to each parameter, and then validated using model spectra generated using the NEMESIS radiative transfer and retrieval code (Irwin et al. 2008) as developed for Venus (Tsang et al. 2008a).

The spatial variation of sulphuric acid concentration in the cloud particles is estimated; the concentration is found to be higher in regions of optically thick cloud. The retrieved cloud base altitude varies with latitude, reaching a maximum height near -50° before falling by several km towards the pole. An increase in average particle size near the pole (Wilson et al. 2008) and latitudinally-variable CO abundance at 35—40 km altitude (Tsang et al. 2008) are both confirmed. A decrease in tropospheric H_2O abundance at high latitudes is observed, and provides evidence for strong downwelling between ± 60 and $\pm 75^\circ$ latitude, which marks the poleward extent of the Hadley cell circulation. Long-term secular change is also observed over a period of two Earth years. The measurements presented here provide a reference dataset for microphysical and dynamical modelling of the cloud deck, and the role of the cloud as a dynamical and chemical tracer means that such observations aid understanding of the Venusian atmosphere.

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Chapter 1

Introduction

This chapter provides an introduction to the planet Venus, its cloud layer and the missions that have been designed to study it, including more detail about the Venus Express mission and in particular the Visible and Infrared Thermal Imaging Spectrometer, the instrument used in this work. The final section provides a summary of the following chapters in this thesis.

1.1 The planet Venus

Venus is a rocky planet with a mass $0.81\times$ that of the Earth, orbiting the Sun at ~ 0.72 of the Earth's orbital radius. Despite these superficial similarities to our own planet, it is in reality a very different world. It has a shorter orbital period than the Earth, of 224 Earth days, and an extremely slow retrograde rotation with a period of 243 Earth days. Its obliquity from a fully retrograde rotation axis is less than 3° , so Venus experiences very little seasonal variation in solar radiation as a function of latitude. The eccentricity of the Venusian orbit is also very small, having a value of 0.0067, meaning that the orbit of Venus is almost perfectly circular. Its slow

rotation and lack of seasonal variation result in atmospheric dynamics very different to those on the Earth.

The estimated surface temperature of a Venus in radiative equilibrium with incoming solar radiation would be ~ 240 K, slightly cooler than that of the Earth due to the very high albedo of Venus. However, Venus has a massive atmosphere with a surface pressure of 92 bars, and the atmosphere is composed largely of carbon dioxide which is highly absorbing in the infrared, creating an efficient greenhouse effect. The resulting average surface temperature is closer to 740 K.

Venus is covered in a layer of cloud that extends vertically from ~ 48 –80 km. This cloud is known to be mainly composed of concentrated sulphuric acid droplets in the upper layers (Hansen and Hovenier 1974, Pollack et al. 1974), although the precise composition is still uncertain, especially in the lower regions. The cloud layer contributes to the extremely high bolometric albedo (reflectivity) of Venus, which is ~ 0.7 . High-contrast ultraviolet markings are due to an absorber in the region of the cloud top (Pollack et al. 1980), but the substance responsible is still unidentified. Likely candidates, from comparisons of recent laboratory results with Venus observations, are sulphuric aerosols, either sulphur grains or composite particles formed of liquid sulphuric acid and solid sulphur (Carlson 2010).

1.2 Previous missions to Venus

The Venus Express satellite, launched in November 2005, is the latest in a series of successful missions to Venus that began with the flyby of the NASA Mariner 2 spacecraft in 1962. Mariner 2 data provided an indication that temperatures at the surface reached at least 700 K. Several probes from the USSR successfully entered the atmosphere of Venus during the late 1960s, culminating in Venera 7 becoming the

first probe to send a signal back from the surface of another planet. The Venera series during the 1970s provided the first in-situ data from the surface and atmosphere of Venus, including initial surface rock-type indications from radioactive species abundance, relative abundances of atmospheric constituents, initial cloud profiles and wind speed data, and confirmation that the solar flux at the surface is sufficient for a runaway greenhouse to exist (Marov 1978).

The success of these missions was followed by results from the Pioneer Venus multiprobe and orbiter mission in 1978. Collated data from this mission refined the temperature structure and atmospheric gaseous abundances obtained by the Venera probes 4–10, and also detected two regions of instability in the atmosphere where overturning can occur, from 20–29 km and 52–56 km altitude (Donahue 1979). Data from orbiting infrared and ultraviolet spectrometers and the cloud polarimeter, the nephelometers, the cloud particle size spectrometer and the solar flux radiometer on the descent probes provided constraints on cloud structure and particle size. Surface topography was also observed using a radar instrument on the orbiter.

Data from these probes, combined with results from the Venera series, formed the basis for the Venus International Reference Atmosphere (Kliore et al. 1986). Included are average atmospheric temperatures, pressures and gaseous abundances as functions of altitude, which are often used as a basis for a Venusian model atmosphere in radiative transfer calculations.

The 1985 Vega 1 and 2 lander/balloon probes close to the equator and morning terminator provided surface temperature and pressure values of 733 ± 1 K and 89 ± 1 atm respectively, as well as detecting a temperature inversion between 62 and 64 km (Petropoulos and Telonis 1988). The aim of the next mission to Venus, Magellan, was to gather radar and radiometric data from the surface in order to generate a topographical map of Venus. It also carried a gravity experiment to map

the gravity field of Venus and look for anomalies that may provide an insight to the tectonic structure of the planet. The majority of the planet was covered twice by the radar instrument, allowing the identification of several different terrains from the resulting topography map.

1.3 Venus Express

The Venus Express orbiter is the most recent mission to Venus, and is the first to exploit transparent spectral regions in the infrared to observe the lower atmosphere from space. The varied instrumentation of this mission reflects its multiple goals. Of particular interest and relevance to this work is the Visible and InfraRed Thermal Imaging Spectrometer, VIRTIS, which is designed to provide data for surface mineralogy, cloud properties, temperature and gaseous abundances from the surface to the upper atmosphere (Drossart et al. 2007).

Venus Express (VEX) was launched in November 2005 and entered orbit around Venus in April 2006. The nominal mission was due to last for 2 Venus sidereal days, but at the time of writing has been extended until at least December 2014. Seven science instruments are on board VEX. These are the Analyser of Space Plasma and Energetic Atoms (ASPERA), a magnetometer (MAG), the Planetary Fourier Spectrometer (PFS, not usable due to a scanning fault), SPectroscopy for Investigation of Characteristics of the Atmosphere of Venus (SPICAV), the Venus Radio Science Package (VeRa), the Visible and InfraRed Thermal Imaging Spectrometer (VIRTIS), and the Venus Monitoring Camera (VMC). Data from VIRTIS has been used in this work and the instrument is described below in more detail.

Venus Express is the first dedicated mission to Venus since the discovery by Allen and Crawford (1984) of spectral regions in the near-infrared within which radiation

originating from the surface and troposphere is observable from space. These so-called “window” regions were discovered when near-infrared images of the nightside of Venus taken using the Anglo-Australian telescope were analysed, and found to exhibit significant spatial variation in radiance at specific wavelengths. The presence of these regions in a 90-bar CO₂ atmosphere is due to the sub-Lorentzian nature of the CO₂ absorption lines; inelastic collisions of CO₂ molecules mean the profile of individual CO₂ absorption lines is narrower than the pressure-broadened case assuming purely elastic collisions, so there are a few regions of the infrared spectrum in which the atmosphere is not entirely opaque.

The regions in which the surface can be observed occur at 1.02, 1.10 and 1.18 μm , windows, with regions sensitive to thermal radiation from the troposphere occurring at 1.27, 1.31, 1.51, 1.55, 1.74 and 2.3 μm . The 2.3 μm window is very broad, with sensitivity between 2.15 and 2.6 μm and altitude sensitivities ranging from 30—55 km. The spectral range of the VIRTIS instrument makes it especially suited to studying these atmospheric window regions.

1.3.1 The Visible and Infrared Thermal Imaging Spectrometer

VIRTIS was originally designed for the cometary mission Rosetta, to study the nucleus and coma of the comet P/Wirtanen (Coradini et al. 1998), and was subsequently included on Venus Express. It consists of three unique data channels, two of which are mapping channels, one operating in the visible wavelength range 0.25–1.0 μm (VIRTIS-M-VIS) and the other in the range 1.0–5.0 μm (VIRTIS-M-IR). The spectral sampling of VIRTIS-M is 0.01 μm . The third channel is a higher resolution (~ 1 nm) echelle spectrometer operating in the range 2.0–5.0 μm (VIRTIS-H). The work presented here uses data from the VIRTIS-M-IR channel. A schematic of the

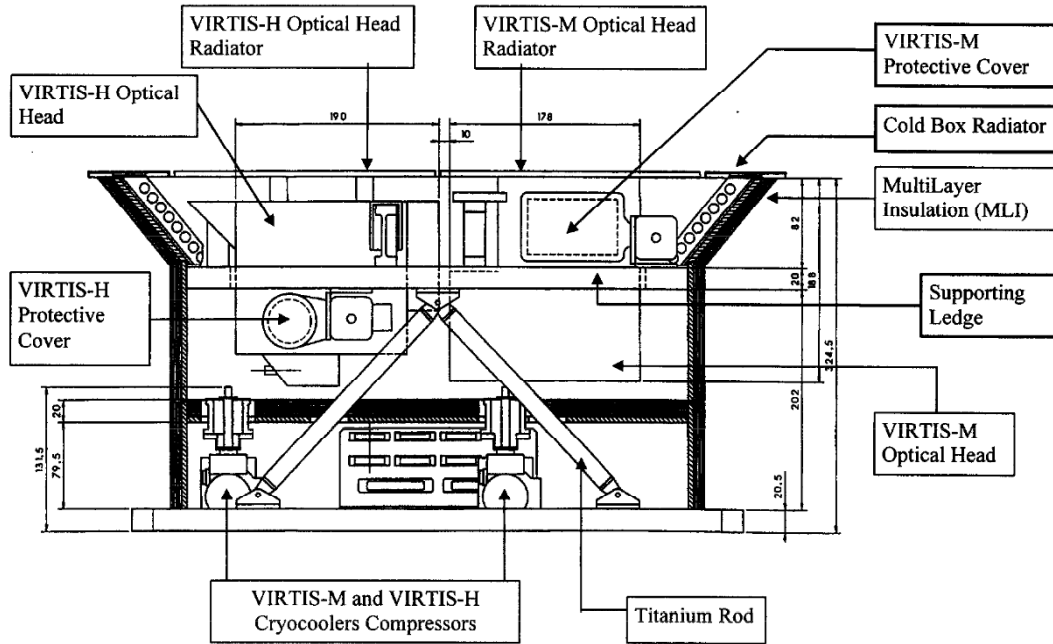


Figure 1.1: A schematic of the VIRTIS optics module, taken from Coradini et al. (1999).¹

instrument is shown in Figure 1.1, from Coradini et al. (1999).

The VIRTIS-M part of the instrument consists of a matched Shafer telescope and Offner grating spectrometer. VIRTIS-M-IR and -VIS share the optical system; the visible channel detector is a CCD and the infrared channel a HgCdTe detector. VIRTIS-H uses a similar detector to the IR channel of the mapping spectrometer, and both must be cooled to a maximum temperature of 130K.

The instantaneous field of view of VIRTIS-M over the whole slit is 0.25×64 mrad, which corresponds to a distance of $\sim 1/3$ of the diameter of the planet at apocentre. After taking into account scanning by the secondary mirror, the total field of view is 64 mrad^2 (Drossart et al. 2007, Piccioni et al. 2008). The spectral resolution of VIRTIS-M is given by Svedhem et al. (2007) as $(\lambda/\Delta\lambda) \sim 200$, and the size of a

¹Reprinted from Advances in Space Research, vol. 24, issue 9; Coradini, A., Capaccioni, F., Drossart, P., Semery, A., Arnold, G. and Schade, U; “VIRTIS: The imaging spectrometer of the Rosetta mission”; pages 1095—1104, with permission from Elsevier.

single pixel is 0.25 mrad. This corresponds to a spatial resolution of ~ 20 km even at apocentre (60,000 km from the planet).

Current observations by VIRTIS allow the study of the Venusian cloud using the infrared window regions between 1.0 and 2.6 μm . Radiance at these wavelengths is heavily attenuated by the cloud and as such measurements in this spectral region provide a good indication of cloud opacity and an opportunity to study other properties of the Venusian cloud. This instrument is the first to provide global coverage of Venus in the near-infrared, and so is ideal for this study of the Venusian cloud.

1.4 Key properties of the Venusian atmosphere and surface

1.4.1 Atmospheric dynamics

The atmosphere of Venus rotates at a much greater speed than the solid body of the planet. This phenomenon is known as super-rotation. It is also observed on Titan, another slowly-rotating body, suggesting a possible link between slow rotational period and this dynamical regime. Zonal wind speeds in the troposphere and mesosphere of up to 90 ms^{-1} have been recently inferred from the temperature field as measured by VIRTIS on Venus Express by Piccialli et al. (2008). The mechanism for this super-rotation is still not understood, although circulation models of Venus suggest that there are several possibilities. Above 100 km, solar heating creates a strong diurnal temperature gradient which results in a strong sub-solar – anti-solar flow. Meridional mean transport below 100 km is dominated by a Hadley cell between the equator and $\sim 50^\circ$ latitude. The meridional extent of the Hadley cell has been inferred from an observed decrease in cloud top altitude at $\sim 50^\circ$ (Titov et al. 2008).

This conclusion is supported by the observed increase in the concentration of carbon monoxide at 35 km altitude and $\sim 60^\circ$ latitude, caused by a downward transport of CO-rich air with the downwelling branch of the Hadley cell (Tsang et al. 2008).

Many General Circulation Models (GCMs) have been used to try and replicate the observed Venusian atmospheric rotation. These include the models described by Yamamoto and Takahashi (2004), Takagi and Matsuda (2005), Hollingsworth et al. (2007), Lee et al. (2007) and Lebonnois et al. (2010). However, the results of these models are not all in agreement; the magnitudes and altitudes of the zonal wind speed maxima vary by as much as 80 ms^{-1} and 20 km, and these maxima do not always take the expected form of mid-latitude jets. Phenomena that could be responsible for generating the super-rotation include momentum transport towards the poles by Hadley cell-style meridional circulation, and return transport by eddies or waves, or momentum transport via diurnal and semidiurnal thermal tides.

At $\sim \pm 65^\circ$, the downwelling branch of the Hadley cell coincides with a region of cooling above the tropopause. This cold region surrounds the polar region and is referred to as the cold collar. It extends from ~ 55 to 80° latitude. There is a temperature inversion between 60 and 70 km altitude in this latitude region (Seiff et al. 1985, Tellmann et al. 2009). The polar collar is colocated with bands of optically thick cloud, a decrease in cloud top altitude that continues towards the pole, and ultraviolet-bright features at the altitude of the cloud top (Titov et al. 2008). It marks the transition between the low-to-mid-latitude dynamical region and the polar vortex.

Atmospheric vortices that are most often dipolar in shape have been observed close to both poles, and these are thought to be driven by the meridional Hadley cell transport. They are characterised by infrared-bright double-eye features (Piccioni et al. 2007). The polar vortices in the northern and southern hemispheres have both

been observed (Taylor et al. 1979, Piccioni et al. 2007) and are found to display similar features, although the southern vortex has a faster rotation speed (Piccioni et al. 2007). Detailed infrared observation of the southern vortex indicates that the shape is broadly dipolar, although a double-eye structure is not always observed (Piccioni et al. 2007). The shape and position of these vortices vary between observations, and the exact mechanism for their formation is poorly understood. Similar vortices on Titan are thought to act as a mixing barrier in the stratosphere and mesosphere (Teanby et al. 2008), and it is possible that such considerations apply to the Venusian mesosphere.

1.4.2 Atmospheric composition

The atmosphere of Venus is approximately 96 % CO_2 , and the mean surface pressure is 92 bar. Therefore, Venus has a much higher abundance of CO_2 , as well as CO and SO_2 , than the Earth, but its atmosphere is much drier (Table 1.1). The reasons for these compositional differences are unclear, particularly if the initial atmospheres of Earth and Venus were identical in composition, but the relatively high abundance of SO_2 is probably due to high levels of volcanic activity, since SO_2 is a major constituent of volcanic gas on the Earth. An observed decrease in the SO_2 abundance could be attributed to a large volcanic event succeeded by a more quiescent period (Esposito et al. 1988).

Donahue et al. (1982) interpret the high deuterium-hydrogen abundance ratio obtained from mass spectroscopy as evidence that Venus was once much wetter than it is today. The D/H ratio is enriched by two orders of magnitude compared to that on Earth, and Donahue et al. (1982) postulate that this came about from the greater likelihood of exospheric escape of hydrogen over the heavy isotope deuterium. The high enrichment indicates that a large amount of hydrogen from the dissociation

of H_2O has escaped from Venus in the past, and this is perhaps why Venus is dry. Recent measurements of the ion escape rate at the top of the atmosphere indicate that H^+ and O^+ ions escape with a ratio close to the stoichiometric ratio of water, providing support for this theory (Barabash et al. 2007).

The low abundance of atmospheric CO_2 on Earth compared to that of Venus may be linked to Venus' lack of a water ocean; the high uptake of CO_2 by the oceans on Earth facilitated the rapid formation of carbonate minerals, which has sequestered much of the Earth's carbon and prevented CO_2 from becoming a major atmospheric constituent.

	Venus	Earth
CO_2	0.96	0.0003
N_2	0.035	0.770
Atomic O	trace	trace
H_2O	0.00003	~ 0.01
SO_2	0.00018	0.2 ppb
CO	0.000025	0.12 ppm
Surface Pressure	92 bar	1 bar
Surface Temperature	~ 740 K	~ 290 K

Table 1.1: A comparison table for the atmospheres of Earth and Venus. Abundances are taken from Taylor and Grinspoon (2009) and are given as mole fractions unless otherwise specified.

Other trace gases present in the Venusian atmosphere include HCl , HF , OCS , H_2S and H_2SO_4 . The presence of sulphuric gases in higher abundances than those found on Earth is attributed to high levels of volcanic activity on Venus. The sulphuric acid clouds that cover the planet are a result of the high abundance of sulphuric compounds in the atmosphere. Distributions of the gases can provide information about circulation and dynamics on the planet, as they act as tracers; for example, volume mixing ratio gradients with altitude of OCS and CO are anticorrelated, with OCS decreasing with increasing altitude below the clouds and CO increasing (Pollack et al. 1993). OCS is also potentially less abundant at $\sim 60^\circ$ latitude, where

the CO volume mixing ratio is increased, and this behaviour has been attributed to the downwelling branch of the Hadley cell (Marcq et al. 2006).

H₂SO₄ condenses at ~ 45 km to form the cloud droplets in solution with H₂O. The sulphur chemistry on Venus is therefore intrinsically linked to the radiative balance, as the clouds play a significant role in the radiation budget on the planet. Climate models have shown that the surface temperature is sensitive to the altitude and optical thickness of the cloud, which is in turn affected by the abundances of sulphuric acid and water vapour (Bullock and Grinspoon 2001). These authors study the variation of the Venusian climate in response to various volcanic emission scenarios, demonstrating the likelihood that volcanic activity on Venus has some responsibility for the current climate.

1.4.3 Surface

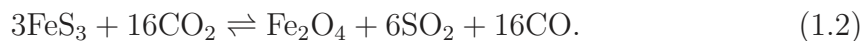
As discussed in the previous section, volcanism is likely to have played a significant role in the evolution of the Venusian climate and therefore the formation of the global cloud deck. Venus has the greatest number of volcanic topographic features in the solar system, and areas of high surface emissivity have been interpreted as evidence of recent lava flows (Smrekar et al. 2010). Radar-bright features from ground-based measurements were interpreted as volcanic in origin by Saunders and Malin (1977), and the topographical maps generated using data from the Magellan probe have provided evidence that over 90% of the surface is covered by features that bear a close resemblance to volcanic features on Earth (Head et al. 1992). With data from VIRTIS, correlations between high emissivity regions and volcanic features interpreted from Magellan topography data have been observed (Helbert et al. 2008). Whereas the presence of past volcanism on Venus is widely accepted, it is unknown whether it occurred in sporadic bursts of high activity or continuously.

Bullock (1997) completed evolutionary model simulations of both possibilities, and concluded that the most likely evolutionary scenario was an epoch of massive volcanic plains emplacement between 600 and 1100 million years ago, although this has been debated. Esposito et al. (1988) suggest that an observed decrease in sulphur dioxide concentration above the cloud tops during the Pioneer Venus mission could be evidence that volcanic activity has occurred more recently, possibly favouring a more constant outgassing model.

The relationship between the atmosphere of Venus and the surface mineralogy is complex and not yet well understood. Hashimoto and Abe (2005) discuss the relative merits of carbonate and pyrite models for surface-atmosphere equilibrium. The carbonate model is based on the Urey (1952) equilibrium reaction as studied by Bullock and Grinspoon (2001). This carbonate buffer reaction is



However, Hashimoto and Abe (2005) postulate that the amount of carbonate rock reservoir required to buffer a 90 bar atmosphere of CO_2 would be equivalent to a layer 1 km thick across the entire surface of Venus. Instead, they suggest that a pyrite equilibrium model may be more appropriate:



Fegley et al. (1992) compare surface composition measurements from Venera and Vega missions (Section 1.2) to compositions of mid-ocean ridge basalt and alkali olivine basalt. Whilst correspondence with these rocks is possible, instrument limitations, the paucity of data and restricted coverage leave several open questions, including the abundance of carbonate rocks and the composition of the high radar

reflectivity regions. Currently, reaching a conclusion as to the precise nature of surface-atmosphere interaction on Venus is difficult, and further observation and measurement are required. The composition of the surface rocks, if known, could provide useful clues about previous and current volcanic activity and the history of the planet.

1.4.4 Mesosphere, upper atmosphere and escape processes

Chemistry in the atmosphere above the clouds is important for their formation. In particular, H_2SO_4 is a photochemical product that is formed in this region from the photo-oxidation of SO_2 into SO_3 , which then combines with H_2O to form sulphuric acid vapour. The supply of SO_2 and H_2O to this altitude region is therefore necessary for cloud formation.

Significant variation in SO_2 abundance in the 70 km region has recently been observed, using the SPICAV instrument on Venus Express (Marcq et al. 2011). The mechanism is so far unclear, although these authors favour a dynamical process uplifting SO_2 from the deep atmosphere. Volcanic plumes cannot be ruled out as an alternative. These fluctuations may be linked to variations in the cloud, or may affect cloud formation processes.

Escape processes are not important for short-term evolution of the cloud, but may have an impact over longer timescales. Venus has no significant intrinsic magnetic field, so the solar wind interacts directly with the upper atmosphere. This direct interaction contributes to the escape of gases from the top of the Venusian atmosphere. The escape of H^+ and O^+ ions, leading to the loss of water, is the process of most interest in this work as it has had and will have consequences for both the past and future evolution of the cloud layer. The ASPERA instrument on Venus

Express has been the first to directly observe the escape rates of these two ions, and Barabash et al. (2007) have found that the escape ratio corresponds closely to the stoichiometric ratio of water. They find that there is significant escape through the plasma wake. Significant water loss would impact the acid concentration in the cloud layer and would eventually lead to a cessation of cloud cover if there was no replacement of water vapour through volcanic outgassing; in his atmospheric evolution model for Venus, Bullock (1997) shows that the clouds begin to disappear if the deep atmospheric water vapour volume mixing ratio falls below 0.3 ppmv, a factor of 100 smaller than the current value. This is because the equilibrium cloud droplet acid concentration increases as the volume mixing ratio of water decreases, resulting in a higher saturation vapour pressure of sulphuric acid over the solution, whilst at the same time the production rate of sulphuric acid vapour is decreasing as it is a product of water vapour and SO_2 . Eventually, the partial pressure of sulphuric acid becomes insufficient for condensation to occur.

1.5 The Venusian cloud

The clouds on Venus play a significant role in the energy balance of the atmosphere. The high albedo of the clouds prevents much of the solar radiation from penetrating to the surface, and the sulphuric acid aerosol particles that form the clouds are also strong scatterers in the near-infrared and strong absorbers at wavelengths above $\sim 3 \mu\text{m}$, contributing to the greenhouse effect by preventing thermal radiation from the surface from escaping into space.

After brightness temperatures derived from microwave observations provided initial evidence that the surface temperature of Venus was at least 600 K (Barrett 1960), Sagan (1962) discussed the possibility of a greenhouse model for Venus, having pos-

tulated that water clouds were partially responsible for this effect (Sagan 1960). Evidence of a stronger compositional candidate for the cloud began to emerge a decade later, when Young (1973) summarised the inferred properties of the cloud particles from optical polarisation data. He concluded that the only substance consistent with the available spectroscopic and polarimetric data was concentrated sulphuric acid in liquid droplets, containing about 75% by weight H_2SO_4 . Young also pointed out that the presence of sulphuric acid is to be expected on a planet with a high level of volcanic activity, as it is a naturally-occurring constituent of volcanic gas and can also be formed from other outgassed substances (H_2O and SO_2). He concluded that other suggestions such as the acids HCl , HF and HNO_3 could be ruled out, at least as candidates for the upper cloud layer.

This work was closely followed by that of Hansen and Hovenier (1974). These authors collected data from several sources for the linear polarisation of sunlight reflected by the clouds in the 0.3—2.0 μm wavelength range, and concluded that the only candidate substance compatible with these data was concentrated $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$. The effective radius they determined for the cloud particles was 1.05 μm , and the particles were found to be spherical. The size distribution was found to be very narrow, with a width of only 0.07 ± 0.02 . As the authors comment, this is much narrower than values for terrestrial clouds (for example, see distribution widths quoted by Kokhanovsky (2004) of 2—8). The apparent monodispersion suggested great differences in the clouds on Venus and on Earth; these results were however restricted to the region of the cloud tops only and did not provide constraints on the lower cloud.

The conclusions of Hansen and Hovenier (1974) are supported by the work of Pollack et al. (1974), who interpreted reflectance spectra in the 1.2–4.1 μm wavelength region as also indicative of a sulphuric acid cloud layer. Pollack et al. compared

Venusian reflectance spectra with synthetic spectra for several possible candidates and determined that the only substance that matched a cloud absorption feature between 3 and 4 μm was a solution of H_2SO_4 , with a concentration of 75 % by weight or higher. It was, however, not possible to distinguish between solutions of 75 and 95 wt % using these data. The possibility of impurities being present in the aerosol particles was invoked to explain a poor match between H_2SO_4 synthetic spectra and data in the ultraviolet region of the Venus spectrum.

The Pioneer Venus mission, described in detail by Colin (1980), featured a range of instruments devoted to studying the Venusian cloud that were distributed between an orbiter and several descent probes. These were the nephelometers on the large and small descent probes (LN/SN), the Large Probe Cloud Particle Size Spectrometer (LCPS) and the Orbiter Cloud PhotoPolarimeter (OCP). The five descent probes entered the atmosphere at different locations. These consisted of three small probes, one entering the dayside (Day) atmosphere, one the nightside (Night) and the third entering the atmosphere at around 60° latitude in the northern hemisphere (North). A large probe (Sunder) and the bus on which the probes were mounted also entered the atmosphere. The cloud vertical profiles obtained by these probes were generally in good agreement with similar profiles derived from backscattering nephelometer data from the Venera 9, 10, 11, 13 and 14 probes, although some variations in the cloud base and cloud top regions were noticeable (Kliore et al. 1986).

The Pioneer Venus mission was the first equipped with an instrument capable of measuring particle sizes at high resolution – the LCPS instrument. Data from this instrument showed a multimodal distribution of particle sizes was present in the Venus cloud, and three separate modes were identified (Esposito et al. (1983), after Knollenberg and Hunten (1980)). These are the small sub-micron mode 1 particles, the mode 2 particles of $\sim 1 \mu\text{m}$ radius (identified with those observed by Hansen and

Hovenier (1974)), and large mode 3 particles, with a mean radius of $\sim 3.5 \mu\text{m}$. The upper cloud down to 58 km has a bimodal size distribution, consisting of mode 1 and mode 2. All three modes are present in the cloud below this altitude, indicating that different dynamical or chemical processes may be responsible for the formation of the two layers. Knollenberg and Hunten (1980) include a plot, reproduced below (Figure 1.2), of the vertical distribution of number density, extinction coefficient and mass loading at the Large Probe descent site, from which these distributions can be inferred.

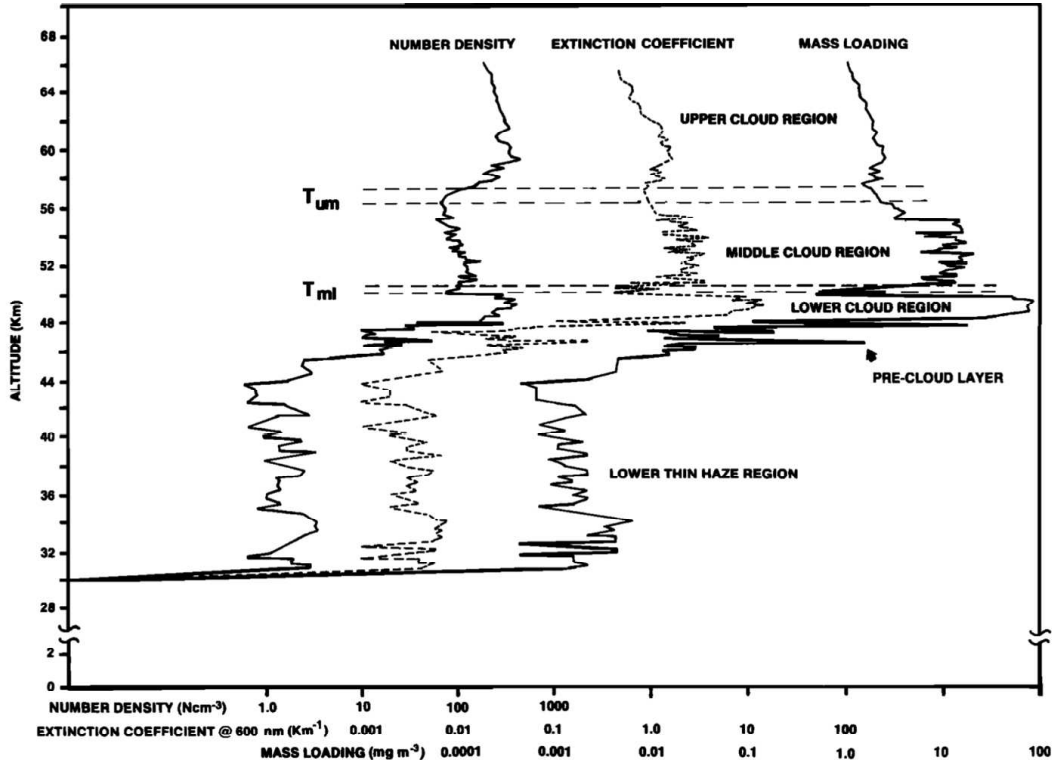


Figure 1.2: Total particle number density, extinction coefficient and mass loading, for all three size modes combined, obtained from LCPS data and presented by Knollenberg and Hunten (1980)². No allowance was made for particles with diameters less than $0.6 \mu\text{m}$ or for sizes greater than the largest actually measured. A density of 2 g cm^{-3} was assumed for mass loading computations. T_{um} and T_{ml} are the boundary regions between the upper/middle and middle/upper layers as identified by these authors.

²Reprinted from Knollenberg, R. G. and Hunten, D. M., “The microphysics of the clouds of Venus – Results of the Pioneer Venus particle size spectrometer experiment”, Journal of Geophysical Research volume 85, pages 8039—8058, 1980. Copyright 1980 American Geophysical Union.

The question of possible variations from a purely $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ mixture, either due to impurities (such as those thought to cause the ultraviolet markings) or a different major constituent (in the lower cloud layers), was revisited after results from the Pioneer Venus mission became available. Cimino (1982) examined data from the radio occultation experiment, and modelled the aerosol particles as a solid dielectric sphere with a coating of liquid sulphuric acid. This increases the absorptivity of the particles compared to a pure sulphuric acid sphere. The mass contents derived from the radio occultation data, assuming liquid concentrated H_2SO_4 aerosols, are more than an order of magnitude greater than mass contents determined by the LCPS, which suggested that particles with a higher absorptivity were required. The spectral dependence of the absorption coefficient determined for the occultation data was also found to be different from that of liquid H_2SO_4 . She concluded that the best-fit model consisted of a solid core making up 97 % of the particle by radius, with a thin coating of liquid H_2SO_4 .

It is now known that the cloud opacity is highly variable, so a cloud mass content observed at one time and in one place could very conceivably differ by an order of magnitude from a content observed elsewhere. However, we cannot yet rule out the possibility of compositional variations or impurities in the cloud particles, especially as the nature of the ultraviolet absorber in the cloud top regions remains unknown. The composition of the largest cloud particles in the lower cloud is also a subject of debate. Esposito et al. (1983) suggested chlorides such as HCl or FeCl_3 , or NOHSO_4 , instead of H_2SO_4 .

Decades of studying the Venusian cloud have yielded much information, but there are still significant gaps in our understanding. The upper cloud has been identified as concentrated liquid sulphuric acid, with a good constraint on the size of the majority of the particles ($\sim 1\text{ }\mu\text{m}$). The lower cloud has been presumed in most

studies to also be composed of sulphuric acid, although this is more questionable. The cloud is found to extend upwards from ~ 45 km to ~ 80 km, with a division at around 60 km between the upper cloud, thought to be photochemical in origin, and the lower cloud which since it lies in a region of convective instability is thought to be condensational. Some larger particles with mean radii of 3–4 μm have been detected in the lower cloud deck, and the composition of these particles is uncertain; the majority of radiative transfer and microphysical models work on the assumption that they are also sulphuric acid, in the absence of compelling evidence for an alternative. The concentration of the sulphuric acid in the cloud droplets is broadly constrained by observations to lie between 75 and 96 wt%. High variability in the cloud opacity, both temporally and spatially, suggests that other properties of the cloud may also vary in similar ways.

1.6 Thesis outline

This chapter has summarised the key properties of the planet Venus, the major results from previous missions and an introduction to the Venus Express satellite. The following chapter includes a description of the radiative transfer model used in this work, including a discussion of the parameterisation of the CO_2 lineshape and continuum absorption. Chapter 3 reviews previous representations of the cloud in radiative transfer models, with justification for the parameterisation adopted in this work. Chapter 4 includes a more detailed description of the VIRTIS data and how they are processed for this work, and also a full description of the method used to retrieve properties of the cloud from the data. The results of this are presented in Chapter 5. Details of validation procedures, error analysis and a discussion of the *a priori* assumptions made follow in Chapter 6. A discussion of the results in the context of previous results, atmospheric chemistry and dynamics is presented

in Chapter 7. The final chapter contains the conclusion and some ideas for further work that may be undertaken to expand this thesis, with some suggestions for future missions to Venus.³

³Preliminary results from this work were published in *Icarus* (volume 217 issue 2, pages 542—560, 2012); Barstow, J. K., Tsang, C. C. C., Wilson, C. F., Irwin, P. G. J., Taylor, F. W., McGouldrick, K., Drossart, P., Piccioni, G. and Tellmann, S.; “Models of the global cloud structure on Venus derived from Venus Express observations”. Figures 3.6, 3.7, 4.3, 4.6, 4.7, 4.8, 4.13, 4.14, 4.15, 5.6, 5.7 and 6.12 were published as part of this article and are reprinted here with permission from Elsevier.

Chapter 2

The Infrared Spectrum of Venus

2.1 Properties of the near-infrared spectrum

Thermal emission from the surface and troposphere of Venus can be observed in the near-infrared, due to the presence of spectral “window” regions between 0.8 and 2.6 μm that are relatively free from absorption by CO_2 . Whilst the radiation from the lower atmosphere in these regions is attenuated, it is not completely absorbed and can be observed from space. This property has been exploited by the inclusion of the VIRTIS instrument on Venus Express, making this the first mission to perform dedicated global remote sensing of the troposphere and surface thermal properties.

The amount of absorption due to CO_2 in and at the edges of the window regions is dependent on several factors, which are discussed below in Section 2.2.4. In addition, there is dependence on the atmospheric temperature profile, the structure of the cloud layer and abundances of trace gas species such as CO and H_2O . The cloud in particular has a significant effect on the near-infrared radiance, as sulphuric acid aerosol droplets of the observed size are highly scattering in this spectral range and the atmospheric path length is increased by the multiple scattering events within the

cloud. The scattering parameterisation is described in Section 2.2.3. The high single-scattering albedo means that each individual cloud droplet scatters the majority of the incoming radiation and absorbs very little; however, due to the increased path length the number of cloud droplets encountered as radiation passes through the cloud is high, and so absorption by the cloud droplets is significant when taken over the whole thickness of the cloud. The scattering and absorptive properties of the cloud droplets vary strongly as a function of particle size and acid concentration, and as a consequence the near-infrared attenuation by the cloud is affected by variations in the cloud. These spectral effects are very broad, but the atmospheric windows span a large enough spectral range to allow their observation.

Trace gas effects on the spectrum are more localised. CO and H₂O are the most significant contributors in the near-infrared, H₂O having broad absorption bands at 1.13, 1.37, 1.38, 1.46, 1.88, 2.4 and 2.57 μm and CO absorption at 2.33 μm (Figure 2.1). The bands of interest in this work are the H₂O bands at 1.37, 1.88, 2.4 and 2.57 μm and the CO band.

A more detailed discussion of the spectral sensitivities to the cloud and trace gases, and how these are exploited in this work, is presented in Section 4.2.2.

2.2 Radiative transfer modelling of Venus in the near-infrared

2.2.1 NEMESIS

The inference of cloud properties from remotely-measured infrared spectra requires a powerful and well-validated radiative transfer modelling tool; NEMESIS, the Non-linear optimal Estimator for MultivariatE spectral analySIS (Irwin et al. 2008), was

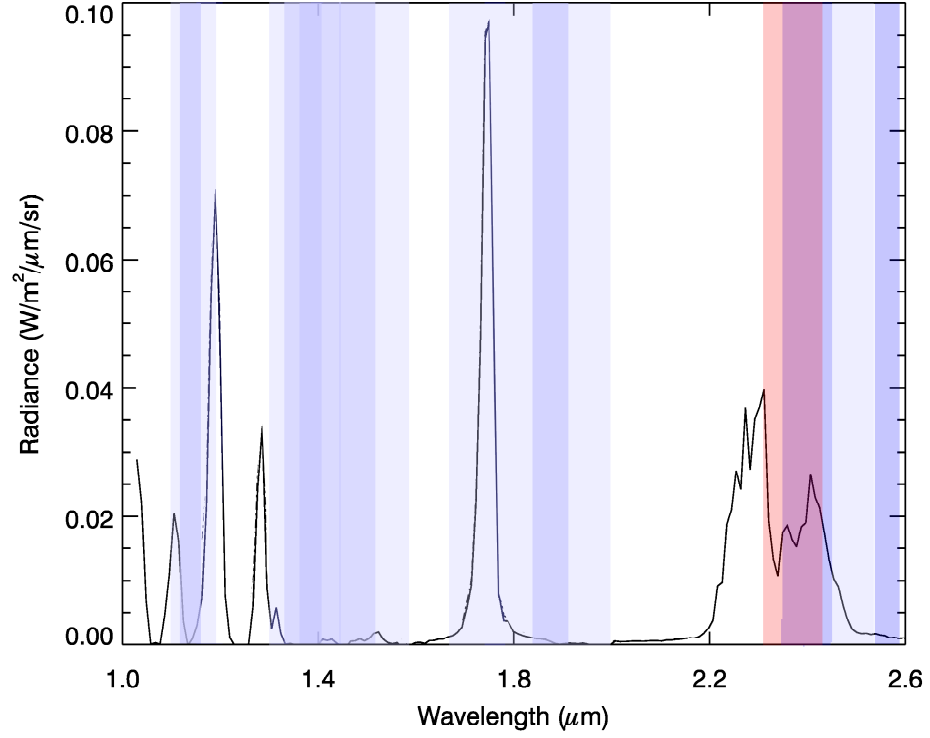


Figure 2.1: An example VIRTIS-M spectrum between 1.0 and 2.6 μm , with the CO (red) and H₂O (blue) absorption bands marked by shading. There are many H₂O lines which overlap, and the bands are relatively broad. Darker blue indicates the central regions of the absorption bands. The characteristic shapes of the regions of high emission in this diagram are qualitatively representative of all spectra. The shorter wavelength windows increase in strength relative to the windows longward of 1.27 μm in regions of thick cloud, and the relationship between the strengths of the 1.74 and 2.3 μm windows is heavily influenced by variation in the properties of the cloud, although the 1.74 μm peak radiance is always brighter than that at 2.3 μm .

chosen for this work. NEMESIS was designed for use with planetary atmospheres, and utilises a non-linear optimal estimator formalism to find the best-fit forward model to a spectrum for up to four different variables simultaneously, allowing the solution of an under-constrained problem.

Important features in a radiative transfer model for Venus are the capability to perform multiple scattering calculations, due to the presence of the highly-scattering clouds, and to rapidly calculate the absorption at each wavelength. NEMESIS uses the correlated-k approximation (Lacis and Oinas 1991) to perform fast forward model calculations, which approach is described below. The correlated-k approximation provides an efficient method for calculating absorption in multiple scattering atmospheres; models based on line-by-line calculations are slow, and band-model-based tools are not suitable for use in multiple scattering environments. It is particularly important to use an approach like this for a planet such as Venus, which has a very dense, high-pressure and high-temperature atmosphere composed of a gas that has many absorption lines in the infrared. The advantage of the correlated-k approach is that the absorption data is pre-tabulated and therefore only needs to be calculated once; all subsequent model calculations use a look-up table (k-table). In addition to the efficiency of this approach, NEMESIS has already been modified and validated for application to Venus (Tsang et al. 2008), making it a good choice for this work.

For a detailed description of NEMESIS as used to model Venus, and a discussion of its direct use for atmospheric retrievals, see Tsang et al. (2008). This work follows on from that performed in Tsang et al. (2008) and most aspects of the model are unchanged; those that differ are highlighted. The forward modelling capabilities of NEMESIS, which are those relevant for this work, are briefly discussed in this chapter, along with different ways of parameterising and describing the spectral

absorption by CO₂, which is by far the most abundant gas on Venus. The sources for other gaseous absorption data, temperature and pressure values are also given.

2.2.2 Correlated-k approximation

The correlated-k approximation assumes that the precise location of a spectral line of absorption coefficient k within a small frequency interval $\nu \rightarrow \nu + \Delta\nu$ is of no importance to the calculation of the transmission in that interval. It is in fact sufficient to know what fraction of the frequency domain $f(k)dk$ is occupied by absorption coefficients between k and $k + dk$ (Irwin et al. 1997). Then, the mean transmission within this interval can be written as:

$$\bar{T}(m) = \int_0^\infty f(k)e^{(-km)}dk \quad (2.1)$$

where m is the number of molecules per square metre of atmosphere. Equation (2.1) has the form of a standard Laplace transform of the frequency distribution of k , and it is independent of the ordering of the absorption coefficients. Therefore we can define the cumulative frequency distribution

$$g(k) = \int_0^k f(k)dk \quad (2.2)$$

and if Equation (2.2) is inverted such that $k(g) = g^{-1}(k)$ then we can rewrite $\bar{T}(m)$ as

$$\bar{T}(m) = \int_0^1 e^{(-k(g)m)}dg. \quad (2.3)$$

If we divide the space between $g = 0, 1$ into N intervals such that g is well-sampled,

we can then express $\bar{T}(m)$ as a sum rather than an integral:

$$\bar{T}(m) = \sum_i^N e^{(-\bar{k}_i m)} \Delta g_i. \quad (2.4)$$

NEMESIS uses a Gaussian quadrature scheme with N quadrature points to calculate this mean transmission.

A diagrammatic representation of this process is shown in Figure 2.2. It can be seen that the shaded areas are equal in both the plot of absorption with wavenumber and the distribution function, demonstrating that for a small wavelength interval the calculated absorption across the interval is independent of the position of absorption lines within the interval.

These approximations would be valid for a homogeneous path through an atmosphere (i.e. a path where temperature and pressure are constant). In reality, temperature and pressure change considerably as a function of altitude. As NEMESIS interpolates the k-tables for each gas to the required temperature and pressure, the correlated-k approximation is required. This relies on the assumption that the ordering of the k-coefficients within a spectral interval is in general well-correlated between adjacent atmospheric layers, ie. the strongest k coefficient in one layer corresponds to the strongest k-coefficient in adjacent layers. The name ‘correlated-k’ arises from this fact (Tsang 2007). Instead of equation 2.4, the transmission over a path through the atmosphere is then given by

$$\bar{T}(m) = \sum_i^N \exp\left(-\sum_j^M (\bar{k}_{ij} m_j)\right) \Delta g_i, \quad (2.5)$$

where M is the number of layers summed over (Irwin et al. 2008). For multiple gases, the k-tables for different gases are combined assuming no correlation between the gases, and the volume mixing ratios are used as weights.

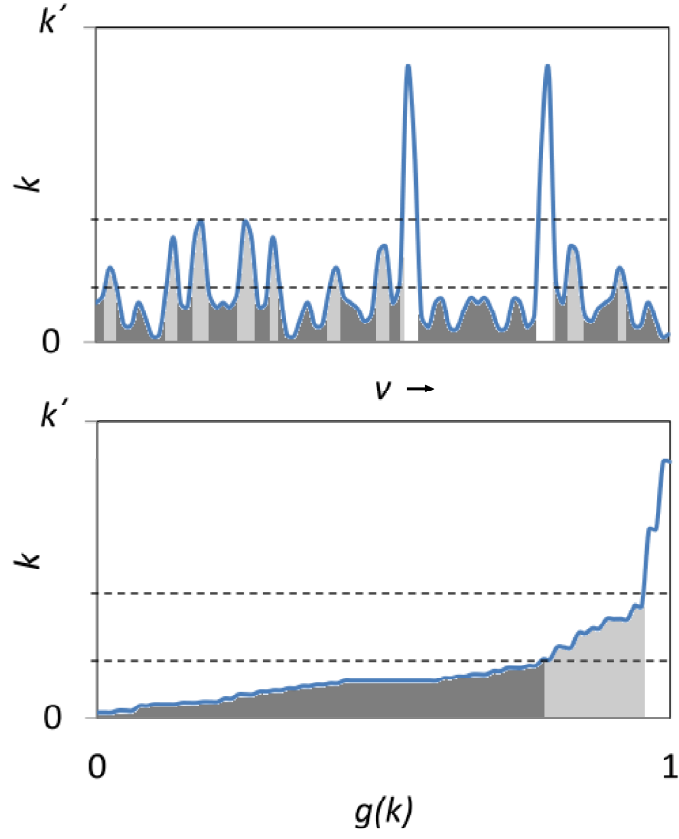


Figure 2.2: This diagram shows how the correlated-k method works. The absorption across the spectral interval from ν to $\nu + d\nu$ is shown in the top panel. The distribution function $g(k)$ of the absorption lines is shown in the bottom panel. Dark grey shaded areas in both plots represent the regions in which $k < 0.2k'$, light grey areas the regions in which $0.2k' < k < 0.45k'$. It can be seen that the shaded areas are equal in both plots.

2.2.3 Synthetic spectrum calculation

A simple block diagram for the radiative transfer calculation part of the NEMESIS code is shown in Figure 2.3. It outlines the steps of the forward model calculation, and lists the input information required.

The model atmosphere for NEMESIS is set up with *NPARAM* vertical profiles, including temperature, clouds/aerosols and spectrally-active gases. These are specified at *NPRO* vertical levels in the atmosphere, with a sufficient number of levels

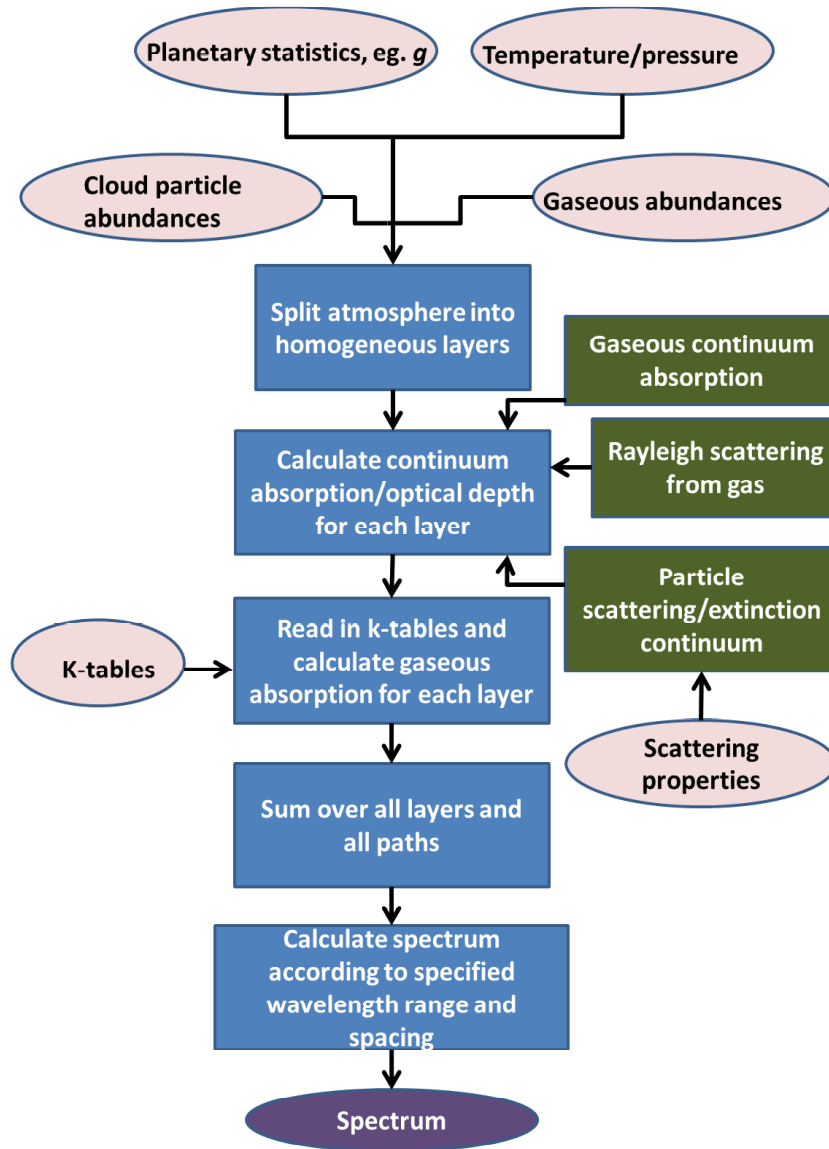


Figure 2.3: A block diagram showing the basic structure of the NEMESIS radiative transfer calculation. Pink ovals list the input information about the Venusian atmosphere that is required by NEMESIS. The main steps of the calculation are shown in blue rectangles, subsidiary calculations are shown in green rectangles. Output is shown in purple ovals.

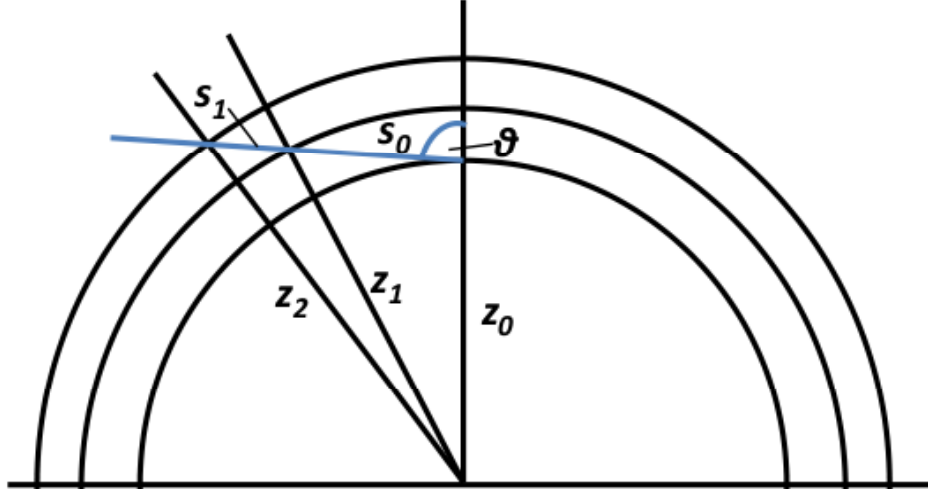


Figure 2.4: Schematic showing how NEMESIS calculates path lengths through layers. NEMESIS uses the cosine rule to calculate the length s_0 ; this can be expressed as a function of z_0 , z_1 and θ . $s_0 = -z_0 \cos(\theta) + \sqrt{z_1^2 - \sin^2(\theta) z_0^2}$

to resolve important variation (Irwin et al. 2008). NEMESIS then splits up the atmosphere into a number $NLAYER$ of equivalent homogeneous layers sufficient to resolve the transmission weighting functions over the spectral range considered. This splitting can be done in several different ways, but for Venus layers are split by equal changes in log pressure over layers. Path lengths through these layers are then calculated so that the mean properties of each layer can be determined. This calculation is represented in Figure 2.4. The length of a path through a layer s_0 can be calculated using the cosine rule. The mean temperature and pressure are calculated as absorber amount weighted means along the viewing angle path, and the integration is performed using Simpson's rule. Similar integrations are performed for absorber amount and aerosol amount along the line of sight.

The clouds on Venus are formed of highly scattering particles, and as such it is necessary to include multiple scattering in a Venus radiative transfer model. The scattering properties of spherical particles, for wavelengths of the same order of magnitude as the particle size, can be described by the Mie parameterisation (Mie

1908). This is an analytical solution to Maxwell's equations for a spherical particle, and can be applied to spherical particles of any size with respect to the wavelength of light considered. In the near infrared, the Venusian cloud particle sizes are of the same order of magnitude as the wavelength (so Rayleigh scattering cannot be used as the condition $r \ll \lambda$ is not met) and as the particles are assumed to be liquid they are also assumed to be spherical, so the Mie parameterisation is appropriate in the context of this work. The source function can be expressed as

$$S_\nu = B(\bar{\nu}, T)(1 - \omega_\nu) + \omega_\nu \oint I_\nu P(\theta) d\Omega, \quad (2.6)$$

where $B(\bar{\nu}, T)$ is the Planck function evaluated at wavenumber $\bar{\nu}$ and temperature T , ω_ν is the single-scattering albedo and I_ν is the spectral radiance. The phase function $P(\theta)$ is here approximated using a variant of the Henyey and Greenstein (1941) approximation to the full phase function, as in Tsang et al. (2008). Whilst this approximation has inaccuracies, it is computationally efficient when calculating synthetic spectra and since the errors on the refractive index data used to calculate the phase functions (Palmer and Williams 1975) are likely to be significant in the near-infrared due to the very small imaginary refractive indices it is unlikely to introduce much greater uncertainty into the results. The Henyey-Greenstein phase function approximation used here is given by

$$P(\theta) = \frac{1}{4\pi} \left[f \frac{1 - g_1^2}{(1 + g_1^2 - 2g_1 \cos\theta)^{3/2}} + (1 - f) \frac{1 - g_2^2}{(1 + g_2^2 - 2g_2 \cos\theta)^{3/2}} \right], \quad (2.7)$$

where θ is the scattering angle, f has a value between 0 and 1 and g_1 and g_2 are asymmetry parameters, measures of the anisotropy of the scattering. The two terms in the equation represent the forward- and backward-scattering peaks respectively, making it more useful for modelling particles with strong scattering in both the forward- and backward-scattering directions than the single-peaked function pro-

posed by Henyey and Greenstein (1941).

A triangular instrument function is assumed for VIRTIS with a full-width-half-maximum of 13.5 nm, as in Tsang et al. (2008).

2.2.4 CO₂ spectral line properties under Venusian conditions

As the Venusian atmosphere is composed of ~ 90 bars of CO₂ at high temperatures, absorption lines that are weak for Earthlike conditions become important contributors. In particular, these lines influence the shape of spectra at the edge of the atmospheric window regions. Some discrepancies between the shape of a synthetic spectrum and spectra from VIRTIS are noted in the wings of the 1.74 μm window region (Figure 2.5; see Section 6.2 for more detail). The model is slightly too absorbing at the shortward edge of this region relative to the central peak; this may be a result of too little absorption in the far wings of absorption lines, resulting in too much emission at the window peak, or excessive absorption by weak lines at the band extremities. Further testing of the CO₂ line data and lineshape after Tsang et al. (2008) was deemed necessary, as the work of Tsang et al. optimised the model between 2.15 and 2.5 μm whereas the current work uses a broader spectral range, and these tests are described below.

Spectral line databases

The linelist used for CO₂ in this work is taken from the HITEMP (Rothman et al. 2010) database, which was found by Pollack et al. (1993) and later Tsang et al. (2008) to better reproduce Venusian spectra than the other commonly used database, HITRAN (Rothman et al. 2003), due to its inclusion of a greater num-

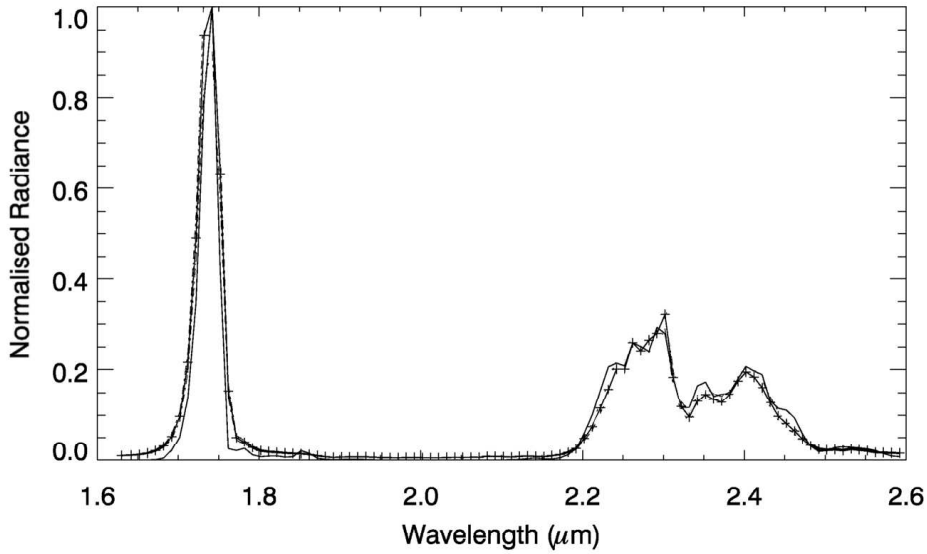


Figure 2.5: An example VIRTIS-M-IR spectrum in the 1.6—2.6 μm range (joined crosses), shown with a synthetic spectrum (solid line). The fit produced is in general good, although there is a small discrepancy at 1.71 μm , which persists in fits to the majority of spectra. This example illustrates the main features common to all near-infrared nightside spectra; emission occurs in a broad region between 2.15 and 2.6 μm with the characteristic shape shown here, and also more strongly between 1.7 and 1.78 μm , again with the same characteristic peak at 1.74 μm .

ber of weak lines. A potentially viable alternative is the Carbon Dioxide Spectroscopic Databank linelist, which has more recently been made available (Tashkun et al. 2004). A list specifically for Venus has been produced by these authors, and I have used this list to generate model spectra for comparison with the standard HITEMP spectra, to test which best reproduces the observed spectral features for Venus. A direct comparison of the two linelists shows that CDSD in general contains fewer weak absorption lines than HITEMP (Figure 2.6). A comparison of two spectra generated using the different line databases (Figure 2.7) shows that CDSD contains too few lines in the short wavelength wing of the 1.74 μm window. Although a discrepancy exists for synthetic spectra produced with HITEMP (Figure 2.5), CDSD produces an even poorer fit in the wings of this window, albeit in the opposite direction, and therefore HITEMP is preferred. Whilst spectra produced

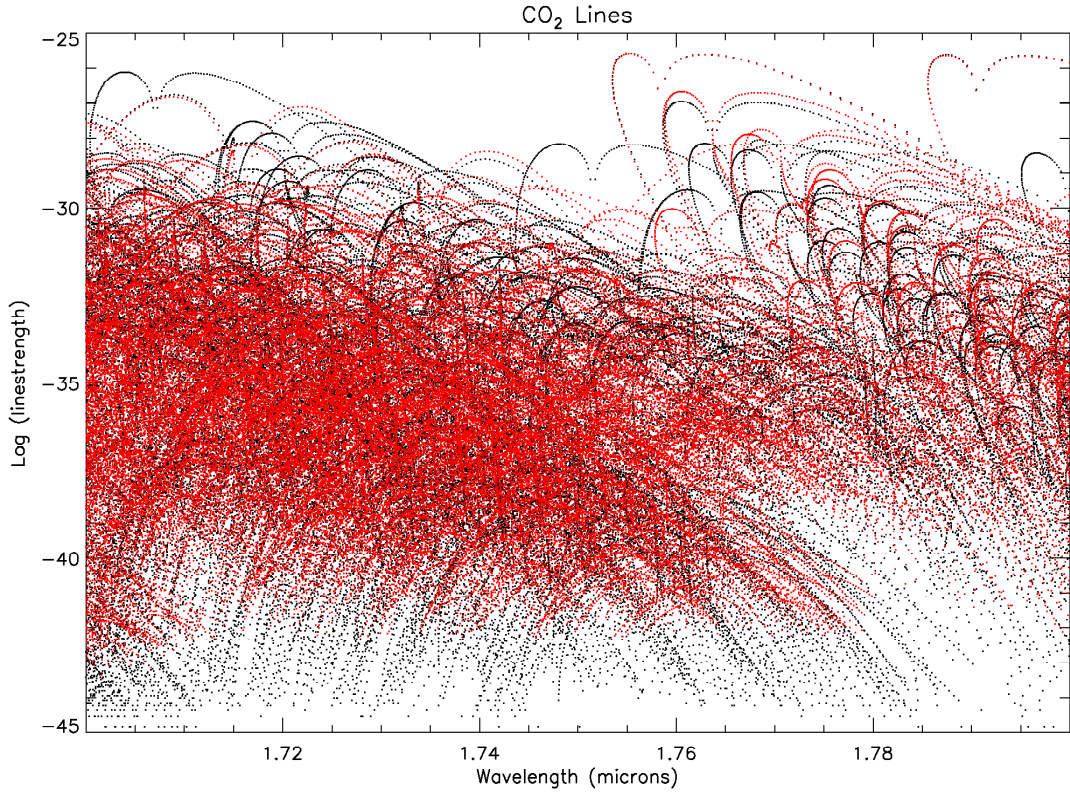


Figure 2.6: Lines in the 1.74 μm window from the HITEMP and CDSD databases. HITEMP lines are marked in black, CDSD in red. It can be seen that HITEMP contains many weak lines not included in the CDSD database, but also some strong ones, notably the strongest lines at 1.71 μm .

using HITEMP are inaccurate for model atmosphere temperatures above 1000 K (Bharadwaj and Modest 2007), the temperature on Venus is cooler and so this is not a cause for concern here.

CO₂ lineshape

Due to the high temperatures and pressures in the Venusian atmosphere, pressure (Lorentzian) broadening and temperature (Doppler) broadening of the absorption lines are both important. This superposition of the Lorentz and Doppler broadening effects creates a Voigt lineshape, which is calculated by convolving the Lorentz and Doppler lineshapes. The Voigt and Lorentzian lineshapes are equal at high pressures

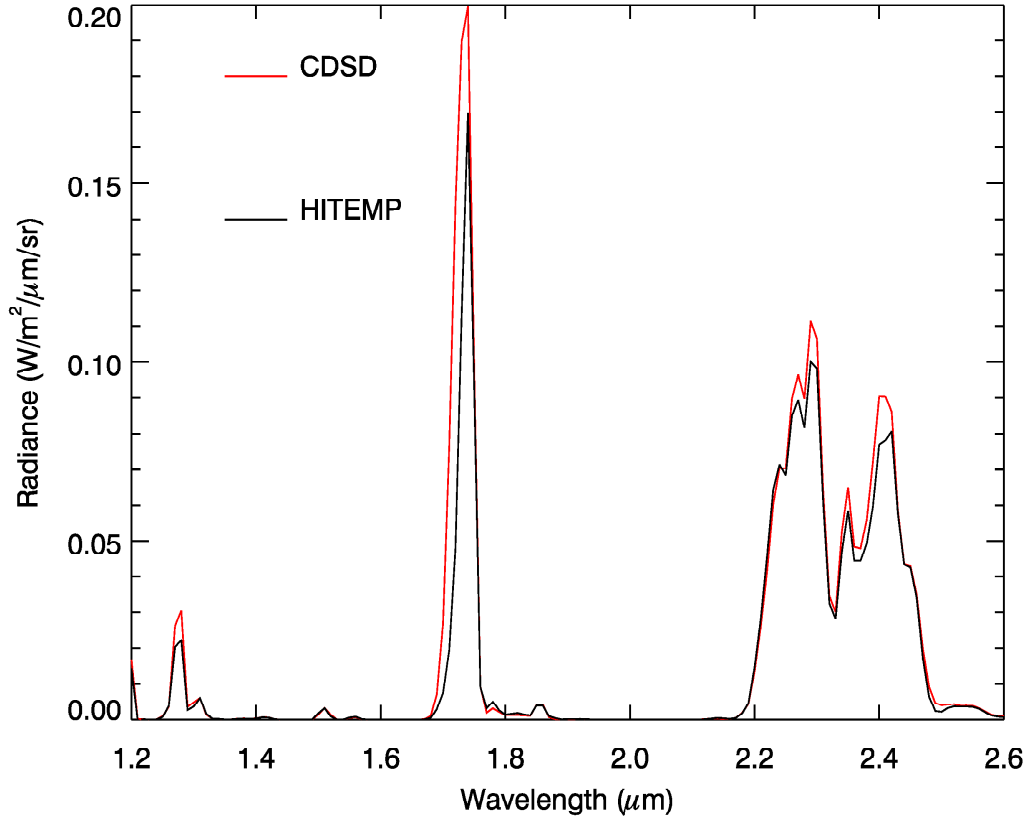


Figure 2.7: Spectra generated using CO₂ line data from CDS and from HITEMP. In general, CDS contains fewer lines and so the spectrum has generally higher radiances. In particular, CDS has fewer lines in the short wavelength wing of the 1.74 μm window.

as the Doppler profile tends towards a δ -function (Goody and Yung 1989), and this is the case in the regions below the cloud on Venus. Pre-tabulated gaseous absorption data existed for the Voigt case from Tsang et al. (2008), so this was used; the Voigt lineshape was also adopted by previous authors such as Pollack et al. (1993). It is calculated here as described in Humlíček (1982), and this lineshape is used for all gases included in the model, excepting CO₂. The extremely high CO₂ pressures on Venus result in collisional line mixing (Lévy et al. 1992), an effect caused by the transfer of energy between rotational lines due to inelastic collisions between atoms. This is important for CO₂ on Venus since the atmosphere is 96.5 % CO₂, and it means

that the CO₂ lineshape is better modelled by a sub-Lorentzian profile, as found by Winters et al. (1964) and Burch et al. (1969). For sub-Lorentzian behaviour the far wing absorption of each line is reduced from the standard Lorentzian case, and it is this fact that results in the presence of significant radiance in the near-infrared spectral window regions. The sub-Lorentzian behaviour can be parameterised by convolving the Lorentzian/Voigt profile with a correction factor χ , which takes the form of a cutoff a certain distance beyond the centre of the absorption line (Kamp and Taylor 1990, Pollack et al. 1993, Tonkov et al. 1996, Tsang et al. 2008). An example, using the χ factor proposed by Tonkov et al. (1996), is shown in Figure 2.8.

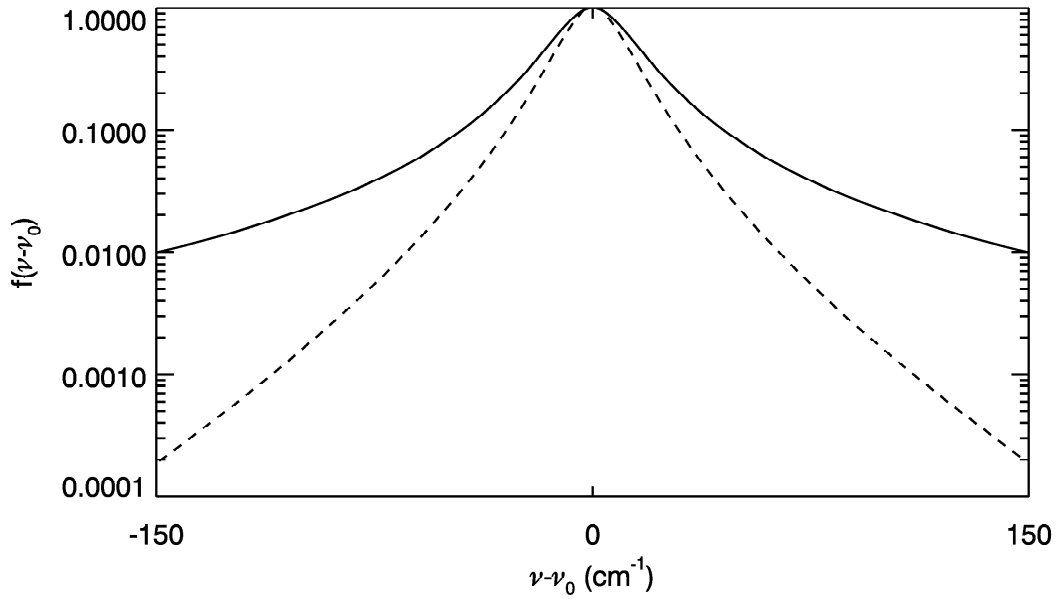


Figure 2.8: A Lorentzian line profile (solid line) shown compared with a sub-Lorentzian profile (dashed line) as parameterised by Tonkov et al. (1996). It is clear that the absorption in the line wings is much reduced in the sub-Lorentzian case.

The effect of different χ factors has been tested here, specifically to examine the effect on the wings of the 1.74 μm band and the small windows between 1.5 and 1.6 μm . The χ used by Tsang et al. (2008) is that of Tonkov et al. (1996), and the alternative χ factors tested were those proposed by Pollack et al. (1993) and Fukabori

et al. (1986). There was very little observed difference between the normalised spectra at 1.74 μm generated using the three different factors (Figure 2.9), suggesting that the choice has little effect here, especially since the error in the correlated-k approximation relative to a full line-by-line calculation is greater than these observed differences. The differences are somewhat more noticeable in the 1.5—1.6 μm region however, the Fukabori et al. (1986) χ factor being more absorbing at 1.56 μm than the other two (Figure 2.10). The mathematical representations of the three χ factors are shown below.

Tonkov et al. (1996):

$$\begin{aligned}\chi &= 1, \quad |\nu - \nu_0| < 3\text{cm}^{-1}, \\ \chi &= 1.084 \exp(-0.027|\delta\nu|), \quad 3 \leq |\nu - \nu_0| \leq 150\text{cm}^{-1}\end{aligned}\tag{2.8}$$

Pollack et al. (1993):

$$\begin{aligned}\chi &= 1, \quad |\nu - \nu_0| < 3\text{cm}^{-1}, \\ \chi &= 1.35 \exp(-|\delta\nu|/10), \quad 3 \leq |\nu - \nu_0| \leq 10\text{cm}^{-1}, \\ \chi &= 0.614 \exp(-|\delta\nu|/47), \quad 10 \leq |\nu - \nu_0| \leq 120\text{cm}^{-1}\end{aligned}\tag{2.9}$$

Fukabori et al. (1986):

$$\begin{aligned}\chi &= 1, \quad |\nu - \nu_0| < 5\text{cm}^{-1}, \\ \chi &= \exp(-0.05(|\delta\nu| - 5)^{0.8}), \quad |\nu - \nu_0| \geq 5\text{cm}^{-1}\end{aligned}\tag{2.10}$$

Tsang et al. (2008) already tested a series of correction factors to the Voigt profile for the 2.3 μm window region, and concluded that the parameterisation of Tonkov et al. (1996) was preferable in this spectral region since it was developed with a view

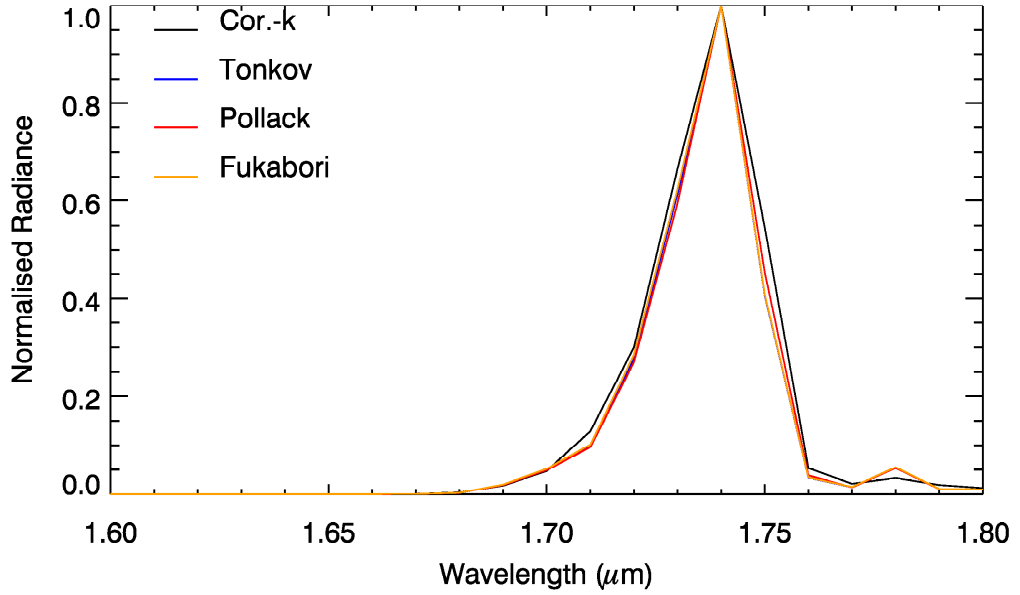


Figure 2.9: The effect of different line wing parameterisations on the shape of the 1.74 μm window, labelled by author name. The line-by-line calculations for these tests are also compared to the correlated-k spectrum (generated using the Tonkov et al. (1996) parameterisation).

to modelling the Venusian atmosphere. A far-wing cut-off was also imposed at 120 cm^{-1} from the line centre, as empirically determined by Tsang et al. (2008). The results of the comparison for the shorter wavelength windows do not suggest any reason to change from the preferred profile of Tsang et al. (2008) as the spectral shapes in the wings of the 1.74 μm window and at 1.51 μm are very similar. The difference apparent at 1.56 μm is of less importance as this window has very low radiances that are on the order of the noise level for VIRTIS (Wilson et al. 2009), and as a consequence is not used in this work. Therefore, the Tonkov et al. (1996) line wing parameterisation as used by Tsang et al. (2008) can be used.

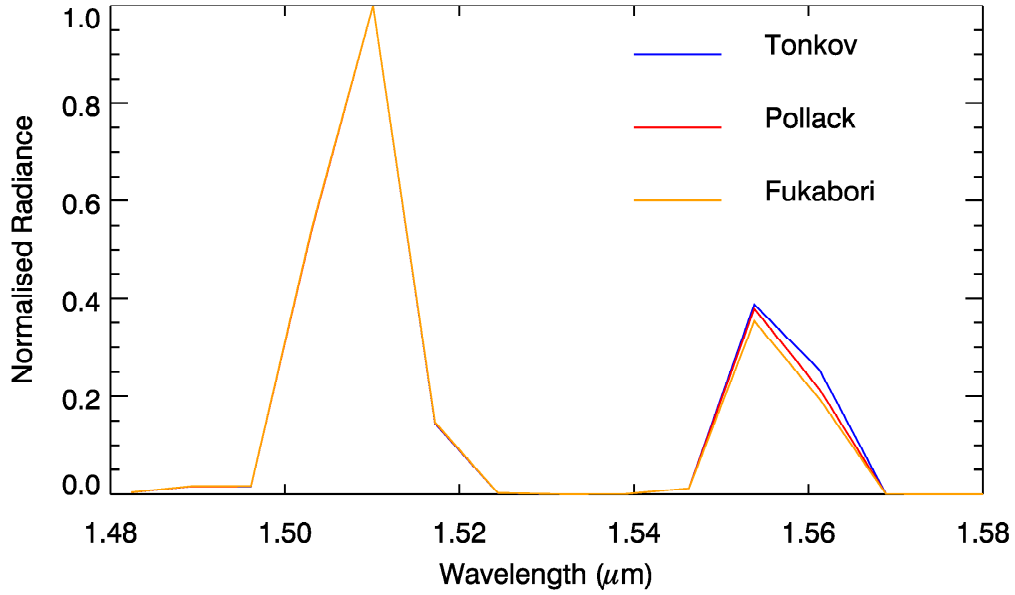


Figure 2.10: The effect of different line wing parameterisations on the shape of the low radiance 1.5 μm windows. The synthetic spectra created using three different parameterisations are labelled by author name.

Collision-induced absorption

The CO_2 lines in a Venusian spectrum are also affected by collision-induced absorption. This is a result of the collisional deformation of CO_2 molecules, which induces a temporary dipole moment and allows transitions that are normally forbidden to take place. Such lines are very broad and the many broad lines in the Venus spectrum result in what is effectively a continuum absorption. The long path lengths of CO_2 in the atmosphere mean this absorption contributes noticeably to the spectral shape (de Bergh et al. 1995).

Several different laboratory experiments have been performed to investigate CO_2 collision-induced absorption in the 2.3 μm region, which are discussed briefly by Tsang et al. (2008). Such measurements are, however, difficult to obtain and in many cases synthetic spectra created using laboratory-derived continuum absorption

values do not match observed Venusian spectra. More success has been achieved with model estimates of the continuum absorption, for example by Pollack et al. (1993) and de Bergh et al. (1995), and in general the amount of absorption is allowed to vary between the different spectral window regions but is assumed to remain constant within a single window. Estimates for the main spectral window regions are of order $1 \times 10^{-9} \text{ cm}^{-1} \text{ amagat}^{-2}$ (de Bergh et al. 1995) at $1.18 \text{ }\mu\text{m}$, 5×10^{-9} (de Bergh et al. 1995)— $8 \times 10^{-9} \text{ cm}^{-1} \text{ amagat}^{-2}$ (Bézard et al. 1990) at $1.74 \text{ }\mu\text{m}$ and 2.5×10^{-8} (Pollack et al. 1993)— $7 \times 10^{-8} \text{ cm}^{-1} \text{ amagat}^{-2}$ (Bézard et al. 1990) at $2.3 \text{ }\mu\text{m}$. These model estimates are determined from high-resolution spectral fits to observations in these window regions, which is possible since an increase in continuum absorption does not just decrease the radiance in the window regions but also has a damping effect on the high-resolution spectral features (Tsang et al. 2008). In the $2.3 \text{ }\mu\text{m}$ window we use the value deduced by de Bergh et al. (1995) of $4 \times 10^{-8} \text{ cm}^{-1} \text{ amagat}^{-2}$, and the $1.74 \text{ }\mu\text{m}$ window value of $6 \times 10^{-9} \text{ cm}^{-1} \text{ amagat}^{-2}$ is a compromise between the values proposed by de Bergh et al. (1995) ($5 \times 10^{-9} \text{ cm}^{-1} \text{ amagat}^{-2}$) and Pollack et al. (1993) ($7 \times 10^{-9} \text{ cm}^{-1} \text{ amagat}^{-2}$). I include $1.5 \times 10^{-9} \text{ cm}^{-1} \text{ amagat}^{-2}$ continuum absorption in the $1.31 \text{ }\mu\text{m}$ window, close to the value of 1×10^{-9} given by de Bergh et al. (1995) and more recently Bézard et al. (2011) for the $1.18 \text{ }\mu\text{m}$ window; none is included at 1.51 and $1.55 \text{ }\mu\text{m}$, as little study has been made of these windows.

2.2.5 Model atmosphere properties

In order to create a synthetic spectrum for Venus, temperature and pressure at each altitude level in the model need to be specified. Tropospheric temperatures cannot be retrieved using VIRTIS due to problems of degeneracy; whilst the near-infrared spectrum is everywhere sensitive to atmospheric temperature fluctuations,

all regions are also sensitive to variation in cloud properties and the two effects are indistinguishable. As the tropospheric temperature has been measured by in-situ probes and exhibits little variation between different locations on the planet, values obtained from these descent probes are specified and fixed in the radiative transfer calculation. I use collated pressure and temperature values from the Venera and Pioneer Venus probes as presented by Seiff et al. (1985) and the recent results from the VeRa radio occultation instrument on Venus Express as presented by Tellmann et al. (2009) to produce representative vertical profiles at 0, -50 -70 and $\sim$ -90° latitude (Figure 2.11). VeRa data are only available over a limited altitude region ($\sim$ 50—95 km, from 45 km for the polar profile), but this is the region where the largest temperature changes as a function of latitude occur, so at all other altitudes the equatorial temperature profile from Seiff et al. (1985) can be used whilst the latitudinal variation is still represented. Tsang et al. (2008) use only data from Seiff et al. (1985) as their work predates the release of the temperature data from VeRa.

Occultation data from VeRa were from orbits 1241, 672, 109 and 105 respectively, as these were part of an initial, limited dataset released by the VeRa team to the Venus Express community. The data were interpolated onto an altitude grid consisting of 111 altitude levels ranging from the surface to 150 km. The Seiff equatorial data is used below $\sim$ 45 km as the VeRa data do not extend below this altitude, and the temperatures below this altitude are assumed to be constant as a function of latitude. The Seiff data are also used above 95 km for the same reason, but temperatures above this altitude have no effect on modelled radiances in the infrared window regions (see Figures 4.7 and 4.11) so this is unimportant. The use of these profiles in the retrieval will be discussed in Chapter 4. This approach does not allow local variations in temperature to be explicitly accounted for, but comparing synthetic spectra created using these representative profiles indicates the error in the retrieved quantities that would be expected from local variation (see Figure 6.6).

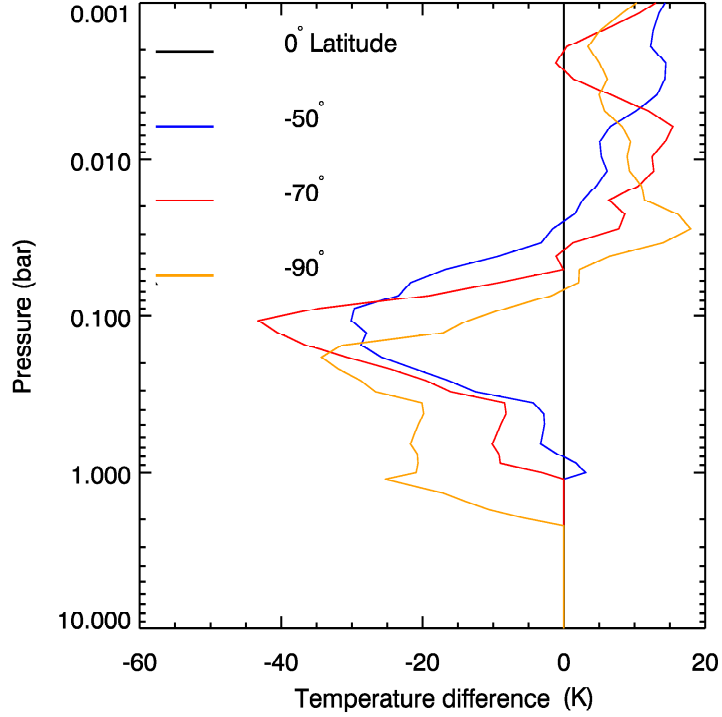


Figure 2.11: Differences from the equatorial temperature profile at different latitudes, from data provided by the VeRa team. Differences are of the form $\Delta T_{lat} = T_{lat} - T_0$. 1 bar is approximately equivalent to 50 km altitude, which is near the base of the cloud.

Gaseous volume mixing ratio vertical profiles are mostly taken from Kliore et al. (1986), as in Tsang et al. (2008). The CO and H₂O profiles are exceptions; these are similar to those used by Marcq et al. (2005), Marcq et al. (2006) and Marcq et al. (2008), which take into account recent high-resolution remote sensing measurements, and are shown in Figure 2.12. These data are chosen because they have been optimised to incorporate the results from high spectral resolution spectroscopy, using both VIRTIS-H and ground-based instruments, and as such represent the current best guess. The water vapour abundance in the deep atmosphere is assumed to be fixed at 30 ppmv up to 28 km. Above this, the whole profile is multiplied by a common factor to model water vapour variations, although above 65 km the retrieval is no longer sensitive to variations in H₂O abundance (see Figure 4.7 in

Section 4.2.1, which shows the vertical extent of the weighting function). The CO abundance is allowed to vary over the whole vertical profile down to the surface, but again the retrieval is insensitive to variation above the cloud. The gaseous absorption properties, except for CO₂ as discussed above, are obtained from the HITRAN2K database. This has been shown to be acceptable for H₂O in the spectral range of interest by Tsang et al. (2010). The Voigt lineshape is used for all trace gases, although the effect of the precise lineshape chosen is negligible for all gaseous components except CO₂ (Afanasenko and Rodin 2005).

The k-tables for the all gases are as used by Tsang et al. (2010); all use air-broadened half widths from HITRAN2K, except for CO₂ which has CO₂-CO₂ half widths from HITEMP and CO₂-H₂O half-widths from Delays et al. (1989). The relative abundances of H₂O and HDO are set assuming a D/H ratio enhancement on Venus of $130 \times$ the terrestrial value, after Donahue et al. (1982). All are as used by Tsang et al. (2010) after Tsang et al. (2008).

The *a priori* cloud model is discussed in detail in Section 3.3.4. The properties specified for a single-mode cloud are the extinction cross-section, single-scattering albedo and Henyey-Greenstein parameters as functions of wavelength; the top and bottom altitudes; the total optical depth at some reference wavelength; and the fractional scale height relative to the atmospheric scale height. As I will explain in Chapter 3, the Venusian cloud is represented in the model by four different particle modes with different modal sizes (see Section 3.2.2), and these parameters need to be specified for each of the four modes.

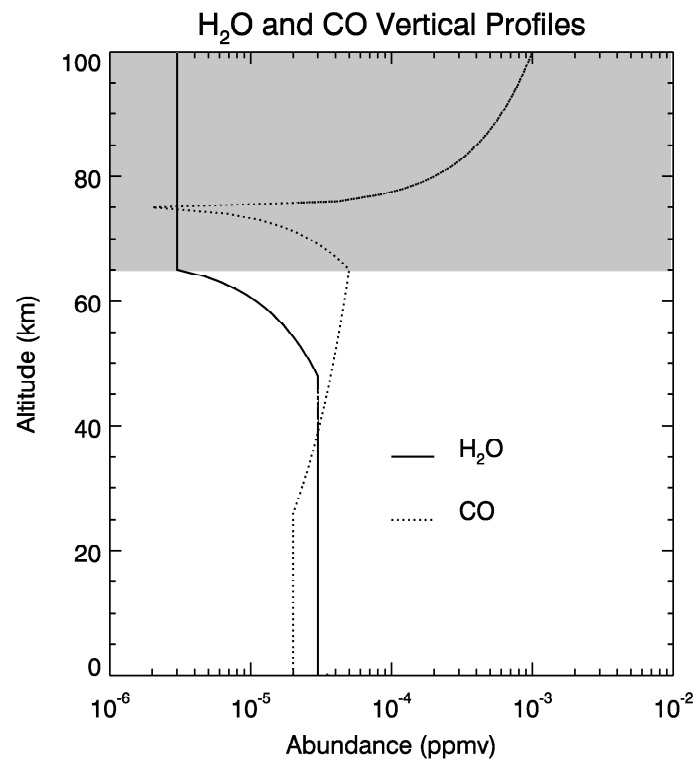


Figure 2.12: CO and H₂O *a priori* vertical profiles used in this work. The shaded region indicates altitudes for which the *a priori* profile chosen does not affect the retrieval.

Chapter 3

Models of the Venusian Cloud

This chapter explores the task of modelling the Venusian cloud, from microphysical and radiative transfer perspectives. In particular, cloud parameterisations used by previous authors in radiative transfer models are discussed in detail, and I describe the approach adopted to arrive at the parameterisation used in the retrieval of global cloud properties from Venus Express data.

3.1 Introduction to size distributions

An important factor when including the Venusian cloud in radiative transfer models is the treatment of particle size. The combined literature indicates that the size distribution of the cloud droplets on Venus has several peaks; very small particles of less than $0.5\text{ }\mu\text{m}$ radius are common at the cloud top, as are particles with a modal radius of close to $1\text{ }\mu\text{m}$. In the lower regions of the cloud, the dominant particle size is slightly larger than $1\text{ }\mu\text{m}$, and there are also some larger particles with modal radii of between 3 and $4\text{ }\mu\text{m}$. These size distributions were directly observed by the Pioneer Venus Large Probe particle size spectrometer (LCPS), and

whilst representative of only one data point in space and time they provide a basis for a Venusian cloud model.

This complex size distribution is represented here and in the models of Crisp (1986), Pollack et al. (1993) and Grinspoon et al. (1993) by four different ‘modes’, or four separate particle size distributions, each with a specified effective radius and distribution width. The smallest particles, which are present throughout the cloud and also in hazes near the cloud top, are called mode 1 and have a modelled effective radius between 0.3 and 0.5 μm . The 1 μm radius particles in the upper cloud are called mode 2. The particles in the lower cloud that are of similar size to mode 2 (although with slightly larger modelled radii of 1.4 μm) are referred to as mode 2', and the largest particles are named mode 3, with a modelled effective radius of 3–4 μm .

In this work, all the size distributions used are of the log-normal form, with the calculated distribution given by $n(r) \propto r^{-1} \exp[-(\ln r - \ln \bar{r})^2 / (2\sigma^2)]$, where $\bar{r}$ is the mean radius and σ the width of the distribution.

3.2 Cloud in microphysical models

3.2.1 Cloud formation on the Earth

Cloud formation on the Earth must share similarities with cloud formation on other planets, Venus included. Cloud formation on the Earth relies on convective processes, and there is evidence that the lower and middle cloud deck on Venus may be formed in the same way as stratocumulus clouds on Earth (McGouldrick et al. 2008). On Earth, parcels of moist air rise due to convection in the atmosphere, and when the temperature of such a parcel falls below the dew point temperature it reaches sat-

uration with respect to water (Rogers and Yau 1989). Once saturation is achieved, water vapour can condense out and form cloud droplets.

$$\frac{de_s}{dT} = \frac{\Delta s}{\Delta \alpha} = \frac{L}{T\Delta \alpha} \quad (3.1)$$

$$e_s = e_0 \exp\left(-\frac{L}{R_v T}\right) \quad (3.2)$$

The Clausius-Clapeyron equation 3.1 gives the temperature dependence of the saturation vapour pressure, e_s , for a given latent heat of evaporation L and volume change $\Delta \alpha$. The saturation vapour pressure defines the point at which condensation of water vapour is energetically favourable. This equation can be simplified and integrated to give equation 3.2, where e_0 is a reference vapour pressure and R_v is the water vapour gas constant; from this it is clear that the lower the temperature, T , the lower the vapour pressure e_s required for condensation to be favourable. The predominant mechanism on the Earth for creating supersaturations is therefore cooling, usually by adiabatic expansion as an air parcel rises.

However, this rather simplistic model does not entirely describe the full requirement for cloud formation. The Clausius-Clapeyron equation does not take into account the free energy barrier for condensation of water into small droplets (Rogers and Yau 1989), so in fact condensation into droplet form might not be expected to occur until large supersaturations of water vapour are reached. The saturation vapour pressure for a spherical droplet is dependent on the radius of curvature, and is given below by the Kelvin equation:

$$e_s(r) = e_s(\infty) \exp\left(\frac{2\sigma}{R_v \rho_l T r}\right), \quad (3.3)$$

where r is the radius of curvature of the droplet, σ is the surface tension and ρ_l is the

density of the liquid. It is clear from this equation that the required supersaturation is highest for very small particles, which makes the initial formation of water droplets only possible where the supersaturation is very high. Once droplets are initially formed, growth of the particle reduces the required supersaturation. Growth of droplets can occur by a variety of processes, listed by Houze, Jr. (1993), an important case being growth by collision.

The major barrier to cloud formation as defined by the Kelvin equation is the extremely high supersaturation required for the initial formation of small droplets (Rogers and Yau 1989). This can be overcome if the cloud droplet contains impurities. Raoult's law states that the vapour pressure of water over a flat solution with a mole fraction x of water is given by

$$e_s^{sol} = e_s(\infty)x. \quad (3.4)$$

As x is less than 1, the vapour pressure is reduced by the presence of the impurity, so the saturation vapour pressure is also reduced. The full equation for the saturation vapour pressure of water over impure cloud droplets is given by a combination of the Kelvin and Raoult equations, and this theory is called Köhler theory. The Köhler equation can be written as

$$e_s^{sol} = e_s(\infty) \left(1 - \frac{B}{r^3} \right) \exp \left(\frac{A}{r} \right), \quad (3.5)$$

where A and B are constants (Rogers and Yau 1989). The $1/r^3$ term is the Raoult term and the exponential term can be compared with that in Equation 3.3. For small values of r , the Raoult term dominates and the saturation vapour pressure becomes small, so the formation of small cloud droplets is energetically favourable. An increase in supersaturation will gradually increase the equilibrium particle radius

until the critical radius is reached, beyond which the Kelvin term dominates and the supersaturation decreases as particle size increases. Particles that have achieved this critical radius are said to be activated, as growth is now energetically favourable. The critical radius can also be achieved by collisional rather than condensational growth, which removes the requirement for high supersaturations.

Small aerosol particles on the Earth provide the necessary impurities to reduce the required supersaturation; substances such as black carbon and seasalt suspended in the air can be dissolved or coated in liquid water. These particles generally have sizes of order a few tens or hundreds of nm. The process of cloud droplet formation on these nuclei is called heterogeneous nucleation.

As mentioned above, growth of cloud droplets can also occur as a result of collisions between droplets. Growth by collision and coalescence is best modelled as a discrete process called stochastic collection. A stochastic collection model results in a more realistic size distribution than an assumption of continuous growth, as it takes into account the possibility that two drops of the same initial size may not attain the same size after a time Δt , having experienced different numbers of collisions. This process can lead to the formation of clouds with complex multi-modal size distributions, such as those observed on Venus.

3.2.2 Cloud microphysics on Venus

The mechanisms discussed for convective cloud formation on Earth are also relevant to convective cloud formation on Venus. The Venusian cloud between 48 and 60 km is located within a region of convectively unstable atmosphere, so can be considered as a convective cloud. The region of cloud above this is more likely to be photochemically produced. A possible cloud formation scheme for Venus is shown

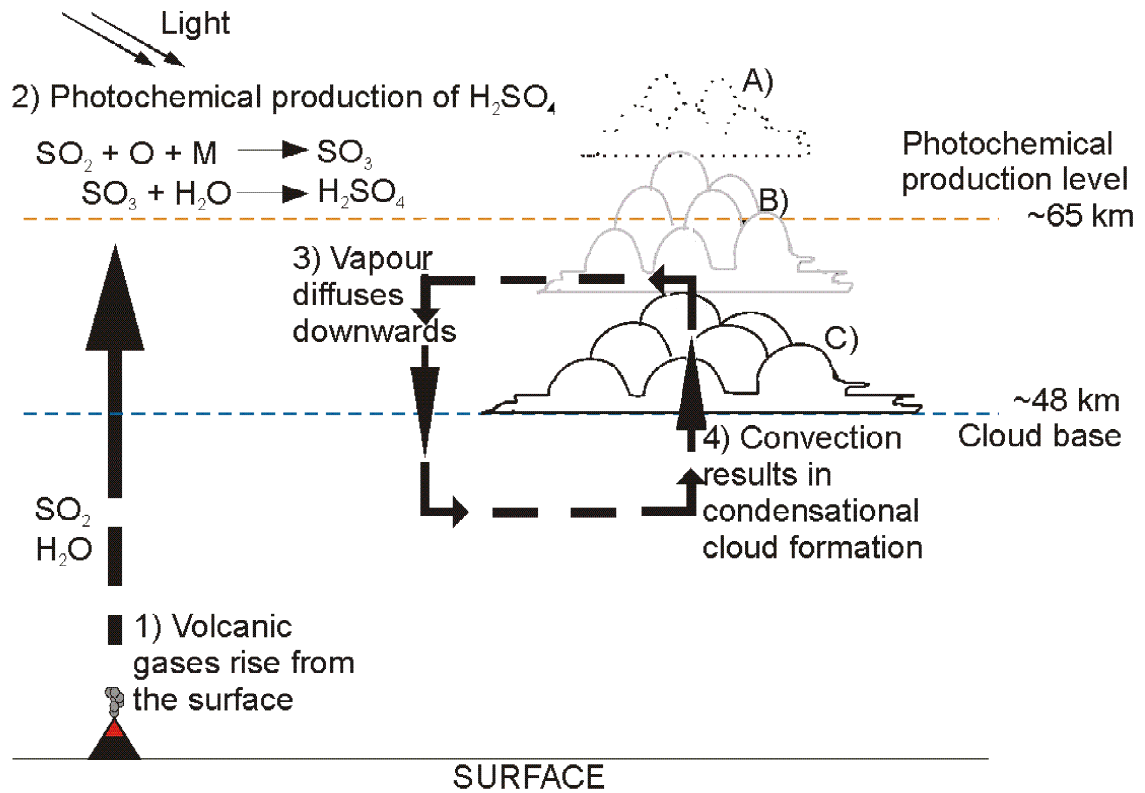


Figure 3.1: A simple schematic of how sulphuric acid clouds may form on Venus. A) marks the upper haze, B) is the upper cloud composed of mode 1, mode 2 and UV absorber particles, and C) is the lower cloud made mostly of mode 2' and mode 3 particles (after Crisp (1986) and Pollack et al. (1993)).

in Figure 3.1.

As stated in Section 3.2.1, multi-modal distributions such as that observed in the Venusian cloud favours a stochastic collection model for the initial growth and activation of cloud droplets. Knollenberg and Hunten (1980) suggest that the smallest (mode 1) particles have not yet reached the critical radius and are not yet activated, so remain small as they can only grow if the supersaturation increases (Rogers and Yau 1989), whereas mode 2 particles have achieved this critical radius and so can grow to larger sizes more easily, explaining the marked difference in average size between these two modes. CCN are believed to be an important part of this process – indeed, Knollenberg and Hunten (1980) suggest that the smallest mode one

particles detected by the Pioneer Venus LCPS in the lower cloud may be just bare CCN, with little sulphuric acid content. Imamura and Hashimoto (2002) assume the CCN to be made of elemental sulphur, with a single radius of $0.17\text{ }\mu\text{m}$, based on the LCPS measurements discussed by Knollenberg and Hunten (1980).

The formation mechanism for mode 3 particles is less certain. Knollenberg and Hunten (1980) suggest that these particles may be crystalline. Other models treat all modes as composed of concentrated sulphuric acid (see Section 3.3.2). The microphysical model of Imamura and Hashimoto (2002) results in mode 3-sized particles being produced by condensation of sulphuric acid as a result of vigorous mixing in the region of the lower clouds.

Bullock (1997) in his thesis on the stability of the Venusian climate utilised a simple chemical and microphysical model for cloud feedback processes. This model took into account the photochemical formation of H_2SO_4 aerosols and the subsequent diffusion/convection/condensation processes as shown in Figure 3.1. A relationship between particle size and number density was obtained by setting equal the Stokes drift timescale of the particles and the Brownian coagulation timescale of aerosols. The aerosol vapour was assumed to be destroyed at a temperature of 432 K, which occurs around 40 km altitude. The resulting particles were then binned according to size and composition, and this distribution was used in the radiative transfer calculations.

McGouldrick and Toon (2007,2008) also implement a microphysical cloud model to investigate the mesoscale spatial evolution of the Venus condensational clouds. They investigate the evolution of ‘holes’ in the cloud and the effect of convection cells and gravity waves. They use the values of Knollenberg and Hunten (1980) at 40 km as the CCN input distribution for their microphysical model.

The results of these different microphysical models suggest that simple microphysical

parameterisations can be useful in modelling the behaviour over time of the Venusian cloud. The work of Knollenberg and Hunten (1980) provides a good physical basis for a multi-modal cloud as observed on Venus. In summary, it seems likely that the size distribution on the Venusian cloud is achieved through stochastic collection followed by preferential condensational growth of larger particles, although this does not rule out the possibility that the mode 3 particles may have an entirely different origin.

3.3 Cloud in radiative transfer models

3.3.1 Building a cloud model

Generating an accurate, globally-relevant representation of the Venusian cloud in a radiative transfer model is a complex process, mainly due to the paucity of in-situ data combined with the known variability of the cloud. Backscattering nephelometer data from a handful of descent probes and one profile from LCPS on the Pioneer Venus Large Probe do not provide global constraints, since they only show the state of the cloud at one place and time on the planet. Combining these results with remote sensing data at different wavelengths is necessary if we want to produce generally applicable cloud models for use in radiative transfer simulations and GCMs. To demonstrate this and to justify the type of cloud model that is eventually used in this work, the following examines the effect on model spectra of introducing cloud models of increasing complexity.

Whilst the presence of the ultraviolet absorber and the uncertainty about the composition of the mode 3 particles makes the presence of impurities likely (Section 1.5), the most useful starting point for a cloud model is an $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ cloud. Initially I

assume the concentration is 96% H_2SO_4 to 4% H_2O , after Grinspoon et al. (1993) for the lower cloud; this is supported by the microphysical analysis of James et al. (1997), who find that the equilibrium acid concentration at the cloud base is close to 100 wt%, and then decreases with increasing altitude. The particle sizes are represented by a log-normal distribution with an effective radius of 1 μm (these particles are called ‘mode 2’ when part of a 4-mode particle distribution) and confine the cloud to an altitude range of 45–84 km. The number density of cloud particles is assumed to vary in altitude with the same scale height as the atmospheric density.

A synthetic spectrum generated for the wavelength range 1.6–2.6 μm using this cloud profile is shown in Figure 3.2. This is compared to a VIRTIS-M-IR spectrum with a similar 1.74 μm radiance. It can be seen that for this simplified single-size-mode model the absorption in the 2.3 μm window is much less than is required to fit the observed spectrum. Other models with the same total optical depth at 1.74 μm are also presented in the figure, and it is clear that the problem becomes worse when we add in mode 1 particles, which are smaller haze-like particles with an effective radius of 0.3 μm . The reason for this is that particles are less effective at absorbing radiation once the wavelength has become larger than the particle size, so the addition of smaller particles results in less absorption at 2.3 μm relative to 1.74 μm . It is clear that some larger particles are required to fit the spectrum in this region, and mode 2' ($r_{eff} = 1.4 \mu\text{m}$) and mode 3 ($r_{eff} = 3.65 \mu\text{m}$) are included in the full 4-mode model, which produces a better fit to the observed spectrum.

We can also see that the region between 2.5 and 2.6 μm has a poor fit for models containing a single vertical cloud deck with the scale height equal to the atmospheric scale height (Figure 3.3). If instead we introduce a more complex vertical structure with clear separation at ~ 58 km between the upper cloud deck, which is presumed to be photochemically maintained, and the lower/middle convective cloud deck, the

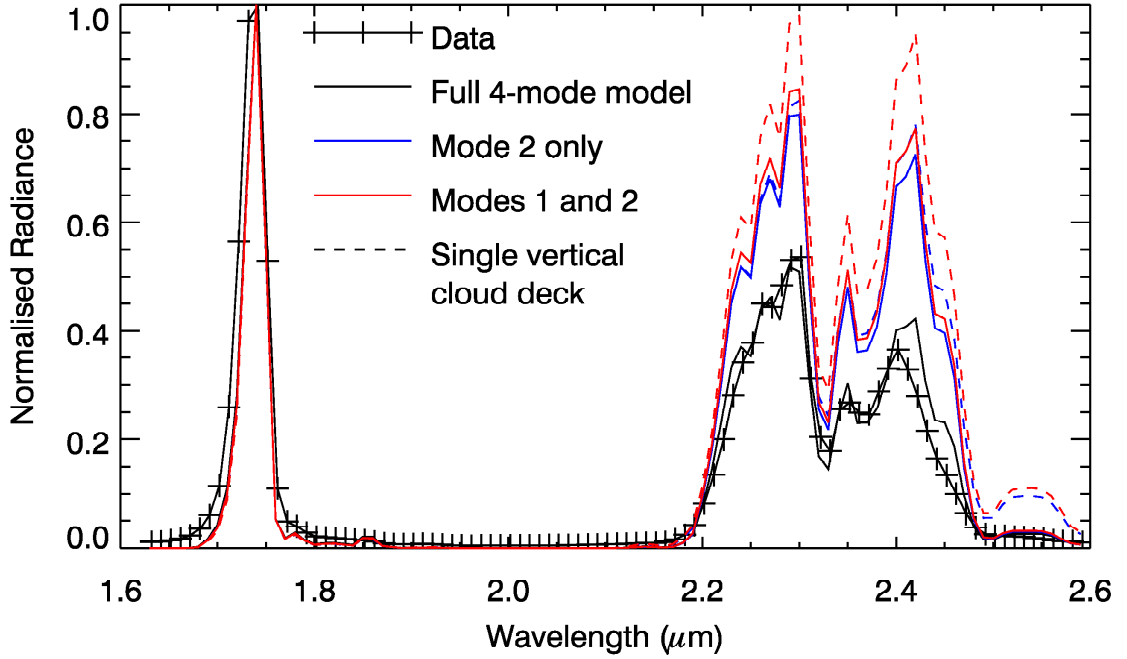


Figure 3.2: Spectra calculated using simplified 1- and 2-mode cloud models for Venus, compared to an observed spectrum and the full 4-mode model. It is clear that more large particles are required than are present in the simple models in order to fit the observed spectrum.

model produces a good fit in this region of the spectrum. This indicates that this spectral region is sensitive to the altitude distribution of the cloud particles.

It is evident that including large mode 3 particles in the modelled cloud results in a good fit to spectra in the near-infrared. This is however not a unique solution. Changing the acid concentration in the cloud droplets alters the spectral properties of the droplets, and lower acid concentrations in the model produce spectra that are more absorbing at 2.3 μm . Also, several different possible values for the CO_2 continuum absorption at 1.74 μm have been derived by previous authors (Section 2.2.4), and if the initial value chosen here is too high the model may be too absorbing in the 1.74 μm range. If the acid concentration is allowed to vary and a lower continuum absorption at 1.74 μm is assumed, it is possible to fit a single observed spectrum without including large particles in the cloud model (Figure 3.4). The cloud is not

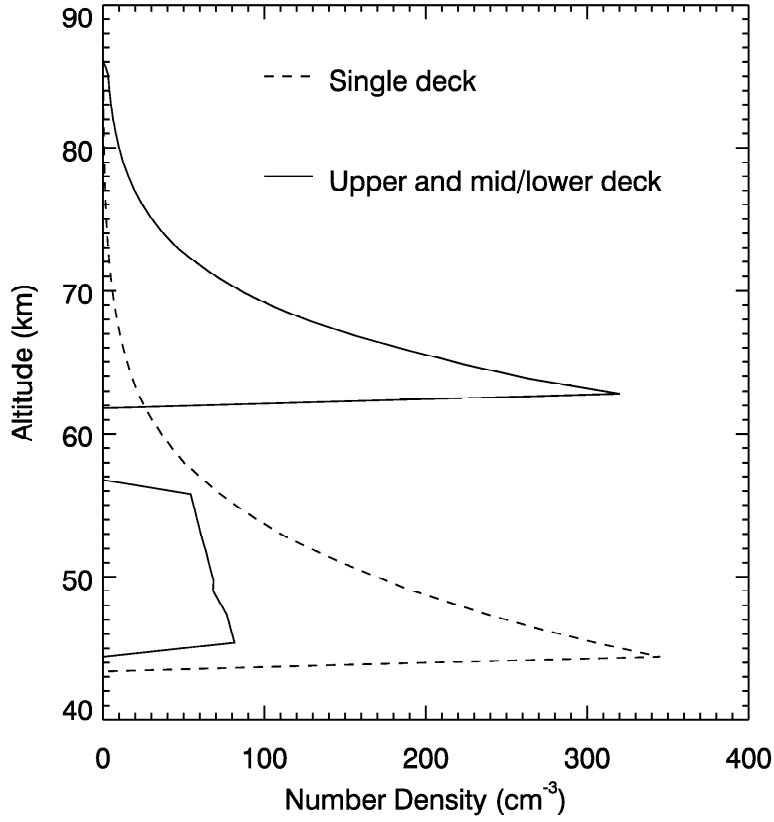


Figure 3.3: The difference between two cloud models with a single particle size mode and the same optical depth, but with different vertical distributions. The distribution shown in the solid line is considered to be the more realistic, based on measurements by descent probes.

however a grey absorber, so an important test is whether or not we can use the same model to fit a different VIRTIS spectrum with a lower or higher $1.74 \mu\text{m}$ radiance (i.e. a spectrum from a region with a greater or smaller cloud optical depth).

In Figure 3.4, a CO_2 continuum absorption value of $3 \text{ cm}^{-1} \text{ amagat}^{-2}$, half the value assumed in the *a priori* model, is used to fit synthetic spectra modelled with mode 1 and mode 2 particles only (no large particles) to observed spectra. A model with 96 % acid concentration, 53 ppmv of CO , 60 ppmv of H_2O and 3.75 ppmv of OCS , all at 35 km, can be made to fit the $I_{1.74}=0.09 \text{ W/m}^2/\mu\text{m/sr}$ spectrum in most places, although with a remaining discrepancy at $2.45 \mu\text{m}$. The value of H_2O

at 35 km required to fit the spectrum at 2.4 μm is significantly outside the error bars stated by Marcq et al. (2008), the value quoted by these authors being 31 ± 2 ppmv. The gaseous volume mixing ratios (VMRs) have not been varied from the *a priori* values for the other two spectral fits, but it is obvious that similar increases in VMR for CO, H₂O and OCS would be needed to fit the spectra beyond 2.3 μm . The $I_{1.74}=0.19$ W/m²/μm/sr spectrum is fit up to 2.3 μm by a model with 85 % acid concentration. The $I_{1.74}=0.06$ W/m²/μm/sr spectrum is fit up to 2.2 μm by a model with 96 % acid concentration, but the fit beyond this is poor. The only way to fit a model to this spectrum is to introduce a source of opacity that is more absorbing between 2.2 and 2.3 μm . As there are no minor species absorption lines in this region and the fit up to 2.2 μm indicates that an acid concentration of 96 % is appropriate, the most likely candidate for this extra source of opacity is a population of larger cloud particles. The closest match sulphuric acid concentration and the cloud optical depth for these spectra were fit by eye up to 2.2 μm ; the VMRs for CO, H₂O and OCS for the $I_{1.74}=0.09$ W/m²/μm/sr were retrieved using NEMESIS as described in Tsang et al. (2010). This example sufficiently demonstrates that a fit cannot be achieved to all spectra without sometimes including large mode 3 particles in the radiative transfer model, even assuming an alternative value for collision-induced absorption at 1.74 μm . Therefore, despite the somewhat tenuous observational evidence for the existence of such particles, I follow previous authors in representing the Venusian cloud with four distinct size modes.

3.3.2 Cloud in previous radiative transfer models

The results from the Venera and Pioneer Venus missions provided much-needed measurements of the lower cloud particle properties on Venus. When combined with the upper cloud data, these became a basis for the representation of the cloud

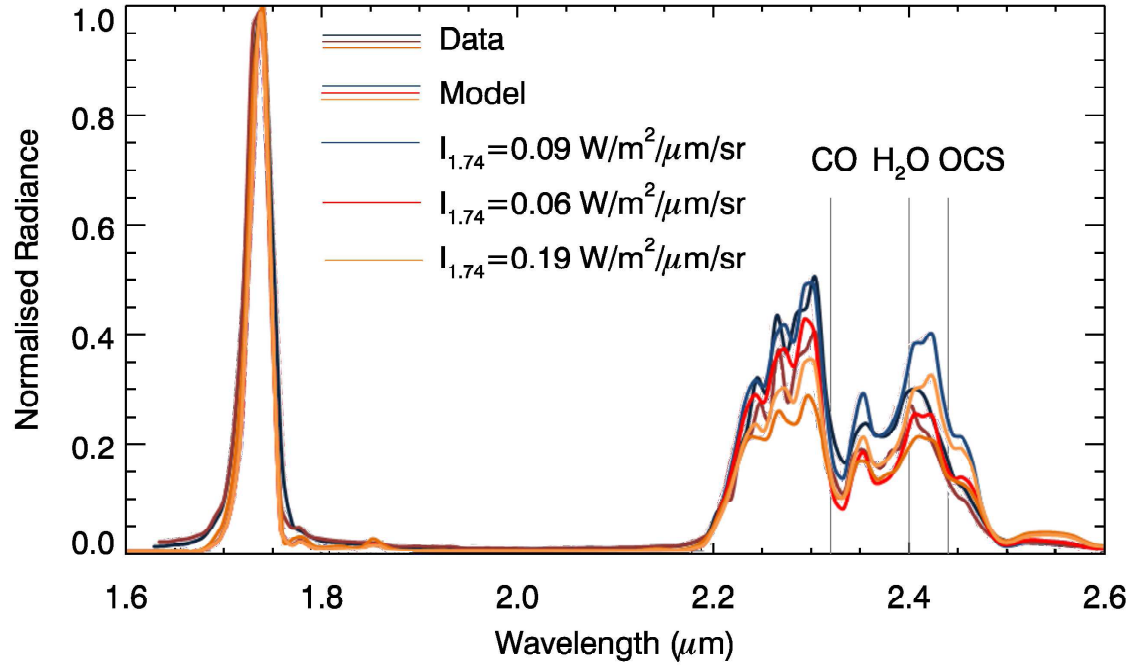


Figure 3.4: A CO₂ continuum absorption value in the 1.74 μm window of half the *a priori* value is used here to fit models containing only mode 1 and mode 2 particles to observed spectra. A model with 96 % acid concentration, 53 ppmv of CO, 60 ppmv of H₂O and 3.75 ppmv of OCS, all at 35 km, can be made to fit the $I_{1.74}=0.09 \text{ W/m}^2/\mu\text{m/sr}$ spectrum in most places, although with a remaining discrepancy at 2.45 μm . The $I_{1.74}=0.19 \text{ W/m}^2/\mu\text{m/sr}$ spectrum is fit up to 2.3 μm by a model with 85 % acid concentration – the gaseous volume mixing ratios have not been altered from the *a priori*. The $I_{1.74}=0.06 \text{ W/m}^2/\mu\text{m/sr}$ spectrum is fit up to 2.2 μm by a model with 96 % acid concentration, but the fit beyond this is poor. The approximate centres of the 35 km CO, H₂O and OCS absorption bands are indicated.

in radiative transfer models. The above discussion shows that the cloud is a non-grey absorber, and therefore accurate representation in radiative transfer simulations is crucial.

The importance of an accurate cloud model for Venus is evident from the number of authors who have spent time on their development. The first multi-modal cloud model to be produced after Pioneer Venus was that of Tomasko et al. (1980), based on the analyses of Hansen and Hovenier (1974), Knollenberg and Hunten (1980) and Knollenberg et al. (1980). The size distributions for each mode have not been substantially changed from those used by these authors in any subsequent cloud model, although this consistency is due as much to a lack of further in situ data after Pioneer Venus as to confidence in the assumptions made.

The cloud model used in this work has been based in particular on three previous representations, which are discussed in detail here. These are presented by Crisp (1986), Pollack et al. (1993) and Grinspoon et al. (1993), and they have been chosen as a basis because taken together they make use of all the available information about the cloud on Venus from in-situ and remote sensing experiments prior to Venus Express.

Crisp (1986) developed a detailed cloud parameterisation for use in a radiative transfer model to study the radiative forcing of the Venusian mesosphere. His cloud model consists of four H_2SO_4 aerosol particle modes, with radii for each mode listed in Table 3.1. These radii are very similar to those suggested by Tomasko et al. (1980) and based on the results of Knollenberg and Hunten (1980). An upper haze is present between 80 and 90 km, the upper cloud above ~ 57 km has a bimodal distribution of mode 1 and mode 2 particles, and the lower cloud from ~ 48 – 57 km has a trimodal particle distribution of modes 1, 2' and 3. The ultraviolet absorber in the upper cloud has the same size distribution as the mode 1 particles, but different refractive

indices. A composition of 75% by weight sulphuric acid is assumed for the four cloud particle modes and haze, but not for the ultraviolet absorber. This assumption was based on measurements of the cloud top (Hansen and Hovenier 1974, Kawabata et al. 1980) which were consistent with this composition, although as Crisp points out the solution is not unique.

Crisp’s cloud model is characterised by a lower cloud for which aerosol particle number density does not decrease noticeably with height, as observed by the Pioneer Venus cloud particle size spectrometer (Knollenberg and Hunten 1980), and an upper cloud with a scale height of the same order as the atmospheric scale height. These vertical distributions and size distributions are based on the interpretation of results from the Pioneer Venus optical cloud particle polarimeter and LCPS experiments, data from both being used to constrain optical depths for the upper cloud and LCPS data being used for the lower cloud.

Mode	Effective Radius at Equator (μm)	Eff. Rad. at Poles (μm)
Mode 1	0.49	0.29
Mode 2	1.18	1.01
Mode 2'	1.40	1.40
Mode 3	3.65	3.65

Table 3.1: Aerosol particle size distribution as used in the radiative transfer model of Crisp (1986). The radii used in practice were the equatorial radii, as the variation was found to make little difference to the mesospheric radiative forcing.

Mode	Mean Radius (μm)	σ
Mode 1	0.30	0.44
Mode 2	1.00	0.25
Mode 2'	1.40	0.21
Mode 3	3.65	0.25

Table 3.2: Aerosol particle size distribution as used in this work, after Pollack et al. (1993). The size distributions are given by $n(r) \propto r^{-1} \exp[-(\ln r - \ln \bar{r})^2 / (2\sigma^2)]$, where $\bar{r}$ is the mean radius.

The cumulative optical depths in the cloud layer for the Crisp model and three other models are shown in Figure 3.5.

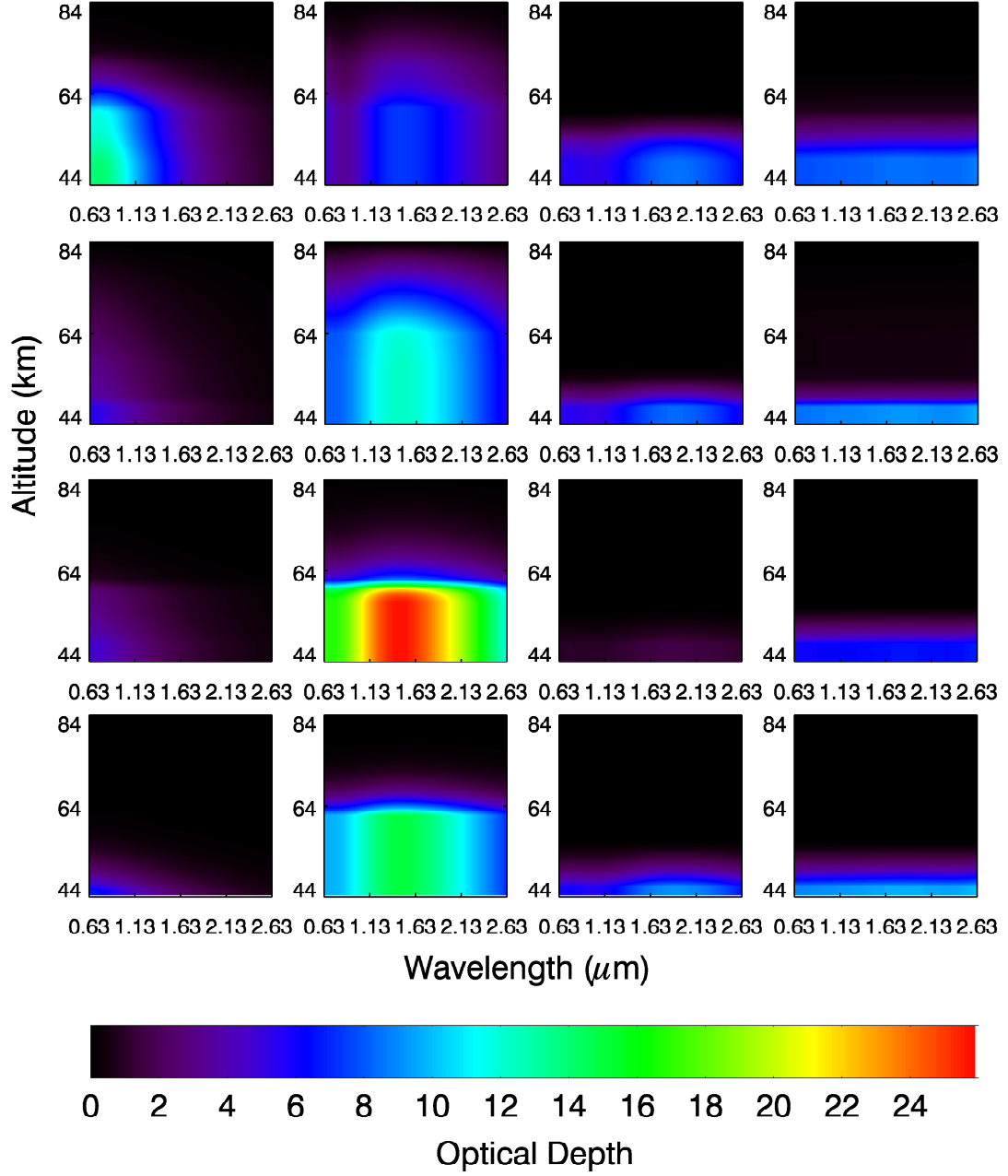


Figure 3.5: Cumulative optical depth from top to bottom in the cloud layer for each of the four particle distributions (from left to right: modes 1, 2, 2' and 3) in the Crisp, Pollack, Grinspoon and Tsang models (from top to bottom of the plot), between 0.63 and 2.63 μm .

The model of Crisp was further developed by Pollack et al. (1993), incorporating ground-based remote sensing data from Bézard et al. (1990) and Crisp et al. (1991). In their cloud model for the nightside of Venus, mode 2 particles are restricted to the upper cloud only, whilst mode 2' and mode 3 are largely restricted to the lower cloud, an approach very similar to Crisp's. Opacity profile modifications were made in order to bring the model into better agreement with the NIMS data. The particle size distribution is also very similar to that used by Crisp (1986), and is given in Table 3.2. The major difference between the two models is the way in which the altitude distribution of the droplets has been parameterised; Crisp's model specifies an optical depth and scale height for each mode for 10 altitude layers, whereas the model of Pollack et al. contains only six separate layers and no scale height is specified. The assumption must be that the optical depth is uniformly distributed within each layer. This is clearly a simpler modelling approach than that adopted by Crisp, but the number of variable cloud parameters in the model is still large (optical depths in six layers for four different cloud modes); this problem is avoided by Pollack et al. by the assumption that cloud variation occurs only in the lowest few km, thus restricting the variation to the two lowest model cloud layers. This approach does not easily facilitate the study of the vertical distribution of cloud particles, as it is based on first removing cloud particles from the lowest layer and then removing particles from the next layer only if the bottom layer is entirely removed.

A similar parameterisation was produced by Grinspoon et al. (1993) by comparing synthetic limb-darkening curves with those obtained from the Galileo/NIMS data. They found that the data were fit best by a model in which the upper cloud optical depth remains constant, and that the majority of the cloud opacity variation occurs in the region from 48–50 km, thus validating the approach of Pollack et al. The results from Crisp (1986), Pollack et al. (1993) and Grinspoon et al. (1993) are

similar, and favour a three- or four-mode cloud model with larger mode 3 particles towards the bottom of the cloud.

More recently, Tsang et al. (2008) developed a cloud model for VIRTIS data analysis with NEMESIS based on the model of Pollack et al. (1993). The parameterisation is further simplified from that of Pollack et al., with each particle mode being described by top and bottom pressures, a total optical depth at a specified wavelength and a fractional scale height relative to the atmospheric scale height. This reduces the number of variable parameters in the model whilst still allowing alteration of the optical depth for each mode separately, thus allowing variation in the average particle size. More importantly, this parameterisation permits a constraint to be placed on the vertical distribution of cloud particles, as both the scale height and bottom altitude are variable quantities for each individual mode.

These four models all have some common features. These are 1) the presence of four distinct particle size distributions, all composed of concentrated sulphuric acid solution and with similar effective radii between models; 2) the restriction of mode 2 to altitudes above ~ 60 km and of modes 2' and 3 to altitudes below this (with the exception of a very small amount of upper-cloud mode 3 in the Pollack model); 3) small mode 1 particles throughout the cloud layer; 4) a cloud base between 45 and 48 km altitude, close to the 1 bar level. There are also some differences, one being that the $\tau=1$ altitude at $1.63\ \mu\text{m}$ in the Pollack model is significantly higher than in the others, at ~ 82 km, whereas those of Grinspoon and Crisp are ~ 74 and 79 km respectively. These values are much closer to those found for low-to mid-latitude cloud by Titov et al. (2008) at $1.6\ \mu\text{m}$. The Tsang model gives a somewhat lower $\tau=1$ altitude of ~ 70 km.

The nominal cloud base is given in Crisp (1986), Pollack et al. (1993) and Grinspoon et al. (1993) as 48 km. The evidence for a cloud base of ~ 48 km is provided by

the Pioneer Venus descent probe results, as summarized by Kliore et al. (1986), and in radio occultation data reanalysed by Kolodner and Steffes (1998). However, the structure of the lower cloud is seen to vary greatly between the individual descent profiles taken from Venera and Pioneer Venus (Knollenberg et al. 1980, Ragent and Blamont 1980) and it is therefore important to consider the possibility that the altitude of the cloud base may be variable. This hypothesis is supported by the work of James et al. (1997). Their microphysical model of the cloud indicates that changes in the VMR of sulphuric acid vapour at the cloud base can result in the cloud base altitude varying on the order of a few km, with the removal of the lower 2 km of cloud in regions where the acid vapour VMR is low. This variation is probably due to lower temperatures (higher altitudes) being necessary for supersaturation where the acid vapour VMR is lower.

All four models described above used refractive index data for sulphuric acid obtained from laboratory measurements by Palmer and Williams (1975). These data were used, together with the assumed size distributions, to calculate the extinction coefficient and single scattering albedo for each mode at each wavelength. The derived scattering properties were then included in the radiative transfer model. Grinspoon et al. (1993) used values of 84.5 in the upper cloud and 95.6 wt % H_2SO_4 in the lower cloud, as opposed to the 75 wt % used by Crisp (1986), Pollack et al. (1993) and Tsang et al. (2008). Palmer and Williams (1975) provide optical data for these three concentrations. Distinguishing between different concentrations of acid using observational data is not straightforward as the problem is underconstrained, and the short duration of the Galileo encounter limited the amount of information that could be extracted from the NIMS observations. Results from the 1-D microphysical model of James et al. (1997) show a decrease in droplet acid concentration with altitude, from ~ 98 wt % at 48 km to ~ 80 wt % at 58 km, which is best represented by the model of Grinspoon et al.

There are other sources of uncertainty for such models. No data were available between the cloud top and the 75 mbar level at the time of Crisp’s model, mode 1 particles were too small to be detected by the LCPS instrument, and the extrapolation of a model based on descent probe data to a planet-wide scale is based on the potentially flawed assumption that the conditions at the probe entry site and time were typical. The Galileo/NIMS data did however provide an opportunity to refine this model using remote-sounding data obtained over a wider area of the planet, and went some way towards removing these uncertainties. The Crisp model as refined by Pollack et al. (1993) and the model of Grinspoon et al. (1993) together gave the most accurate representation of the Venusian cloud that was possible with the data available at the time, showing significant agreement despite different approaches, and therefore these models have been used as a starting point for those developed in this work.

3.3.3 Cloud modelling since Venus Express

With the arrival of Venus Express, global remote sensing of the cloud layer became a possibility for the first time – in particular, using the near-infrared mapping spectrometer VIRTIS-M-IR. Recent work has begun to exploit the potential of this new dataset. Satoh et al. (2009) produce best-fit forward models of the shape of the 1.74 μm peak, and postulate that there may be small haze particles as low in the atmosphere as 30 km, although such particles could not be made of concentrated sulphuric acid as sulphuric acid vapour is expected to decompose at temperatures found below 45 km altitude on Venus (Prinn 1978). The possibility of alterations in the average particle size across the planet is explored by Wilson et al. (2008), after initial findings by Carlson et al. (1993). They find that the ratio of the peak radiances at 1.74 and 2.3 μm is indicative of a ‘size parameter’ for a cloud model with

a single-mode size distribution. When the results of this model are compared with VIRTIS-M-IR data, they find that the average particle size is constant over most of the planet but increases towards the poles, indicating that cloud formation processes are different at latitudes greater than 60° , possibly as a result of a different convective regime. Erard et al. (2009) suggest that their independent component analysis of VIRTIS spectra indicates variation in particle size within the polar region, with regions of different average particle size forming concentric rings around the polar vortex. All these results are examples of the potential of the VIRTIS dataset to solve outstanding questions about the global structure and variability of the cloud on Venus. This work focuses on three of these unknowns: 1) the concentration of the acid in the cloud droplets, 2) the average particle size in the lower cloud and 3) the vertical distribution of the cloud.

3.3.4 The *a priori* cloud model

The cloud parameterisation used in this work has been updated from that used by Tsang et al. (2008), which was developed for VIRTIS data analysis using NEMESIS. A key feature recommending this approach is the relative simplicity of the model in terms of the number of variable parameters, which have been carefully chosen to allow independent variation of the optical depth and the vertical distribution of the cloud, as well as the acid concentration and particle size.

The choice of an *a priori* cloud model is important for the solution of an underconstrained cloud retrieval problem. The *a priori* is an assumed initial set of values for the variable parameters in the model, which represent best guess values or ranges of values and prevent the retrieval from converging on an unphysical or impossible solution. Also important is the choice of which parameters to allow to vary and which to fix; though the model of Tsang et al. (2008) has relatively few variables,

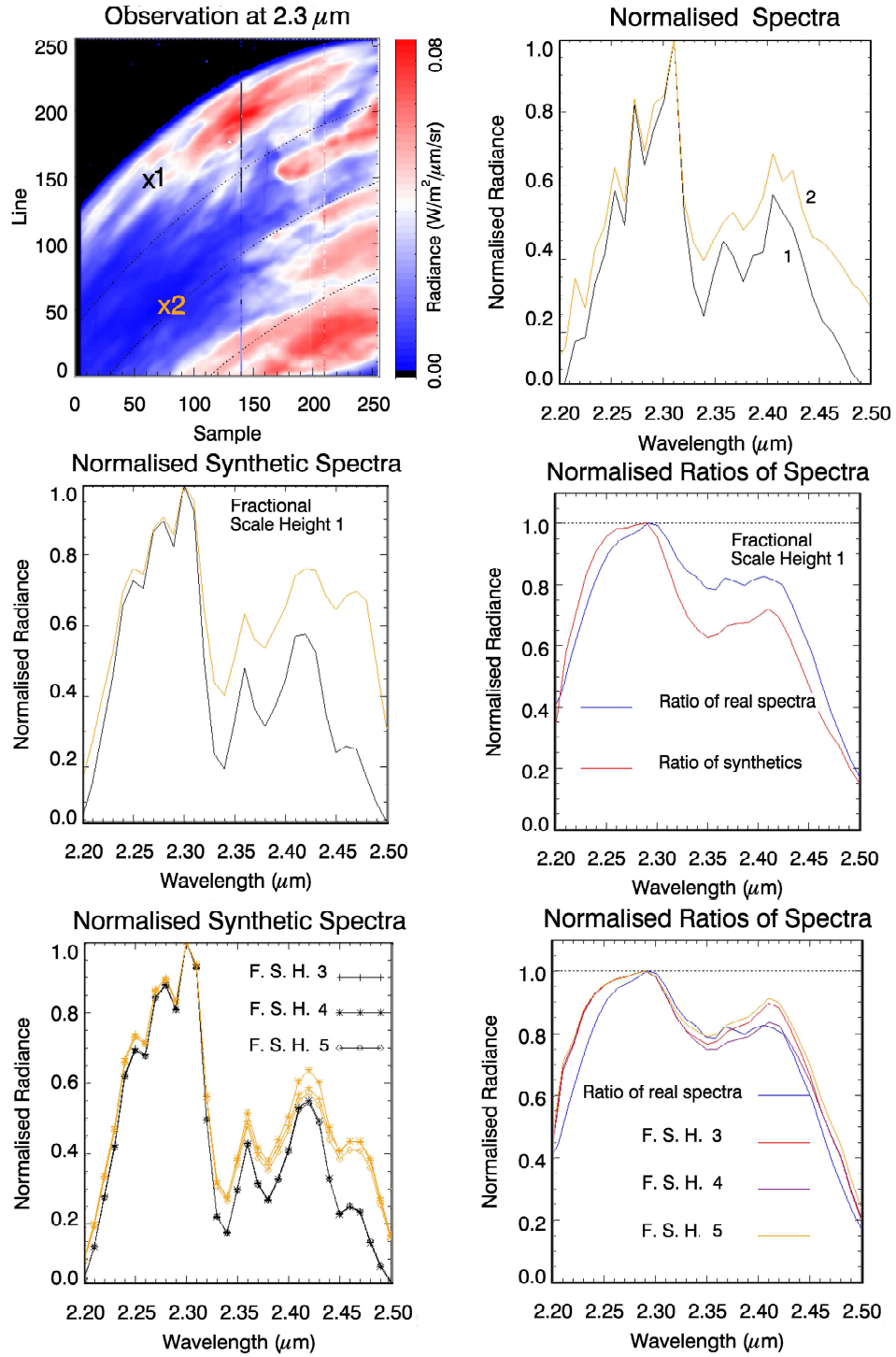


Figure 3.6: An example of the distortion in the synthetic spectrum at 2.45 μm relative to an observed spectrum with the same radiance where the cloud optical depth is high. The black lines are real/synthetic spectra corresponding to Point 1 (bright region), the orange lines correspond to Point 2 (dark region). The lower plots show the improvement in the spectral shape when the lower cloud fractional scale height is increased to 4.

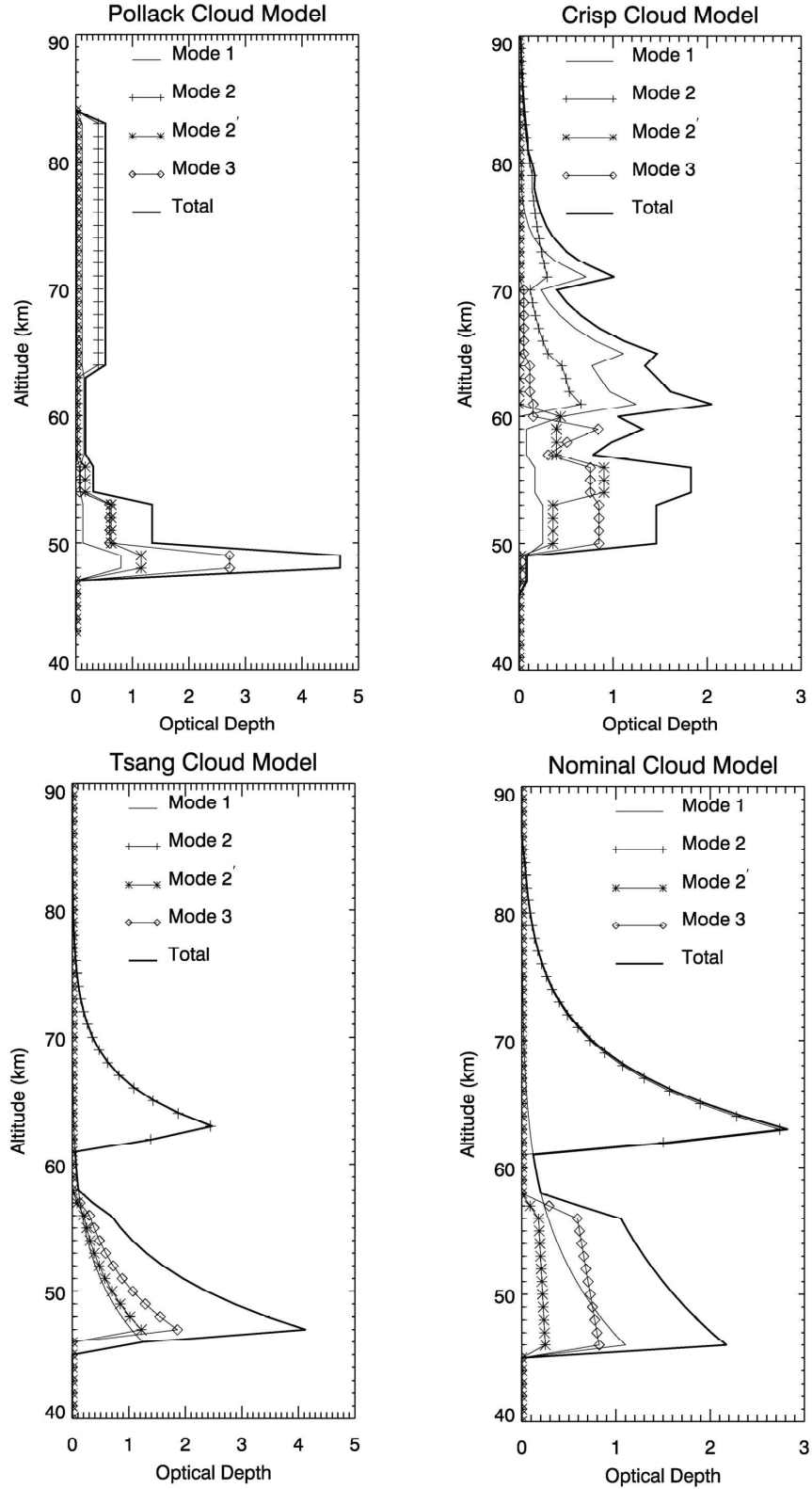


Figure 3.7: Vertical distributions of the four cloud particle size modes used in this work, compared with those in the models of Crisp et al. (1986), Pollack et al. (1993) and Tsang et al. (2008a). Optical depths are at $0.63 \mu\text{m}$.

insufficient information is contained within an infrared spectrum to retrieve the sixteen variables that fully describe the vertical distribution of the four cloud modes, as well as other parameters that I am seeking to constrain.

I have used the same *a priori* cloud top altitudes as Pollack et al. (1993), and these are fixed. The mode 2 optical depth is increased from the values used by Pollack et al. to 14 at 0.63 microns, bringing the model closer to the model of Grinspoon et al., and the mode 1 optical depth is increased to 8, a compromise between the lower values of Pollack et al. and Grinspoon et al. (4—6). and the much higher value of Crisp (14). The total upper cloud (above 60 km) optical depth is 15, similar to that suggested by Grinspoon et al. and Crisp. The effect of changing the mode 1 and mode 2 optical depths is investigated in Section 6.3.4, but for the majority of the following work these parameters are fixed, as the upper cloud is relatively uniform across the planet, although the altitude of the cloud top decreases with latitude polewards of $\sim \pm 50^\circ$ (Ignatiev et al. 2009). The effect of including this variation in the model is discussed in Section 6.3.4.

The fractional scale heights have been increased from the profile suggested by Tsang et al., to $1 \times H_{atm}$ in the upper cloud and $4 \times H_{atm}$ in the lower cloud, and are fixed. This removes cloud particles from the line-forming region in the lower cloud without reducing the optical depth, which corrects for some spectral distortion observed between 2.3 and 2.5 μm in models with high cloud optical depths (Figure 3.6). It also brings the distribution of particles in the model closer to that suggested by Crisp (1986), particularly in the lower cloud, and reflects the mostly-uniform distribution with altitude seen by the Pioneer Venus and Venera descent probes. The mode 2' and mode 3 base altitudes (representative of the cloud base altitude) are allowed to vary in the model, although the two altitudes are forced to be equal, and are shown in Figure 3.7 as 45 km. The mode 2' and mode 3 optical depths are allowed

to vary in the model. The values shown in Figure 3.7 are for a combined optical depth of 6 at $0.63\ \mu\text{m}$, which is typical of lower optical depth regions on the planet. The *a priori* cloud particle distributions are shown in Figure 3.7, with profiles from Pollack et al. (1993), Crisp (1986) and Tsang et al. (2008) for comparison.

Refractive index data for sulphuric acid are taken from Palmer and Williams (1975). Values for 75, 85 and 96 wt % are used. The size distribution used is the same as that used by Pollack et al. (1993) (Table 3.2).

The number of variable cloud parameters has been reduced to only four; the total lower cloud optical depth, the cloud base altitude, the relative particle size and the acid concentration. The relative particle size is parameterised as the ratio of the mode 3 to mode 2' number densities, as the best representation of the particle size in the lower cloud, hereafter referred to as the particle size parameter. This is considered to be the most useful parameterisation as 1) two distinct larger modes, as well as the ubiquitous mode 1 particles, are persistently identified in descent probe data (Knollenberg and Hunten 1980), and 2) the majority of the optical depth variation occurs in the lower cloud, where opacity variations in mode 2' and mode 3 dominate. This provides a more realistic picture than modelling the variation with a single-mode cloud and changing the effective radius of the particles. The effective radii in the size distributions are not changed, although the effect of altering the mode 3 effective radius is discussed in Section 6.3.2. These four variables encompass the majority of the observed variation in the cloud, and there is sufficient information in the infrared spectrum to reliably retrieve them, plus VMRs of CO and H₂O in the lower atmosphere.

3.4 Summary

The Venusian cloud is complex, and therefore requires a level of complexity in parameterisations for radiative transfer calculations. Various modelling approaches and parameterisations have been discussed. I have shown in Section 3.3.1 that it is necessary to model the Venusian cloud with multiple size modes and at least two discrete layers, supporting the previous work of Crisp (1986), Pollack et al. (1993), Grinspoon et al. (1993) and Tsang et al. (2008). I describe the rationale behind my chosen *a priori* parameterisation in the context of the previous work; instead of splitting the cloud into many vertical layers and specifying properties for each layer, the procedure employed by Crisp, Pollack et al. and Grinspoon et al., each of the four particle modes is parameterised by top and bottom altitudes, a fractional scale height and a total optical depth. These sixteen parameters are reduced to three – lower cloud total optical depth, cloud base altitude and mode 3:mode 2' ratio, plus the acid concentration in the cloud droplets, and provide the fullest description of local and global cloud variability for the fewest retrieved parameters. *A priori* values are based on the previous work of Crisp, Pollack et al., Grinspoon et al. and Tsang et al., and as such reflect the accumulated knowledge prior to Venus Express. In the next chapter, I will discuss how I exploit the new VIRTIS dataset and use this cloud parameterisation to determine mean values for these cloud parameters for different conditions on Venus.

Chapter 4

VIRTIS Data and Analysis

Technique for Cloud Parameter Retrieval

This chapter details the analysis technique used to extract global information about the clouds from the VIRTIS dataset. Further processing of the VIRTIS calibrated data product was necessary before it could be used with this technique, and this is discussed in Section 4.1. Next, a study of the spectral sensitivities to various model parameters in the 1.2—2.6 μm range was necessary to determine what information about the cloud could be independently extracted from VIRTIS spectra (Section 4.2.2). The information acquired is then used to formulate a computationally-inexpensive, hierarchical method to determine cloud properties using VIRTIS data, as described in Section 4.2.4. The results are presented in Chapter 5, and the associated error analysis and validation are presented in Chapter 6.

4.1 Dataset and processing

Data from VIRTIS-M-IR are transmitted in the form of three-dimensional cubes, with two spatial dimensions and one spectral dimension. The VIRTIS-M spectrometer slit is 256 pixels across, and during each observation VIRTIS-M scans in a direction perpendicular to the orientation of the slit, recording a 256×256 pixel image. The third dimension of the cube is provided by the 432 spectral channels (Drossart et al. 2007, Piccioni et al. 2008). This makes for a very versatile dataset, as variation in the radiance at a given wavelength can be investigated by looking at an image in one of the 432 spectral bands, or a spectrum can be extracted from a specific location in the image.

The data used in this work are taken from 922 VIRTIS cubes between orbits 100 and 898. The selection has good coverage of the southern hemisphere on the night-side; it also provides good temporal coverage, spanning more than two Earth years of observations from July 2006 until October 2008 (when VIRTIS-M-IR ceased to function). This selection does not include all observations taken during this time, but represents a compromise between good coverage and efficiency. The selection within this time interval is made on the basis of observation geometry – only images with at least 256×256 pixels are included. This is important for the averaging described below (Section 4.1.1). Observations with the shortest exposure time of 0.026 s are excluded, as these would have a low signal-to-noise ratio. The total number of individual spectra is 484050, after the averaging described below, although some of these are rejected during the retrieval process.

The VIRTIS-M-IR component of the instrument has already been calibrated to a very high standard, which process is described in detail by Cardesin Moinelo et al. (2010). The majority of the processing is performed on the ground, in three main stages. Thermal background, bad frame and dead/saturated pixel removal

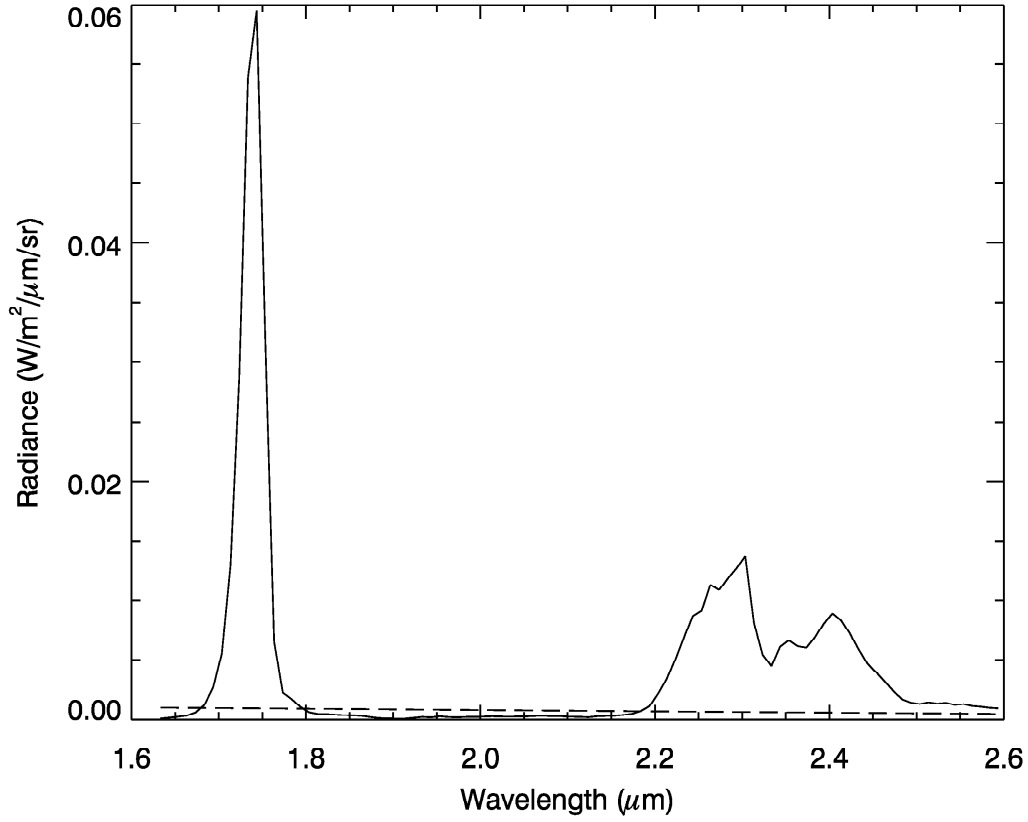


Figure 4.1: The noise-equivalent spectral radiance for a 1 s VIRTIS observation (dashed line) compared with a low-radiance spectrum (solid line). After averaging over several hundred spectra the NESR decreases by a factor of ~ 10 .

and identification are performed prior to radiometric conversion, and the spectral registration is also determined at this stage. The radiometric calibration is then performed, and the pixel counts are converted into radiances; some post-calibration processing is then necessary, to remove spikes and stripes from the data. This calibration process is intended to remove, as far as possible, systematic radiometric errors from the dataset.

The signal-to-noise ratio (S/N) has been maximised in this work by the averaging process described in Section 4.1.1; it can be calculated using the VIRTIS-M noise-equivalent spectral radiance (NESR) from the ground calibration of the instrument

(Piccioni, G. and Drossart, P. 2004). The NESR was calculated from the standard deviation of measurements of a cold background source, and is provided based on an exposure time of 1 s; the NESR used here is based on a few spectral points, and is then interpolated to provide a smooth, conservative NESR for the whole spectrum. It is then scaled for the actual exposure time, and where several spectra are averaged to produce a single spectrum the number of spectra averaged is also accounted for. The formula used is $\text{NESR}_{\tau,n}(\lambda) = \text{NESR}(\lambda) / \sqrt{\tau n}$, where τ is the exposure time and n the number of spectra. An example of the 1 s exposure time NESR, compared to a typical low-radiance VIRTIS spectrum, is shown in Figure 4.1. It can be seen that the radiance exceeds the NESR in all spectral regions in the 1.74 μm window, and between 2.18 and 2.6 μm , which are the regions used in this analysis. Since in most cases several hundred spectra are averaged over for each retrieval, the actual NESR is generally lower by an order of magnitude than that shown in the figure. It is stated in Piccioni, G. and Drossart, P. (2004) that the NESR may be overestimated, so I take this to be a conservative estimate of the noise; the S/N for the averaged spectra used in the analysis is therefore high.

Cardesin Moinelo et al. (2010) place a similar, slightly reduced estimate on the NESR based on the calibration of the flight data. It must be remembered, however, that this NESR is a measure of the random noise only, and does not take into account any potential systematic error. The greatest concern is spectrally-varying systematic error, as the method relies upon the comparison of radiances at different wavelengths. Spectrally varying radiometric offsets due to problems with the instrument itself are unlikely to persist beyond the radiometric calibration, but there are other possible sources of such errors which require consideration, discussed below in Sections 4.1.1 and 4.1.2. Two acknowledged outstanding issues after calibration (Cardesin Moinelo et al. 2010) are an offset in the spectral registration and a persistently uneven response in odd and even spectral pixels – the so-called “odd-even effect”. The

first issue is mostly consistent from observation to observation, but is known to vary in extent along the slit direction in the image (Cardesin Moinelo et al. 2010). The second issue is most pronounced in observations with short exposure times, and though it is more important for observations of the dayside, it has a noticeable effect on the nightside in the spectral region between 2.5 and 2.6 μm . The approach used in this work to correct for both issues is discussed in Section 4.1.1.

4.1.1 Averaging and spectral registration

As described above, data from VIRTIS-M-IR are transmitted as a 3-dimensional cube, with dimensions $432 \times 256 \times 256$ pixels. Geometry files are also distributed with the calibrated data, which contain geometrical data for each individual pixel. The data used in this work have been spatially co-added in boxes of 20×20 pixels, shifted every 10 pixels to ensure Nyquist sampling. This reduces a 256×256 pixel image to a 25×25 pixel image, and increases the signal to noise ratio. These data have also been corrected for the spectral registration shift mentioned above, using a cross-correlation method similar to that described in Tsang et al. (2009) but over the whole 1.6—2.6 μm range. A synthetic reference spectrum in the range 1.6 to 2.6 μm normalised to the radiance at 1.74 μm is compared with normalised spectra from VIRTIS that have been interpolated onto the model wavelength grid, and a cross-correlation routine is used to determine the wavelength offset between the two normalised spectra. This offset is then subtracted to obtain the real wavelength registration, before co-adding (Figure 4.2).

Single radiances closest to 1.31, 1.51, 2.2, 2.29, 2.32, and 2.4 μm have then been extracted for each coadded spectrum. Due to the wavelength registration shift, the 1.74 μm radiance peak is often not sampled - instead, two points of similar radiance either side of the peak are sampled. As the radiance gradient is large in this region of

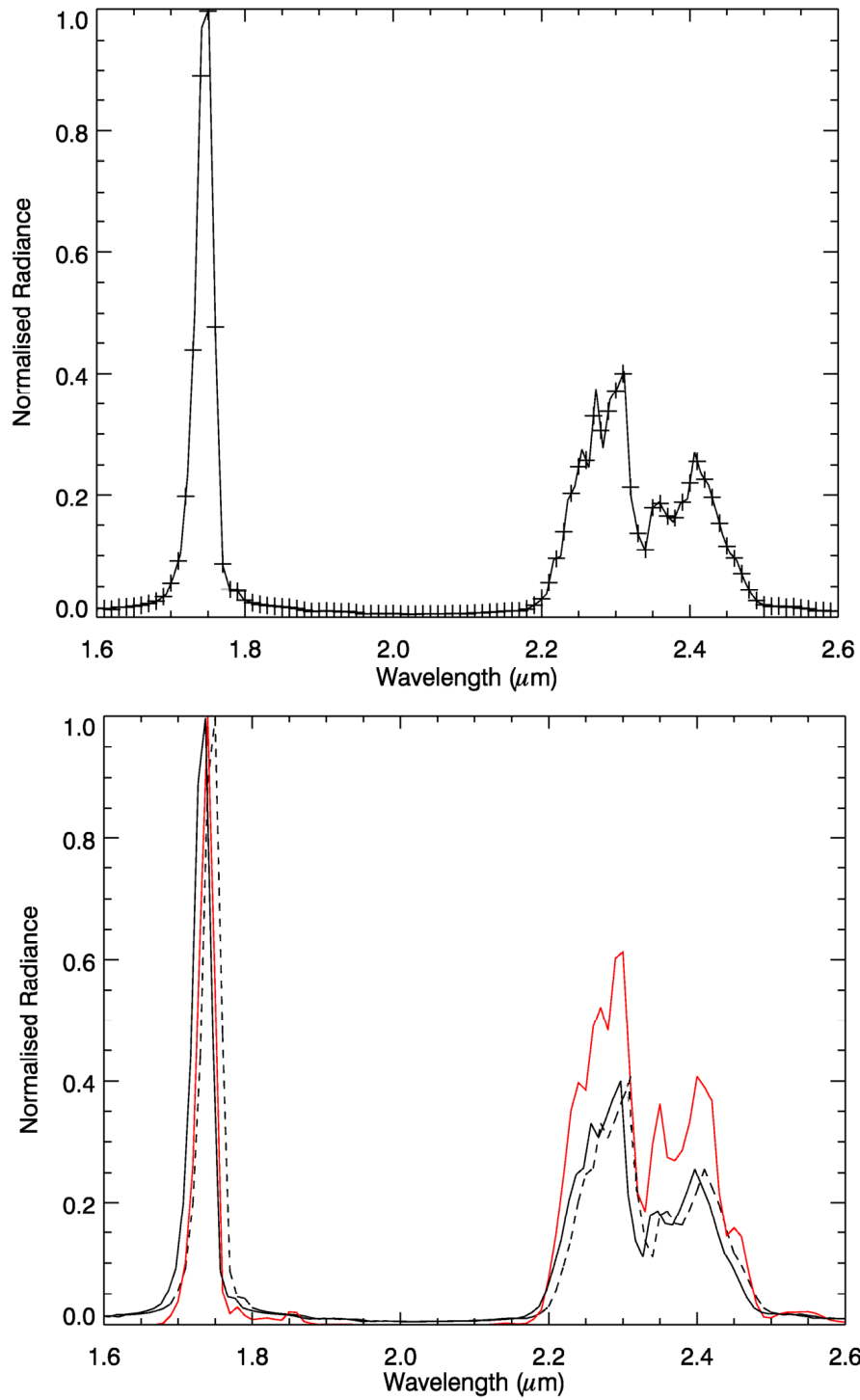


Figure 4.2: An example of the spectral registration correction process. The top figure shows a spectrum from VIRTIS normalised to the radiance at 1.74 μm (solid line). The crosses are points where the spectrum has been interpolated onto the same grid as a reference synthetic spectrum with 0.01 μm resolution. The figure below shows the interpolated spectrum (dashed line), the reference synthetic spectrum (red line) and the shifted interpolated spectrum, now corrected for the spectral registration shift.

the spectrum, this results in a much lower maximum radiance at 1.74 μm than would be the case if the true peak was sampled. To correct for this, a third order polynomial function is fit to the four spectral points closest to 1.72, 1.73, 1.74 and 1.75 μm , and the maximum value of this function determined. That maximum value is then taken to be the 1.74 μm radiance. The 1.71 μm radiance is determined by interpolating between the two sampled points on either side of 1.71 μm , since the maximum value for 1.74 μm is usually part way between the points closest to 1.73 and 1.74 μm and this best maintains the distance in wavelength space between the 1.71 and 1.74 μm points. The 2.53 μm radiance has been smoothed using a triangular filter in order to remove the above-mentioned odd-even effect. This smoothing calculates the 2.53 μm radiance as $I'_{2.53} = 0.25 \times I_{2.52} + 0.5 \times I_{2.53} + 0.25 \times I_{2.54}$.

4.1.2 Scattered and stray light

VIRTIS is susceptible to contamination from various unwanted sources of radiance. As VIRTIS is an infrared instrument, one of these potential sources is heat from the instrument itself, hence for operation to be possible the infrared detector is cooled to a maximum temperature of 130 K. The filter window also reduces the thermal contribution from the instrument housing. The VIRTIS-M-IR filter window is designed to prevent contamination from higher diffraction orders, and the window is also covered with an anti-reflection coating to further reduce scattering and noise. The instrument is designed to minimise stray light effects; only the primary and secondary mirrors are illuminated by potential stray light in VIRTIS-M, as other optical elements are situated behind the field stop (VIRTIS Team 2002). The aperture stop is situated as close to the detector as possible to minimise the number of critical objects that can be seen directly by the detector (VIRTIS Team 2002), which also acts to minimise the stray light. VIRTIS-H is baffled to reduce the stray light

contribution to that part of the instrument, but this is not the case for VIRTIS-M, which means the data used in this work may still be contaminated by stray light.

Because reflected sunlight from the dayside of Venus has a contribution in the infrared that far exceeds the nightside thermal emission in intensity, most of the nightside spectra are to some degree contaminated by this. This dayside radiance is scattered into regions of the VIRTIS image that are looking only at the nightside, either because a bright sunlit crescent is present in the image and the light is scattered within the instrument, or the light is scattered within the upper atmosphere of Venus itself. The latter effect is most prominent within 5° incidence angle of the terminator, with the contribution decreasing with increased distance from the dayside; close to the terminator the scattered light is of the same order of magnitude as the nightside signal. The former effect is generally smaller, but is also more widespread as many of the observations considered contain a sunlit crescent. Instrument design cannot avoid problems with light being scattered within the atmosphere of Venus itself; the anti-reflection coating on the filter window may minimise the scattering within the instrument, but some contribution is still present and must be accounted for.

This scattered light can be removed from the spectra by taking a reflected sunlight spectrum from the dayside, scaling it and then subtracting it from the nightside spectrum. I use here a dayside spectrum from orbit 0129, which was obtained near the subsolar point and smoothed with a square wave averaging function of 5 spectral pixels in width. The longer wavelength region was further smoothed to remove the pronounced odd-even effect longwards of $2.1\ \mu\text{m}$. The spectrum is scaled against the CO_2 absorption band near $1.4\ \mu\text{m}$, in a similar procedure to that adopted by Meadows and Crisp (1996), as in this region nightside spectra should show zero emission.

At wavelengths shorter than 1.74 μm , stray light directly from the sun can significantly affect the spectra obtained by VIRTIS if the observation geometry is unfavourable. This stray light is not scattered into the field of view of VIRTIS, but is sunlight directly striking (and heating) the VIRTIS instrument, although the night-side of the planet is under observation here (Arnold et al. 2008). The effect of this is to increase the zero radiance level of the spectrum with decreasing wavelength. The amount of stray light contamination depends on the angle between the observation and the instrument-to-Sun vector and therefore varies between observations. To remove this effect, a range of stray light curves from pixels looking to space are smoothed with a square wave averaging function of 10 spectral pixels width and then averaged to give a representative stray light curve, preserving the features present in the stray light. This curve is then scaled to fit the ‘zero level’ for each observed spectrum (with the dayside scattered light already removed) and the scaled curve subtracted. ‘Zero level’ points are selected by comparing the observed spectrum including stray light with a spectrum generated from a radiative transfer model. Combinations of polynomial functions are then fitted to the ‘zero level’ points from the observed spectrum and the stray light spectrum. The scaled stray light has the form:

$$\Delta I(\lambda)' = \Delta I(\lambda) \times (F(\lambda)_{obs} / F(\lambda)_{\Delta I}) \quad (4.1)$$

where $\Delta I(\lambda)$ is the representative stray light curve, $F(\lambda)_{obs}$ is the polynomial function fit to the ‘zero level’ points in the measured spectrum and $F(\lambda)_{\Delta I}$ is the polynomial fit to the ‘zero level’ points in the stray light curve. $F(\lambda)_{obs} / F(\lambda)_{\Delta I}$ is therefore the scaling factor. The corrected spectra are then used in the analysis. An example spectrum without any significant contribution from stray or scattered light between 1.6 and 2.6 μm is shown in Figure 4.3. A spectrum corrected for both scattered and stray light compared with the original is shown in Figure 4.4.

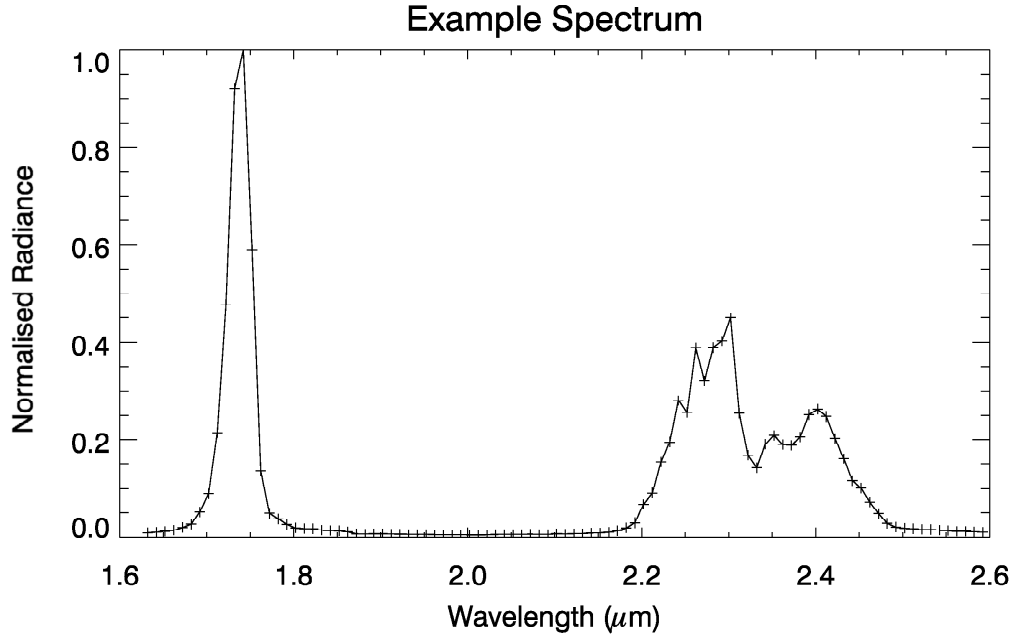


Figure 4.3: A VIRTIS-M-IR spectrum in the 1.6—2.6 μm range, characteristic of a spectrum uncontaminated by stray light.

4.1.3 Limb darkening

The VIRTIS viewing geometry results in the planet being observed at a range of emission angles. The emission angle of the radiation coming from the planet affects the radiance measured, which effect on Venus is mainly due to the scattering properties of the cloud; as the sulphuric acid particles that make up the cloud are highly forward-scattering, less radiation is scattered into the line of sight for high emission angles. (Figure 4.5). A correction for this limb darkening effect is applied to each of the radiances used. The correction is obtained by creating model spectra for different input emission angles, and deriving a relationship between emission angle and radiance at each wavelength. The theoretical limb darkening for the wavelengths used is shown in Figure 4.6. It can be seen from this figure that the dependence on $\cos(\theta)$ is close to linear, and also that there is little dependence on wavelength, although I still derive separate corrections for each channel. The model limb dark-

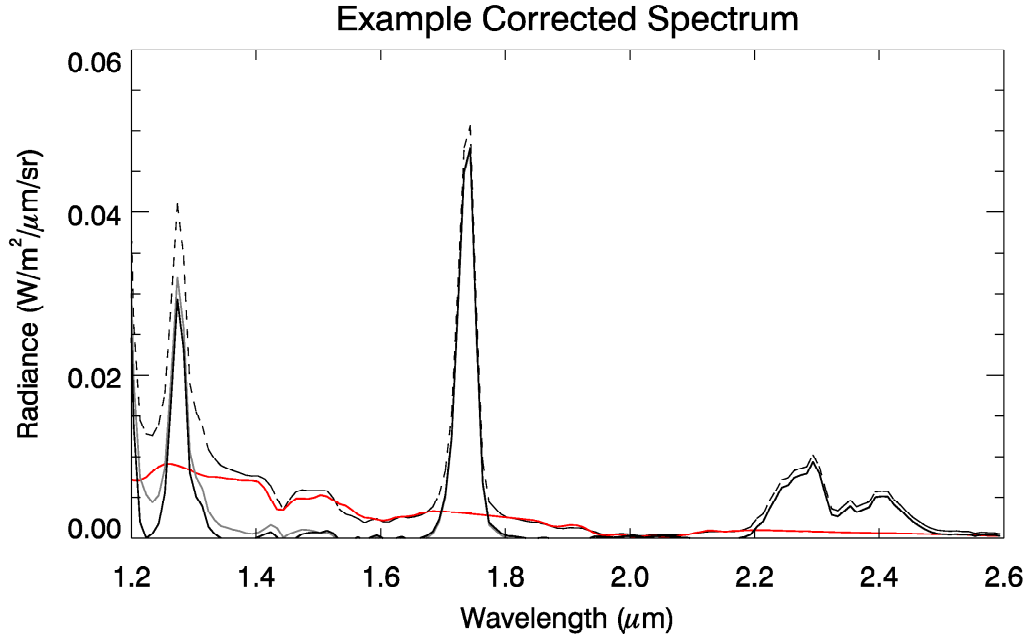


Figure 4.4: An example spectrum contaminated by stray light at short wavelengths (dotted line) compared with the same spectrum corrected for scattered light (solid grey line) and total stray light (solid line). The scaled dayside spectrum used to remove the scattered light is shown in red. This demonstrates the potential extent of contamination by the stray and scattered light and the efficacy of the removal procedure in such cases.

ening correction derived for 1.74 μm is $I_0 = I/(0.6848 \times \cos(\theta) + 0.3211)$, similar to that calculated by Carlson et al. (1993) which is $I_0 = I/(0.685 \times \cos(\theta) + 0.316)$. Carlson et al. (1993) show this theoretical curve to correspond well with the upper boundary of I/I_0 data plotted as a function of $\cos(\theta)$. The calculated value for 2.3 μm used here is somewhat different to that used by Carlson et al. (1993), but more recent calculations (Carlson, R. W. 2007) show agreement with the observed wavelength invariance of the correction in this work, and the new correction exhibits similar behaviour to those used here.

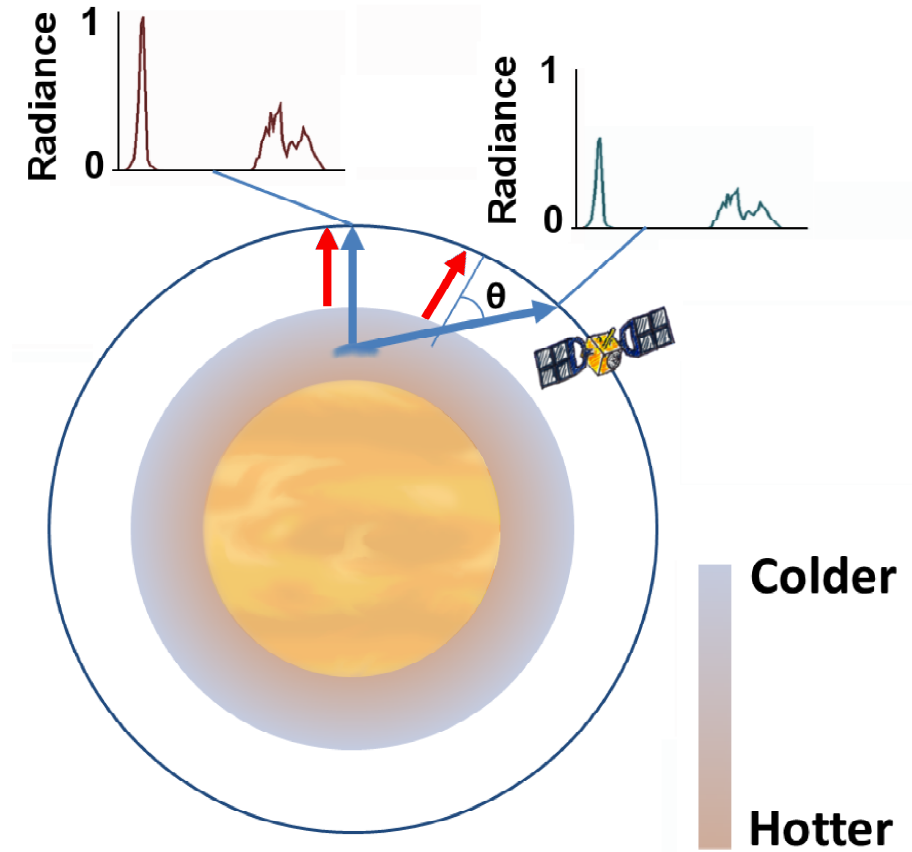


Figure 4.5: When observing at high emission angle θ , less radiation from the hot lower atmosphere is scattered into the line of sight, as the cloud particles preferentially scatter in the forward direction. Blue arrows indicate observation angle, red arrows indicate predominant scattering direction. The signal is therefore attenuated relative to the nadir case.

4.2 Retrieval procedure

4.2.1 The ‘branch plot’ method

The branch plot method is a computationally-efficient way to determine values for a range of atmospheric parameters by fitting computed spectra to measured spectra (Carlson et al. 1993, Wilson et al. 2008). In this method, pairs of wavelengths are selected such that one is sensitive to variations in, for example, particle size or gaseous species VMR, and the other not or less so. Different pairs are chosen

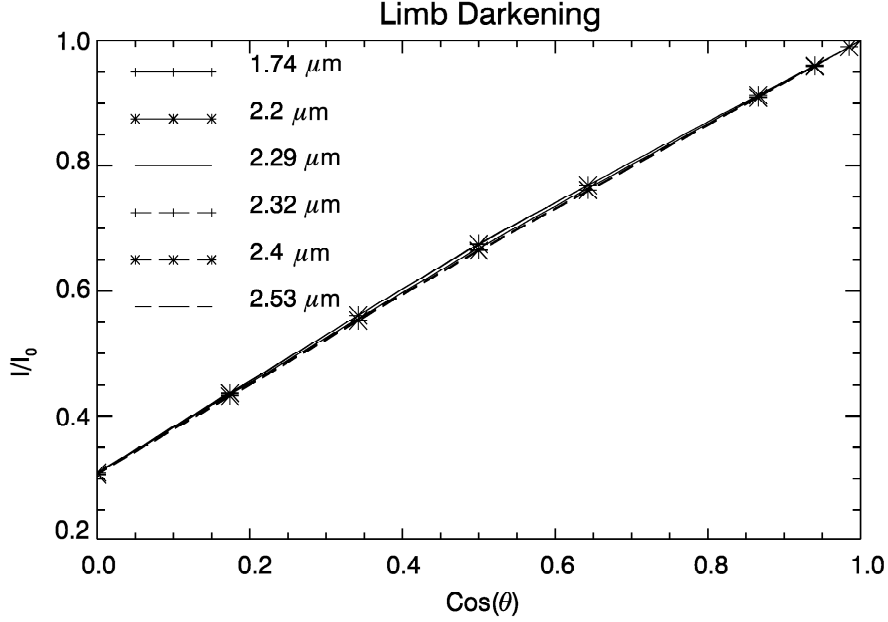


Figure 4.6: The theoretical limb darkening obtained by creating model spectra for different emission angles. The dependence is very close to linear, so a linear correction in $\cos(\theta)$ of the form $I_0 = I/(a\cos(\theta) + b)$ was used.

for each of the key parameters that have a measurable signature in the spectrum, as determined by model sensitivity studies detailed in Section 4.2.2. An example plot is shown in Figure 4.13. The results of the retrieval can be used to compute a synthetic spectrum, which is compared to the full observed spectrum as a check if desired, as in Section 6.1. The method is designed to extract sufficient information from the spectrum to perform the retrieval, but without wasting computer power in fitting regions of the spectrum where there is no information content; the full spectrum can still however be utilised to check the retrieval.

4.2.2 Selection of wavelengths

Near-infrared radiation in the 1.6—2.6 μm range (Figure 4.3) is scattered and absorbed by the cloud on Venus. The values of the variable cloud properties in the model parameterisation discussed in Section 3.3.4 impact the shape of a synthetic

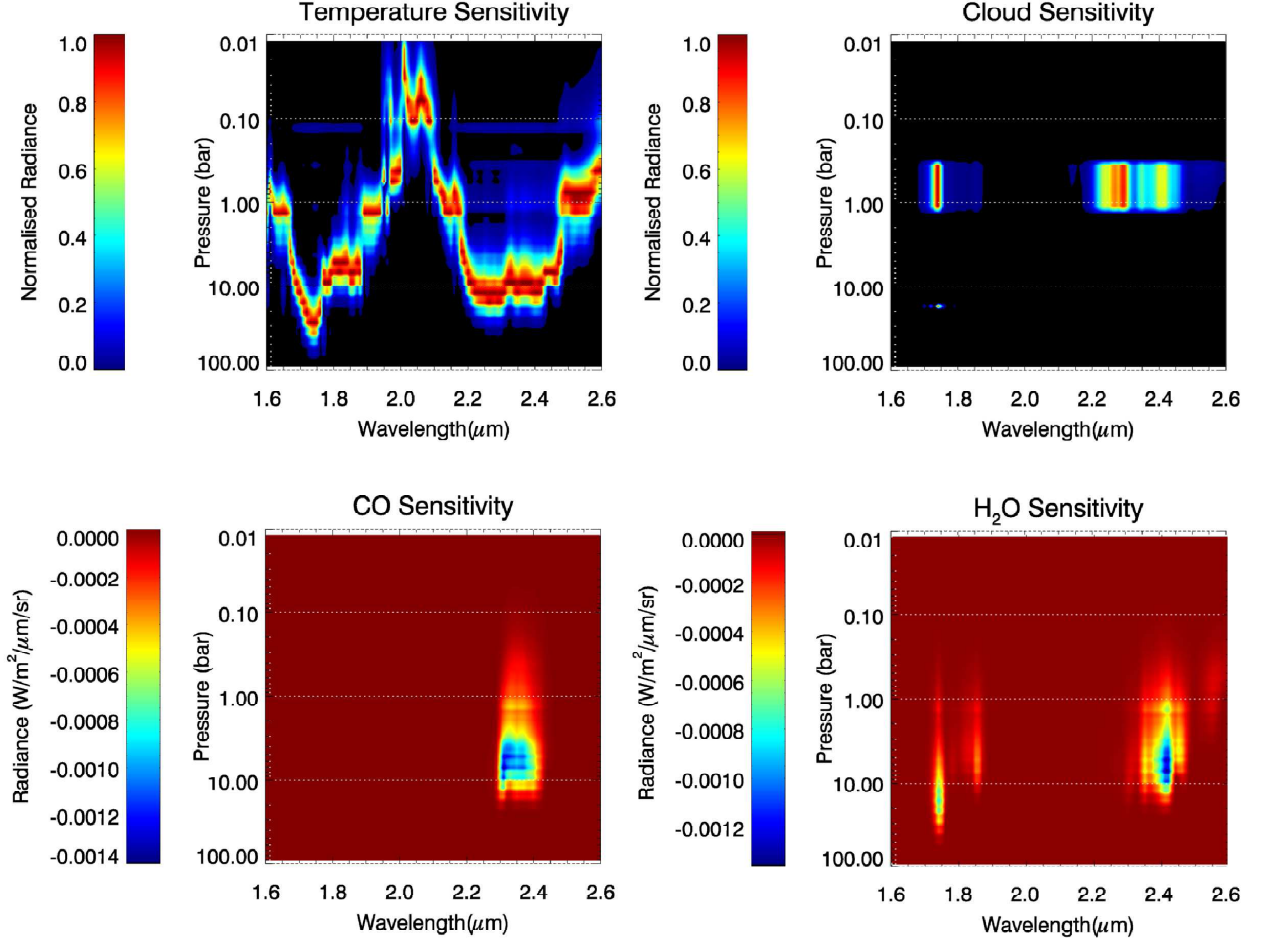


Figure 4.7: Sensitivity to temperature structure, lower cloud optical depth, CO and H₂O between 1.6 and 2.6 μm, demonstrated by contribution function plots generated using NEMESIS. The temperature contribution function is normalised to the maximum sensitivity at each wavelength in order to highlight the altitude of maximum sensitivity. The cloud opacity sensitivity is normalised to the sensitivity at 1.74 μm. Contribution functions for gaseous VMRs are expressed as absolute change in radiance per ppmv VMR increase. We see from the temperature contribution function that the altitude that contributes most to the emission (where the weighting function peaks) between 2.2 and 2.5 μm is ~35 km (10 bar), whereas between 2.5 and 2.6 μm it is ~50 km (1 bar), within the cloud deck; since the observed radiance is sensitive to the absorption and scattering by any cloud particles located above the altitude of emission, comparison of radiances at these two wavelengths provide a constraint on the vertical distribution of the cloud.

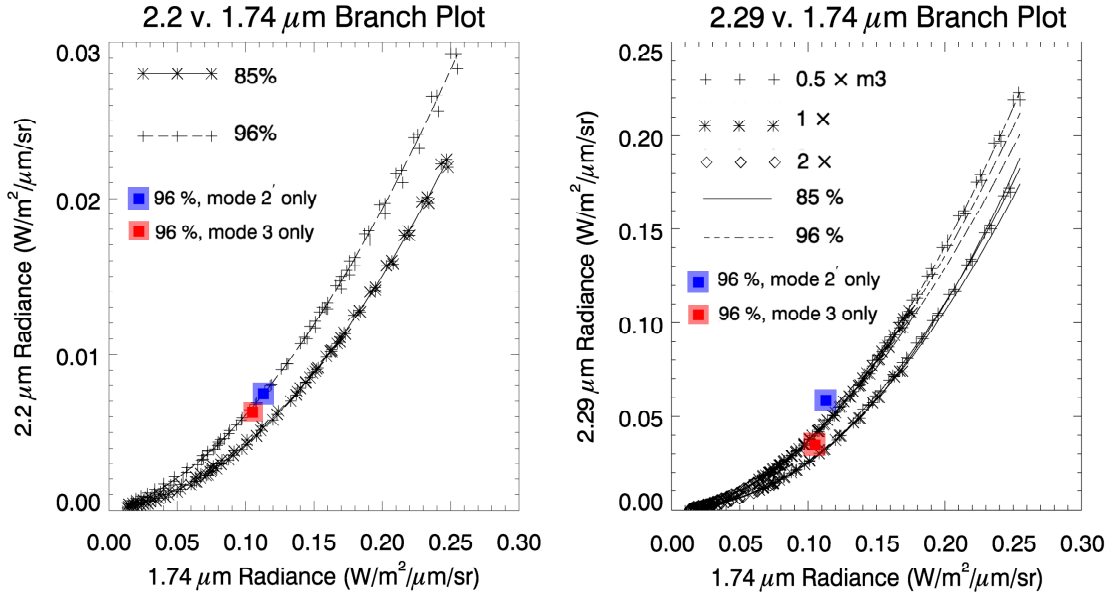


Figure 4.8: Branch curves generated by varying the total lower cloud optical depth, for models with different acid concentrations, base altitudes and ratio of mode 3 to mode 2' relative to the *a priori* case. These plots show variation in the 2.2:1.74 μm and 2.29:1.74 μm radiance ratios. It can be seen that in the 2.2 μm plot that models with only mode 2' and only mode 3 both lie on the same branch, whereas the 2.29 μm plot shows significant sensitivity to this variation. Both plots show two distinct branches for models with different acid concentrations. The altitude of the cloud base has little effect in these plots.

spectrum in this wavelength range; different regions of the spectrum are sensitive to each of these properties in varying degrees. In the spectral window regions at 1.74 μm and between 2.15 and 2.6 μm there are absorption bands due to CO, H₂O and OCS (carbonyl sulphide), with relatively insignificant contributions from HF and SO₂. Absorption due to HCl is present at 1.74 μm , but measurements of the HCl volume mixing ratio in the deep atmosphere show that VMR of the gas at a given altitude. The temperature contribution function is normalised to the maximum sensitivity at each wavelength to make the altitude of maximum sensitivity clear.

The retrieval method, described below in Section 4.2.4, depends on the selection of pairs of narrow spectral bands at wavelengths that are uniquely, or predominantly, sensitive to each of the parameters in the model. The sensitivity to acid concentration and particle size parameter for two specific bands are shown in Figure 4.8. The plots shown are produced using model data for two different acid concentrations (range 85—96 %), three particle size parameters (0.5—2) and three base altitudes (44—52 km). The red and blue squares show radiances from two extreme models, one with only mode 2' and the other with only mode 3 in the lower cloud. The figure demonstrates that at 2.2 μm relative to 1.74 μm there is sensitivity to acid concentration but very little signature from particle size parameter, even for the extreme case, and from Figure 4.7 we see there is no absorption from CO or H₂O at this wavelength either. The relationship between 2.2 and 1.74 μm is therefore used to determine acid concentration, since sensitivity to acid concentration predominates. The sensitivity to particle size parameter is more significant near 2.29 μm and there are similarly no CO or H₂O absorption lines in this region, so this wavelength relative to 1.74 μm is used to determine the particle size parameter after accounting for variation in acid concentration.

The 2.5—2.6 μm region is sensitive to temperature changes at the 1 bar level (about 50 km), which is within the lower cloud (Figure 4.7). This is in contrast to radiation at wavelengths of 2.2—2.5 μm , which originates below the clouds at 30—45 km (~ 10 bar). To constrain the vertical distribution of the cloud, a pair of wavelengths with weighting functions peaking at these different altitudes is required. Whilst the altitude of maximum sensitivity is also ~ 50 km between 2.15 and 2.17 μm , the radiance at these wavelengths is significantly lower than that at 2.53 μm , so the signal to noise ratio is much smaller. Stray and scattered light (see Section 4.1.2) also become problematic in this spectral region due to the very low radiances and the presence of a feature in the dayside reflectance spectrum, and they are difficult to correct for with the required level of accuracy. Therefore, the region between 2.5 and 2.6 μm is preferred for the determination of the cloud base altitude. The optimum choice uses 2.53 and 2.4 μm radiances – since radiances at both wavelengths are sensitive to absorption by water vapour, the branching relationship is insensitive to variations in the water vapour VMR, assuming no significant deviations from the assumed vertical profile. At 2.53 μm the radiation is coming from within the cloud deck, whereas at 2.4 μm the radiation passes through the whole vertical thickness of the cloud, allowing constraints to be placed on the vertical distribution for a given total cloud optical depth. This is parameterised by changing the cloud base altitude. The scale height is fixed, since I have already placed some constraint on it as described in Section 3.3.4, although the possibility of scale height variation cannot be ruled out; the effect of varying the scale height is discussed further in Section 6.3.4.

Water vapour absorption lines are present at 2.4 and 2.57 μm , with weighting functions peaking below the cloud at 2.4 μm and within the cloud at 2.57 μm . The significant weighting function overlap and large vertical extent of the functions means that the water vapour variation is best treated as correlated between these two alti-

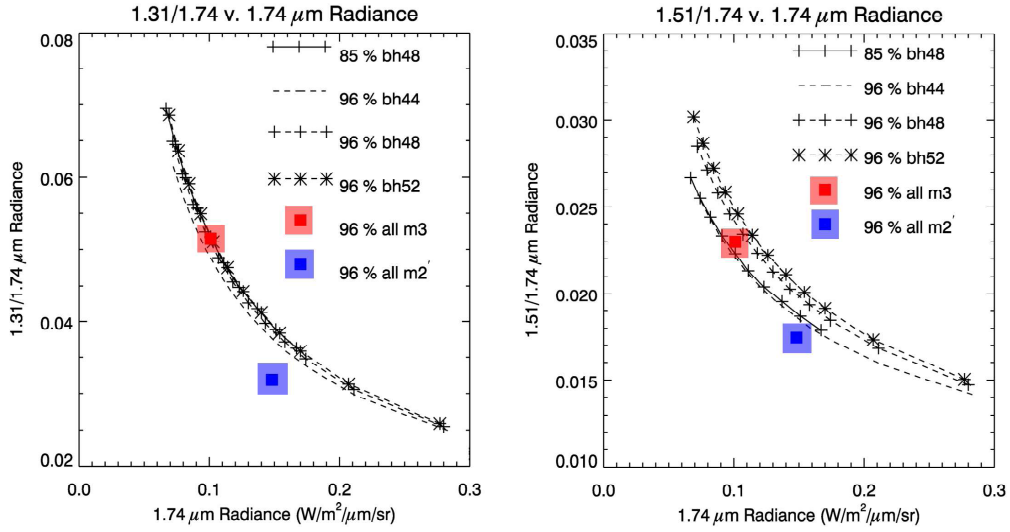


Figure 4.9: Sensitivity to cloud parameters at 1.31 and 1.51 μm . The sensitivity is mainly due to relative mode 3:mode 2' abundance, although there is some contribution from base altitude variation at both wavelengths and some sensitivity to acid concentration at 1.51 μm .

tudes. The wavelength pair 2.4:2.29 μm is used to constrain the water vapour VMR in the troposphere above 30 km, and the VMR within the cloud deck is assumed to scale with the same ratio. There is also absorption due to CO at 2.4 μm , the effect of which needs to be accounted for as well. The ratio between 2.32 and 2.29 μm radiances is used by Tsang et al. (2009) to retrieve CO VMRs below the cloud, and a similar technique using these radiances is applied here.

4.2.3 The short wavelength windows

There are regions of the spectrum at shorter wavelengths than 1.74 μm that also have sensitivity to variation in atmospheric and cloud properties; the three main regions are at 1.31 μm , 1.51/1.55 μm and 1.71 μm . Sensitivities in these regions are shown in Figures 4.9, 4.10 and 4.11. The short wavelength windows at 1.31 and 1.51 – 1.56 μm are less well-studied than those at 1.74 and 2.3 μm . The 1.51 – 1.56 micron region was first investigated by Wilson et al. (2009). They show that

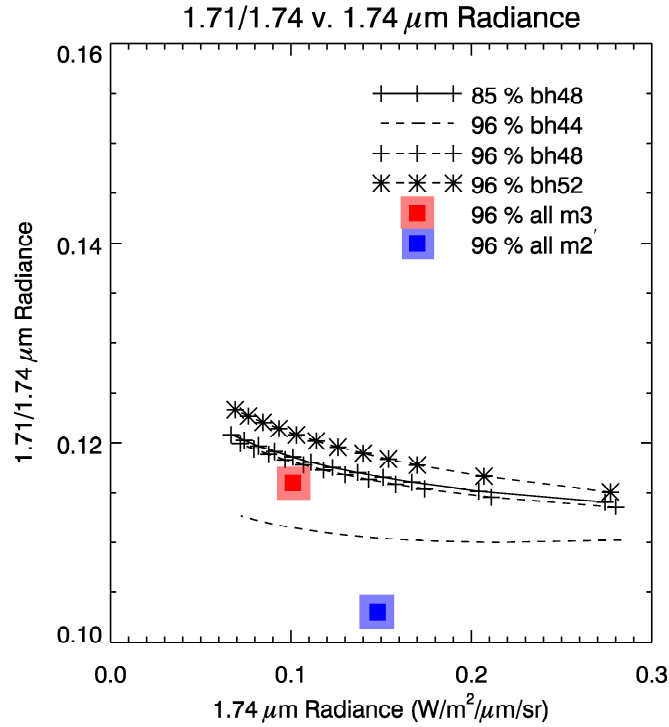


Figure 4.10: Sensitivity to cloud parameters at 1.71 μm . The sensitivity is mainly due to relative mode 3:mode 2' abundance and base altitude, with little contribution from acid concentration.

for a observation time of 1 s with VIRTIS, the 1.55 μm peak is below the noise level, so the radiance at this wavelength is not used here. The 1.51 μm peak is large enough to be above the noise level even for shorter observation times, but the subtracted scattered daylight spectrum (Section 4.1.2) also has a feature at this wavelength, and the combination of this with the low signal radiance limits the reliability of the radiance obtained after processing. The 1.31 μm peak is somewhat higher in radiance; however, there is a strong oxygen airglow band at 1.27 μm (Connes et al. 1979). The level of contamination depends on the relative strength of the airglow compared with the brightness of the thermal radiation. To avoid this problem, all spectra for which the radiance at 1.27 μm exceeds that at 1.74 μm have been rejected for use in the short wavelength comparison (Section 6.2), although they have been retained for the majority of the work as the spectral region between

1.6 and 2.6 μm is not affected. A comparison of spectra (Figure 4.12) shows that the thermal signal at 1.31 μm is not significantly contaminated by the airglow signal if this criterion is applied, and this filtering errs on the side of caution.

Water vapour lines are present at both 1.31 and 1.51 μm , as shown in Figure 4.11. Ideally, there would not be sensitivity to water vapour in any branching ratios used, since the cloud properties are of greater interest. Therefore, the ratios chosen to examine the variability present at these wavelengths are $I_{1.31}/I_{1.74}$ vs. $I_{1.74}$ and $I_{1.51}/I_{1.74}$ vs. $I_{1.74}$. This has the effect of minimising the sensitivity to variation in acid concentration and water vapour VMR. There is sensitivity to the mode 3: mode 2' relative abundance for both ratios, with smaller contributions from the other variables. These ratios provide a good opportunity to validate the results obtained using the longer wavelength windows.

4.2.4 Retrieval technique

Synthetic spectra at the VIRTIS-M resolution of 0.01 μm are created using NEMESIS for different amounts of mode 2' and mode 3 particles, increasing the total cloud optical depth whilst keeping the mode 1 and mode 2 abundances fixed. The abundance of these particles increases with a constant ratio down each branch, implicitly taking into account variation in cloud optical depth, and different branches are produced by changing the ratio of mode 3 to mode 2' and other model input parameters. Ranges of variability used are chosen to make use of existing constraints as presented in the literature. Tests described in Section 6.3 show that there is little sensitivity to the chosen *a priori*. If the parameter space so defined depends on only one variable, the position of a data point from a real spectrum on the branch plot allows the variable to be fixed for that data point. Once this variable is fixed, branch plots that are sensitive to this variable and one other can be used to fix a second variable,

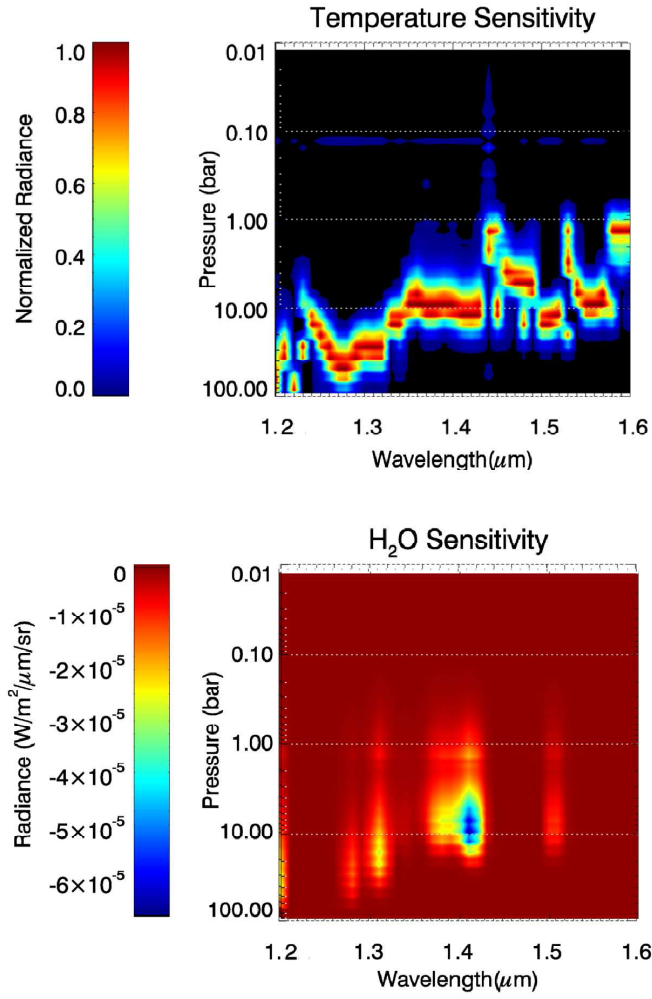


Figure 4.11: Normalised temperature sensitivity and water vapour sensitivity in the short wavelength windows. It can be seen from the temperature plot that the altitude of maximum sensitivity at 1.31 is similar to that for 1.74 μm (see Figure 4.7) whereas the altitude for 1.51 μm is a few km higher at the 10 bar level, similar to 2.3 μm . There are water vapour absorption lines at 1.31 and 1.51 μm .

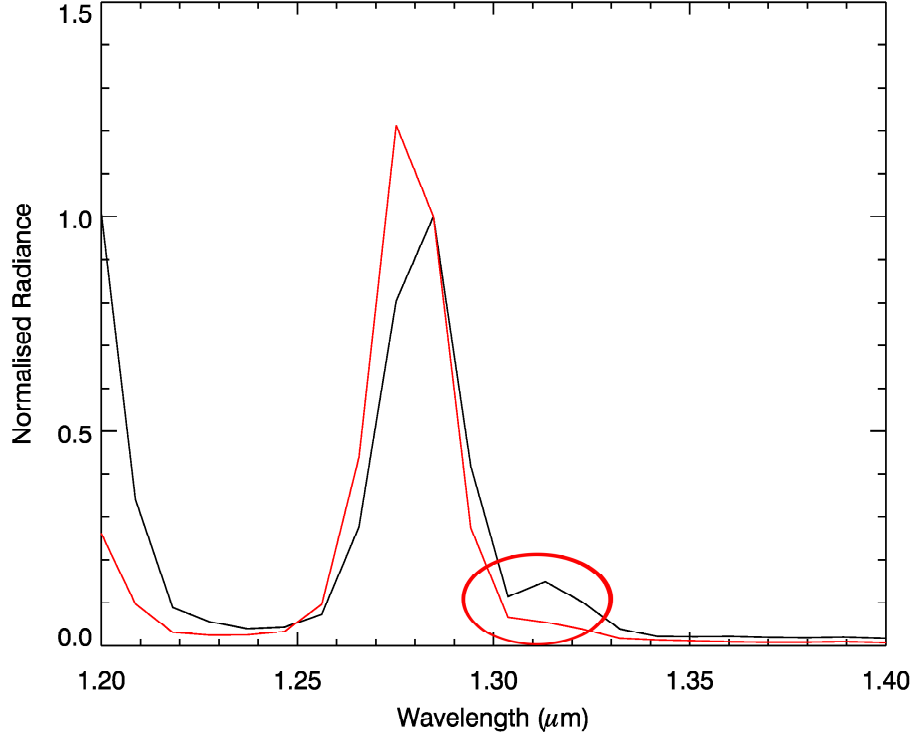


Figure 4.12: Two normalised example spectra between 1.2 and 1.4 μm . The black spectrum meets the condition $I_{1.27} < I_{1.74}$; the red spectrum does not. The circled area shows the characteristic change in the spectral shape at 1.31 μm for a spectrum with a high airglow radiance at 1.27 μm .

and so on. Due to the overlapping sensitivities of some of the parameters in this study, calculations are performed in a specific order, such that the variables that can be independently constrained are computed first and the solutions carried forward in subsequent calculations. For example, the 2.2:1.74 μm radiance ratio is sensitive only to the acid concentration in the droplets, so this variable is calculated first. I can then calculate the mode 3:mode2' relative ratio (particle size parameter) from the 2.29:1.74 μm ratio, having accounted for the variation that is due to changes in the acid concentration. The calculation steps are listed below:

1. Determine acid concentration using 2.2:1.74 μm ratio
2. Calculate CO volume mixing ratio (VMR) using 2.32:2.29 μm ratio

3. Correct 2.29:1.74 μm ratio for acid concentration
4. Calculate particle size parameter using 2.29:1.74 μm ratio
5. Correct 2.4:2.29 μm ratio for acid concentration and CO VMR
6. Calculate water vapour VMR using 2.4:2.29 μm ratio
7. Correct 2.53:2.4 μm ratio for acid concentration and CO VMR
8. Calculate base altitude using 2.53:2.4 μm ratio

Figure 4.13 shows 2.2 μm radiances plotted against 1.74 μm radiances, as in Figure 4.8. Two distinct branches are produced by varying the acid concentration in the model input, between 85 and 96 wt %. Data from VIRTIS observation 0319_00¹ are shown and lie mostly between the two branches. The two branches are fitted using third-order polynomials, and a linear relationship between these coefficients and acid concentration can be derived. This can be rearranged to form an equation for acid concentration as a function of 2.2 and 1.74 μm radiances. The radiance data from VIRTIS are then used to derive acid concentrations for each data point. I adopt a linear approximation for the variation in 2.2 μm radiance relative to 1.74 μm with acid concentration to yield qualitatively representative results for acid concentration and all other retrieved quantities.

The retrieval process was automated using the IDL language. The functions used in each calculation step are listed in the Appendix at the end of this thesis to facilitate reproduction of the analysis. These functions are determined by fitting low-order polynomials to branches taken from synthetic spectra; this provides a set of polynomial coefficients for each branch. Further polynomials are then fitted to each of these coefficients as a function of the variable to be retrieved. By these means, an

¹Observations are named using a combination of the orbit number (4 digits) and the observation number within that orbit (2 digits).

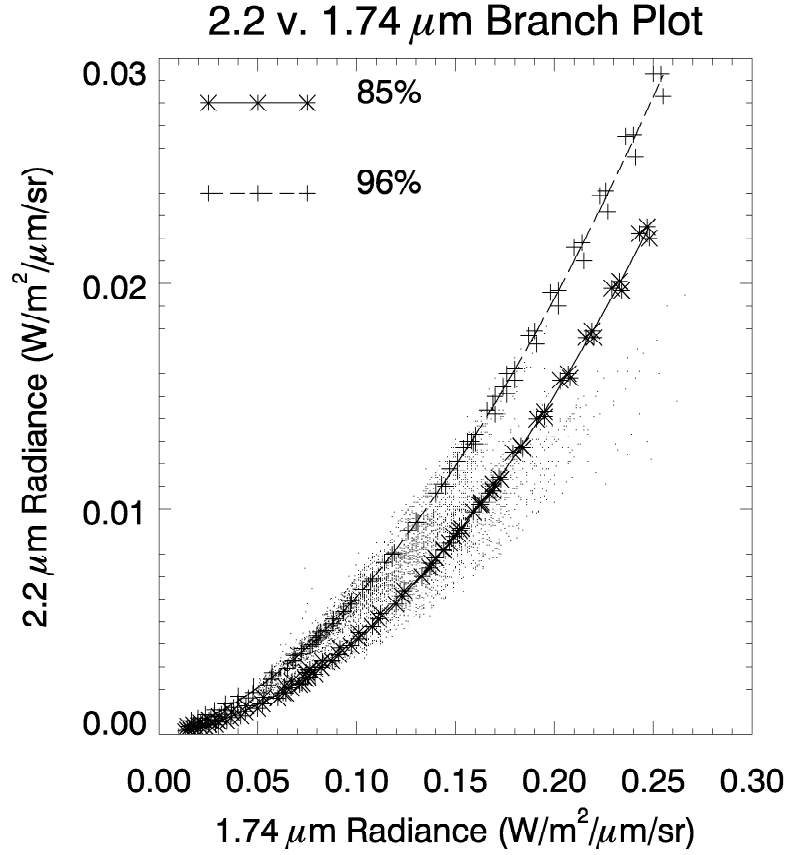


Figure 4.13: Branch curves for the 2.2:1.74 μm ratio as in Figure 4.8, with the addition of example VIRTIS data from observation 0319_00 (small dots). These data mostly lie between the two distinct branches formed by models with different acid concentrations. Solid and dashed lines are polynomial fits to the model branches for the different concentrations.

expression relating the two branch plot radiances to the variable is derived, which for the correct choice of polynomial functions can be uniquely inverted. The position of a data point on the branch plot hence determines the value of the retrieved variable. Using a series of branch plots one after the other allows the retrieval of further properties.

Variations in the atmospheric temperature structure as a function of latitude are taken into account. Branches generated for different temperature profiles for the same 2.2:1.74 μm radiance ratio are shown in Figure 4.14. The four temperature

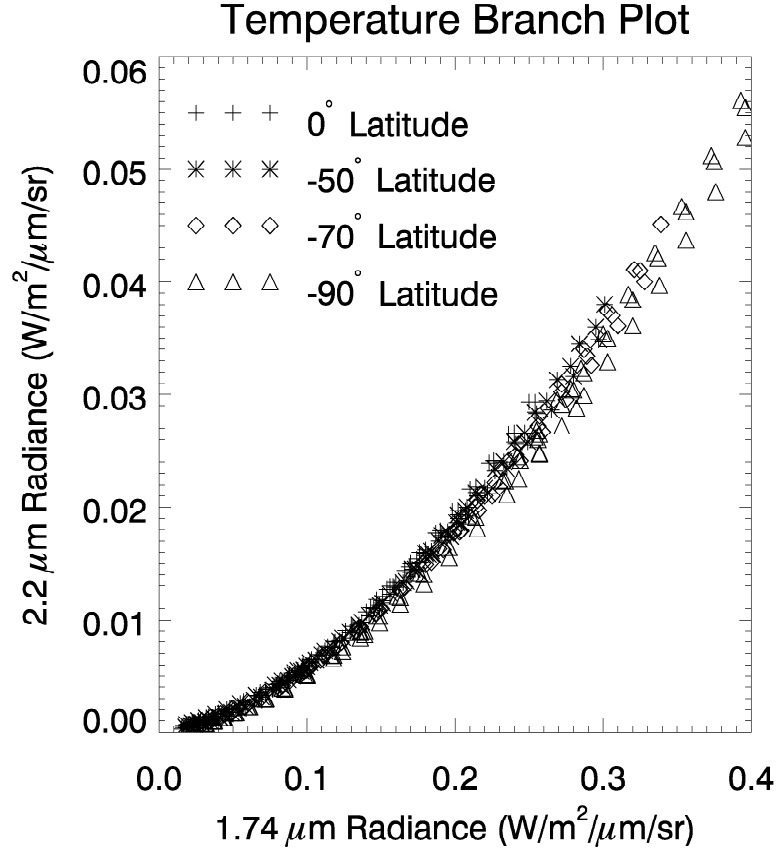


Figure 4.14: Branch curves generated as in Figure 4.13, except the different branches are produced by different model temperature structures, which vary with latitude. The acid concentration is 96 wt %.

profiles for 0, -50, -70 and $\sim$ -90° latitude are generated using temperature/pressure data from a limited data set provided by the VeRa team down to $\sim$ 45 km altitude, and data from Seiff et al. (1985) below this that are constant with latitude (Figure 2.11). A relationship similar to the one for acid concentration can be derived, expressing 2.2 μ m radiance ($I_{2.2}$) in terms of 1.74 μ m radiance ($I_{1.74}$) and latitude (θ). I then define a new value, $I'_{2.2} = I_{2.2} - F(\theta, I_{1.74})$, where F is a function of latitude and $I_{1.74}$, and $I'_{2.2}$ is the value of $I_{2.2}$ for 0° latitude. Effectively, this correction alters the 2.2 μ m radiance to compensate for the variation in temperature with increasing latitude. This new value is used in calculations of acid concentration. Temperature variation with local solar time is less significant than latitudinal

variation at the altitudes sensed in the near-infrared window regions and has not yet been taken into account (see Section 8.2.1).

Latitudinal temperature variations within the cloud layer are of order 10 K, so this correction is very important for the determination of cloud base altitude. Other variables are less affected since the weighting functions at other wavelengths peak lower in the atmosphere, where the temperature is more stable. Random temperature variations within the cloud layer of similar magnitudes to this latitudinal variation have been observed, for example by the Vega balloons (Linkin et al. 1986), and this would introduce an error in the retrieved base altitude of $\sim \pm 2$ km. Extensive averaging over many hundreds of spectra to obtain the trends presented in Chapter 5 is designed to remove such effects from the final results.

Once the acid concentration is known, other branching ratios can be used to determine the particle size parameter, cloud base altitude and gaseous abundances, after taking into account the observed variation in acid concentration in a similar way to temperature as described above. A schematic showing an example of this process is in Figure 4.15. A low-radiance cut-off at $I_{1.74}=0.05 \text{ W/m}^2/\mu\text{m/sr}$ is imposed because for low radiances the effect of the variables on the spectral shape is too small to detect relative to noise, and the method therefore breaks down.

4.3 Summary

In this chapter, the post-calibration processing of the data and the retrieval method have been outlined. In the following chapter, average retrieved values of acid concentration, the particle size parameter, the cloud base altitude and VMRs of CO and H₂O are presented for a range of different conditions on Venus. The validation and error analysis related to the retrieval method are discussed in Chapter 6.

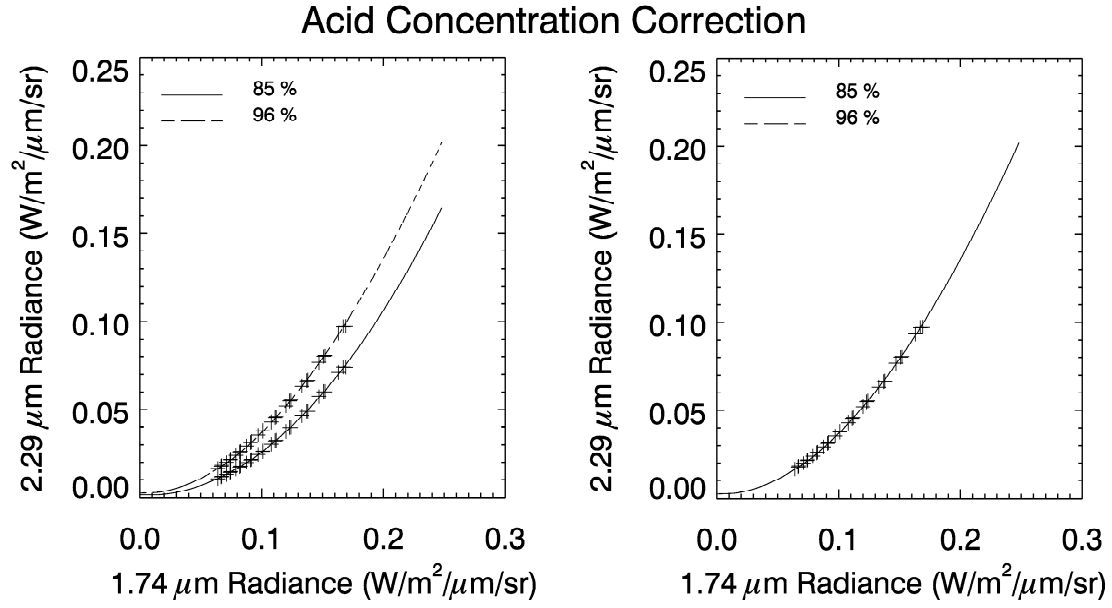


Figure 4.15: The left panel shows branches for 2.29 v. 1.74 μm , as in the right-hand panel in Figure 4.8. Model fits are shown for separate branches with different acid concentrations and the a priori particle size parameter. In the right panel, the branches for 85 wt% acid have been mapped onto those for 96 wt% using a numerical correction for acid concentration. The particle size parameter can now be determined independently of acid concentration using these wavelengths.