

Global Cloud Properties on Venus from Orbital Infrared Spectroscopy

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Chapters 5 to 8

Chapter 5

Derived Global Cloud Properties

The Venusian lower cloud is known to vary spatially in optical depth, as observed by Allen and Crawford (1984), Crisp et al. (1989) and many subsequent authors. Venus Express, and VIRTIS in particular, has provided an unprecedented opportunity to study this spatial variation over the whole near-infrared spectral region. There is already evidence that meridional circulation and zonal wind gradients produce latitudinal variations in gaseous volume mixing ratios in the sub-cloud region (Tsang et al. 2008, Tsang et al. 2009), cloud morphology (McGouldrick et al. 2008, Titov et al. 2008, Ignatiev et al. 2009) and particle size (Carlson et al. 1993, Wilson et al. 2008). Similar variation in the vertical structure and acid concentration in the droplets might be expected as a function of latitude. Thermal tides may also produce variation in the zonal direction as a function of local solar time. Due to the high altitude of the clouds above the surface topography, significant effects as a function of planetocentric longitude are not expected but need to be ruled out.

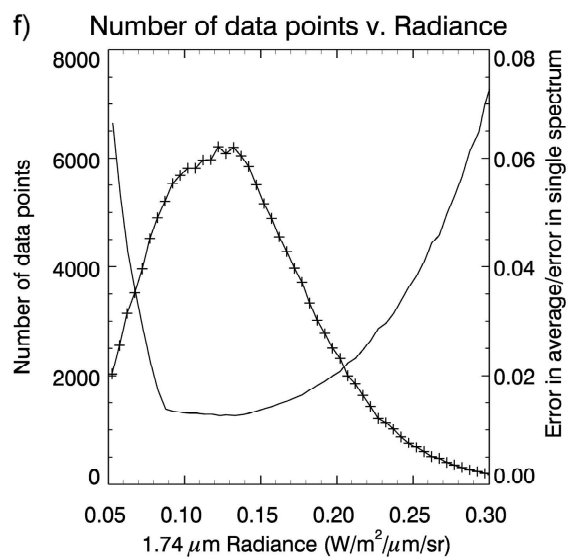
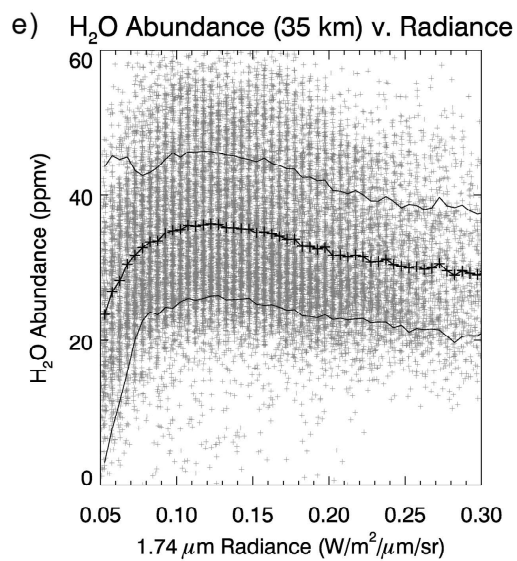
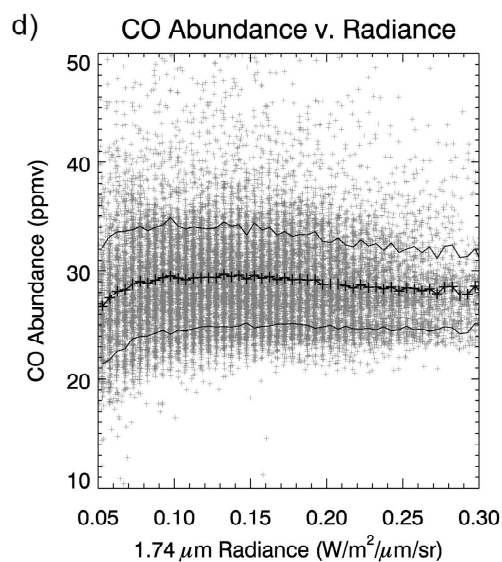
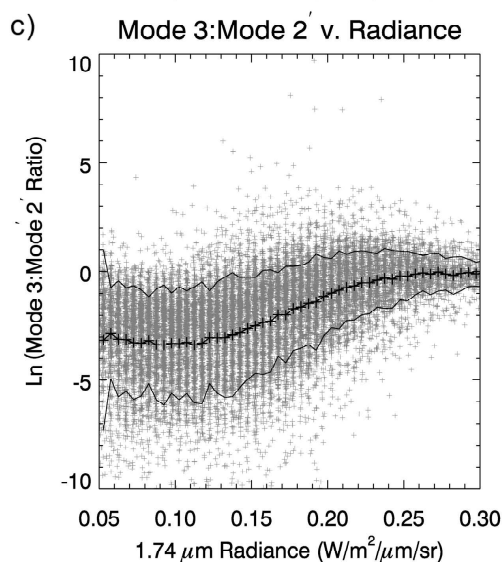
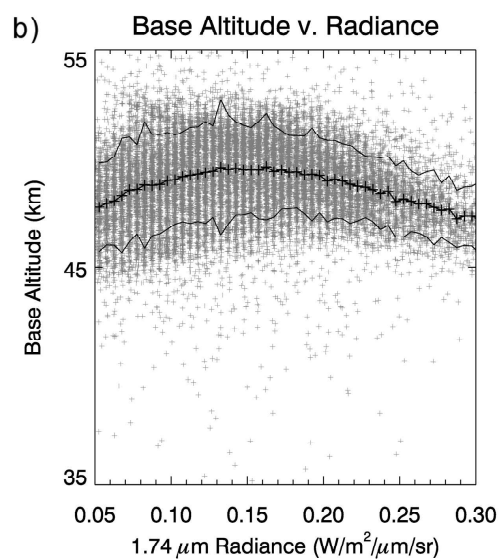
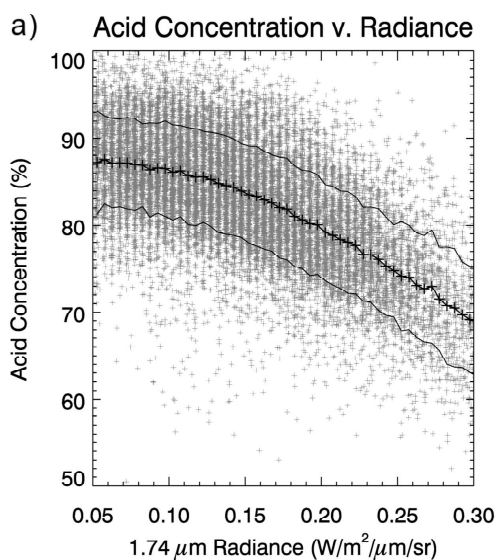
As well as cloud variation due to global-scale dynamics, more localised variation has been observed by ground-based campaigns (Crisp et al. 1991), the NIMS instrument during the Galileo flyby (Carlson et al. 1991), and VIRTIS on Venus Express. Such

variation is attributed by Allen (1987), Kamp et al. (1988) and Crisp (1989) to optical depth variations in the cloud; Crisp (1989) refers specifically to the middle and lower cloud layers, here encompassed in a single lower cloud deck. McGouldrick et al. (2008) use VIRTIS data to examine the lifetimes and evolution of such features, which appear as infrared-bright holes in the cloud and dark patches of thicker cloud. McGouldrick et al. (2008) attribute these variations to convective activity. Correlated variations in other cloud properties with the optical depth variations are a possibility, and so variations as a function of the $1.74\ \mu\text{m}$ radiance, a proxy for total cloud optical depth as used by McGouldrick et al. (2008), are also examined. The $1.74\ \mu\text{m}$ wavelength is chosen because it yields the highest radiance, and therefore has the highest S/N ratio, out of those window regions that are insensitive to variation in surface properties.

The clouds are observed to change over timescales of order 1 day by McGouldrick et al. (2008), but detection of longer timescale changes was precluded by the small subset of VIRTIS-M-IR observations considered. As the results presented here use data spanning most of the working lifetime of VIRTIS-M-IR, covering a period of just over two Earth years, they can be used to look for longer-term changes in the cloud. Best-fit properties are therefore also plotted as a function of orbit number.

Results for acid concentration, the natural log of the relative ratio of mode 3:mode 2' compared with the *a priori* (particle size parameter), cloud base altitude, CO abundance and H₂O abundance (VMRs) are presented in Figures 5.1—5.5. Within

Figure 5.1 (*following page*): Variation of retrieved quantities with $1.74\ \mu\text{m}$ radiance, which is inversely proportional to cloud optical depth. Grey points are radiance-binned data for each observation. Black points represent the average value in each radiance bin for all observations, and thin black lines represent the standard deviation on this value. In the coverage plot, the black points represent the number of data in each bin (left-hand axis) and the solid black line shows the error on each average value, relative to the error for a single spectrum as stated in Table 5.1.



the limitations imposed by the instrument and orbit, the coverage of different conditions on Venus is very good, as demonstrated by the coverage plots included in the figures. Results as a function of $1.74\text{ }\mu\text{m}$ radiance are shown in Figure 5.1, those as a function of latitude in Figure 5.2, local solar time in Figure 5.3 and longitude in Figure 5.4. The results are plotted as a function of orbit number (Figure 5.5), to look for possible long-term temporal changes. The results are briefly summarised in this chapter, and a more detailed discussion of potential mechanisms is presented in Chapter 7.

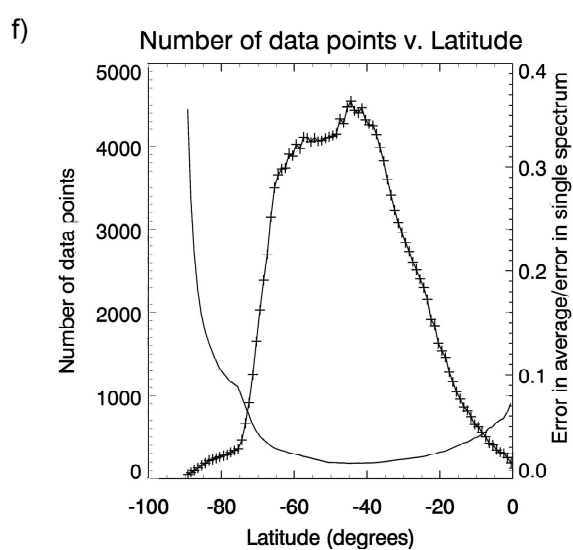
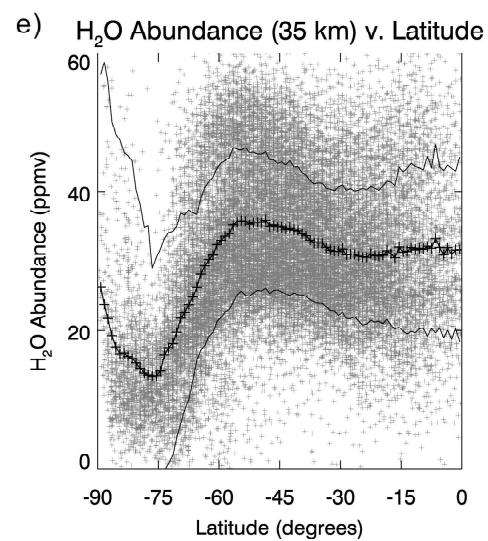
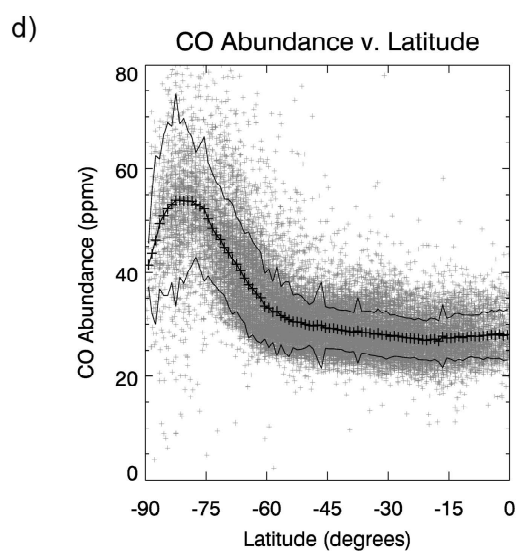
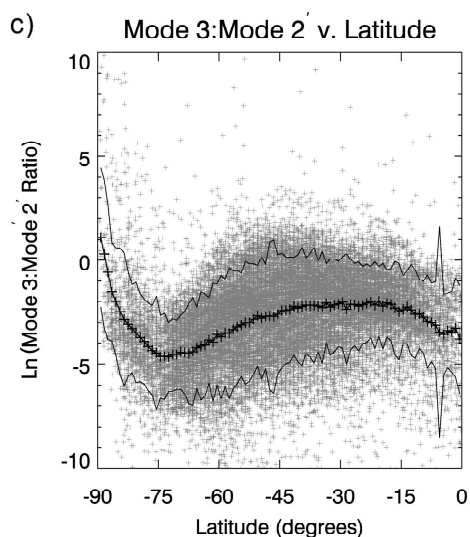
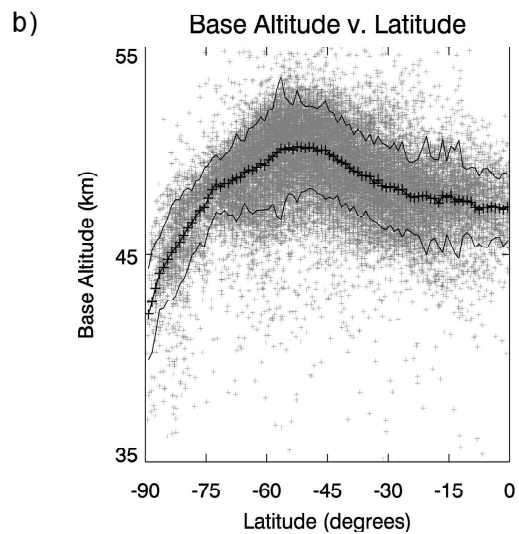
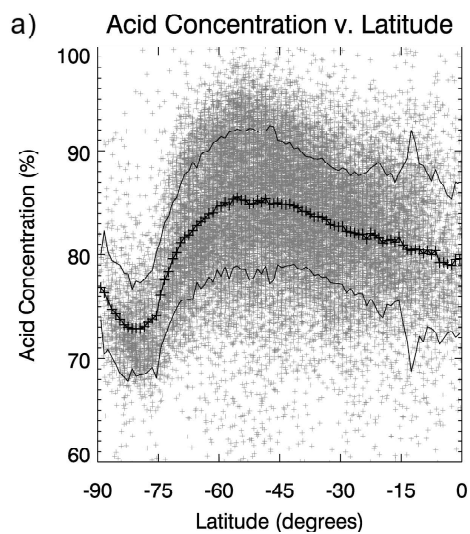
Similar results were presented in Barstow et al. (2012). The results here have been derived using observed spectra that have been corrected for stray light and scattered light, which was not the case in Barstow et al. (2012). As the scattered light in particular has a significant contribution at $2.2\text{ }\mu\text{m}$, one of the wavelengths used to determine the acid concentration, the results are not identical, although the major conclusions presented in Barstow et al. (2012) remain unchanged; in general, the variation in the cloud properties is preserved although the absolute values have shifted. No results for water vapour within the cloud deck are presented here, and the reason for this is explained further in Section 6.3.6.

The error on each retrieved quantity for a single coadded spectrum is given in Table 5.1. The origin of these error values is explained in Section 6.1.

5.1 Variation with radiance

Figure 5.1 shows that the acid concentration in the clouds has a strong dependence on $1.74\text{ }\mu\text{m}$ radiance. As discovered by Allen (1987), Kamp et al. (1988) and Crisp

Figure 5.2 (*following page*): Variation of retrieved quantities with latitude, details as in Figure 5.1.



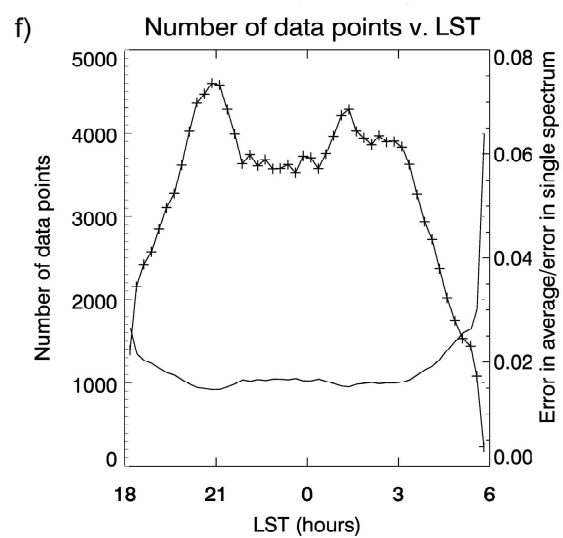
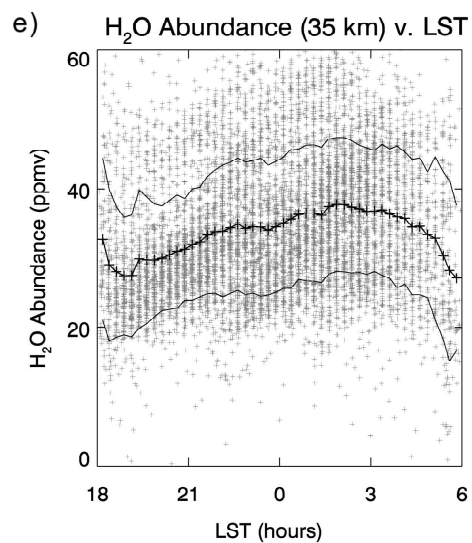
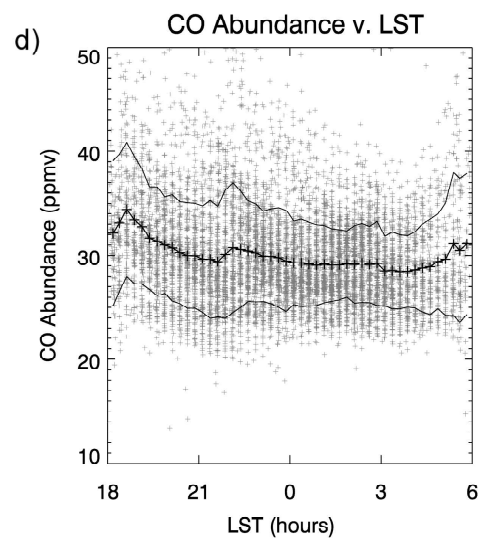
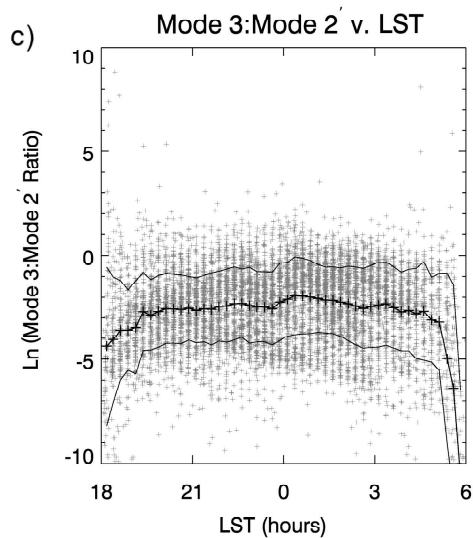
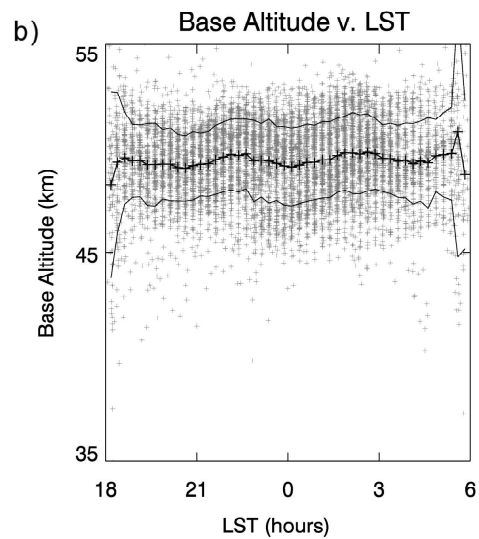
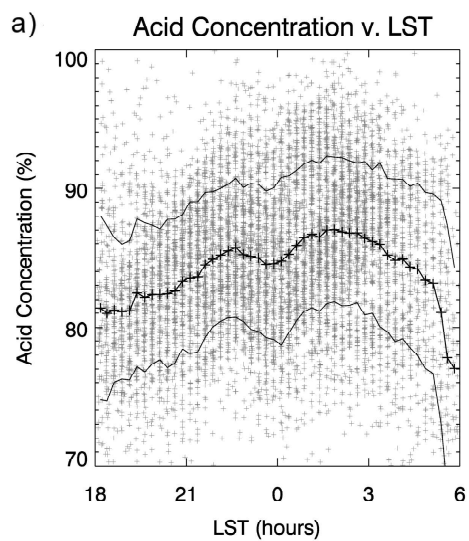
Variable	Error	Unit of Measurement
Acid Concentration	± 7	wt%
Base Altitude	± 3	km
Ln Mode 3:Mode 2' Relative Ratio	± 2	
CO Abundance	± 5	ppmv
H ₂ O Abundance	± 10	ppmv

Table 5.1: Errors in an individual measurement. Errors in averaged values are shown in Figures 5.1–5.4. For the full error analysis see Section 6.1.

et al. (1989), the variation in this radiance is mostly due to variations in the absorption by the cloud, and so this radiance is inversely proportional to the total optical depth of the cloud; it follows that the average concentration of sulphuric acid in the cloud particles is higher in regions of thick cloud. A likely explanation for this is that the acid concentration in the cloud droplets decreases with increasing altitude (James et al. 1997). The opacity variation in the cloud is assumed in the model used here to take place below 57 km, so the variation is occurring at altitudes where the cloud acid concentration is high. In regions of thick cloud, the amount of more acidic lower cloud has increased relative to the amount of less acidic higher cloud, so the overall acid concentration is higher. The reverse is true in regions where the cloud is less optically thick.

The base altitude undergoes little change with total cloud opacity. The altitude retrieved in the model is slightly lower in regions of very high or very low 1.74 μm radiance. This may indicate a lower cloud base in regions of high convective activity, since high radiance contrasts occur more frequently in convectively active regions (McGouldrick et al. 2008). Values cluster around 47–48 km, which is in very good agreement with the findings of Kliore et al. (1986) from the Venera and Pioneer Venus descent probe data. It may be noted that ~ 50 km is typically where the

Figure 5.3 (*following page*): Variation of retrieved quantities with local solar time, details as in Figure 5.1.



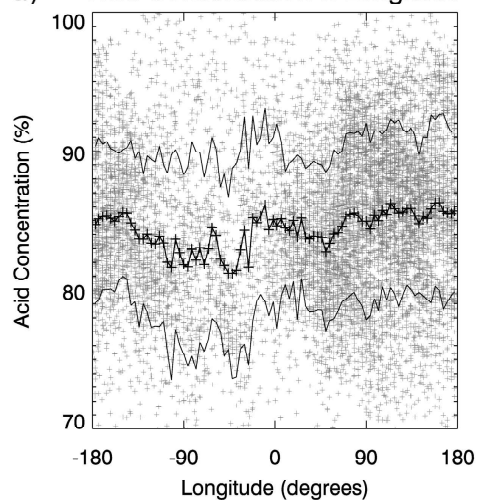
base of the convective cloud zone is found in radio occultation profiles (Tellmann et al. 2009), but the retrieved cloud base altitude indicates that some convective processes must occur below this if the lower cloud is convectively formed.

The particle size parameter (ratio of mode 3:mode 2' particles) is relatively constant with radiance, with a slight increase in the number of large particles in bright regions. This may be due to larger particles having increased stability, whereas the smaller mode 2' particles may evaporate more easily. Alternatively, it may indicate a different composition for the mode 3 particles, which would explain their persistence in regions where the mode 2' sulphuric acid particles evaporate. The average ratio is $\sim 0.25 \times$ the *a priori*.

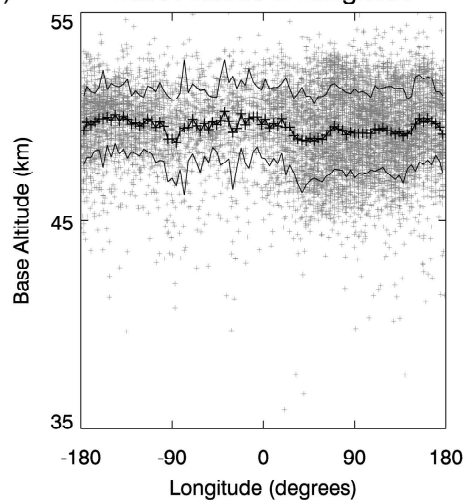
The abundance of CO below the cloud does not change appreciably with radiance, although there is a slight decrease in CO in regions of very thick cloud. This may be due to vigorous upwelling in regions of thick cloud drawing up comparatively CO-poor atmosphere from lower down, as CO VMR is known to increase with altitude (Pollack et al. 1993, Marcq et al. 2006). However, there is a decrease in H₂O vapour below the cloud in regions of very thick cloud, although the low radiances here mean that the H₂O vapour retrieval is less reliable than that in brighter regions. This result is quantitatively consistent within the errors with the findings of Pollack et al. (1993), de Bergh et al. (1995) and Marcq et al. (2008), who all find a water vapour VMR of 30 ppmv at 35 km.

Figure 5.4 (*following page*): Variation of retrieved quantities with longitude, details as in Figure 5.1.

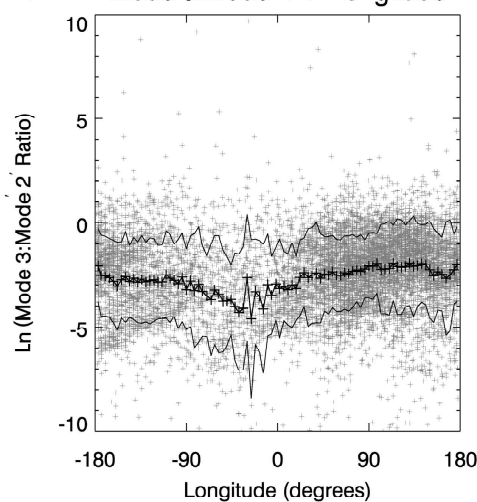
a) Acid Concentration v. Longitude



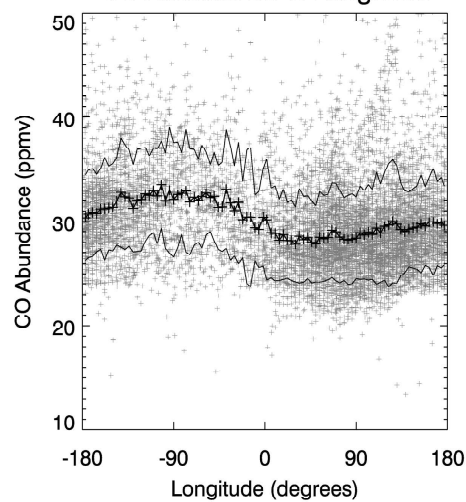
b) Base Altitude v. Longitude



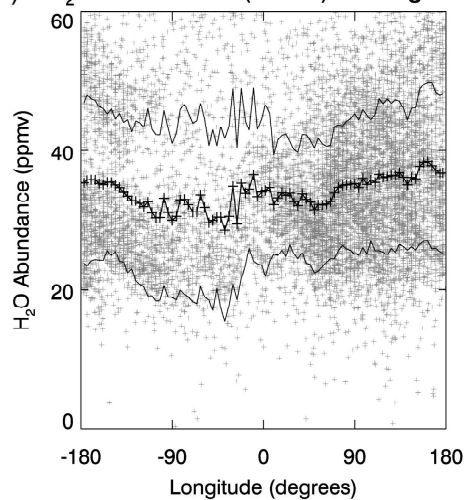
c) Mode 3:Mode 2' v. Longitude



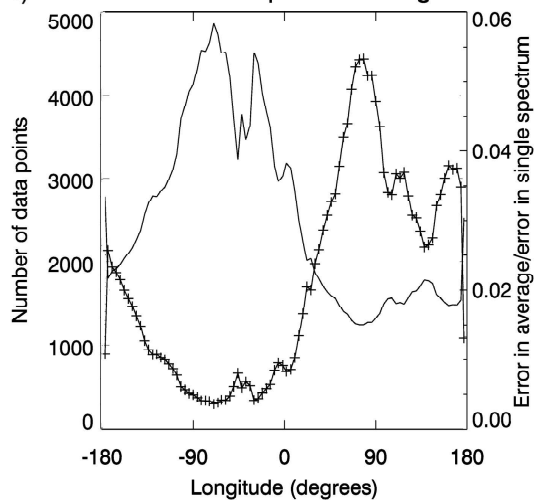
d) CO Abundance v. Longitude



e) H₂O Abundance (35 km) v. Longitude



f) Number of data points v. Longitude



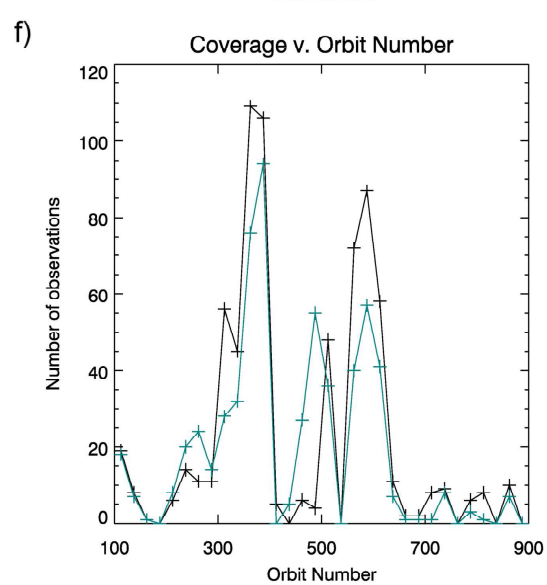
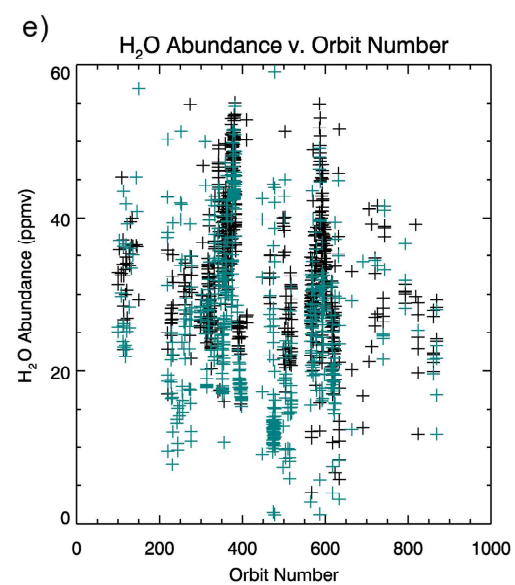
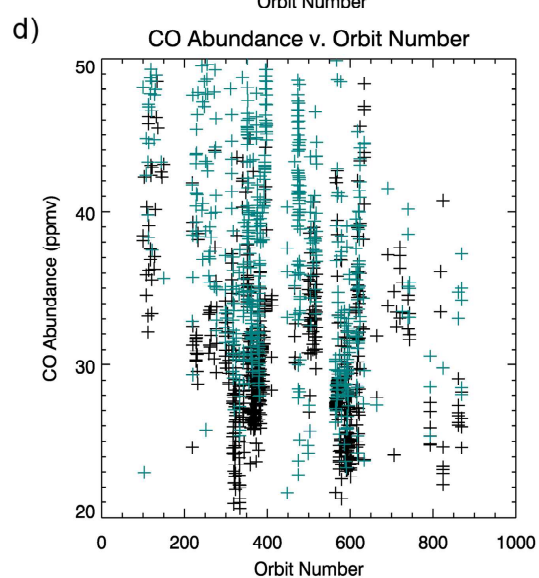
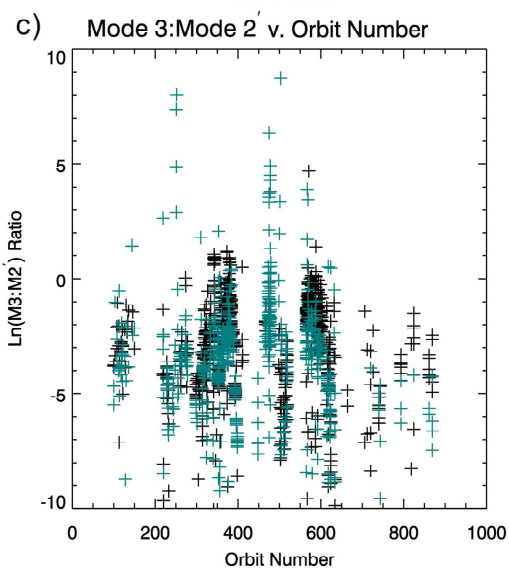
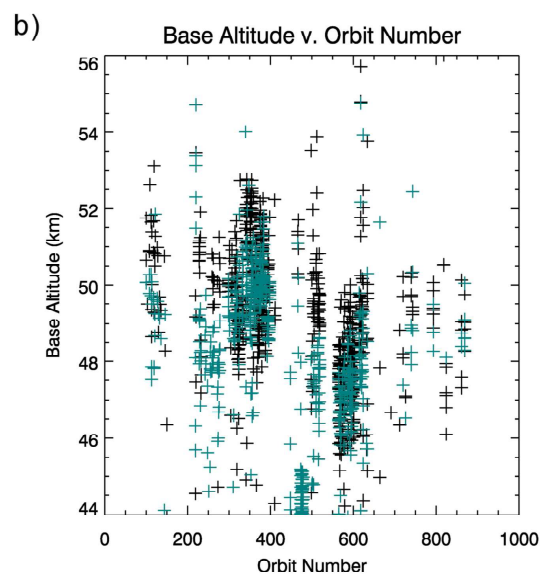
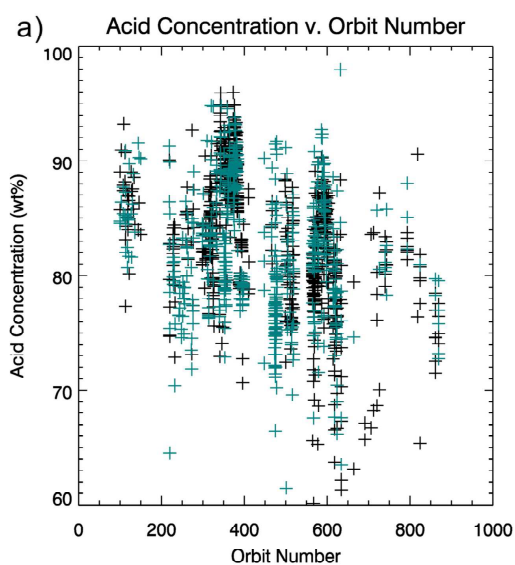
5.2 Variation with latitude

As expected, the properties of the cloud vary as a function of latitude, as seen in Figure 5.2. The acid concentration is found to increase between the equator and the mid-latitudes between -50 and -60° . It then begins to decrease slightly towards -70° before rapidly decreasing towards the pole. The cloud base altitude displays a similar trend, also peaking at $\sim -55^\circ$ before decreasing towards the pole. There are similarities between this behaviour and the variation in tropopause temperature as observed by Tellmann et al. (2009), suggesting that global dynamics play a key role in the observed variation. There are also similarities with the variation of the $1.74\ \mu\text{m}$ radiance as a function of latitude (Figure 5.6); however, the variation in acid concentration is the opposite to what would be expected if it was only a result of the latitudinal variation in cloud opacity, and the magnitude of the variation in the water vapour VMR is far greater than would be expected from cloud opacity-correlated variation only.

As found by Wilson et al. (2008), the relative number of large cloud particles increases towards the pole, shown by an increase in the particle size parameter. Wilson et al. (2008) postulate that the downwelling at the poles removes the more volatile smaller particles from the cloud and results in their evaporation. An alternative suggestion is that the composition of the cloud particles changes towards the poles. As discussed in Section 6.1, this is still an open question and a conclusive explanation for this phenomenon is deferred until the next in-situ Venus mission.

The VMR of CO below the clouds (referenced to 39 km) increases from 28 ppmv at low latitudes to 55 ppmv in the region of the cold polar collar. Similar varia-

Figure 5.5 (*following page*): Variation of retrieved quantities with orbit number. Black points are averages for latitudes $>-60^\circ$ and teal for $<-60^\circ$.



tion is observed by Tsang et al. (2008) and Tsang et al. (2009); at their reference altitude of 35 km I find, with the assumed CO vertical profile, VMRs of 25 ppmv at low latitudes and 35 ppmv at -70° latitude, in good agreement with their results. This is a good test of the method used here, which is not identical to that of Tsang et al. (2008) and Tsang et al. (2009), although the radiative transfer model is very similar (Section 2.2). The explanation of this phenomenon offered by those authors is that comparatively CO-rich air is transported from above the clouds by the downwelling branch of the Hadley circulation, which we expect to be present in the cold collar region. The abundance of CO is higher well above the clouds, where it is produced by photodissociation of CO_2 , than it is in the region below (von Zahn et al. 1983, Clancy and Muhleman 1985, Marcq et al. 2006). There is a subsequent decrease in abundance from the collar region into the polar vortex, which supports the hypothesis that this is a localised enhancement due to downwelling, although the abundance at the pole is still higher than it is in equatorial regions. Collard et al. (1993) observed a similar phenomenon in the northern hemisphere with the near-infrared mapping spectrometer (NIMS) on Galileo.

The abundance of H_2O vapour increases towards 50° latitude (Figure 5.2 e), then drops sharply within the polar collar. This result appears to be correlated with the change in $1.74\text{ }\mu\text{m}$ radiance with latitude (Figure 5.6), but the magnitude of the H_2O variation with latitude is greater than the observed variation with radiance (Figure 5.1 e), so the observed change is not just a result of the latitudinal variation in cloud optical depth. It may, like the CO variation, be due to the polar collar downwelling, as the atmosphere above the cloud is known to be drier than the regions below (Fedorova et al. 2008).

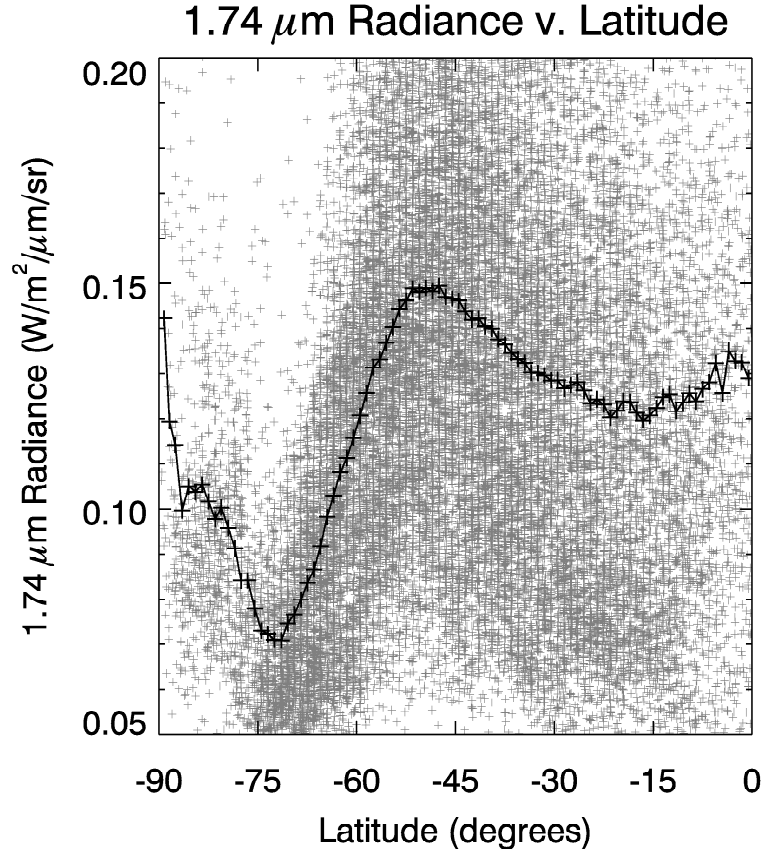


Figure 5.6: Variation of $1.74 \mu\text{m}$ radiance with latitude. The large variation is due to the local variation in cloud optical depth, which contrast is observed to be particularly large at equatorial latitudes (McGouldrick et al. 2008). Grey and black points are as in Figure 5.1.

5.3 Variation with local solar time

Since diurnal heating variation has little effect on the Venusian atmosphere below 60 km, we expect little variation in the cloud structure and tropospheric gaseous abundances; this expectation is largely confirmed (Figure 5.3). Apparent excursions from the mean value towards the terminators in acid concentration, particle size parameter, base altitude and H_2O abundance should be viewed with caution as the data coverage is comparatively poor in these regions (Figure 5.3 f) and the contamination from the dayside scattered light is significant. Slight increases in

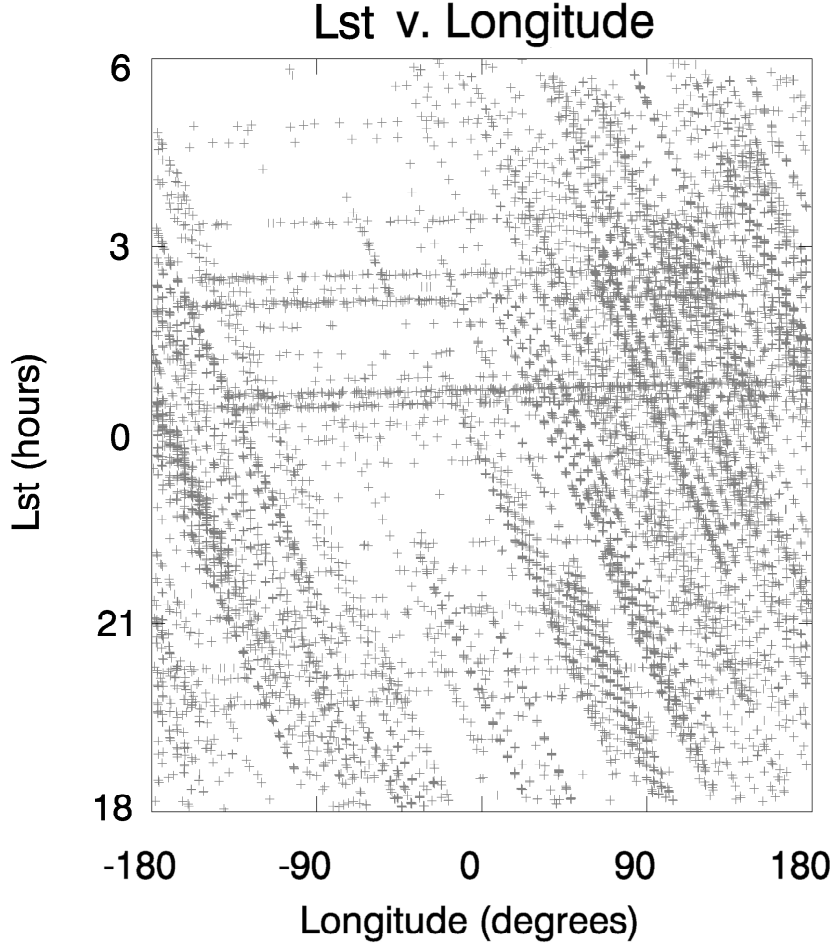


Figure 5.7: Coverage in local solar time-longitude space, which is good except between -180 and -45° longitude, where there are few data in the early morning between 3 and 6 hours local time. Grey points are as in Figure 5.1.

acid concentration and H_2O abundance from the evening to the morning and a decrease in the CO abundance are not outside the error bars on the plot. There is little observed variation as a function of local solar time.

5.4 Variation with longitude

Little variation in cloud structure and gaseous abundances is expected with planetocentric longitude, and most retrieved quantities do not change with longitude

(Figure 5.4). There is a small peak in CO abundance at -90° longitude, but since there are few data between -90° and 0° this is difficult to confirm. The apparent peak may be due to observational bias, since there are more evening observations compared with morning observations at longitudes between -180 and -45° (Figure 5.7) and CO abundance is higher towards the evening terminator (Figure 5.3).

5.5 Long-term temporal variation

Acid concentration, CO and water vapour abundances all decrease with time from the start of the mission, although there is significant scatter (Figure 5.5). Possible explanations for this phenomenon are changes in the rate of active volcanism, if present, and changes in the solar radiation in the upper atmosphere due to solar cycle variation, as solar photons are responsible for the photochemical production of CO and sulphuric acid. There is no correlation between these decreases and the variation in mesospheric SO₂ abundance as observed by Marcq et al. (2011). As H₂SO₄ is produced by photolysis of SO₂ to SO₃ and subsequent reaction with H₂O vapour, a decrease in the amount of H₂SO₄ due to a decrease in solar photons should be accompanied by an increase in SO₂ at the cloud top, as less would be removed by photolysis. Marcq et al. (2011) do observe a sharp increase in the abundance of SO₂ during early 2007 (orbit 310), but after this the SO₂ abundance is approximately constant. The data analysed by Marcq et al. (2011) only extend to mid-2007 so far, so an overall increase in SO₂ abundance during the period considered in this work cannot be ruled out, but no obvious anti-correlation is observed in the period between orbits 100 and 400. In particular, I observe no sudden decrease in cloud acidity that might be linked to the sharp increase in SO₂ in orbit 310.

The lack of observed decrease in SO₂ abundance (Marcq et al. 2011) does, on the

other hand, appear to preclude a volcanic explanation for the decrease in cloud acid concentration, as if this was the case a decrease in SO_2 abundance with time would be expected. Esposito et al. (1988) postulated that a long-term decrease in SO_2 abundance at the cloud tops during the Pioneer Venus mission was due to a cessation or decrease of active volcanism; if this is proposed as a mechanism for a decrease in other volcanic gases such as H_2O and H_2SO_4 , the SO_2 abundance would be expected to decrease also.

There is considerable scatter in the temporal variation, which indicates the extreme variability of the cloud between observations. Some of this scatter is due to the variability already discussed as a function of radiance and latitude, but there is also a large component of random variation between observations. The latitude/radiance coverage does not change significantly as a function of observation number, so the retrieved latitude- and $1.74\text{ }\mu\text{m}$ radiance-dependent variation is not greatly influenced by the secular variation, although it contributes to the scatter on the results.

5.6 Summary

It is clear from the results presented in this chapter that the Venusian clouds are highly variable, and the variation is likely to be related to both planetary-scale and more localised dynamical processes. The average acid concentration of the cloud droplets is 17 wt% higher, at 87 wt%, in the regions of high cloud optical depth than it is in very bright regions; there are also slight decreases in particle size and sub-cloud water vapour abundance in regions of thick cloud. The CO and H_2O VMRs in low- to mid-latitude regions are on average 28 (at 39 km) and 32 ppmv (between 28 and 50 km altitude), in good agreement with previous results as summarised by Bézard and de Bergh (2007) and more recent results presented by

Marcq et al. (2008) and Tsang et al. (2009).

The cloud structure shows significant variation as a function of latitude; the acid concentration and cloud base altitude both peak in the mid latitudes, at 85 wt% and 51 km respectively, and both have minima in the polar regions (of 75 wt% and 42 km). The variation is correlated with the decrease in atmospheric temperature towards the poles in the region of the cloud (Figure 2.11), and also shows some correlation with the zonal wind, which peaks at the mid-latitude jet. The H₂O VMR varies similarly, with a peak of 35 ppmv in the mid-latitudes and a minimum of 15 ppmv at -75° latitude. This is correlated with the peak in CO VMR at the same latitude, of 55 ppmv at 39 km altitude. The particle size parameter reaches a maximum value at the poles, corroborating the findings of Wilson et al. (2008).

There is little variation as a function of local solar time and longitude; variation observed is not outside the errors. I tentatively find that acid concentration, CO abundance and H₂O abundance decrease steadily between orbit 100 and orbit 900, over a period of around two Earth years (3 Venus years).

A full error analysis for the results presented here is given in the following chapter.

Chapter 6

Validation and Error Analysis

This chapter discusses the various sources of uncertainty present in this work, describes the error analysis, and presents validation of the method, using complete spectra rather than wavelength pairs and incorporating channels outside the wavelength range used for the retrieval. The first section contains error analysis performed using the wavelength range between 1.6 and 2.6 μm ; the following section exploits the shorter wavelength atmospheric windows. This two-stage check ensures consistency within the spectral region used for the retrieval, then uses a part of the spectrum outside the retrieval range for further validation. The final section of this chapter discusses the different assumptions that have been made in the analysis, and examines the impact of changing or removing these assumptions on the results obtained.

6.1 Validation and error calculation between 1.6 and 2.6 μm

The branch plot method is extremely computationally efficient, but does not use all of the available spectral information. To test the validity of the results obtained using the branch plot method, these results are used as inputs to produce synthetic spectra for comparison with the full spectra between 1.6 and 2.6 μm . Examples of this are shown in Figures 6.1 and 6.2. It can be seen that the characteristics of the different spectra are for the most part well-matched by the model spectra, except for some discrepancies in the shape of the low-wavelength shoulder of the 2.3 μm window between 2.21 and 2.25 μm where there seems to be opacity in the observed spectrum that is not accounted for in the model. Possible candidates for this are weak CO_2 absorption lines that are missing from the line database but are important at Venusian temperatures; incorrect assumptions about the CO_2 collision-induced absorption, which is poorly understood; or the presence of an unknown absorber. Further work is needed to elucidate this. The large differences on either side of the 1.74 μm absorption line have already been mentioned in Section 2.2.4 and are further discussed in Section 6.2. The random differences in the 2.3 μm window observed in Figure 6.2 may be due to random noise, and in part perhaps to the odd-even effect mentioned in Section 4.1.

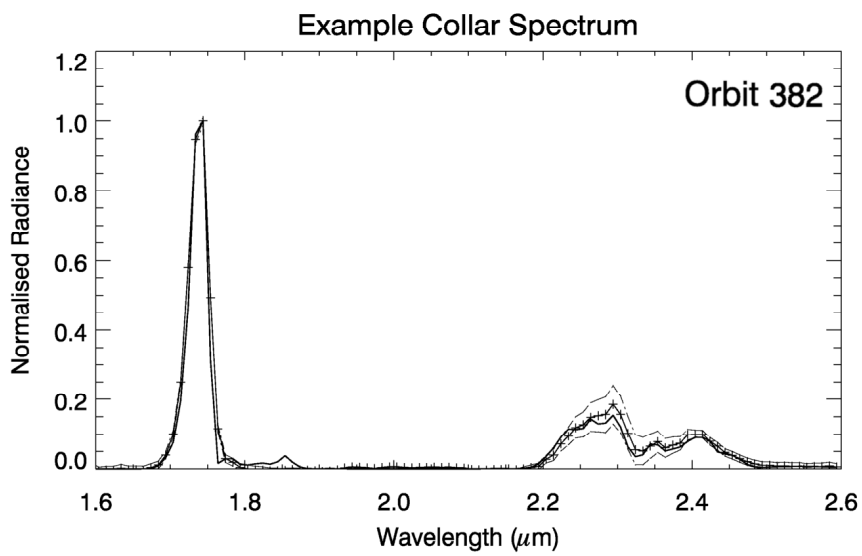
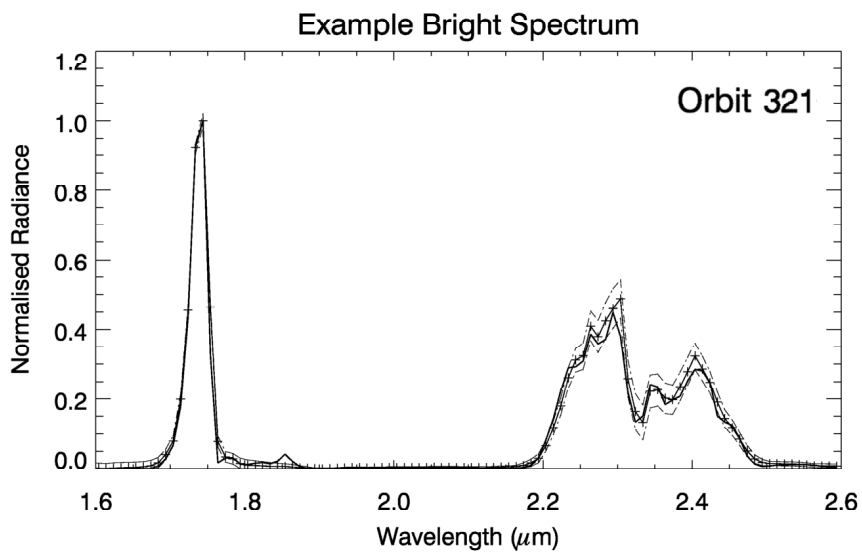
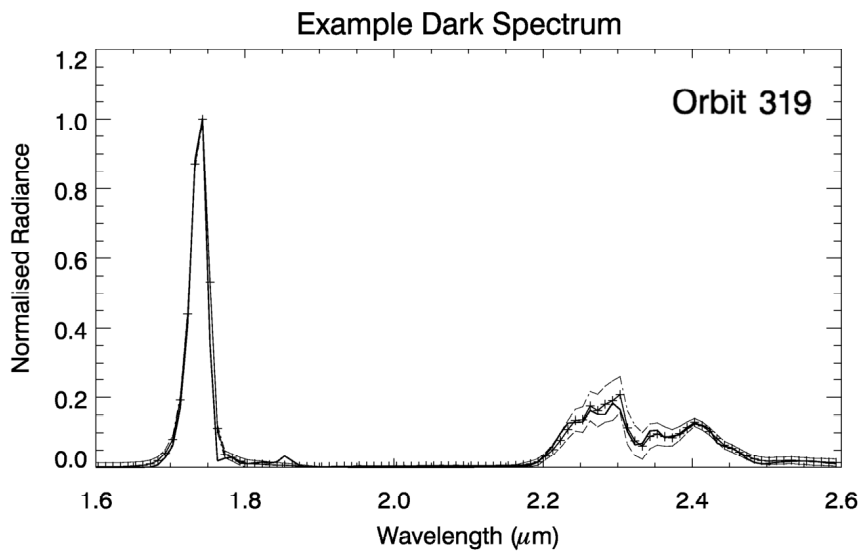
In Figure 6.1 it can be seen that the three spectra shown have distinctly different shapes across the 1.6-2.6 μm range, especially the relative radiances in the 1.74 and 2.3 μm windows. These shapes are typical of spectra obtained in the different locations and conditions on Venus and are a direct consequence of the scattering and absorptive properties of the cloud; they were chosen to best display the variability in spectra. It is encouraging to note that the fit achieved is of similar quality for each

of these representative cases; however, the error bars on an individual spectrum are seen to be large due to the approximate nature of the method (see Table 5.1), and hence the results presented are averages over all considered spectra as functions of radiance, latitude etc. (see Section 5).

The errors presented in Figures 6.1 and 6.2 are calculated by taking the errors for each variable presented in Table 5.1 and calculating synthetic spectra to encompass the spread of the error bars for each variable. The differences between these synthetic spectra at 2.2, 2.29, 2.32, 2.4 and 2.53 μm relative to 1.74 μm were then calculated to give the relative error on the spectrum at that point. At 2.2 and 2.29 μm , the error is dominated by changes in acid concentration; at 2.32 μm , by CO; at 2.4 μm , by H₂O; and at 2.53 μm by the cloud base altitude. The error at 2.2 μm is therefore the change in radiance at 2.2/1.74 μm for a 7 wt% change in acid concentration, and so on; the errors in the intervening regions are calculated by interpolating between these points. The calculation process for the errors presented in Table 5.1 is described below.

It can be seen in Figure 6.2 that the discrepancy in the short wing of the 2.3 μm window is most pronounced in the bright spectrum, and may indicate a poor fit at 2.2 μm , which is the wavelength used to determine the acid concentration. Lower acid concentrations are found in brighter regions, and in these regions it may be possible that the assumed linear approximation for spectral radiance variation due to changes in acid concentration is no longer valid; this is discussed in Section 6.3.1. The large discrepancy at 2.3 μm in the bright spectrum is probably due to spectral registration

Figure 6.1 (*following page*): Three spectra, representing typical dark, bright and polar collar ($\sim 70^\circ$) spectra (line with crosses), with model fits (solid black line). The model spectra have been produced by using the values obtained by the branch plot method as inputs for NEMESIS. The error on the spectrum is represented by broken lines, and is calculated from the error on the retrieved values and the resulting differences in radiance as a function of 1.74 μm radiance.

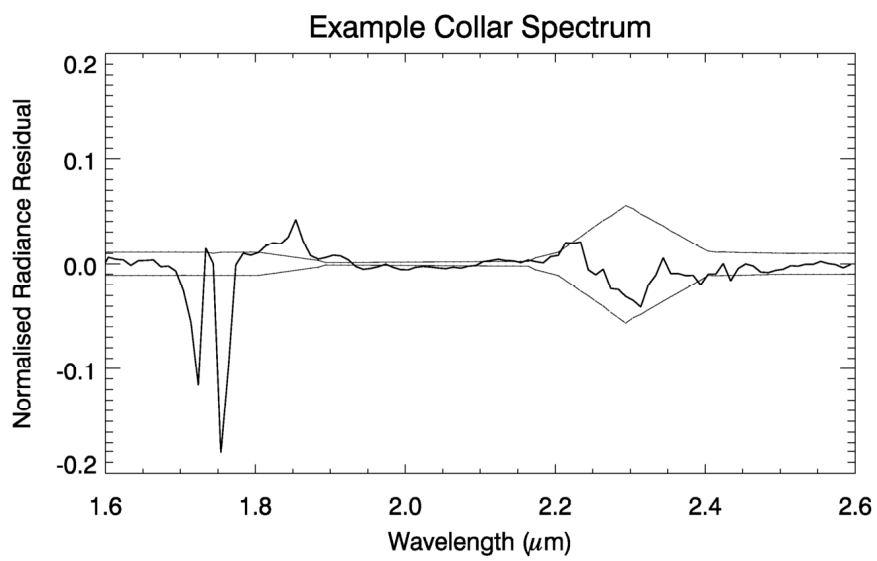
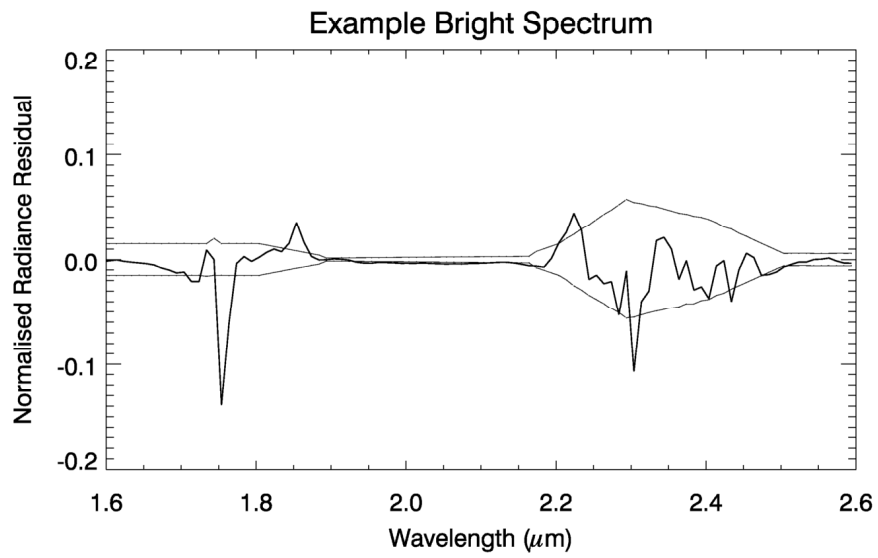
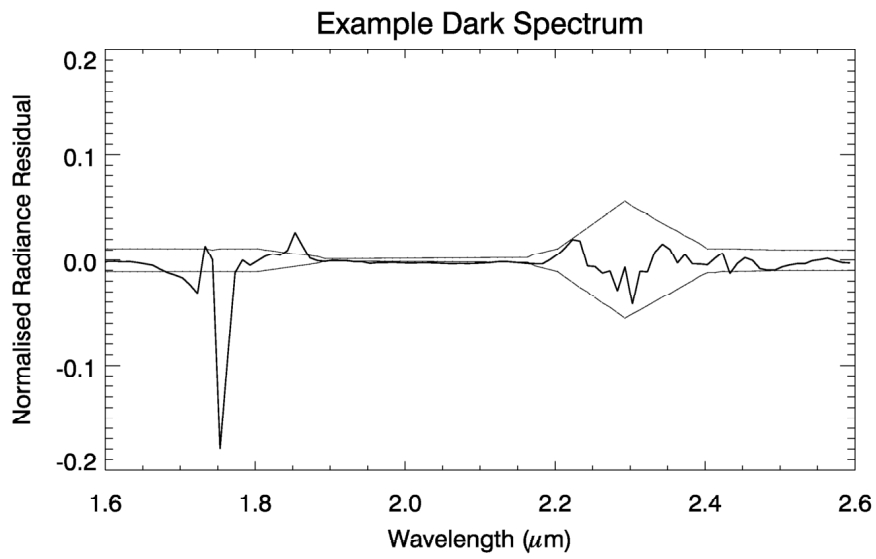


issues (see Section 4.1.1). The peak radiance at 2.3 μm is not consistently registered by VIRTIS, as the radiance gradient is very steep between 2.3 and 2.31 μm ; small offsets in spectral registration can result in the closest radiance to 2.3 μm being either a high value, if the wavelength recorded falls on the peak, or a much lower value if not. The spectral registration correction cannot easily account for this aspect of the problem, which is why the 2.29 μm radiance was used in the retrieval instead of the 2.3 μm peak value, as this radiance is more consistent.

These three spectra all demonstrate reasonable concurrence between the models and data over the 1.6–2.6 μm range; it is, however, a different matter when spectra closer to the poles are considered. If latitudinally-binned radiances are plotted on a 2.3 v. 1.74 μm branch plot, it is clear that beyond $\sim 70^\circ$ there is a change in the behaviour (Figure 6.3). More absorption at 2.3 relative to 1.74 μm is required to fit the spectra. Equatorwards of this region, variation in the abundance of mode 3 particles relative to mode 2' particles is sufficient to fit the data, but here it is clear that no change in this ratio produces a significant enough increase in 2.3 μm absorption to fit these data (Figure 6.4). Therefore, an alternative source of increased opacity at 2.3 relative to 1.74 μm needs to be sought. In Section 6.3, the assumption of an invariant upper cloud is discussed; varying the upper cloud optical depth provides a potentially viable alternative.

The exposure times considered in this work range from a shortest time of 0.3 s to a longest time of 18 s, the 0.026 s observations having been rejected (Section 4.1). As the NESR scales with $\sqrt{\tau^{-1}}$ (see Section 4.1), the shorter exposure time observations may have a low S/N . To examine the effect of this, the analysis was performed with and without a data selection criterion based upon the S/N ratio at 2.53 μm , one

Figure 6.2 (*following page*): As Figure 6.1, except the difference $I_{\text{model}} - I_{\text{observation}}$ is shown. The noise envelope is shown by thin lines.



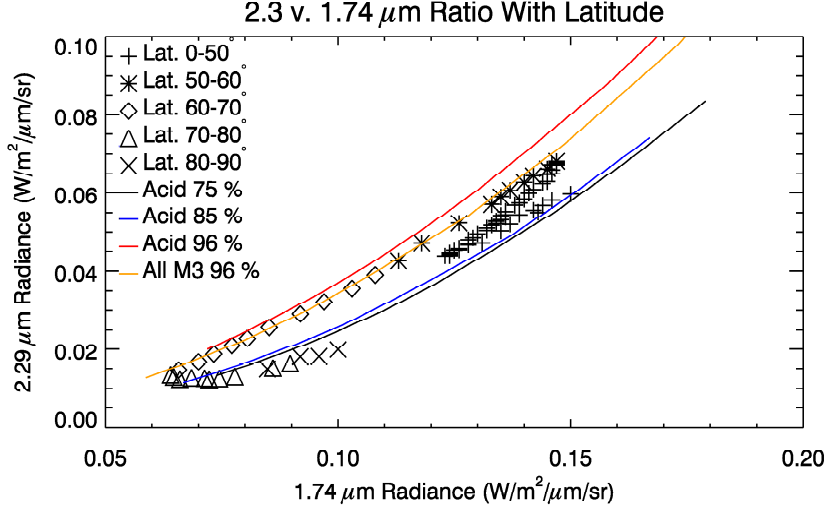


Figure 6.3: 1.74 and 2.29 μm radiances taken from the VIRTIS dataset, binned in latitude, are plotted against a range of models. Models with the nominal particle size parameter at both 85 and 96 wt % are included, and also a series at 96 wt % with only mode 3 in the lower cloud. The VIRTIS radiances are corrected for latitudinal temperature structure changes. It can be seen that the points polewards of -70° lie well below the branches shown on the plot, whereas equatorwards of this they follow the model branches more closely.

of the lowest-radiance points in the spectrum. All averaged spectra with a S/N value lower than 20 at this wavelength were rejected by this criterion. $\sim 90\%$ of the data considered pass the test, and the mean and standard deviation of the retrieved quantities obtained when the remaining 10% are rejected are almost identical to the results when all data are included. This suggests that even where the S/N for a single averaged spectrum is low, the retrieval is reliable and produces internally-consistent results.

In order to investigate the reliability of the method and uncertainties in retrieved values, I perform an input-versus-retrieved test. I calculate a range of model spectra with different input values, and add random noise similar to that expected in the observations. This is of the order of 1% of the radiance except for the 2.2 and 2.53 μm radiances, which have noise of the order of 5% of the radiance added. These values arise from the exclusion criterion discussed above, where it is found that the

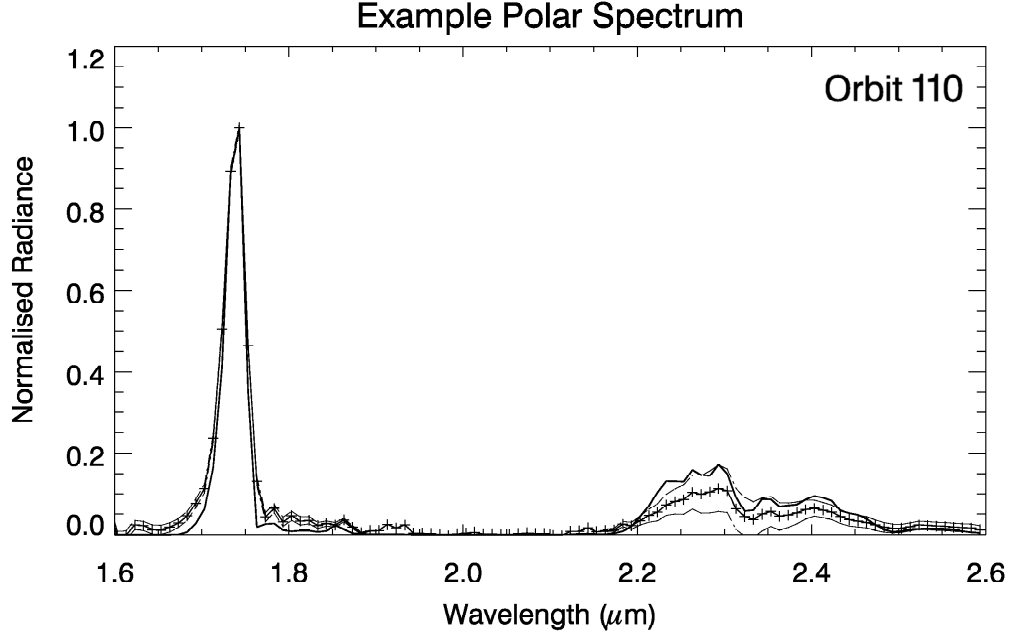


Figure 6.4: Model fits to a spectrum at $\sim 85^\circ$. The observed spectrum is represented by the line and crosses, the error on the spectrum is represented by dashed lines, and the model fit by the heavy solid line. The model fit is poor longwards of 2.2 μm . There is insufficient absorption here to fit the spectrum well.

majority of data points used meet the criterion that the S/N ratio is above 20 at 2.53 μm , where the noise is calculated from the VIRTIS instrumental noise-equivalent spectral radiance. For the case where the S/N at 2.53 μm is at least 20, the same is considered to be true for the S/N at 2.2 microns, and at all other radiances used in this work it is approximately 100. This is due to the slowly-varying behaviour of the NESR in the spectral region of interest (Figure 4.1), and the consistency of the near-infrared spectral shape as observed by VIRTIS-M-IR.

The random noise is calculated by generating Gaussian random numbers with a mean of zero and a standard deviation of one, which are then multiplied by $0.05I_\lambda$ (where λ is 2.2 and 2.53 μm) or $0.01I_\lambda$ (where λ is 1.74, 2.29, 2.32, or 2.4 μm) to provide the noise on each radiance. The noise is assumed to be Gaussian as I expect it to be dominated by thermal noise, which has a Gaussian amplitude

distribution. This provides a good, conservative, general noise estimate for a single averaged spectrum; of course, the actual noise on the mean values presented for the retrieved parameters is considerably less, as this noise is reduced during the averaging processes by a factor $\sqrt{n_{(spectra)}}$, where $n_{(spectra)}$ is the number of averaged spectra in each radiance, latitude, longitude or local solar time bin. Due to the high level of coverage, this is at least a factor of 10 for all results presented, except in the region polewards of -88° latitude.

The branch plot method is used to retrieve all the parameters of interest from the modified synthetic spectra, and I then compare the “retrieved” atmospheric state with the model input values used to create the spectrum. This provides an estimate of the error on a single measured value, and is a useful check that the retrieved values are consistent with the real values. Figure 6.5 shows that in all cases the input-versus-retrieved correlation coefficient is greater than 0.7, except for particle size parameter for which it is 0.2812. This poorer result is due to the small level of variation between branches of different relative mode 3 abundances. The dependence of other retrieved quantities on this variable is however very low (and not taken into account explicitly in the retrieval), so the poor retrieval has no effect on the retrieval quality for other variables. A systematic error of $\sim + 0.5$ can also be seen in the particle size parameter input v. retrieved plot, which since we are interested mainly in the abundance variation is of little importance. All of the retrieved variables are independently and simultaneously varied during this test, so the errors take into account any correlation between variables that is not explicitly accounted for. This also ensures correct error propagation; for example, errors in the determination of acid concentration that may subsequently affect the retrieval of other variables are implicitly included in the error for those variables.

There is also a systematic error in the particle size parameter of as much as -1 at

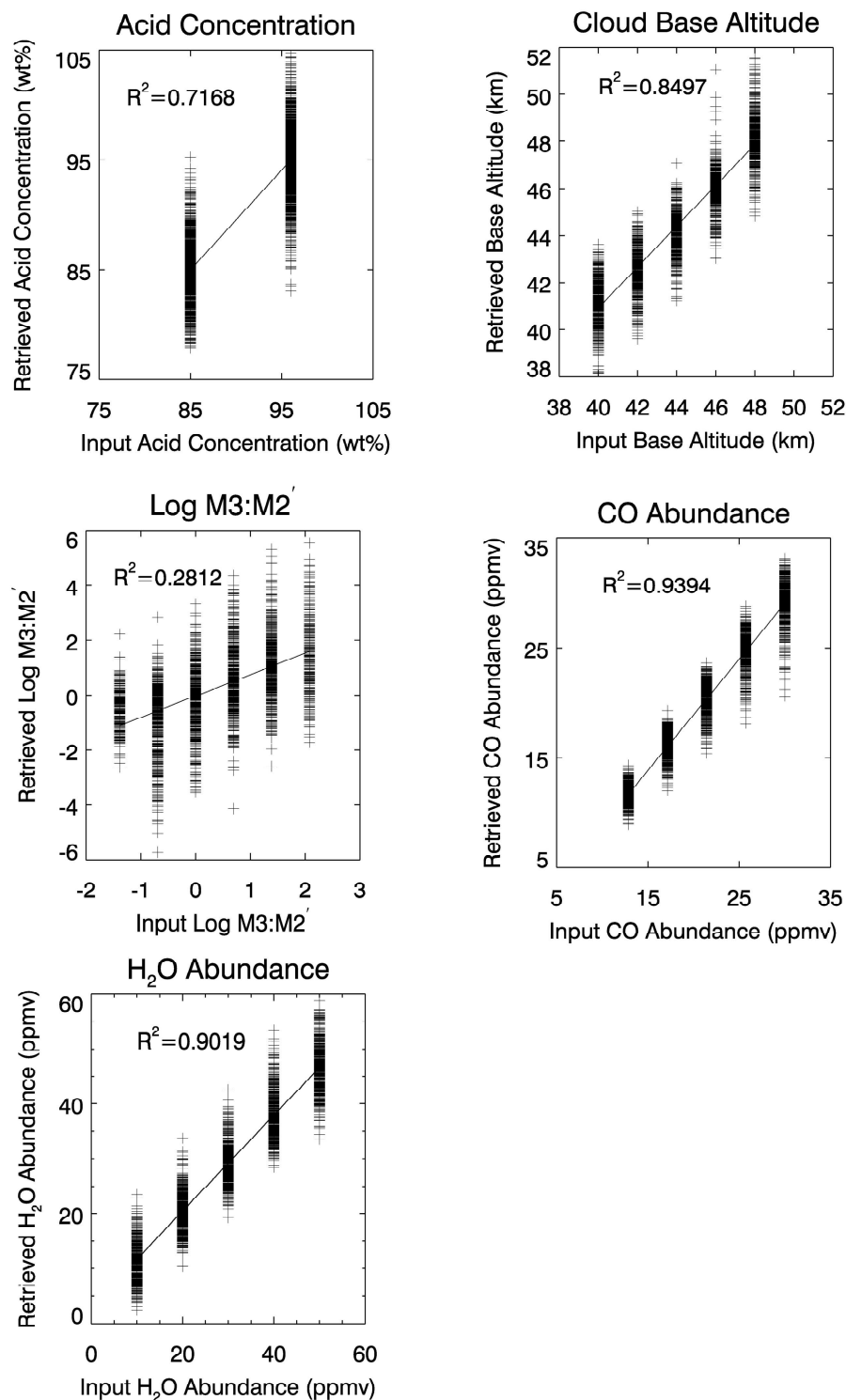


Figure 6.5: Input-versus-retrieved values for the five parameters investigated. Robust retrievals are obtained for acid concentration, base altitude, CO volume mixing ratio (VMR) and H₂O VMR. Mode 3:Mode 2' ratio is expressed as a natural logarithm and is the least well-retrieved variable, due to the small changes in radiance at 2.3 microns caused by particle size variation relative to acid concentration variation.

Variable	Error	Unit of Measurement
Acid Concentration	± 7	wt%
Base Altitude	± 3	km
Ln Mode 3:Mode 2' Relative Ratio	± 2	
CO Abundance	± 5	ppmv
H ₂ O Abundance	± 10	ppmv

Table 6.1: Errors in an individual measurement. Errors in averaged values are at least a factor of 10 smaller for each value.

high latitudes relative to spectra assuming an equatorial temperature profile, but this has no effect on the retrieval of other quantities, as variation in particle size is not taken into account when calculating the values for other variables.

The errors from the input-vs-retrieved calculation in each variable for an individual measurement are listed in Table 6.1. These errors are estimated from the full spread of retrieved values as shown in Figure 6.5, excluding extreme outliers, and combine the errors due to instrument noise and the errors introduced during the analysis (modelling error). The majority (90 %) of the data considered have S/N ratios higher than the threshold discussed here, so these errors are conservative estimates. They become very small when the data are averaged, since there are at least several hundred data in each final averaged value, so I take the standard deviation to be the best representation of the error on the mean retrieved values. The errors shown in Table 6.1 are approximately equal to the observed standard deviations. The observed standard deviation represents a combination of the spectral and modelling errors, and actual variation in the cloud properties between observations. The largest contributor is the scatter due to cloud variation; if the combined modelling and instrument noise error is reduced by at least a factor of 10 in the mean value compared with the error for a single spectrum, this error is small compared with the observed standard deviation.

A correction for the variation in temperature structure with latitude is implemented

in the calculations of acid concentration, mode 3:mode 2' relative abundance and cloud base altitude, but due to the small amount of data used to calculate this correction, its reliability may be questionable and therefore its effect on the results needs to be well understood. The calculations were therefore also performed without this correction (Figure 6.6). The qualitative results are unchanged. The base altitude at the pole is 2 km higher in this case than with the temperature correction, however, which provides a useful indication of the importance of taking into account latitudinal temperature variation when studying spectral regions sensitive to altitudes above ~ 45 km.

The extensive averaging is shown to reduce the random error on the mean value such that the real variation in the cloud properties is the main source of random noise. However, this does not account for sources of systematic error; some of these are discussed in detail in Section 6.3. The possibility of long-term changes in the response of the VIRTIS instrument is also not accounted for by this error analysis; whilst no such drift has been reported, degradation of detectors and other components may have introduced changes in, for example, the width of the instrument response function, which would introduce systematic differences between spectra taken at the beginning and end of the instrument working lifetime. Such changes are unlikely to affect the majority of conclusions presented here as they are based on an average over the working lifetime of the instrument, and the radiance and latitude coverage in particular are consistent throughout the mission. However, the trends reported as a function of orbit number are tentative, and long-term change in the behaviour of the instrument could conceivably account for the observed temporal variation (Figure 5.5); these trends, whilst interesting, must be viewed with caution. Other systematic effects related to the instrument itself have been discussed in Section 4.1, and the effects of stray light and odd-even response inequalities are removed as far as possible. Stray light removal becomes difficult within 5° of the

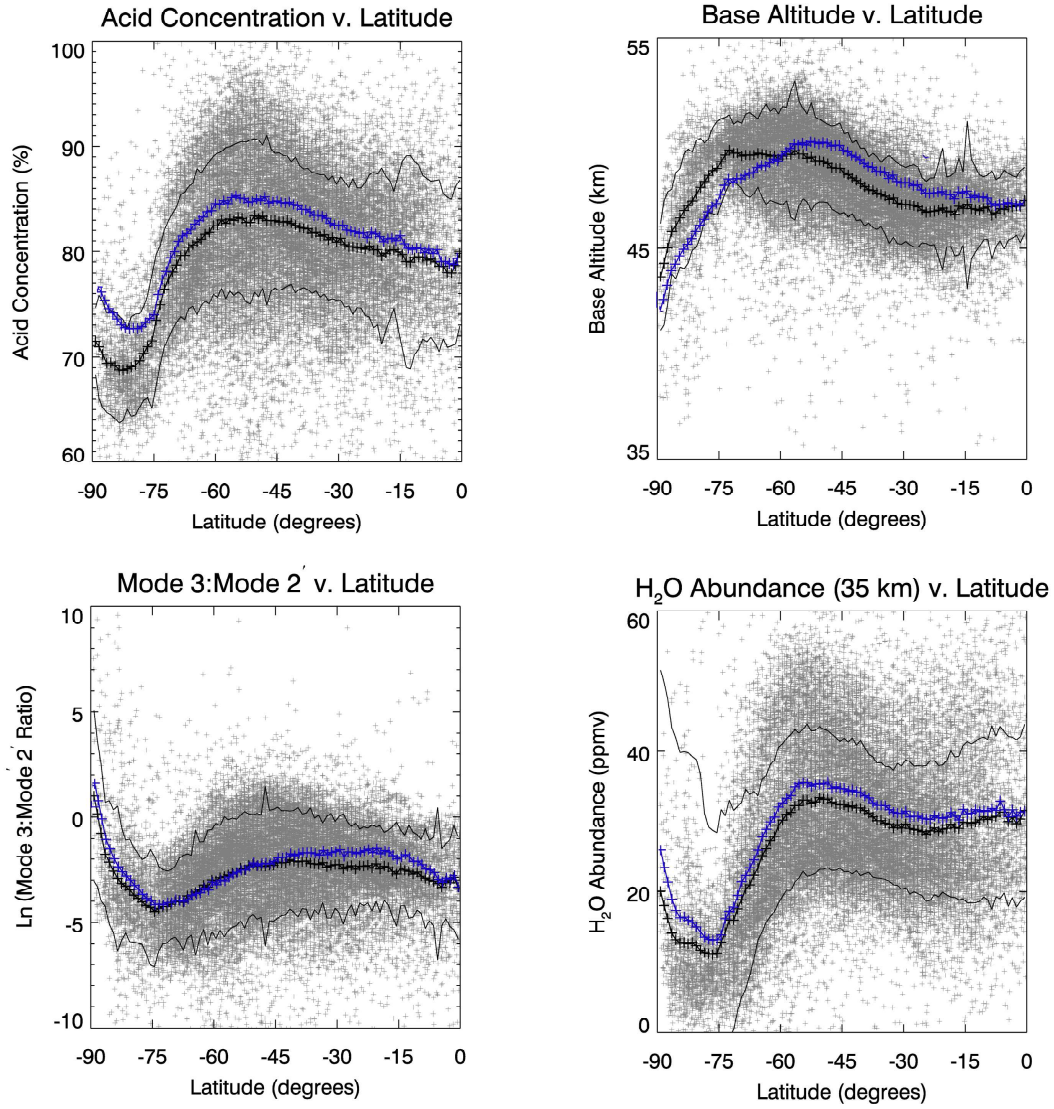


Figure 6.6: Retrieved quantities for acid concentration, cloud base altitude, particle size parameter and water vapour VMR where the standard equatorial temperature profile is assumed everywhere. Grey points are latitudinally binned for each observation, black joined points are the average over all observations used, and thin black lines are the standard deviation on this average. The blue points are the average values when a temperature structure correction is used, taken from Figure 5.2.

terminator, which contributes to the lack of reliability of spectra close to the pole and day/night terminators.

6.2 Validation using short wavelength windows

To provide further constraint and to test the conclusions previously arrived at using the 1.6—2.6 μm spectral range, I now extend the analysis to include the shorter-wavelength windows at 1.31 and 1.51 microns, and the wing-to-centre ratio of the 1.74 μm band. These radiances are not used as part of the retrieval process, and their inclusion therefore constitutes a strong test of the results. The sensitivities of these windows to the cloud properties investigated have been discussed previously in Section 4.2.3. Firstly, the 1.31:1.74 μm ratio is used as a test of the retrieval, as the 1.31 μm radiance is higher than that at 1.51 μm and therefore has a better signal to noise ratio. There are known to be problems with the 1.74 μm wing-to-centre ratio, as there is consistently too much absorption in the shortward wing of the 1.74 μm band in the synthetic spectra (see Sections 2.2.4 and 6.1). Using 1.74 μm radiance-averaged results from Section 5.1, together with radiance values at 1.31 and 1.74, the 1.31/1.74 μm ratio is adjusted to take into account latitudinal temperature variation and retrieved variations in particle size. The sensitivity to other variables is not significant enough to require a correction. The resulting values for the 1.31/1.74 μm radiance are then compared with the model spectra.

If all modes of variability are taken into account by the analysis performed using the longer wavelength windows, the points should lie exactly on the model branches for the nominal mode 3:mode 2' ratio. From Figure 6.7 we see this is not the case in bright regions, where the points lie somewhat below the model branches, but the fit is very good elsewhere. It is also not the case polewards of -70° latitude

(Figure 6.8), which is probably the result of the high level of contamination from dayside scattered light and solar stray light and imperfections in the technique for removing this, since stray and scattered light contributions are larger at shorter wavelengths. The closeness of the fit equatorwards of -70° , although it is not exact, is good evidence that the retrieval is reliable as this wavelength was not originally included.

A similar procedure is then implemented for the $1.51:1.74\ \mu\text{m}$ ratio to provide a further constraint, except in this case corrections are also implemented for acid concentration and cloud base altitude. However, in all cases the points lie well below the model branches (Figures 6.7). This is likely to be a result of imperfections in the method of correcting for dayside scattered stray light, as the dayside reflectance spectrum has a peak close to $1.51\ \mu\text{m}$. The radiance at $1.51\ \mu\text{m}$ is low and the scattered dayside radiance that is subtracted is of very similar magnitude to, and sometimes larger than, the thermal signal, so the remaining signal after subtraction is below the noise level. The points taken from the polar regions (Figure 6.7) show higher radiances at $1.51\ \mu\text{m}$ relative to $1.74\ \mu\text{m}$, but the scatter is very high and the high uncertainty introduced by the stray light correction renders this ratio unsuitable for the task.

The $1.71/1.74\ \mu\text{m}$ ratio is sensitive to mode 3: mode 2' ratio and base altitude. Once the $1.71:1.74\ \mu\text{m}$ radiance ratio has been corrected for latitudinal temperature structure variations and retrieved cloud parameters, however, it can be seen that the values in the data are much higher than for any of the models. This is difficult to explain, even with the addition of sub-cloud haze, which reduces this ratio rather than increasing it (Figure 6.9). It is possible that this is also due to an imperfect correction for stray light at $1.71\ \mu\text{m}$, but this is unlikely as the correction is in general seen to be good here; the thermal signal at $1.71\ \mu\text{m}$ is higher than that at

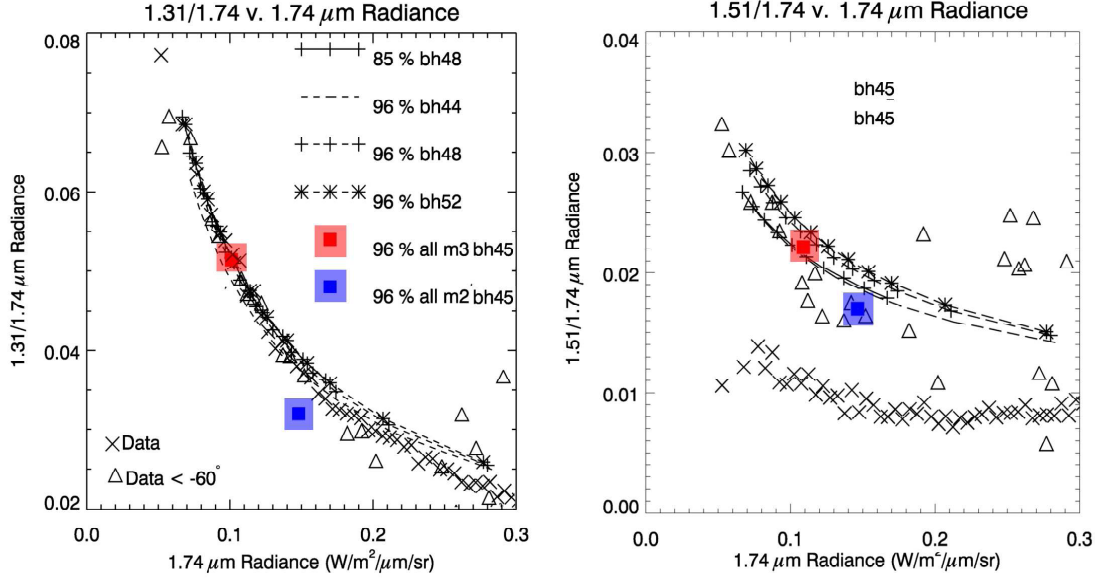


Figure 6.7: Sensitivity to cloud parameters at 1.31 and 1.51 μm microns. After correction for all variation in cloud properties, the data for 1.31 lie on the model branches except in the brightest regions. At 1.51 the data lie below the branches in low latitude regions, but closer to the branches at the poles. The data are binned as a function of 1.74 μm radiance for all latitudes equatorwards of -60° and for latitudes polewards of -60° .

1.51 μm and the scattered light contribution is smaller, so the 1.71 μm radiance escapes the problems experienced at 1.51 μm . It is possible that scattering within the spectral dimension of the instrument from the high radiance peak at 1.74 μm results in the excessive radiances at 1.71 μm .

In Section 6.3 I will discuss potential origins of these discrepancies discussed in the last two sections and attempt to correct for them.

6.3 Assumptions

The results in Chapter 5 were calculated using a model with six variables. Several assumptions were made, as discussed in Chapter 3.3.4, to reduce the number of independent variables to this manageable quantity. The Venusian cloud is in reality

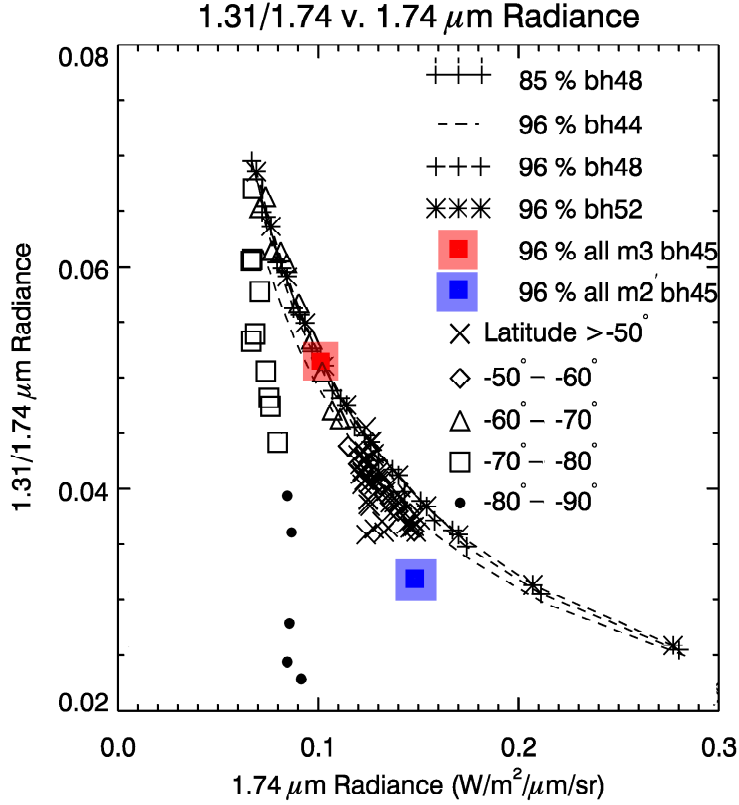


Figure 6.8: Sensitivity to cloud parameters at 1.31 microns. The difference between this and the corresponding plot in Figure 6.7 is that the data has been averaged in latitude instead of radiance. After correction for all variation in cloud properties, the data for 1.31 lie on or close to the model branches for latitudes equatorward of -70° , but below them for polar latitudes. This is likely to be due to the high level of contamination from scattered light, and difficulty in perfectly correcting for this at short wavelengths.

more complex than the model used here, and therefore it is necessary to investigate the possibility that some of these assumptions may be imperfect or incorrect, and if that is the case, what the effect will be on the retrieved results. These include i) assumptions about the refractive indices of the sulphuric acid cloud droplets; ii) the parameterisation of the mode 3 size distribution; iii) the absence of a haze layer below the cloud in the model; iv) the assumed invariance of the upper cloud, and fixed scale heights in the lower cloud; v) the constant temperature profile assumed in the deep atmosphere; vi) the CO and H₂O vertical profiles; vii) the fixed H₂O

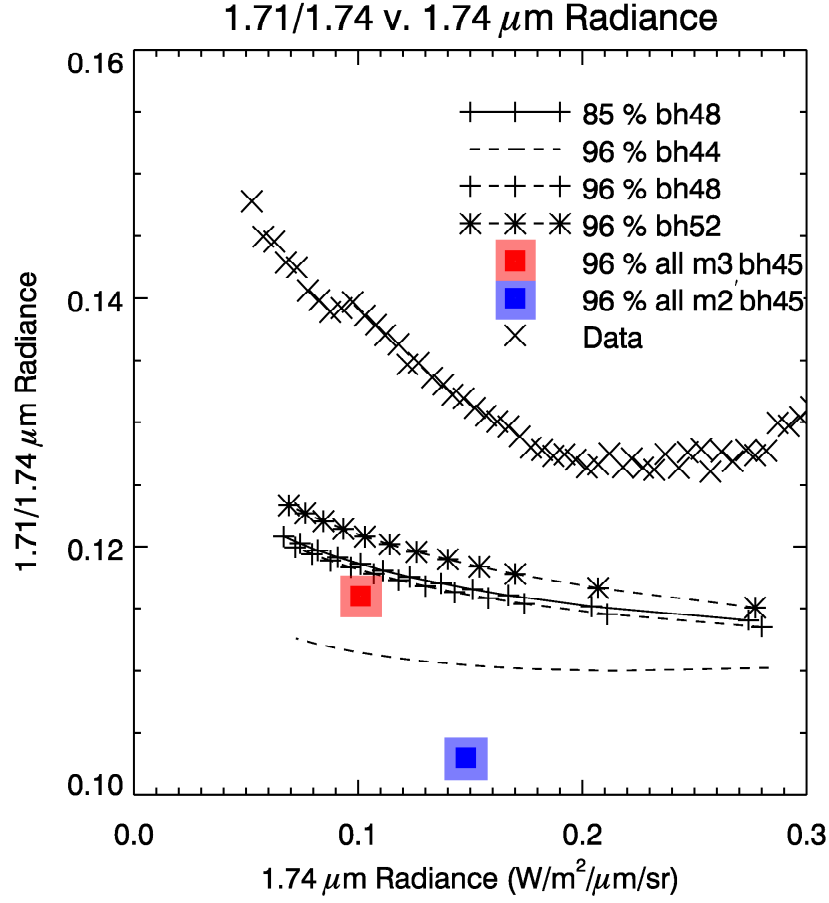


Figure 6.9: Sensitivity to cloud parameters at 1.71 microns. After correction for all variation in cloud properties, the data still lie far above the model branches.

and HCl VMRs in the deep atmosphere; and viii) the lack of retrieval of other minor species, such as OCS. This section provides further detail about the robustness of the results presented and the limitations of the branch plot technique.

6.3.1 Linearity of refractive index variation

The initial assumption has been made for simplicity that the wavelength dependence of the refractive indices due to changes in acid concentration is linear. Data for only three concentrations in the expected range for Venus are available from Palmer and Williams (1975), for 75, 85 and 96 wt%, and the data for lower concentrations

do not contain imaginary refractive index information between 1.8 and 2.5 μm . Until very recently, Palmer and Williams (1975) was the only reliable source of imaginary refractive index data for high acid concentrations in the wavelength range of interest. Measurements by Myhre et al. (2003) also exist in this range, but the highest concentration they considered was 81 wt% and the spectral proximity of their short-wavelength cutoff to the 1.74 μm window rendered their results unreliable for the purposes of this work. I use the 85 and 96 wt% results from Palmer and Williams (1975), with the assumption of linear interpolation for intermediate concentrations. If I also include 75 wt%, however, the assumption of linearity becomes invalid. Since Palmer and Williams provide no data for intermediate concentrations in this range the linear approximation is taken to be the most appropriate as this is the simplest approximation given the limitations of the available dataset.

Between 2.5 and 2.6 μm , no optical data is available from Palmer and Williams (1975), so the values used are interpolated between the measurements that exist outside of this range. The wavelengths used to determine the cloud base altitude include a wavelength in this range, 2.53 μm . An examination of the interpolated Palmer and Williams (1975) data for 75, 85 and 96 wt% indicates that a linear approximation for the spectral variation due to acid concentration changes between 2.4 and 2.53 μm is potentially flawed, although the reliability of the optical data is questionable since no direct measurements were made at 2.53 μm . Two examples of alternative approaches to account for acid concentration variation when determining the cloud base altitude are presented, the first being a quadratic correction, and the second no correction. The base altitude results as a function of 1.74 μm radiance are shown for these two assumptions in Figure 6.10, with the result presented in Section 5.1 overlaid for reference. It can be seen that, for the case with a quadratic correction, the base altitude is ~ 48 km in dark regions, rising to ~ 52 km in the brightest regions. In the case where the acid concentration variation is not explicitly

taken into account, little variation between bright and dark regions is observed, and the results are consistent with a constant cloud base altitude.

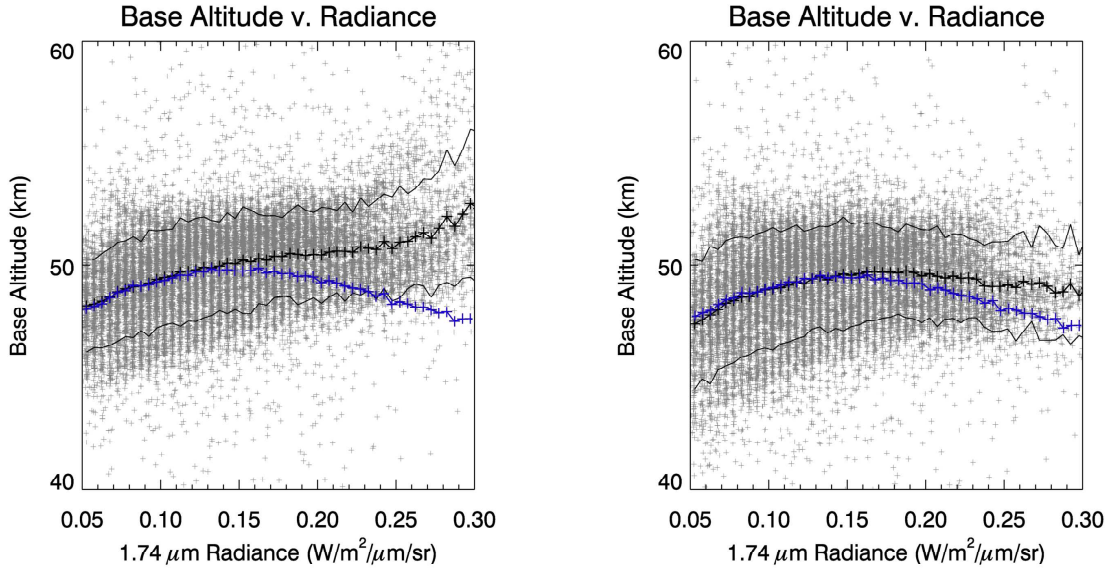


Figure 6.10: Cloud base altitude results as a function of $1.74\ \mu\text{m}$ radiance where the variation of the $2.53/2.4$ ratio with acid concentration is a) approximated as quadratic and b) assumed not to vary. Grey points and black lines show averages as described in the caption to Figure 5.1. Blue joined points show the result from Figure 5.1 for comparison.

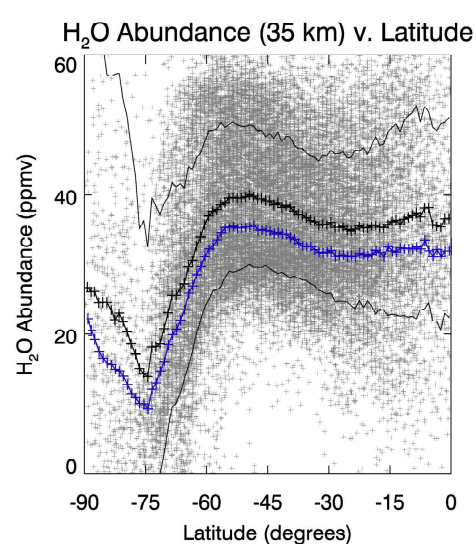
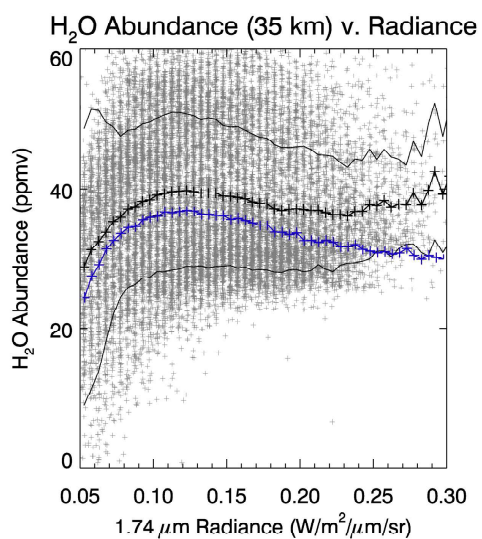
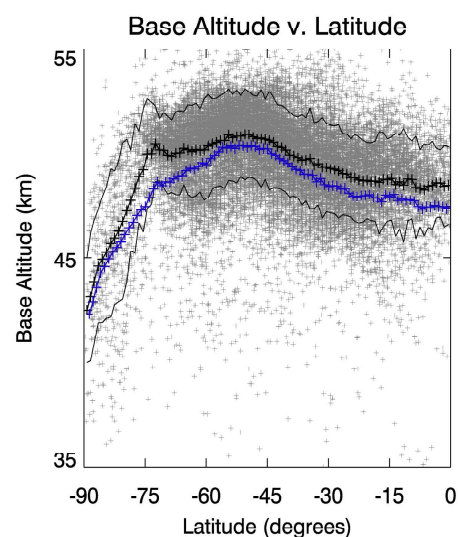
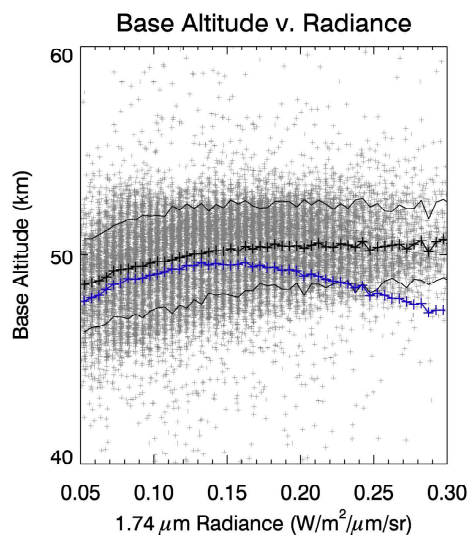
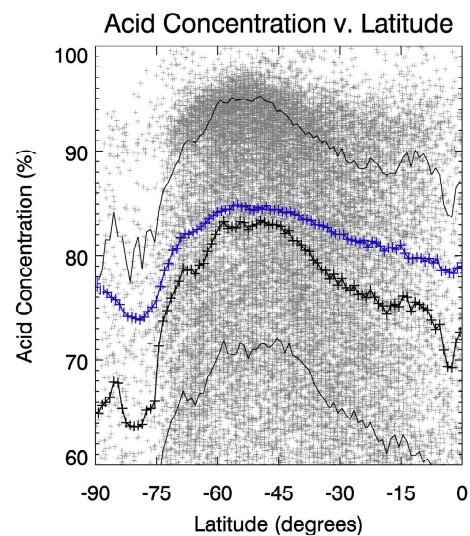
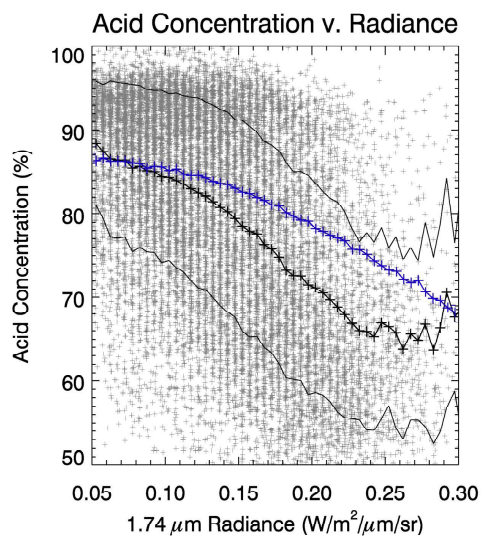
Carlson and Anderson (2010) and Carlson and Anderson (2011) have obtained new laboratory measurements of the imaginary refractive index of sulphuric acid, over a range of concentrations from 68—96 wt %. Their results are very consistent with those of Palmer and Williams (1975) where they overlap, and the greater number of concentrations measured provides more information about the variation of spectral properties as a function of acid concentration than was hitherto available. The region between 2.5 and $2.6\ \mu\text{m}$, where the Palmer and Williams (1975) results were interpolated and not directly measured, shows some differences between the two sets of measurements, which may have an effect on the retrieved base altitude. To test the impact of this new information on the results, the real refractive indices from Palmer and Williams (1975) were interpolated and extrapolated to provide values

for use with the Carlson and Anderson (2011) imaginary indices, and new branching ratio formulae were derived based on models created using the new indices.

Comparing the results of these calculations with those obtained using the linear approximation shows that the qualitative results are largely unchanged (Figure 6.11), although lower acid concentrations are found in bright regions for this case; this explains the discrepancy at $2.2\text{ }\mu\text{m}$ seen in the example bright spectrum in Figure 6.2. The error on the mean acid concentration is somewhat larger, and this increases the error on the retrieved particle size and water vapour VMR. The cloud base altitude is increased from the linear case in bright regions and is slightly higher at the pole, although the latitudinal trend is unchanged. In this instance the acid concentration variation has not been taken into account when calculating the base altitude; the error introduced by the assumption of constant acid concentration in the base altitude calculation is $\sim \pm 2\text{ km}$, whereas if the retrieved acid concentration was taken into account the error in the brightest regions was as high as 6 km , due to the large error in the retrieved acid concentration. This case is not identical to that presented in Figure 6.10 b), as the Carlson and Anderson optical data were used to generate the forward models instead of the Palmer and Williams optical data.

The slight increase in the base altitude in bright regions when the Carlson and Anderson optical data are used is similar to that seen in Figure 6.10 for the quadratic correction for acid concentration. This indicates that, whilst an approximately constant base altitude cannot be ruled out, an increase in base altitude as a function of $1.74\text{ }\mu\text{m}$ radiance is an equally viable result and must also be considered. This

Figure 6.11 (*following page*): Results as a function of $1.74\text{ }\mu\text{m}$ radiance and latitude where the variation of spectral properties with acid concentration is taken from the results of Carlson and Anderson (2010, 2011). The grey points are binned values from each observation, the joined black points are averaged over all observations, the thin black lines represent the standard deviation on this average and the joined blue points are the average values for the linear acid approximation.



may indicate that the model suggested by Pollack et al. (1993), in which the lower cloud optical depth is altered by removing the lowest layer of the cloud, is an appropriate model to describe the cloud formation process. Within the limitations of the method, neither result can be confirmed over the other. Possible explanations for both cases are discussed in more detail in Section 7.1.2.

6.3.2 Mode 3 size distribution and composition

The mean radius of the mode 3 particles has been assumed to be the same everywhere, fixed at the value taken from Pollack et al. (1993), which was based on the cumulative data from Pioneer Venus, Venera and ground-based observations. Only one instrument on Pioneer Venus, the Large Probe Cloud Particle Size spectrometer (LCPS), was capable of directly distinguishing between particles of different effective radii, so this is the only measurement of the mode 3 particle size. It can be seen from Esposito et al. (1983) that great uncertainty about the precise nature of the mode 3 particles remained after analysis of the Pioneer Venus descent probe data – in particular, the size and aspect ratio were called into question. There was a discrepancy between measurements by the Pioneer Venus LCPS instrument, which identified a distinct distribution of larger particles, and nephelometer backscatter data; the two results were incompatible if the assumed refractive indices for the particles were correct. The LCPS size distributions did not yield the same optical depths as those measured by the solar flux radiometer (LSFR), if the particles were assumed to be spherical. There were also internal inconsistencies in the LCPS data, as overlapping size ranges gave conflicting measurements. The hypotheses suggested by Esposito et al. (1983) were that either the mode 3 particles were non-spherical, solid particles of unknown composition, or that the particles identified as a separate larger size mode were a mis-identified tail of the mode 2 distribution. In either

of these hypotheses, however, large particles with average radii close to the chosen mean radius of 3.65 μm would be present.

Due to these uncertainties, it is important to consider the effect of changing this mean radius $\bar{r}$. A branch plot showing the 2.2:1.74 μm ratio for different mode 3 effective radii is given in Figure 6.12. It can be seen first of all that the mean radius has a significant effect on this ratio, but also that the effect is highly non-linear. Most importantly, this ratio could not be used to determine the mean radius even assuming constant acid concentration; finding a single-valued function to describe the variation is impossible as branches for $\bar{r} = 2.5\mu\text{m}$ and $\bar{r} = 5\mu\text{m}$ both lie above the branch for $\bar{r}=3.65 \mu\text{m}$ on the plot. There is variation in 2.2:1.74 μm radiance due to the relative number of mode 3:mode 2' particles for choices of mode 3 radius other than 3.65 μm , and this is due to the different variations in extinction cross-section and scattering phase functions over the wavelength range of interest. It can be seen in Figure 6.12 that the cross section does not change very rapidly for a mean radius of 3.65 μm , hence for 3.65 μm the ratio is insensitive to the relative number density of mode 3:mode 2' particles, but for both 2.5 and 5 μm the change is significant between 1.74 and 2.2 μm . A full explanation for the different spectral behaviour of particles with different sizes involves a combination of variation in the extinction cross section and phase functions of both mode 3 and mode 2' particles.

Changing the mode 3 mean radius affects the retrieval of acid concentration, H_2O abundance and cloud base altitude. If the actual mode 3 mean radius is 2.5 μm , a systematic error of +8 wt % is introduced into acid concentration values, -10 ppmv into H_2O at 35 km, and -1 km in base altitude. If it is 5 μm , systematic errors are +10 wt %, -2 ppmv and -2.5 km for acid concentration, H_2O VMR and base altitude respectively. Other quantities are unaffected.

The possibility of variation in mode 3 mean radius introduces further uncertainty,

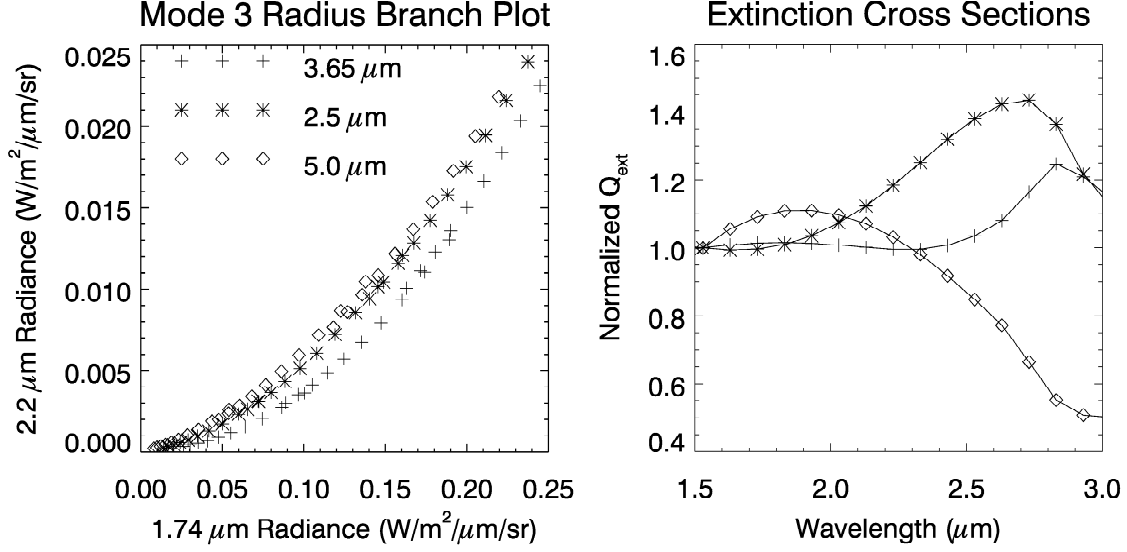


Figure 6.12: 2.2:1.74 μm branching curves for different mode 3 mean radii. This ratio is sensitive to the mean radius chosen in the model, but the behaviour is non-linear. The acid concentration is 85 wt %. The extinction cross-sections, normalized to the value at 1.53 μm , are shown in the right panel.

which provides alternative possibilities for explaining the spectral behaviour of the Venusian cloud. The mode 3 mean radius cannot be uniquely constrained using VIRTIS – to do so will probably require future in-situ measurements using descent probes or balloon platforms. However, the best estimate mean radius of 3.65 μm is well-supported by previous data analysis and modelling work (Crisp 1986, Pollack et al. 1993, McGouldrick and Toon 2008). The McGouldrick and Toon (2008) study in particular is significant, as the results of this microphysical model show effective radii for a single-mode cloud of no more than 4.5 μm , which is consistent with our choice of 3.65 μm for the nominal mean radius of mode 3.

The poor spectral fit in the polar regions with the nominal model cannot be explained by invoking a different mode 3 mean radius, as a mean radius of 3.65 μm maximises the absorption at 2.3 relative to 1.74 μm , as can be seen in Figure 6.12.

The mode 3 mean radius has little effect at 1.31 and 1.51 μm relative to 1.74 (Figure 6.13), even for radii of up to 10 μm . A larger effect can be seen at 1.71 μm , which

as at 2.2 μm is highly non-linear – the model branches for 3.65 and 2.5 μm cross at high 1.74 μm radiances. Whilst larger effective radii result in a higher 1.71:1.74 μm ratio in dark regions, as observed in Figure 6.9, the increase is not sufficient to bring the models into line with the data, and in any case this would make the spectral fit in the polar regions considerably worse. The persistent discrepancy between the model and data at 1.71 μm is more likely to be due to imperfect carbon dioxide line information, or instrumental scattering effects than a significant difference in the cloud properties from the nominal model.

Another area of uncertainty is the composition of the mode 3 particles. Their precise chemical nature has long been questioned, with several suggestions put forward by various authors. The uncertainty is mainly due to apparent discrepancies between results from different instruments on Pioneer Venus, which arise if the particles are assumed to be liquid sulphuric acid droplets. Cimino (1982) examined Pioneer Venus S- and X-band radio occultation data; she found that the wavelength dependence of the absorption in this spectral region is inconsistent with pure sulphuric acid liquid droplets, and the occultation mass content results for the sulphuric acid case suggested a particle number density an order of magnitude greater than was observed by LCPS. She concluded instead that the best-fit model mode 3 particle consisted of a solid dielectric core making up 97 % of the particle by radius, with a thin coating of liquid H_2SO_4 . The core material was not identified, although metal chlorides, solid sulphur and rock fragments are all possible candidates. This would undoubtedly have a significant effect on the scattering properties of the mode 3 particles, but laboratory measurements to obtain refractive index data are likely to be very complex, and these values would depend on the nature of the solid core, which is not known.

Other problems exist in the lower cloud region, which contains high abundances

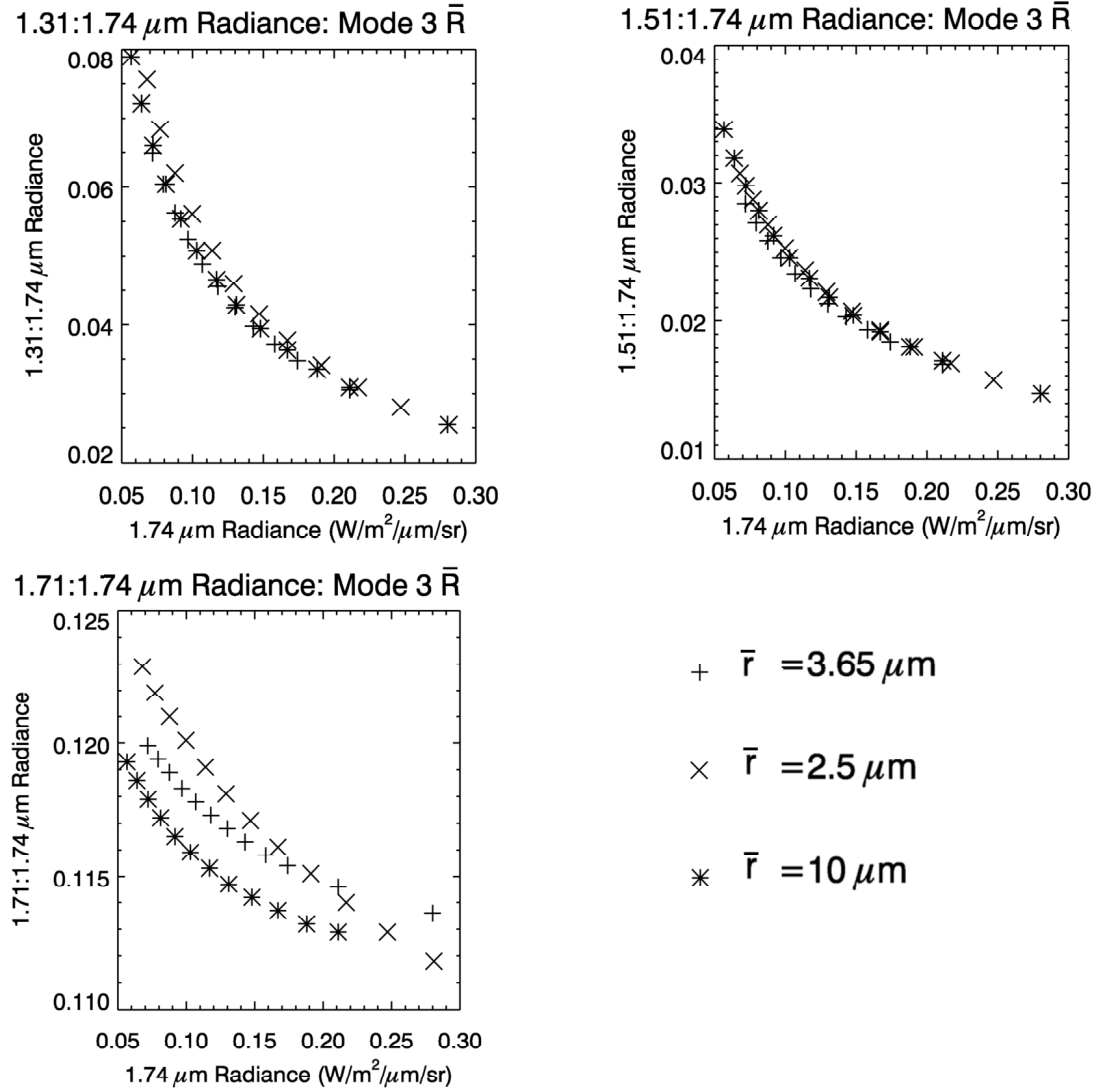


Figure 6.13: Shortwave branching curves for different mode 3 mean radii. Only a small effect is observed at 1.31 and 1.51 μm , but the effect at 1.71 μm is more significant.

of mode 3 particles. Knollenberg and Hunten (1980) state that the low real refractive indices measured in the altitude region between 49 and 52 km (Blamont and Ragent 1979, Marov et al. 1979) are not consistent with liquid sulphuric acid droplets. The method used to determine these refractive indices assumes conservative scattering, and closer values to the expected index are achieved if some absorption by the particles is assumed, but this may also indicate that the mode 3 particles

are crystalline. The LCPS measurements support this hypothesis, as different ranges in the instrument are seen to measure different numbers of particles above a certain size, whereas for spherical particles this number should be equal. Toon et al. (1982) suggest that re-calibration of the LCPS instrument would remove this discrepancy. The presence of crystalline particles would complicate the modelling process, as a new scattering parameterisation for high-aspect-ratio particles would be required (the Mie parameterisation is only valid for spherical particles). The composition of the particles is also called into question by this hypothesis, as in the lower cloud sulphuric acid should be liquid and would therefore form spherical particles.

Several alternative chemical compounds have been proposed by Krasnopolsky (1989) and Esposito et al. (1983), including aluminium chloride and hydrogen phosphate (Krasnopolsky 1989), and NOHSO_4 or chlorides such as HCl or FeCl_3 . Krasnopolsky (1989) describes the results from the X-ray radiometer instrument on the Vega-2 probe; X-ray fluorescence measurements within the cloud layer indicate the presence of chlorine and phosphorus as well as sulphur. Phosphoric acid in the lower cloud may explain the apparent extent of the cloud to altitudes as low as 33 km at the Vega sites, whilst at this altitude sulphuric acid would thermally dissociate due to high temperatures. Esposito et al. (1983) suggest that NOHSO_4 is the only solid particle candidate with an adequate vapour reservoir; problems are posed by its high solubility in sulphuric acid, which means the observed coexistence of mode 2' and mode 3 would be unlikely assuming these compositions. A different composition for mode 3 near the poles may be an explanation for the poor spectral fit in the polar regions that is shown above (Figure 6.4), but the problem is highly underconstrained and the question is only likely to be fully resolved by future in-situ measurements.

6.3.3 Sub-cloud haze

Nephelometer results from the Venera descent probes as presented by Marov et al. (1980) indicate some scattering particles present in a layer below the cloud, extending down to 32 km. They suggest that mostly sub-micron particles, with $r \sim 0.1 \mu\text{m}$, would produce the best fit to the available data, with possibly a very few larger particles. Scattering particles below the cloud are referred to by Satoh et al. (2009) as haze, and are not necessarily sulphuric acid droplets. No such sub-cloud haze was introduced into the cloud model used here. Satoh et al. (2009) use the wing-to-centre ratio of the $1.74 \mu\text{m}$ band to provide constraint on the optical depth of this haze; they find, for a small subset of VIRTIS-M-IR observations, that the optical depth of haze varies from 0 to 3 at $1.74 \mu\text{m}$, with the largest values observed in dark regions of the planet. They do not however present a full sensitivity study of this ratio, and in fact it can be seen in Figure 4.10 that the ratio is sensitive to the particle size parameter and cloud base altitude as well as the optical depth of sub-cloud haze. This window cannot therefore be used to uniquely constrain sub-cloud haze optical depth without first accounting for changes in the other variable cloud parameters.

This being the case, the effect of adding sub-cloud haze is tested here. It is assumed to be made of particles with an mean radius of $0.1 \mu\text{m}$ (a mean value of $0.13 \mu\text{m}$ is given by Marov et al. (1980)), with a log-normal distribution having the same variance as that assumed for mode 1 (see Table 3.2). The particles are assumed to have the same optical properties as sulphuric acid, in the absence of any other candidate substance with known optical properties. Satoh et al. (2009) use similar optical properties for the haze and for the other cloud particles in the model in most cases.

A series of models with different haze optical depths between 30 and 45 km is created. The haze optical depths range from 1—3 at $1.73 \mu\text{m}$, similar to the values

quoted by Satoh et al. (2009). All have a cloud base altitude of 45 km and contain only mode 3 particles in the lower cloud; from Figures 4.8, 4.9 and 4.10 it can be seen that models close to the nominal ratio of mode 3:mode 2' have very similar properties at the wavelengths we are interested in as models with no mode 2', so this is a reasonable approximation and reduces the number of variables in the model.

It may be possible to use the ratios of 1.31/1.74 and 1.71/1.74 to constrain the amount of sub-cloud haze present, if any, having taken into account variation in the quantities already determined. Branch plots are shown below in Figures 6.14 and 6.15, with the corrected data included. The 1.31/1.74 points are almost all fitted well by a model with no haze, the brightest points and those furthest towards the pole perhaps with some haze, although the reliability of the polar points is questionable due to the high levels of contamination by scattered light. The 1.71/1.74 μm ratio data are not fitted by any of these models. If there is some sub-cloud haze present in bright regions but not in darker regions, the conclusion arrived at is the opposite to that of Satoh et al. (2009), who find in general that high haze optical depths occur in dark regions. However, Satoh et al. (2009) suggest that the haze particles may act as cloud condensation nuclei (CCN) for the lower cloud. This being the case, the presence of haze below the cloud in bright regions may be a result of downwelling and subsequent evaporation of sulphuric acid, leaving the bare CCN present in the atmosphere below the cloud; this could explain the observations presented here. It is quite feasible that the haze particles could be solid and act as efficient CCN, and being solid at cloud-level temperatures they would have a higher boiling point than sulphuric acid so would evaporate at lower altitudes. The removal of CCN into a sink below the clouds may also account for the increased average particle size in bright regions, as fewer CCN generally leads to the formation of larger particles (see Section 7.2.3 for a more detailed discussion of this phenomenon).

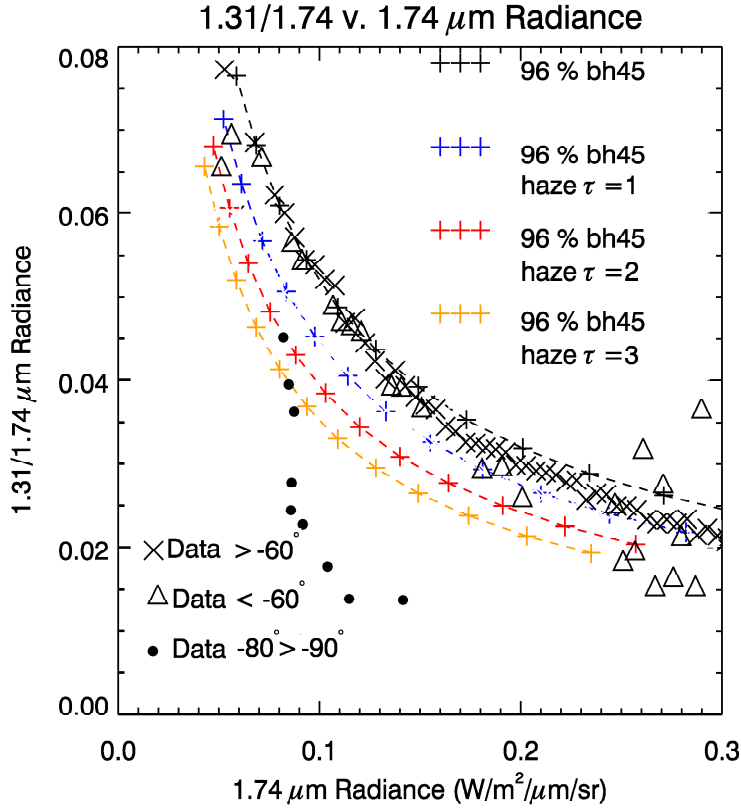


Figure 6.14: Models with different amounts of sub-cloud haze for 1.31:1.74 μm , including corrected data. bh 45 stands for a base height of 45 km, acid concentrations are 96 wt%. τ is the haze optical depth at 1.73 μm .

If sub-cloud haze with an optical depth of approximately 1 is present in bright regions, as indicated by the 1.31 μm ratio, this may have an effect on the parameters already retrieved. The magnitude of this effect is for the most part small – the most significant effects are on the retrieved acid concentration and water vapour VMR. If $\tau_{1.73\mu\text{m}}=1$ haze is present and unaccounted for, then retrieved acid concentrations from synthetic spectra are 5 wt % higher than the input value, and water vapour VMRs are 5 ppmv higher. Other retrieved quantities are unaffected. This would mean that acid concentration and water vapour VMR are overestimated in bright regions, and would alter the actual retrieved acid concentration range to ~ 65 – 90 instead of ~ 70 – 90 wt %, and the retrieved water vapour VMR in the brightest regions to 25 instead of 30 ppmv. Acid concentrations as low as 65 wt% do not

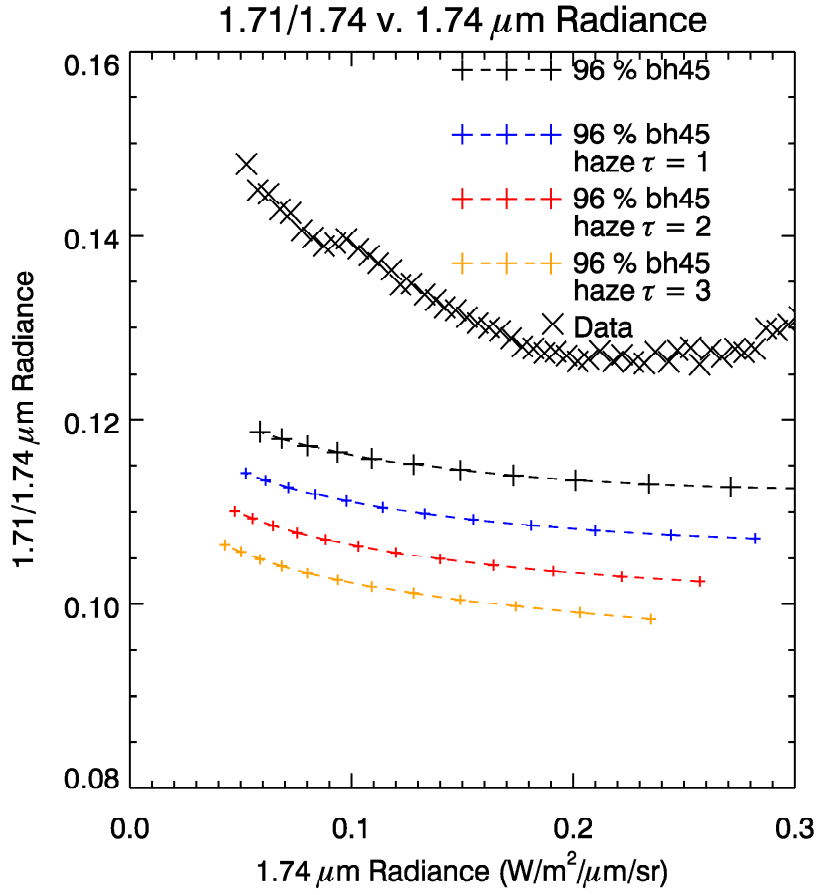


Figure 6.15: Models with different amounts of sub-cloud haze for 1.71:1.74 μm , including corrected data. Labelling is as Figure 6.14.

seem likely from calculation of equilibrium acid concentrations (James et al. 1997), which may indicate that the presence of haze is not the reason for the discrepancy. If significant amounts of sub-cloud haze are present in the polar regions as indicated, the acid concentration and water vapour VMR would be significantly over-retrieved, making these values in reality much lower. Again, as these values are already low, it does not seem likely that this is the case and the discrepancy at 1.31 μm in the polar regions is more reasonably attributed to the severe stray and scattered light contamination.

6.3.4 Mode 1/Mode 2 variability and base altitude v. scale height

The assumption has been made that the upper cloud, consisting of mode 2 and also the ubiquitous mode 1 particles, has a constant optical depth and the same vertical distribution everywhere on the planet. Ignatiev et al. (2009) show that whilst this is the case over the majority of the planet, the altitude for which the optical depth $\tau=1$ (at $1.63\text{ }\mu\text{m}$) is 10 km lower at the pole than it is at latitudes up to $\pm 50^\circ$, with a roughly linear decrease in altitude in between (Figure 6.16). This could be due to either a change in the altitude distribution of the particles in the upper cloud or a change in the optical thickness of the entire upper cloud, both of which could reduce the optical depth in the highest altitude regions.

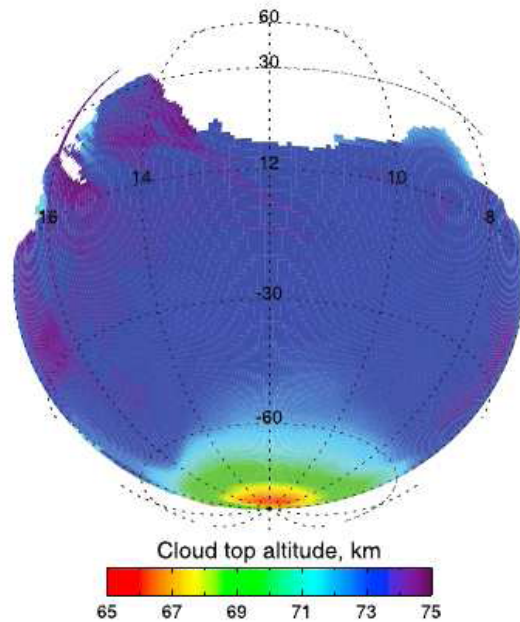


Figure 6.16: Mean $\tau=1$ altitude as a function of latitude and local solar time. This figure is taken from Ignatiev et al. (2009)¹.

¹Reprinted from Ignatiev, N. I., Titov, D. V., Piccioni, G., Drossart, P., Markiewicz, W. J., Cottini, V., Roatsch, T., Almeida, M. and Manoel, N. “Altimetry of the Venus cloud tops from the Venus Express observations”, *Journal of Geophysical Research (Planets)*, volume 114, E13, E00B43, 2009. Copyright 2009 American Geophysical Union.

Ignatiev et al. (2009) model the polar cloud by entirely removing mode 2 particles from the upper cloud. As the removal of particles from the upper cloud is a plausible cause of the observed cloud top altitude decrease, it is necessary to test the effect of implementing this on the quantities retrieved here. I reduce the number of mode 2 particles such that the $\tau=1$ altitude decreases at $1.63\text{ }\mu\text{m}$ by 10 km, as observed by Ignatiev et al. (2009). I then make the assumption that this altitude decrease is linear from -50° to the pole, and compute a latitude-dependent correction for each of the wavelength ratios used in this work, before recalculating each of the parameters. This decrease in the upper cloud optical depth may be a result of photochemical H_2SO_4 aerosol being prevented from reaching the upper cloud at the poles due to a transport barrier created by the polar collar downwelling, a similar phenomenon having been observed on Titan by Teanby et al. (2008).

This reduction in mode 2 has the effect of increasing the retrieved average particle size, as to compensate for the loss in total optical depth an increase in the number of mode 2' and mode 3 particles is required. This may therefore solve the problem of the poor spectral fit in the polar regions beyond $\sim 75^\circ$ latitude, as this will increase the absorption at $2.3\text{ }\mu\text{m}$ relative to $1.74\text{ }\mu\text{m}$. If the retrieval is redone for this case and the new model compared with the data as in Figure 6.4, the synthetic spectrum now lies further within the error bars (Figure 6.17). Therefore, with this alternative hypothesis, a more reasonable fit can be achieved even in the polar regions and no alternative composition for the mode 3 particles is required.

In general, very little difference is made to the retrieved results by altering this assumption (less than the standard deviation in the results), the exception being that the retrieved cloud base altitude is higher if the upper cloud optical depth decreases towards the pole (Figure 6.18). This is because the effect of removing opacity higher in the cloud is not distinguishable from the effect of moving the cloud

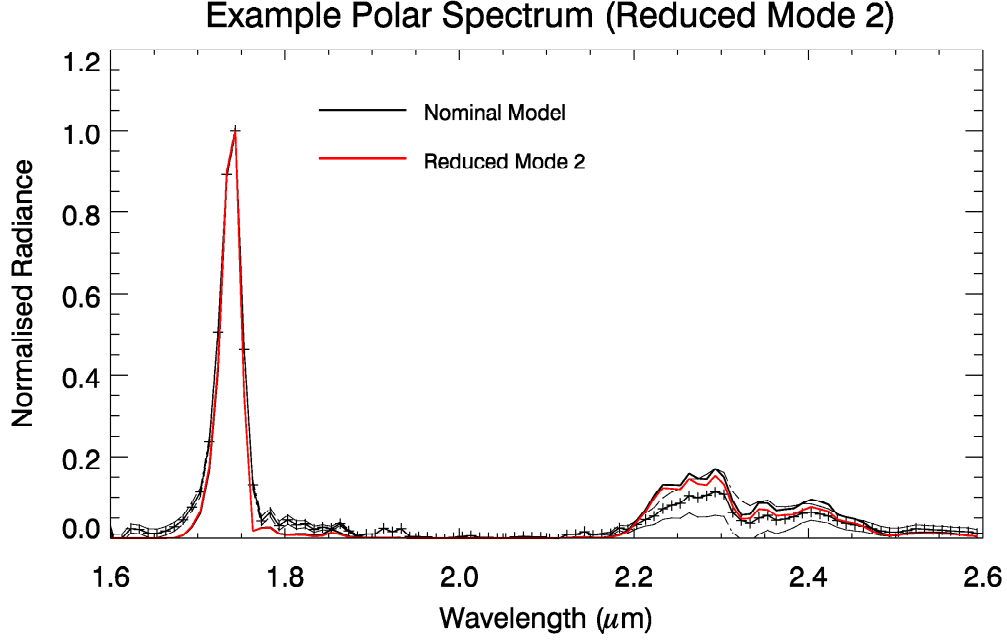


Figure 6.17: Model fits to a spectrum at $\sim 85^\circ$ latitude, as in Figure 6.4, but with an additional model assuming a reduction in the upper cloud optical depth towards the pole as discussed in the text. The fit obtained with this assumption is slightly closer to the data and is just within the errors, except around $1.71 \mu\text{m}$ (see Section 6.2).

base to lower altitudes. The 1.31 , 1.51 and $1.71 \mu\text{m}$ radiances are not significantly affected by this change either; the 1.31 and $1.51 \mu\text{m}$ ratios increase slightly for cases with reduced mode 2 optical depth.

Another way to model the decrease in $\tau=1$ altitude would be to simply move the mode 2 particles to lower altitudes, by decreasing the scale height for this mode. I find that the fractional scale height needs to be decreased from 1.0 to 0.2 at the pole to reduce the $\tau=1$ altitude by 10 km . The scale height reduction has the opposite effect on the retrieved model parameters to the optical depth reduction, but the effect is somewhat smaller. This way of modelling the $\tau=1$ altitude reduction results in a very high abundance of cloud droplets in a very thin band between ~ 62 and 64 km altitude, which is less plausible (although not impossible) than a reduction in mode 2 droplet abundance due to a decrease in photochemically-produced H_2SO_4 . It also

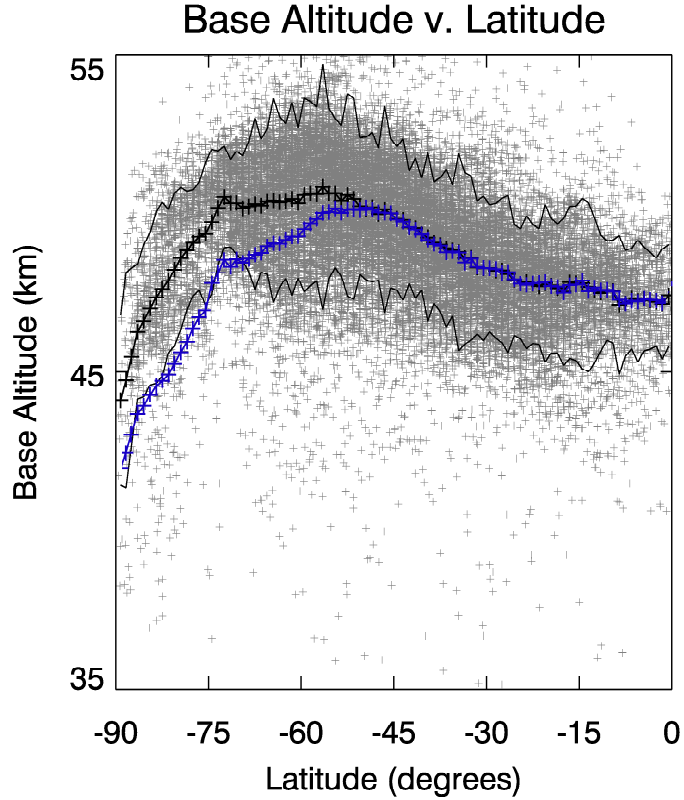


Figure 6.18: Cloud base altitude as a function of latitude, with and without allowing for the varying upper cloud optical depth. Grey and black points are as Figure 5.1, for the case with a correction for variable optical depth, and the blue points are the average values for the nominal case as in Figure 5.2.

does not improve the spectral fit in the polar regions, whereas in Figure 6.17 it is clear that a reduction in mode 2 optical depth does, therefore this work suggests that the model parameterisation adopted by Ignatiev et al. (2009) is the more realistic of these two.

I have also made the assumption that the distribution of the mode 1 particles is invariant. As the cloud base altitude is allowed to vary for modes 2' and 3, it might be expected that the base altitude for the mode 1 particles would also vary, since they extend throughout the vertical thickness of the cloud. Alternatively, if mode 1 particles are cloud condensation nuclei (perhaps of solid sulphur) with a thin coating of sulphuric acid as suggested by Knollenberg and Hunten (1980), the solid

cores would not be expected to evaporate at the same altitude as the sulphuric acid droplets, so the base altitude for mode 1 is not necessarily coupled to that for mode 2' and mode 3. Very little difference is made to the retrieved results if the mode 1 base altitude is allowed to vary with the mode 2' and mode 3 base altitudes – the effect of changing this assumption is well within the errors. Two synthetic spectra are shown in Figure 6.19, both with a mode 2' and mode 3 base altitude of 52 km. The solid line shows a spectrum where the mode 1 base altitude was fixed at 45 km, the dashed line represents a spectrum for which the mode 1 base altitude was allowed to vary and is also at 52 km; the two spectra are virtually indistinguishable.

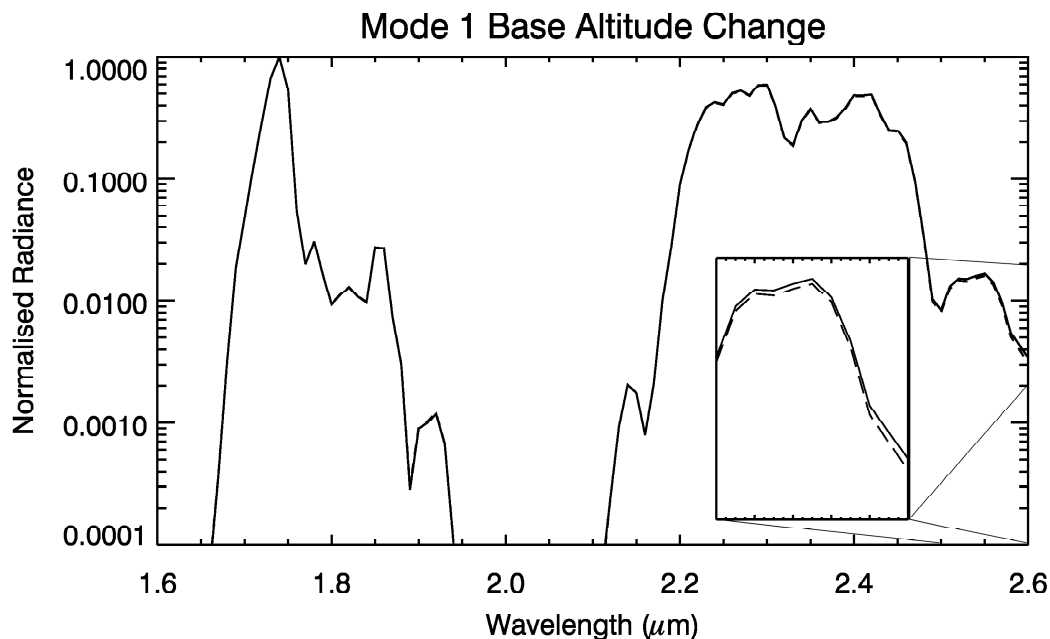


Figure 6.19: Two synthetic spectra with different mode 1 base altitudes. The solid line has the mode 1 base altitude fixed at 45 km, the dashed line is a spectrum for which the mode 1 base altitude was allowed to vary with the mode 2' and mode 3 base altitude. The mode 2'/3 base altitude is 52 km for both spectra.

The optical depth of the mode 1 particles has also been assumed to be constant. As some mode 1 particles are present within the lower cloud, these may increase and decrease with the lower cloud optical depth. If the mode 1 and mode 2' particles are assumed to increase together such that the abundance ratio between them

is constant, some alteration to the retrieved results is observed within the errors (Figure 6.20). The qualitative results are unchanged, except that the increased particle size in bright regions is no longer present outside the scatter. As for the other changes described in this section, the change in the retrieved quantities is small.

As the measurement taken of the $2.53/2.4\ \mu\text{m}$ relative radiances is a direct measure only of the ratio between cloud optical depths at high altitudes versus lower altitudes, it is also necessary to consider whether variation in the scale height of the lower cloud could be misidentified as variation in the cloud base altitude. Whilst some constraint has been placed on the scale height in the lower cloud (see Section 3.3.4), definitively distinguishing between the effects of cloud base altitude variation and other effects is not possible given the underconstrained nature of the problem. Varying the fractional scale height is an alternative method of representing variation in the vertical distribution of the cloud. However, it is apparent from Figure 3.6 in Section 3.3.4 that fractional scale heights of 1 and lower for modes 2' and 3 produce models that do not resemble the observed spectra in dark regions at $2.45\ \mu\text{m}$. Also, a comparison of similar models with fractional scale heights of 3, 4, and 5 shows a difference in retrieved base altitude of less than a kilometre between them. Other retrieved values are also unaffected by these changes. It would be necessary to return to a much lower fractional scale height to fit the observed $2.53:2.4\ \mu\text{m}$ ratio at the poles with scale height variation instead of cloud base altitude variation, and this would re-introduce the distortion discussed in Section 3.3.4. Therefore, it seems most reasonable to conclude that the cloud does indeed extend to much lower altitudes at the pole, along with the reduction in atmospheric temperature and the downwelling in the polar vortex.

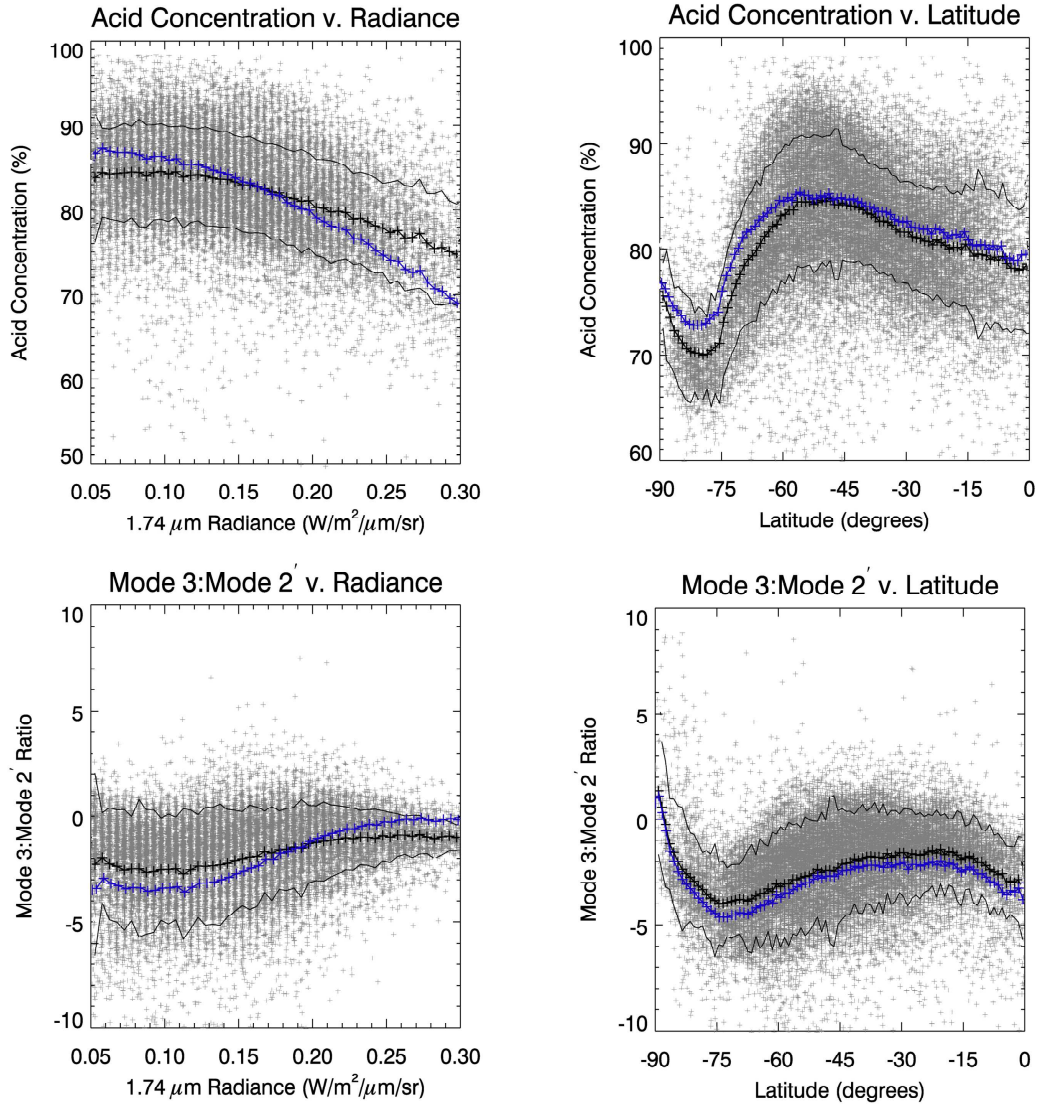


Figure 6.20: Acid concentration and particle size parameter as functions of $1.74\ \mu\text{m}$ radiance and latitude, for the case where the mode 1 optical depth varies with the mode 2' optical depth. Grey and black points are as Figure 5.1, for the case with a correction for variable mode 1 optical depth, and the blue points are the average values for the nominal case as in Figures 5.1 and 5.2. The change in other retrieved quantities is small.

6.3.5 Temperature variations in the deep atmosphere

Variations in the temperature structure in the cloud layer and mesosphere have been taken into account by incorporating the data from the VeRa radio instrument on Venus Express, and the effects of this have been discussed. The temperature below 45 km has been assumed to be invariant, but this may not be the case. There are no temperature data for the polar vortex below 45 km, as no descent probes have entered the polar region and radio occultation techniques are insensitive below this altitude, so temperature variations in the deep atmosphere may provide an alternative explanation for the unique spectral features in the polar regions. This assumption was tested by adjusting the atmospheric temperature profile in the deep atmosphere until a fit was obtained with a representative polar spectrum (Figure 6.21). The temperature of the atmosphere at the surface is increased by 20 K from the nominal profile, and the temperature difference between this and the nominal polar temperature profile then decreases linearly up to an altitude of 50 km, where the profiles merge. In Figure 6.21, it can be seen that this temperature increase makes it possible to fit the spectrum with the retrieved cloud parameters. The effect of such a temperature change on the retrieved acid concentration, however, suggests that if such a temperature profile is in fact usual at the poles, then the acid concentration is under-retrieved in this region by up to 10 wt%, with subsequent effects for all the other retrieved parameters. In particular, it would result in the under-retrieval of water vapour by up to 15 ppmv. A model with 10 wt% more acid, 15 ppmv more water vapour and no mode 2' provides a fit just within the errors assuming an increase in deep atmosphere temperature. If the 1.31 μm channel is also examined, however, it is clear that at the poles the 1.31:1.74 μm ratio decreases (Figure 6.8), and changing the deep atmosphere temperature profile as described above would have the opposite effect.

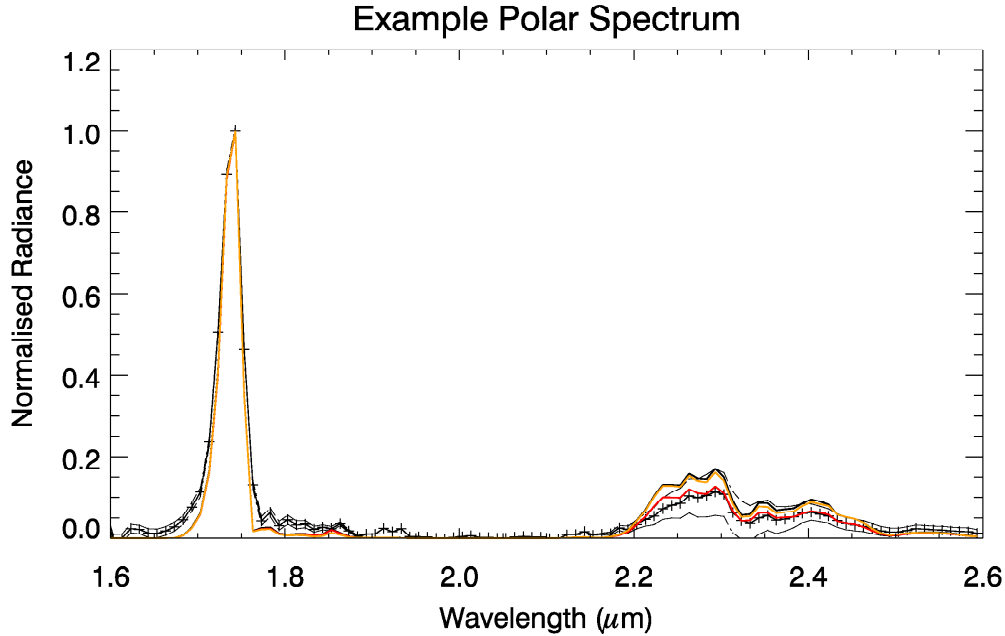


Figure 6.21: Model fits to a spectrum at $\sim 85^\circ$, as in Figure 6.4, but with a temperature increase in the lower atmosphere (red) and with the same increase but adjusted for under-retrieval of acid concentration and water vapour abundance (orange). The error envelope is shown by narrow lines. Some improvement in the fit is observed, as when the upper cloud optical depth is reduced (Figure 6.17) but a perfect spectral fit is still not achieved.

6.3.6 H₂O and CO vertical profiles

The *a priori* vertical profiles for H₂O and CO are based on recent high-resolution spectroscopic analysis using ground-based infrared observations and results from VIRTIS-H on Venus Express for the troposphere (Marcq et al. 2006, Marcq et al. 2008) and the results of the Pioneer Venus measurements in the mesosphere (von Zahn et al. 1983, Krasnopolsky and Parshev 1983). The vertical profiles (Figure 6.22) show that the water vapour VMR in the deep atmosphere is constant as a function of altitude up to the cloud base. Within the cloud deck, the abundance decreases by an order of magnitude, with a constant value above the cloud. The CO VMR is not constant below the cloud, but decreases between the base of the cloud and the surface. This decrease was first observed by Pollack et al. (1993) and

was confirmed by Marcq et al. (2006). It is anti-correlated with an increase in the OCS VMR in the same altitude region, suggesting some chemical process converting CO into OCS in the deep atmosphere and vice versa in the atmosphere immediately below the cloud. Models for different abundances are generated by multiplying the whole vertical profile by a common factor, except for H₂O up to an altitude of 28 km which is assumed to be constant at 30 ppmv (Bézard and de Bergh 2007). Variations at altitudes above 65 km do not affect the retrieval of either quantity.

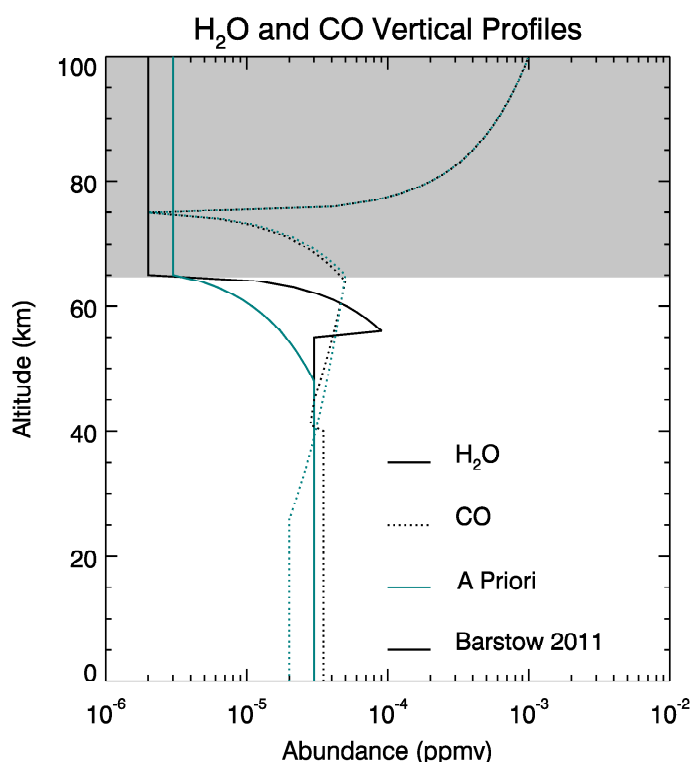


Figure 6.22: Vertical CO and H₂O VMR profiles as used by Barstow et al. (2011). Lines in blue show *a priori* profiles used in this thesis. Dashed lines are CO, solid lines are H₂O. The shaded region indicates altitudes for which the *a priori* profile chosen does not affect the retrieval.

In Barstow et al. (2012) the vertical profiles used were instead those of Tsang et al. (2010) (Figure 6.22), to facilitate comparison between the two sets of results for water vapour and carbon monoxide. The CO VMR profile was constant in the deep atmosphere but otherwise was not significantly different from the one used here.

However, the water vapour VMR profile contained a water vapour abundance peak of 90 ppmv within the cloud deck in the *a priori*. A separate attempt was also made to retrieve the water vapour abundance within the cloud, using the relationship between 2.56 and 2.53 μm radiances. After correction for scattered light from the dayside, the retrieved water vapour VMRs in the cloud layer were extremely high, such that the VMR at 56 km was increased in the polar collar to almost 1000 ppmv, compared with a retrieved lower atmosphere value of 15 ppmv at the same latitude. Such a vast increase would have to occur over only a small altitude range, due to the overlap in weighting functions between the 2.4 and 2.56 micron water absorption bands, and as such is implausible. Also, the water vapour VMR above the cloud has been measured and found to be on the order of a few ppmv only (Fedorova et al. 2008, Cottini et al. 2012). A mechanism for such a large increase in such a narrow altitude range is difficult to construct. The base altitudes calculated assuming this water vapour profile were also several km below the consensus value from the Pioneer Venus and Venera descent probes of 48 km, whereas values presented here are distributed around an average of 47–50 km.

The peak in water vapour abundance was necessary to fit an absorption feature at 2.56 μm . A comparison of model spectra using the current *a priori* profile against that of Tsang et al. (2010) and Barstow et al. (2012), compared with an example spectrum, shows that the relative radiances at 2.56 and 2.53 μm appear to be better fit by a synthetic spectrum with an increased water vapour abundance within the cloud layer (Figure 6.23). However, the extremely low radiances in this wavelength region, coupled with a low spectral resolution, make the identification of this feature with water vapour absorption somewhat suspect. An alternative explanation could be an absorption feature due to sulphuric acid vapour (Hintze et al. 2005), although the feature is very weak. It is suggested by Hintze (2009) that the 2.56 μm line would be unobservable in an atmosphere with water vapour present, as the water

vapour absorption is significantly stronger. The sulphuric acid features are also considerably narrower than the water features, so given the broad effect observed it seems that this can be ruled out as an explanation.

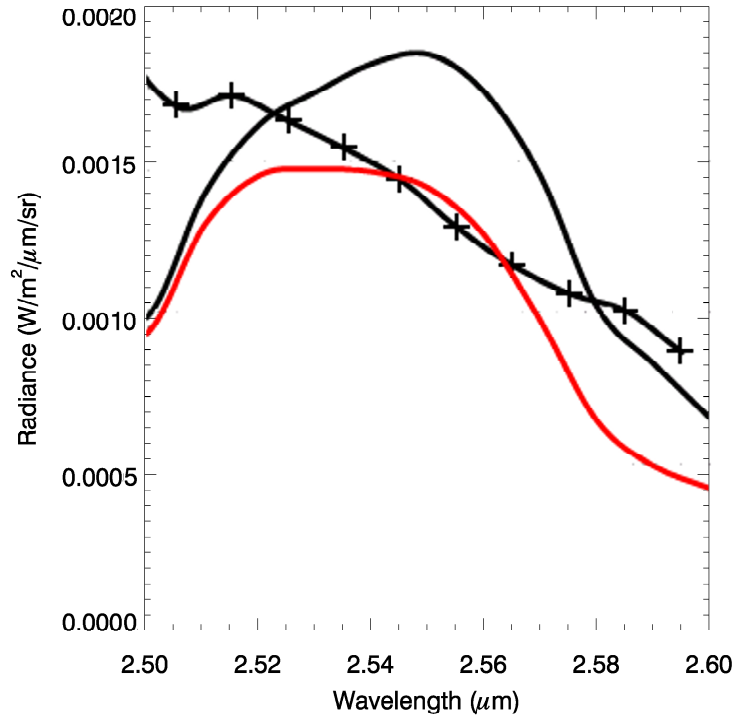


Figure 6.23: An example VIRTIS-M spectrum between 2.5 and 2.6 microns (joined black crosses), compared with synthetic spectra generated using the H₂O vertical VMR profile used in this work (solid black line) and as in Barstow et al. (solid red line).

Errors in the measured refractive indices for sulphuric acid in this wavelength range may also contribute to the difficulty of the spectral fitting. This is likely, as Palmer and Williams (1975) did not make any direct measurements in this wavelength range, instead interpolating between measurements existing at other wavelengths, and whilst Carlson and Anderson (2011) did obtain direct measurements which correspond well with those of Palmer and Williams (1975), they are cautionary about the reliability of the data longwards of 2.5 μm.

Another possibility is that the removal of scattered stray light from the dayside does not sufficiently correct for the shape of the dayside spectrum in this wavelength range. The wavelength region between 2.56 and 2.58 μm is sensitive on the dayside to absorption by water vapour at the cloud top, in the 65 km altitude region, and an absorption feature is present in the dayside spectra. Cottini et al. (2012) find an increase in this absorption due to water vapour in the latitude region between -70° and -80° , corresponding to an increase in the average VMR from 3–5 ppmv. As the dayside spectrum used to remove the scattered stray light is a spectrum from the subsolar point, this enhanced absorption is not corrected for when the stray light is removed, and the signature from the cloud top water vapour increase in the dayside reflected spectrum remains in the corrected nightside spectrum. This signature can be misinterpreted as an increase in the water vapour abundance within the cloud deck. In Figure 6.24, it can be seen that if the dayside spectrum subtracted is taken from the polar region and not the subsolar point, the radiance at 2.56 μm relative to 2.53 μm is slightly higher. It is also clear from this figure that the odd-even effect described in Section 4.1 is very pronounced in this spectral region, especially towards the poles where the contamination from the dayside is more significant, as the dayside spectra are more strongly affected than the nightside spectra. These factors together are likely to contribute to the discrepancy between the model and data at 2.56 μm .

The conclusion is therefore that the observed feature is unlikely to be due to increases in the water vapour within the cloud deck, and should not be treated as such. The most likely explanation is considered to be a combination of inaccuracy in the sulphuric acid refractive index data in this region and the odd-even effect. The *a priori* profile used in this work is felt to be the most plausible given the existing constraints on water vapour abundance below and above the cloud deck.

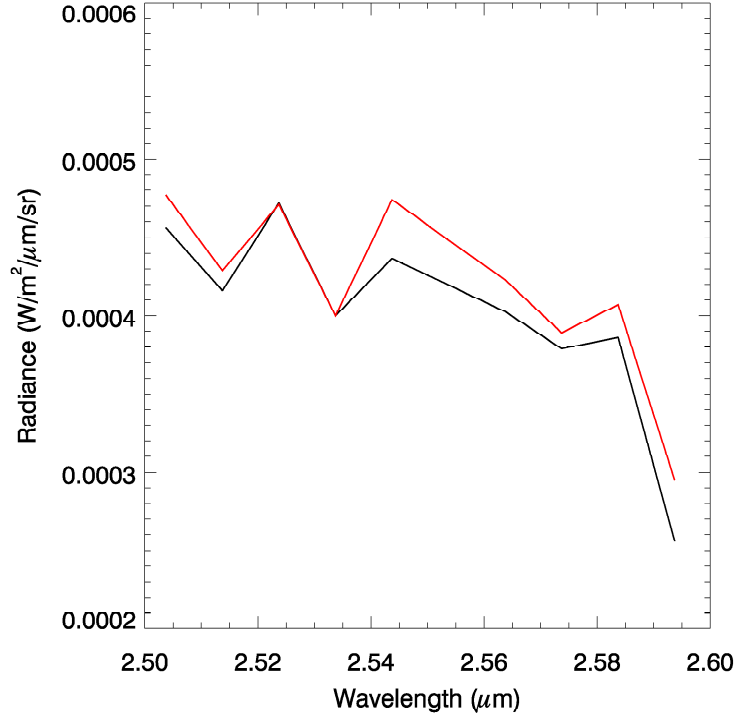


Figure 6.24: An infrared spectrum that has been corrected for dayside scattered light by subtracting a subsolar point dayside spectrum (black) and a high-latitude dayside spectrum (red). The spectrum corrected using the high-latitude spectrum has a lower radiance at 2.56 μm relative to 2.53 μm than the spectrum from which a subsolar point spectrum has been subtracted.

6.3.7 H_2O and HCl in the deep atmosphere

The water vapour VMR in the lower atmosphere at ~ 25 km is assumed to be 30 ppmv, as this is the consensus value quoted in the review by Bézard and de Bergh (2007). The scatter in the results they present is 20—45 ppmv at this altitude. However, since the H_2O is not fixed in the model above 28 km and some variation is observed (Figures 5.1 and 5.2), it is possible that some variation also occurs lower down in the atmosphere. This being the case, we might expect such variation to be coupled with that observed using the 2.4 μm band. If we allow the water vapour at 25 km to undergo coupled variation with the water vapour variation at 35 km in the input-versus-retrieved test, the error in the acid concentration

increases to ± 10 wt%, the error in $\ln(\text{mode 3:mode 2'})$ (the particle size parameter) increases to ± 3 and the error in the H_2O VMR increases to ± 12 ppmv, but errors in other quantities are not greatly affected. The input-versus-retrieved correlations are preserved, although values of retrieved acid concentration and H_2O abundance are somewhat overestimated where the input water content is high and underestimated where it is low. No significant bias is found in other retrieved quantities. The robustness of the acid retrieval to this sort of variation is demonstrated by the comparing the standard retrieval with acid concentration retrieved using the 2.4 to 1.74 μm ratio, which assumes water vapour abundance variation all the way to the surface (Figure 6.25). Since there is sensitivity to H_2O variation at ~ 25 km at 1.74 μm and ~ 35 km at 2.4 μm , if the variation is assumed to be coupled between these two altitudes then the 2.4:1.74 μm ratio is insensitive to the variation in H_2O abundance, but this is no longer the case for the 2.2:1.74 μm ratio. Whilst it is instructive to perform this test, it should be pointed out that Bézard et al. (2009) found the H_2O VMR at 15 km retrieved using the 1.18 μm window to be very constant, so one would not expect large variations to occur at 25 km and the assumption made in this work is therefore appropriate.

There is also a HCl absorption band at 1.75 μm , as measured by Iwagami et al. (2008). Their high spectral resolution measurements indicate that the abundance of HCl and also of water vapour in the deep atmosphere are both globally constant and of similar magnitude to the model input values used here (25 ± 5 ppmv and 0.4 ± 0.05 ppmv for H_2O and HCl, compared with 30 ppmv and 0.5 ppmv in this work). This indicates that the assumption of little gaseous abundance variation low in the atmosphere is a reasonable one to have made, and is unlikely to be a factor in the discrepancies observed between the models and the data at short wavelengths.

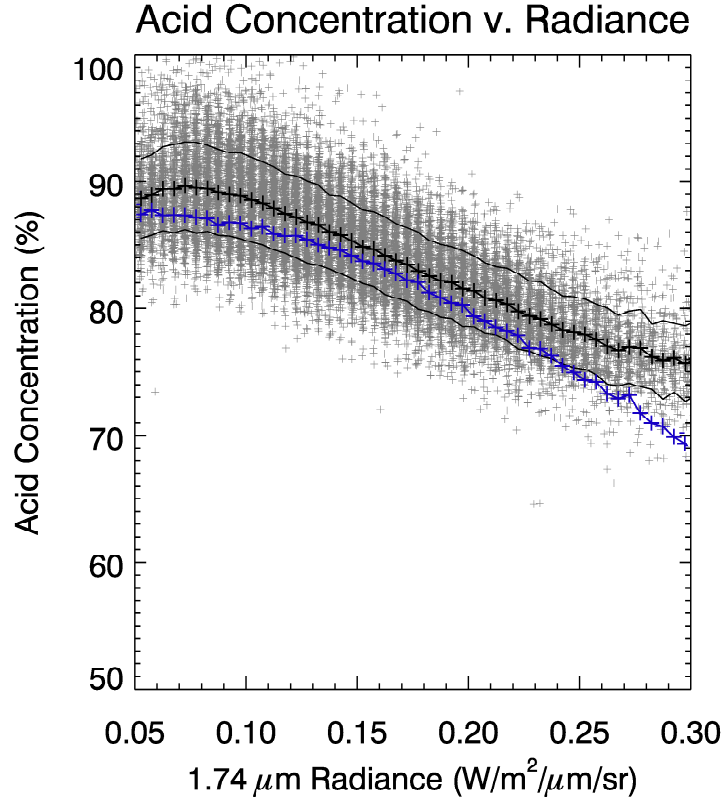


Figure 6.25: Acid concentration as a function of radiance, retrieved assuming H_2O abundance variation down to the surface. The blue points are the nominal retrieved case. Otherwise, the plot is as in Figure 5.1.

6.3.8 Other minor species

Absorption lines for other minor species are present between 2.2 and 2.6 μm , specifically OCS, SO_2 , HF and H_2S . The assumption has been made that variation in the abundances of these gases would not significantly affect the radiances at the wavelengths used. The limits of this assumption need to be tested.

OCS abundance variations have been mapped by Marcq et al. (2008) as a function of latitude using VIRTIS-H observations. They find that the abundance at 33 km, where the OCS weighting function peaks, varies between 2.5 and 4.0 ppmv in the latitude range -60° to $+60^\circ$, although the magnitude of the error bars does not preclude a smaller spread of values. OCS abundance variations have the greatest

impact on the spectrum between 2.41 and 2.46 μm , with a smaller effect at 2.4 μm which is in the wing of the OCS absorption band, and the effect on this wavelength is important for retrievals of H_2O and base altitude. A series of models ranging from 1.6—6.4 ppmv OCS at 33 km, the *a priori* model value being 3.2 ppmv, produces a percentage difference in the 2.4 μm radiance of 2%, corresponding to a difference in retrieved H_2O of 2.2 ppmv at 30 ppmv. This difference is significantly smaller than the error on the H_2O retrieved abundance (± 10 ppmv). The error introduced to the base altitude is only 0.2 km, which is insignificant by comparison with other sources of error.

The magnitude of OCS variation that would be required to mimic a 10 ppmv change in H_2O , such as that observed between -70° and -60° latitude, is from 1.6 ppmv to 26 ppmv, modelled as a multiplication of the whole vertical profile of OCS by 16. Such a value is significantly outside the error bars presented by Marcq et al., and is also not compatible with the results found by Pollack et al. (1993) based on their study of high-resolution spectra. Whilst extreme deviation in the abundance of OCS at the poles cannot be ruled out in the absence of any observations, it seems that OCS abundance variation is unlikely to affect the water vapour retrieval significantly. The error on the retrieved base altitude for a 16-fold change in the OCS abundance is less than 1 km.

An SO_2 band is present, centred at 2.47 μm . There is significant overlap with the OCS band. The *a priori* abundance of SO_2 in the sub-cloud atmosphere in the model is 130 ppmv, but doubling the whole vertical profile of SO_2 has only a small effect on the spectrum, and none on any of the wavelengths used in the retrieval.

There are HF lines around 2.4 μm , at the same location as the centre of the water band. Bézard and de Bergh (2007) state that since the lower atmosphere abundance of 1—5 ppb derived by Pollack et al. (1993) and quoted in Taylor et al. (1997) is

consistent with the results of the first detection in the upper atmosphere by Connes et al. (1967), HF is likely to be in chemical equilibrium. This means the likelihood of any significant abundance variation is very low. Doubling the vertical profile of HF has very little effect on the retrieved water vapour abundance from 2.4 μm and on the base altitude.

There are also HF lines between 2.5 and 2.6 μm , but the effect here of doubling the profile is even less significant than at 2.4 μm , so the assumption that the HF abundance does not vary is extremely unlikely to affect the results obtained. There is also an H_2S band in this region, but no effect on the spectrum is observed at all for doubling and halving the H_2S profile.

6.3.9 Summary

Most of the assumptions made in order to perform the cloud retrieval are unlikely to have an effect outside of the stated errors on the results, either because the effect of changing the assumption is small or because the alternatives are shown to be implausible. There are three exceptions, the first of these being the increased base altitude in bright regions when the spectral response to varying acid concentration is assumed to be non-linear, and when the optical data provided by Carlson and Anderson (2011) are used. The average base altitude is unchanged within the errors and the latitudinal variation remains, but the base altitude appears to be a few kilometres higher in regions of optically thin cloud, possibly indicating preferential removal of the cloud from the lowest few kilometres in regions where the cloud is evaporating. Possible mechanisms for this phenomenon, if real, are discussed in Section 7.1.2.

The second exception is the change in retrieved cloud base altitude between the

nominal case and the case with a decrease in upper cloud optical depth towards the pole. However, the functionality of the result is unchanged - the base altitude still peaks in the mid-latitudes and is lower in the equatorial and polar regions. The third exception is the assumption that mode 3 particles are composed of liquid sulphuric acid droplets with an average radius of $3.65\text{ }\mu\text{m}$; the effect of changing this assumption is clearly significant, but it is difficult to quantify due to the lack of constraint. However, the insensitivity to the majority of the changes made in this section increases the confidence in the results, as they are generally reproducible even with different a priori assumptions.

Chapter 7

Discussion and Interpretation of Results

In Chapter 5, microphysical properties of the cloud are shown to vary both as a function of cloud optical depth (Figure 5.1) and latitude (Figure 5.2). Variations in the abundances of water vapour and CO are also observed, which where correlated with variation in the cloud are likely to be chemically or dynamically linked to this variation. Some secular variation is tentatively observed over a period of 2 Earth years (Figure 5.5). In this chapter, a coherent overall picture of the processes responsible for these changes is sought.

7.1 Cloud opacity variation

The optical thickness of the cloud at $1.74\ \mu\text{m}$ is seen to vary significantly on Venus, with a modal $1.74\ \mu\text{m}$ radiance of $0.13\ \text{W}/\text{m}^2/\mu\text{m}/\text{sr}$ (Figure 5.1) and a range from as low as 0.03 to values higher than 0.3. As discussed in Section 3.3.4, we assume this variation to take place only in the cloud below 57 km, because this is the

extent of the convectively unstable region as observed by VeRa on Venus Express (Tellmann et al. 2009) and also the extent of the lower/middle convective cloud deck; the upper cloud is relatively uniform. The total optical depth change for mode 2' and mode 3 combined between the brightest and darkest regions in this study is from ~ 3 for radiances of $\sim 0.25 \text{ W/m}^2/\mu\text{m/sr}$ to ~ 20 for $1.74 \mu\text{m}$ radiances of $0.05 \text{ W/m}^2/\mu\text{m/sr}$.

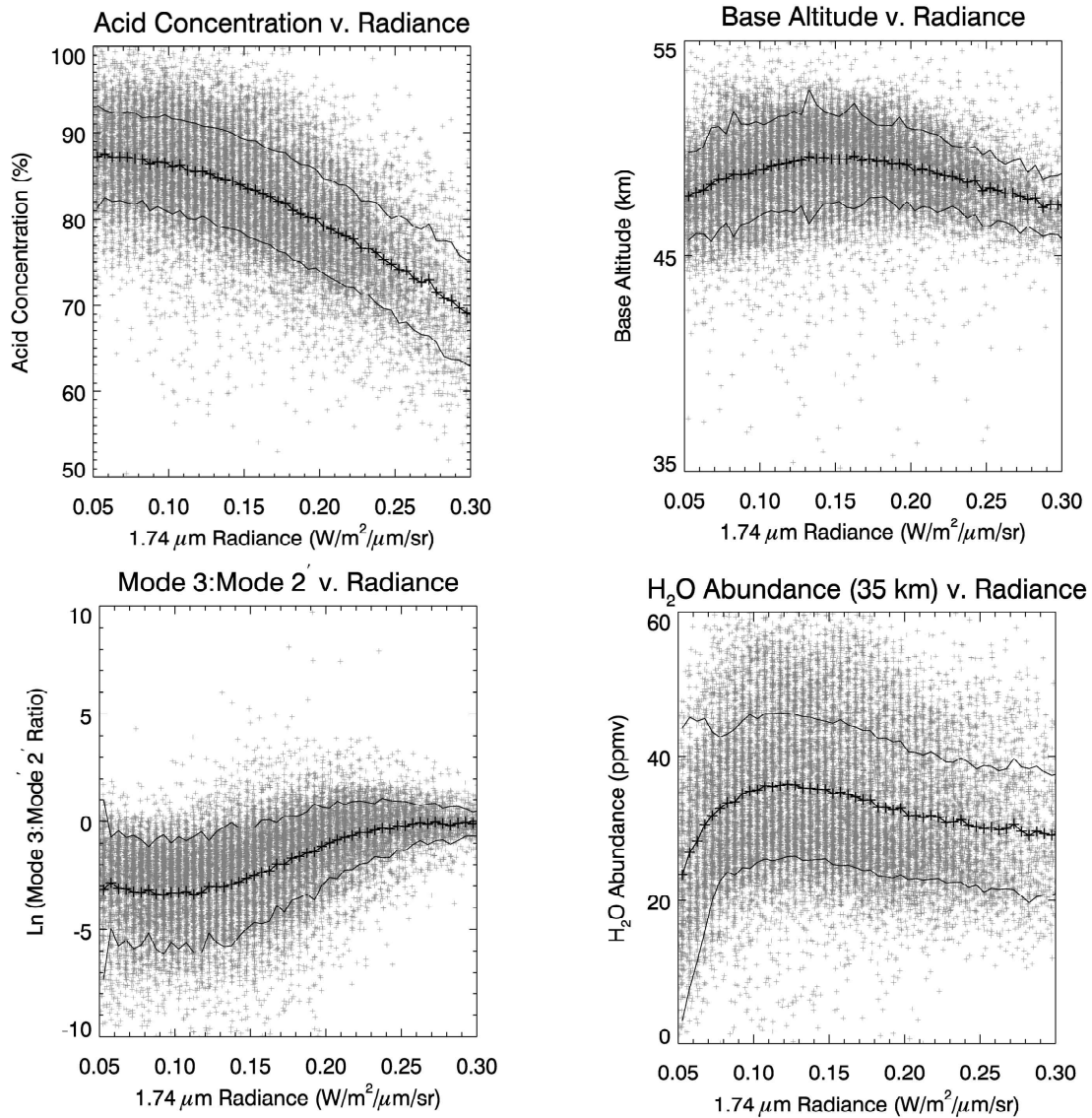


Figure 7.1: Results for acid concentration, cloud base altitude, particle size parameter and H₂O abundance as a function of radiance (as Figure 5.1).

7.1.1 Acid concentration

Figure 7.1 shows that the average acid concentration in the cloud droplets increases as a function of optical depth. There are two possible interpretations of this result. Microphysical modelling results from James et al. (1997) show a decrease in the acid concentration of the cloud droplets with increasing altitude, from very close to 100 wt% at the cloud base to values of around 80 wt% at 60 km. Near-infrared reflectivity measurements presented by Pollack et al. (1978) indicate that the best-fit acid concentration for the upper cloud is ~ 85 wt%. These findings suggest that the cloud becomes less acidic as the altitude increases. As the assumption is made that the optical depth changes occur in the lower cloud only, they also occur only in the region of the cloud with the highest acidity, and thus in bright regions there is less of this more acidic cloud and in dark regions there is more. The average acid concentration is therefore lower in bright regions and higher in dark regions, which is what is observed. However, the magnitude of the variation is obviously greater than can be accounted for with this mechanism, as in the very brightest regions the retrieved acid concentration is as low as 70 ± 6 wt% and in the darkest regions it is 87 ± 6 wt% (Figure 7.1). Therefore this effect can only be partially responsible for the observed variation.

The alternative is that the acid concentration in the droplets actually varies spatially, as well as vertically. A possible mechanism for a decrease in acid concentration in bright regions is variation in water vapour abundance within the cloud layer. For example, James et al. (1997) show that if they increase the water vapour abundance at the bottom boundary of their microphysical model from 30 to 50 ppmv then the acid concentration in $1 \mu\text{m}$ cloud droplets (i.e. mode 2-size droplets) decreases by ~ 2 wt %. This abundance alteration at the base of their model results in a difference of about 15 ppmv at 55 km in the model, within the cloud layer. This

work does not attempt to distinguish water vapour variation within the cloud from that below, as the $2.4\text{ }\mu\text{m}$ radiance is affected by water vapour variation between 28 and 65 km and the retrieval assumes the vertical profile between these altitudes is scaled by a single factor. This does indicate that the water vapour in the cloud is increased in brighter regions compared with the very darkest regions (see Figure 7.1 for the variation of water vapour abundance with radiance, and Section 7.1.4 below for a discussion of these results), but the increase at 55 km would be less than 15 ppmv, so this is insufficient to explain a decrease in acid concentration of almost 20 wt%. None of the other model parameters considered by James et al. (1997) have a significant impact on the acid concentration in the model cloud droplets.

Other factors that are not considered in the work of James et al. (1997) that could affect the acid concentration are the sulphuric acid vapour abundance and the temperature. The sulphuric acid vapour abundance is a function of photochemical production rates at the cloud top and diffusion/convective transport processes. Photochemical production is likely to vary as a function of latitude and local solar time, but any local variation in sulphuric acid abundance is more likely to be a result of convective transport. An influx of sulphuric acid vapour in upwelling regions is probable and is indeed necessary for the formation of a convective cloud, but whether or not there is a corresponding reduction in downwelling regions that is significant enough to reduce the droplet acid concentration is harder to say. James et al. (1997) observed that below 55 km in their model the sulphuric acid vapour pressure remained very close to the saturation vapour pressure, suggesting that any deviations from this are compensated for by changes in the cloud particles, either in their radius or their acid concentration, so changes in the sulphuric acid vapour abundance could be the driver of the acid concentration variation.

The saturation vapour pressures over a droplet of acid for sulphuric acid and water

can be expressed as functions of the temperature, droplet acid concentration and droplet radius. Temperature variations, by changing the saturation vapour pressure for a given particle size and acid concentration, could therefore alter the acid concentration and/or particle size for which the saturation vapour pressures are in equilibrium with the atmospheric partial pressures of the two gases.

If the lower cloud is convective, we would expect cloud formation to occur in regions of upwelling and cloud-free regions to be present where there is downwelling. McGouldrick and Toon (2008) observe this in their microphysical simulation of the effect of convection on the Venus cloud. They also observe deviations from the original model temperature profile as the simulation progresses. After an hour, the temperature at the top of the upwelling plume has increased by ~ 20 K, and it has decreased by the same amount at the base of the downwelling plume. This indicates that horizontal differences of up to 20 K may occur locally within the cloud, which would alter the saturation vapour pressure of water vapour over a given acid concentration and would therefore dictate the acid concentration that is in equilibrium with the water vapour abundance.

The saturation vapour pressure of water over a given sulphuric acid solution can be modelled simply if the sphericity of the droplet, and thereby alteration in the particle size, is ignored and the saturation pressure over an infinite flat surface is calculated. The saturation pressure is not independent of the sphericity, but pretabulated constants are available for the flat surface case and are sufficient to indicate the magnitude and direction of variation in equilibrium concentration as a function of temperature. The saturation pressure over an infinite flat surface has the form

$$\ln P_{\text{water},\infty}^{\text{sat}}(T, W) = A \ln \left(\frac{298.15}{T} \right) + \frac{B}{T} + C + DT + ET^2 \quad (7.1)$$

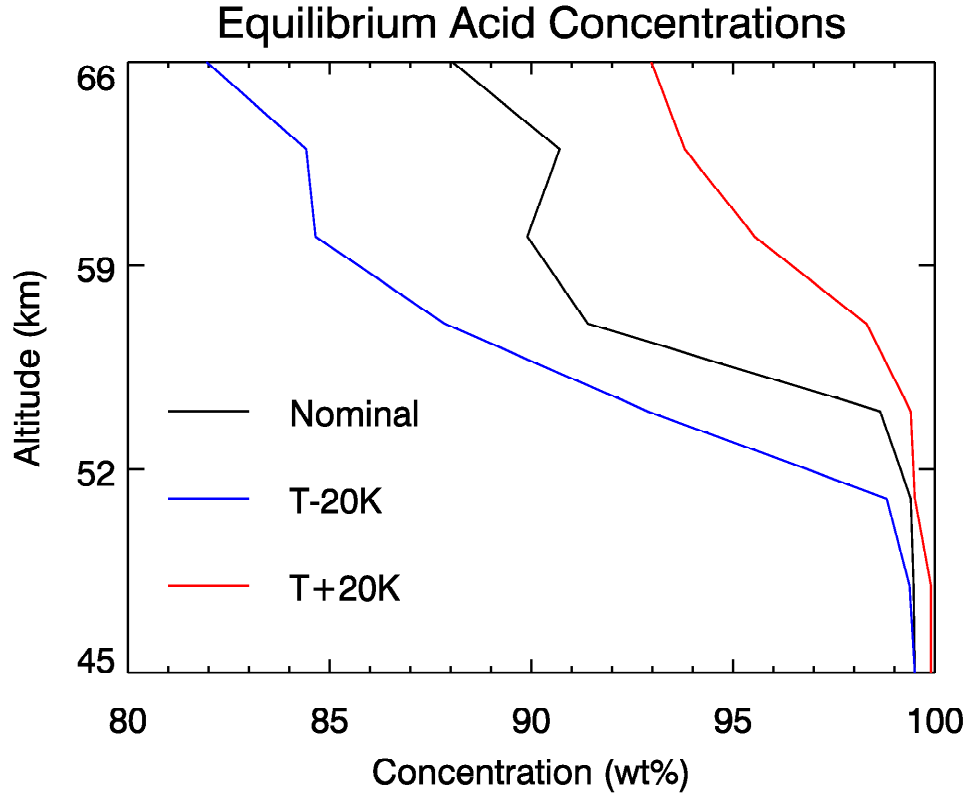


Figure 7.2: The effect of temperature variations on the acid concentration for which the saturation vapour pressure of water is equal to the partial pressure in the atmosphere.

where P is pressure, T is temperature and W is acid concentration in wt %. This equation is taken from the Appendix of James et al. (1997). Gmitro and Vermeulen (1964) provide values of the coefficients A—E for different concentrations of sulphuric acid. These pressures can be calculated for water vapour over a range of altitudes in the Venusian atmosphere and can be easily converted into an equivalent water vapour volume mixing ratio in ppmv. A computational routine for performing this calculation was provided by McGouldrick (2011). The calculation has been performed for a range of altitudes within the cloud deck at the nominal equatorial temperature profile, and profiles with temperatures ± 20 K from the nominal profile. The equilibrium acid concentration is taken to be the concentration for which the

water vapour saturation VMR is closest to the VMR in the *a priori* vertical profile at that altitude. The calculated profiles are shown below in Figure 7.2. It can be seen that a 20 K decrease in temperature results in a considerable decrease in the equilibrium acid concentration, and vice versa. Although these modelled temperature gradients are unrealistically large compared with observations, this may be a potential mechanism for the decrease in acid concentration in cloud-free regions, where we expect downwelling and therefore a decrease in temperature at a given altitude as demonstrated by McGouldrick and Toon (2008). Local temperature deviations of order 10 K have been observed (Linkin et al. 1986), which could lead to a difference in observed acid concentration of ~ 3 wt%. As the average particle size does not show much variation between bright and dark regions, it is reasonable to assume that deviations in temperature structure are here compensated for mainly by changes in the acid concentration.

It is clear from Figure 6.6 that temperature profile variation can affect the retrieved acid concentration. The case considered in Figure 6.6 is for the temperature variation with latitude. At -90° latitude, the temperature within the cloud deck is ~ 30 K cooler than it is at the equator (Figure 2.11); if this temperature variation is not accounted for, the retrieved acid concentration is 5 wt% lower than the case where it is taken into account. Therefore, a temperature decrease of 30 K would, if unaccounted for, reduce the retrieved acid concentration by 5 wt%. If the temperature within the cloud deck is lower in bright regions, as suggested here, the retrieved acid concentration may therefore be somewhat underestimated. A combination of a slight underestimation and a real decrease in acid concentration as a result of lower temperatures may be present, although as stated above a local 30 K temperature differential is unrealistically large; a more realistic 10 K deviation would result in the acid concentration being underestimated by only 1 or 2 wt %, well within the errors.

7.1.2 Cloud base altitude

As mentioned in Section 5, the retrieved cloud base altitude is a few km lower than would be expected from radio occultation static stability profiles (Tellmann et al. 2009), although it is in excellent agreement with Pioneer Venus/Venera descent probe cloud opacity profiles. The presence of a convective cloud extending down into a region of high static stability is not precluded; possible mechanisms are buoyant convection penetrating downwards through the stable layer, mechanical convection driven by strong vertical wind shear, and changes driven by photochemical or volcanic processes. Baker et al. (1998) suggest that deep buoyant convection is a strong possibility on Venus, which explanation is supported by evidence for significant temperature variability between observations at 46—50 km altitude from Venus Express radio occultation profiles (Tellmann et al. 2009). Similarly, the 6.5 K difference in temperature measured by the two Vega balloons (Linkin et al. 1986) at 55 km provides evidence for possible local deviations from the mean temperature profile at a given latitude, which may lead to regions of convective instability. There is evidence for strong variability in zonal wind and significant vertical wind shear below the clouds from the Pioneer Venus and Venera probes (Counselman et al. 1980), suggesting that mechanically-driven overturning is also possible. A third possibility is that the variations in the cloud from 47—50 km are driven by photochemical, volcanic, or other processes, suggesting perhaps that the lower cloud layer is made up of volcanic ash or some other substance that is not related to the sulphuric acid convective cloud. Infrared spectral analysis cannot differentiate between these possible mechanisms.

If volcanic ash is present in the cloud, it is highly unlikely to have similar spectral properties to sulphuric acid droplets. Particles of ash are more likely to be aspherical than liquid droplets, so the assumption of Mie scattering for these particles would

be flawed. Ash particles from the Mount St. Helens eruption in 1980 were found to exhibit mean sizes of 17 μm close to the eruption, but 4—5 μm further away (Taylor and Lichte 1980), so if volcanic ash could reach the cloud deck on Venus the particle sizes could be comparable to that of the mode 3 particles, and may explain the origin of this particle mode. However, as the clouds on Venus are 50 km above the surface and the lower atmosphere is dense, it is questionable whether or not volcanic ash from an eruption would reach so far above the surface, especially as any magma on Venus would probably be less water-rich than that on Earth and therefore eruptions would be less explosive. Speculation is further hindered by the lack of knowledge about surface composition on Venus (see Section 1.4.3). If volcanic ash is present in the Venusian clouds, it would complicate radiative transfer modelling as non-spherical particles are more difficult to represent, and as its composition is unknown it is difficult to state how its presence would affect retrieval of cloud properties using the near-infrared window regions. However, due to the high altitude of the clouds, I do not favour the explanation that the lowest few km of the cloud is made of volcanic ash, so this complication is not likely to arise.

As discussed in Section 6.3.1, the introduction of optical data provided by Carlson and Anderson (2011) and investigation into the effect of acid concentration variation in the 2.53 μm spectral region suggest the possibility that the cloud base altitude may increase as a function of 1.74 μm radiance (Figure 7.3). This is different to the approximately constant base altitude as shown in Figure 7.1. Assuming a liquid sulphuric acid cloud, the cloud base occurs at the altitude where the theoretical mixing ratio of H_2SO_4 in the absence of condensation equals the saturation mixing ratio of gaseous H_2SO_4 over an $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ solution (Bullock and Grinspoon 2001). The altitude where this occurs would be expected to vary as a function of temperature, acid concentration in the cloud droplets and H_2SO_4 vapour mixing ratio. An increase in temperature would be expected to raise the altitude where condensation

is favourable, and an increase in acid concentration in the cloud droplets would increase the saturation mixing ratio of H_2SO_4 vapour at a given altitude, which would also increase the altitude of the cloud base unless accompanied by an increase in the actual vapour abundance. The observed decrease in acid concentration in bright regions could not therefore be responsible for an increase in cloud base altitude, and if temperature anomalies are invoked to explain the acid concentration variation this is also ruled out as a mechanism, as lower temperatures correspond to lower acid concentrations which would theoretically lead to a lower cloud base altitude in bright regions.

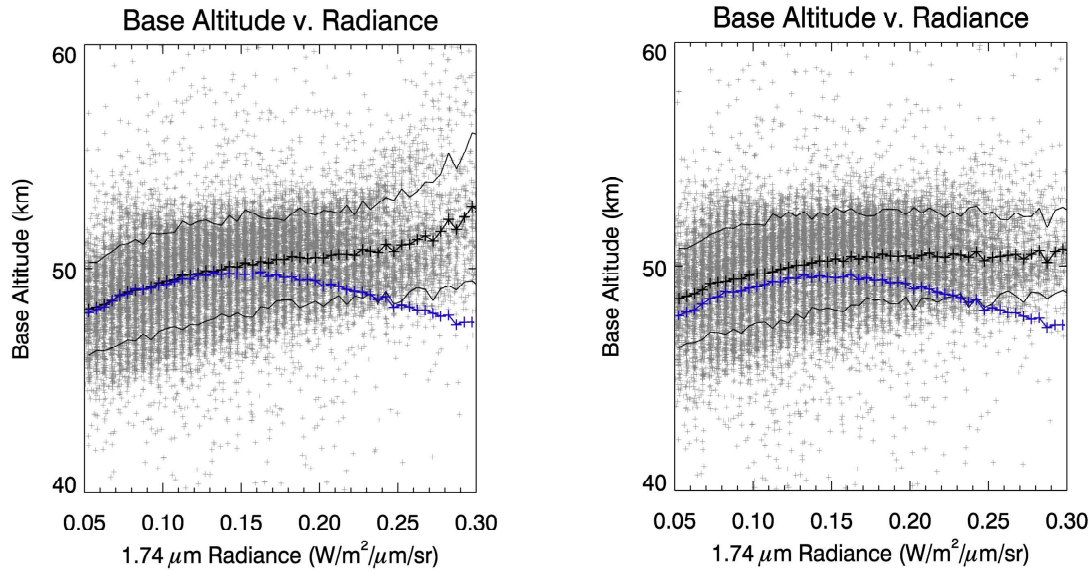


Figure 7.3: The left image shows the retrieved base altitude if a quadratic correction is used for acid concentration variation, with the Palmer and Williams optical data (as Figure 6.10). The right image shows the retrieved base altitude using the Carlson and Anderson optical data, with no explicit correction for acid concentration variation (as Figure 6.11). The blue lines show the result as in Figure 7.1.

Baker et al. (1998) discuss the possibility of deep penetrative convection occurring within a statically stable layer in the atmosphere. Since the static stability between 47 and 50 km is high in non-polar regions, penetrative convection or an alternative

convective mechanism is necessary for a scenario where cloud particles are being added to and removed from this altitude region. The convective model of Baker et al. (1998) shows cold downwelling plumes, with a thin region of heating at the base of the downwelling plume that is caused by compression as the downwelling air penetrates the stable layer below. Such localised heating could evaporate particles at the base of the cloud, but the observed temperature differential is very small, with the localised heating at the plume base only raising the temperature by 4 K. This scenario is also not compatible with the suggestions of McGouldrick and Toon (2008), who find that in their convective model that cooling occurs near the base of the downwelling plume.

A potential mechanism that is not incompatible with the observed acid concentration variation is a reduction in sulphuric acid vapour near the cloud base in downwelling regions; James et al. (1997) find that halving the sulphuric acid vapour abundance in their model from 15 to 8 ppmv raises the modelled cloud base altitude by 2 km. Such a reduction in the supply of sulphuric acid vapour may also influence the acid concentration of the cloud droplets, which is low in bright regions. The possibility that the lower cloud deck between 47 and 52 km is formed of a different substance such as volcanic ash could also explain this variability. Previous radiative transfer modelling by Pollack et al. (1993) and Grinspoon et al. (1993) led both sets of authors to conclude that the cloud variation from dark to bright regions could be modelled well by varying the optical depth only in the lowest few km of the cloud, which supports the hypothesis of a higher cloud base in regions of low optical depth. Raising the cloud base altitude in the model used here from 48 to 52 km by entirely removing the cloud from the lowest 4 km reduces the combined mode 2' and mode 3 optical depth by a factor of 2, which accounts for a significant fraction of the observed optical depth variation.

The results of the Pioneer Venus and Venera descent probes show some variability in the cloud base altitude; the observed range is approximately 47 to 50 km. The volumetric scattering cross sections reported do not show much variation (Kliore et al. 1986), so it is difficult to draw any conclusions about the relationship between cloud base altitude and optical depth from these results. An approximately constant cloud base altitude and an increased cloud base altitude in bright regions are equally compatible with the descent probe results.

This work corroborates the previous findings from Pioneer Venus and Venera of a cloud base altitude in the altitude region $47\text{--}52\pm 2$ km in low- and mid-latitudes, which is also compatible with microphysical and convective modelling results presented by James et al. (1997), Imamura and Hashimoto (1998) and Bullock and Grinspoon (2001). This demonstrates the capability of nadir remote sensing methods to draw conclusions about the vertical distribution of the cloud. A definitive conclusion about the variability of the cloud base altitude between dark and bright regions might be best achieved by a future in-situ mission, such as a long-duration balloon mission making direct measurements within the cloud deck.

7.1.3 Particle size

The average particle size, described by the particle size parameter as discussed in Section 3.3.4, is increased in bright regions (Figure 7.1). The error on this retrieved variable is large, but the variation is outside the range of the standard deviation. For a convective cloud, regions of thick cloud occur in regions of upwelling and cloud is removed in regions of downwelling. It is usually the case on Earth that larger particles are preferentially removed in regions of downwelling, as pointed out by Wilson et al. (2008), but the opposite case is observed here. If the number of cloud condensation nuclei (CCN) is reduced in regions of downwelling, this may result in

the formation of larger particles (see Section 7.2.3 for a more detailed discussion of this process in the context of high latitude clouds), but this is obviously very dependent on the nature of the CCN – if they are photochemical in origin they would be enhanced, not depleted, in regions of downwelling, but if for example they are small particles of volcanic dust they would be enhanced in upwelling regions as they would be transported from regions near the surface. It may also be the case that large particles form preferentially in colder regions, and as explained in Section 7.1.1 cold temperature anomalies can occur in regions of convective downwelling within the cloud deck. The microphysical simulations of McGouldrick and Toon (2008), however, suggest that larger particles are more likely to form in regions of upwelling, so this result is somewhat counter-intuitive.

A different chemical composition for mode 3 as discussed in Section 6.3.2 might also be an explanation for this, particularly if mode 3 particles are partially or completely solid, as they would be more likely to persist in regions where sulphuric acid droplets might evaporate.

7.1.4 Water vapour

A slight decrease in water vapour abundance below the cloud in dark regions is observed (Figure 7.1). It is difficult to explain apparent correlation between water vapour abundance variation in the sub-cloud atmosphere and cloud opacity, as despite the potential for deep penetrative convection on Venus as postulated by Baker et al. (1998) it is highly implausible that such convection could penetrate as deep as 35 km, where the atmosphere is very stable. The higher abundances in relatively cloud-free regions may be due to sedimentation and subsequent evaporation/dissociation of cloud droplets in regions of downwelling; however, a 10 ppmv increase in H₂O vapour over the altitude range required to produce the observed

effect on the spectra could not be caused only by evaporation of cloud droplets.

This calculation can be performed simply as follows: assuming all particles are 85 wt% sulphuric acid, and the radii of all mode 2' and mode 3 particles are the effective radii of 1.4 and 3.65 μm respectively, the column mass of water vapour released for a reduction of the lower cloud optical depth (at 0.63 μm) from 23 to 3 is $5 \times 10^{-4} \text{ g cm}^{-2}$. The column mass required to produce an observed 10 ppmv increase in water vapour abundance between 28 and 50 km altitude is 0.113 g cm^{-2} , which is a factor of 200 larger.

If it was the case that the evaporating cloud particles provided the source for the water vapour increase, we might also expect to see a continued increase towards brighter radiances, but the increase from 25 to 35 ppmv occurs only in the very darkest regions observed, with little deviation from 35 ppmv for 1.74 μm radiances between 0.1 and 0.3 $\text{W/m}^2/\mu\text{m/sr}$.

The large error on the retrieved water vapour abundance (± 8 in the bright regions and ± 22 in the dark regions) makes this result an extremely tentative one. Whilst some corroborative evidence is provided by the results of Bell et al. (1991) and Tsang et al. (2010), these authors did not take into account variations in the acidity of the cloud particles, which is very important since the amount of water in the cloud droplets affects their absorptivity within the water absorption band. If a constant acid concentration of 96 wt % is assumed, the water vapour variation observed is much greater (Figure 7.4), from 30 ppmv in the darkest regions to 55 ppmv in the bright regions. This highlights one example in which the assumed properties of the cloud significantly affect the retrieval of another property of the Venusian atmosphere. It is also worth noting that even the higher spectral resolution of VIRTIS-H is still insufficient to distinguish between variation in water vapour and in acid concentration – three spectra, each with different assumed acid concentrations

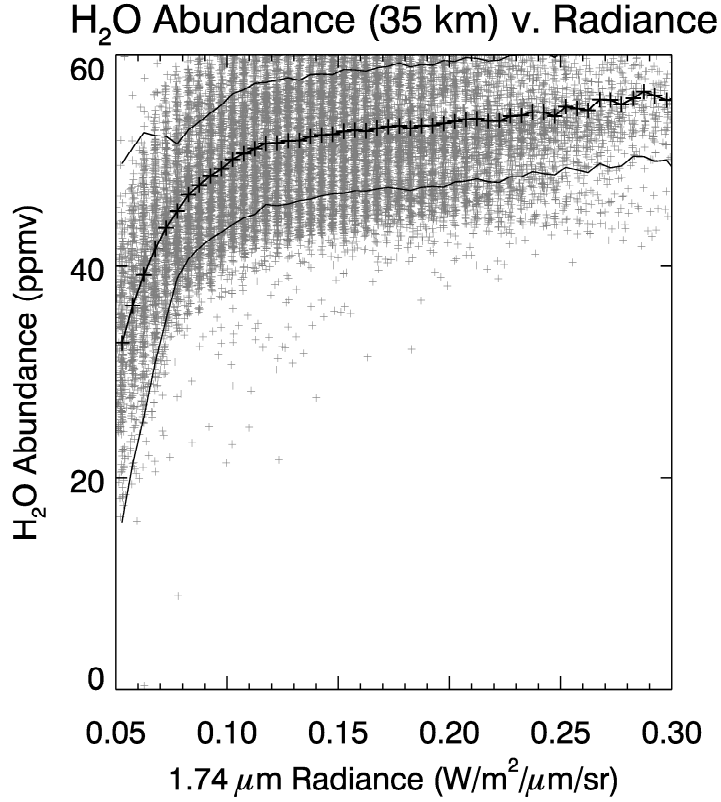


Figure 7.4: The retrieved H_2O abundance if the acid concentration variation is not accounted for. The variation is much greater than that observed if it is taken into account (Figure 5.1).

and retrieved water vapour abundances, all provide an equally good fit to the data.

7.2 Latitudinal cloud variation

The structure of the cloud varies as a function of latitude. Correlated variation in acid concentration, cloud base altitude and sub-cloud water vapour abundance is observed, these quantities all having peak values at $\sim 55^\circ$ latitude followed by a decrease towards the pole. The trends observed are similar in structure to the tropopause altitude variation observed by the VeRa instrument on Venus Express as presented by Tellmann et al. (2009), and in fact the magnitude of the base altitude

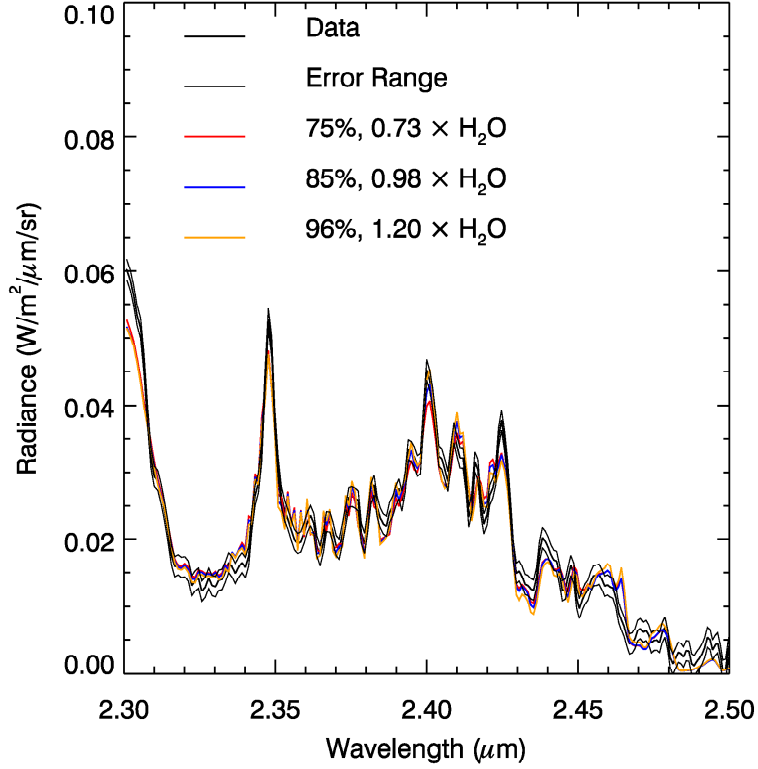


Figure 7.5: Three synthetic spectra with different assumed cloud acid concentrations and different retrieved abundances of H_2O , fit to a VIRTIS-H spectrum. The quality of the fits is similar for all three synthetics.

variation is the same as the magnitude of variation in the tropopause altitude. This indicates that the dynamics responsible for producing the cold collar region at $\sim 65^\circ$, where a temperature inversion is present at ~ 65 km altitude, are probably also responsible for the variation in the cloud properties and are linked to the meridional Hadley cell circulation.

The results in this work, in context with other key results, are summarised in the schematic below (Figure 7.6). The image is intended to be an aid to visualisation, and whilst some suggestions about the dynamics at the pole are made, these are speculative. The structure shown at the pole is that observed in terrestrial hurricanes (Wallace and Hobbs 1977), which have downwelling in the vortex eye but strong

upwelling in the eye wall region, resulting in the formation of thick clouds. It has previously been noted that terrestrial hurricanes share structural features with the Venusian polar vortex (Limaye et al. 2009), and it is therefore possible that the dynamic environment around the vortex eye is similar to that depicted here. The peak in water vapour volume mixing ratio at the top of the cloud layer observed by Cottini et al. (2012) at $\sim 70^\circ$ latitude is evidence of convergence in this latitude region, which may be caused by the presence of the Hadley cell coupled with a polar cell circulating in the opposite direction.

7.2.1 Acid concentration

The acid concentration in the cloud droplets is seen to increase gradually from the equator towards the pole, then drop sharply in the region of the downwelling in the cold collar (Figure 7.7). The peak in the concentration at $\sim 55^\circ$ may be due to the downwelling branch of the Hadley cell polewards of this location resulting in an influx of sulphuric acid from higher in the atmosphere, as sulphuric acid is a photochemical product with the highest production rate in equatorial latitudes. The photochemically-produced sulphuric acid is transported polewards by the meridional circulation and then downwards at $\sim 65^\circ$, and it is then injected into the clouds by convective uplift from the returning branch of the circulation below the cloud layer. This injection of sulphuric acid from the returning branch may result in the peak at 55° .

The sharp decrease in concentration within the polar collar itself and further towards the pole is likely to be due to the temperature decrease within the cloud layer at this latitude. It was shown in Figure 7.2 that a temperature decrease of 20 K can result in a decrease of up to ~ 7 wt% in equilibrium acid concentration. Tellmann et al. (2009) show that the temperature at 50 km decreases by 25 K between 50°

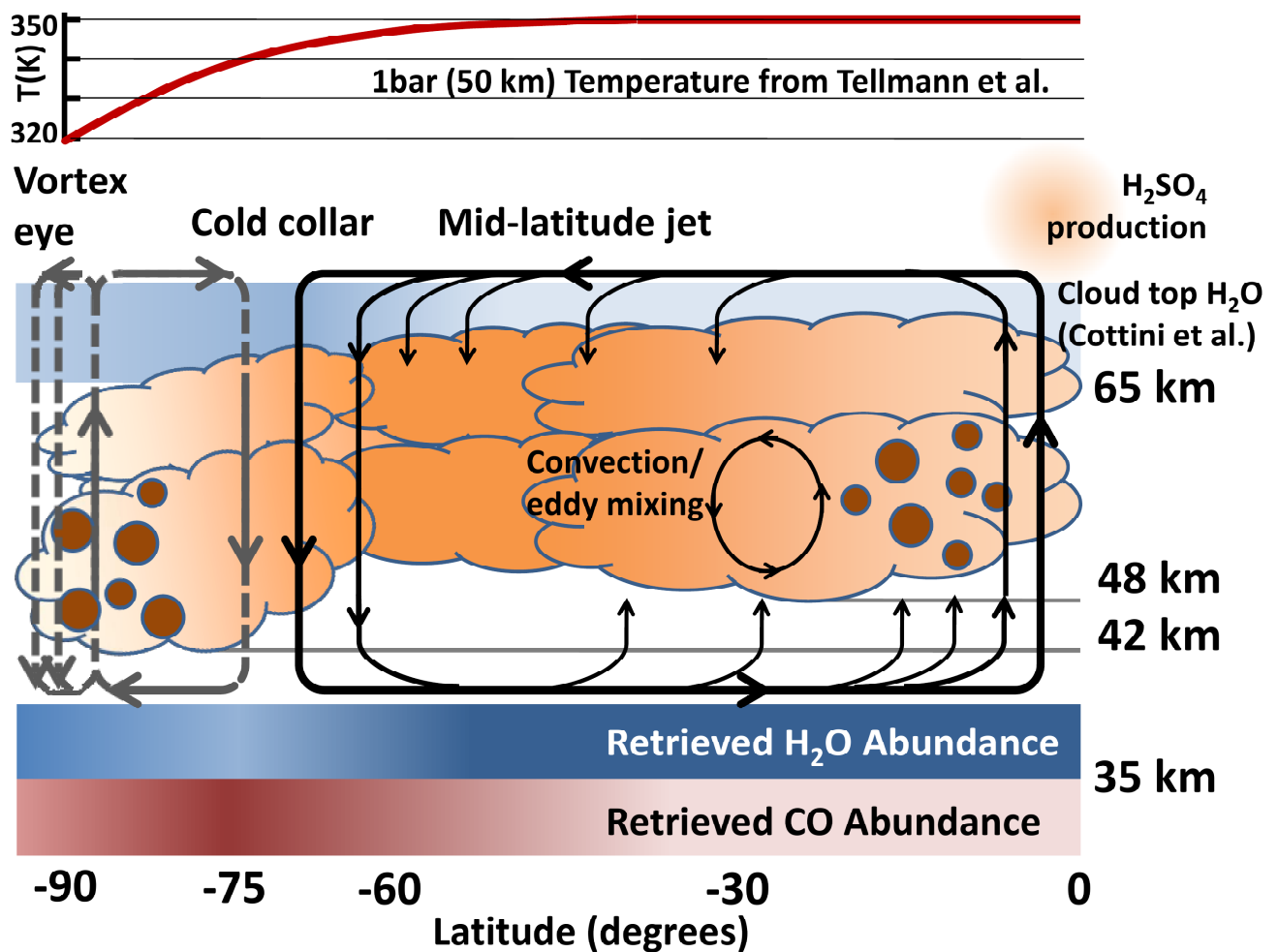


Figure 7.6: A schematic diagram summarising the results presented in this work as a function of latitude, in context with other related results. Orange colouring in the clouds represents sulphuric acid concentration, with darker shades indicative of higher concentrations. Red and blue bars represent abundances of CO and H_2O respectively, again with darker colours indicating higher abundances. The Hadley cell circulation, with small-scale convection in the low-/mid-latitudes, is shown in black as its presence is relatively well-established; the structure of the circulation at the pole, shown with grey dashed lines, is speculative. The polar circulation shown explains the phenomena observed, and gains plausibility from the fact that similar structures are observed in terrestrial hurricanes, which have been observed to have similar morphologies to the Venusian polar vortex (Limaye et al. 2009). The region of downwelling begins at $\sim 65^\circ$ latitude, but is likely to be broad in extent as the related cold polar collar extends from -60 to -80° (Tellmann et al. 2009).

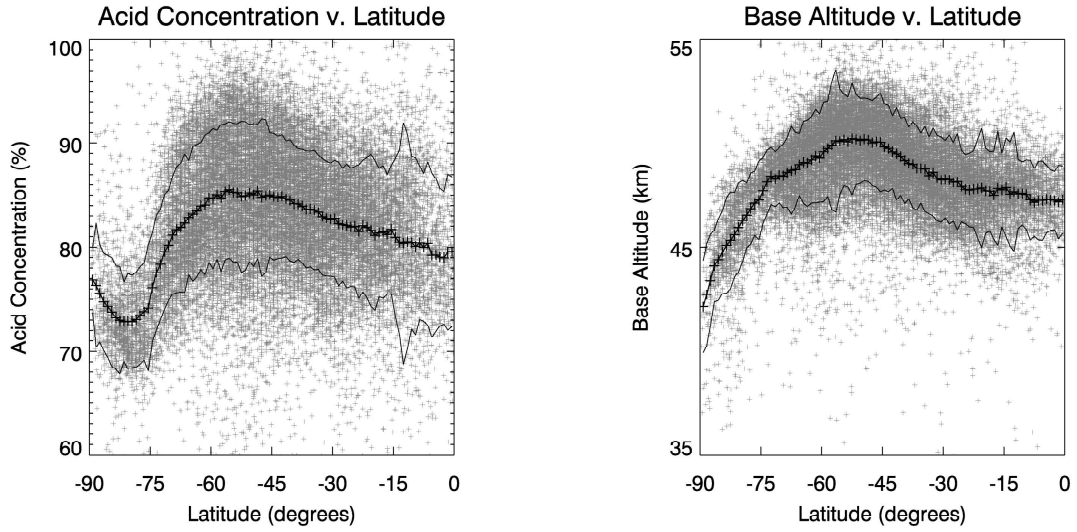


Figure 7.7: Results for acid concentration and cloud base altitude as a function of latitude (as Figure 5.2).

and the pole, with temperatures 20 K lower being reached at -80° latitude. The magnitude of the decrease in average acid concentration between -55 and -80° is 11 ppmv, which is comparable with the predicted decrease within the scatter of the results. It is also possible that the supply of sulphuric acid vapour at this latitude is reduced, since much of it has been drawn down below the cloud by the downwelling.

Whilst a decrease in the water vapour below the clouds is observed in the polar regions, Cottini et al. (2012) observe an increase in the water vapour VMR at the cloud tops in this latitude region on the dayside. An increased water vapour abundance within the upper cloud region would also result in the preferential formation of a less acidic cloud.

7.2.2 Cloud base altitude

The retrieved cloud base altitude in the low-to-mid-latitude regions is in excellent agreement with the results of the Pioneer Venus and Venera descent probe profiles, but towards the pole it decreases sharply, falling to a minimum value of 42 ± 2 km at

-90° (Figure 7.7). The temperature decreases between the equator and pole within the cloud deck such that the isotherms are 4 km lower at the pole than at the equator, and the atmosphere is convectively unstable down to 40 km at the poles (Tellmann et al. 2009). A 6 km decrease in the cloud base altitude between the equator and pole is therefore not incompatible with the thermal and dynamical constraints.

The cloud base altitude peaks at -55° latitude, with a maximum altitude of 51 ± 3 km. This peak cannot be explained by warming within the cloud region resulting in a higher condensation level, as the temperature profiles within the cloud deck are very similar in the equatorial and mid-latitude regions. This result has however been reproduced by two-dimensional microphysical modelling. The results of Ima-mura and Hashimoto (1998) show an optically thinner mid-latitude cloud, with a greater fraction of the cloud mass at higher altitudes when compared with the cloud distribution at the equator and poles, which is very consistent with the observations presented here. These authors postulate that the lowering of the bulk of the cloud at the equator is caused by accumulation of sulphuric acid vapour in the upwelling region of the Hadley cell, and the corresponding lowering of the base in the polar regions is caused by a temperature decrease at the 1 bar (~ 50 km) level, which decrease is observed by Tellmann et al. (2009).

An alternative explanation, which is discussed in Section 6.3.4, is that the upper cloud optical depth at the pole is lower than the *a priori*. The retrieved value is not directly a measurement of cloud base altitude, but a measurement of the relative abundances of cloud higher in the atmosphere to cloud lower down, so a reduction in the optical depth of the upper cloud can be misinterpreted as a reduction in the altitude of the cloud base. The range of different models presented in Section 3.3.2 demonstrates the difficulty of simultaneously placing constraints on the entire cloud deck on Venus. In Section 6.3.4, the upper cloud optical depth is reduced in the

polar regions, and the retrieved base altitude is higher if this is assumed to be the case. No attempt is made in this work to directly place constraints on the upper cloud optical depth, but if the upper cloud model suggested by Ignatiev et al. (2009) is assumed at the poles the retrieved polar base altitude is 44.5 km, 2.5 km higher than the nominal case with an invariant upper cloud. This is closer to the expected value if the altitude decrease is attributed solely to the temperature decrease in the cloud deck, but the results are identical within the errors.

The apparent absence of significant abundances of scattering particles below ~ 48 km in the Pioneer Venus and Venera descent probe profiles (Knollenberg and Hunten 1980, Marov et al. 1980) is not problematic for the retrieved cloud base altitude towards the pole, as none of these probes entered the atmosphere at latitudes polewards of 60° and the retrieved cloud base altitude is 47 km or above in all regions equatorward of this latitude.

7.2.3 Particle size

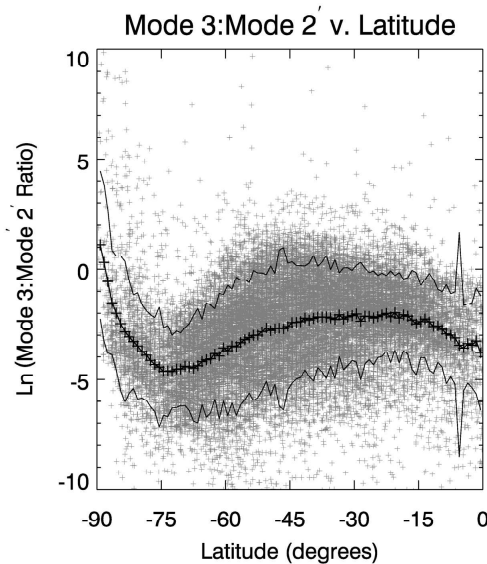


Figure 7.8: Results for the particle size parameter as a function of latitude (as Figure 5.2).

There is an enhancement in the particle size parameter in the polar vortex compared to the abundance at lower latitudes (Figure 7.8). If the mode 3 particles are liquid, the most likely mechanism for such a shift is a decrease in the number of available cloud condensation nuclei (CCN). As discussed in Section 3.2.2, the presence of CCN plays an important role in cloud formation on the Earth, and a similar role is expected for Venus. Such a mechanism for formation of large cloud droplets on Earth is discussed by Squires (1952), and an example of the opposite case, where an influx of CCN from ship engines results in highly-reflective tracks made of many small cloud droplets, is described in Coakley et al. (1987). The precise nature of the CCN on Venus is unknown, although sulphur aerosols are a likely candidate (Imamura and Hashimoto 2002). If these are photochemically produced, the highest abundance at the altitude of production would be expected to occur near the equator, and the meridional Hadley cell transport would be responsible for their distribution. The lowest abundance would be expected near the poles, and a peak at the cloud level would be expected to occur in regions of downwelling, at $\sim 60^\circ$, and upwelling at the equator, which are the regions where a decrease in large particles is observed. The microphysical model of James et al. (1997) showed no change in the particle size distribution for a 10-fold increase in insoluble CCN, but making the CCN soluble was shown to have an effect. No results for different numbers of soluble CCN were presented. To further investigate this hypothesis, information on the composition of the Venus CCN, which is currently lacking, would be required.

If, as suggested by Knollenberg and Hunten (1980), the smallest observed cloud particles are in fact bare CCN, the upper cloud particles themselves may be a source of CCN for the lower cloud. A reduction in upper cloud optical depth is suggested by Ignatiev et al. (2009) to account for the decrease in cloud top altitude at the poles. Although this is modelled as a reduction in the abundance of mode 2 particles, there is nothing to indicate that a removal of smaller mode 1 particles does not also occur,

although the upper haze layer is certainly still present. This reduced upper cloud optical depth may also be a contributing factor to the observed increase in particle size at the poles.

An alternative explanation is that a different chemical species with different absorptive properties than concentrated sulphuric acid is present at the pole. Other chemical species have been proposed as cloud constituents, such as phosphorus anhydride, phosphoric acid and iron chloride (Krasnopolsky 1989). Phosphorus- and iron-bearing rocks are common on the Earth and are assumed to also be present on Venus, providing a source for these chemicals, and detections of these species by the Vega probes were reported (Krasnopolsky 1989). There is however considerably less understanding of potential mechanisms for transport and condensation of these aerosols, although the persistence of the convectively unstable region to altitudes below the cloud deck at the poles (Tellmann et al. 2009) does provide a potential transport mechanism for species generated by chemical reactions near the surface to reach cloud altitudes. Such particles may be more stable under conditions in which sulphuric acid droplets would evaporate, which could also provide an explanation for the increased ratio of large to small particles in regions of low cloud optical depth (Section 7.1.3). The lack of detailed understanding of the dynamics in the polar regions hinders further speculation.

7.2.4 H₂O and CO

A decrease in water vapour abundance below the cloud (Figure 7.9) in the polar collar occurs at the same location as a peak in CO abundance. The peak in CO abundance was also observed by Collard et al. (1993), Tsang et al. (2008) and Tsang et al. (2009), and these authors attribute the enhancement to downwelling bringing down more CO-rich air from higher altitudes. As the atmosphere above the cloud

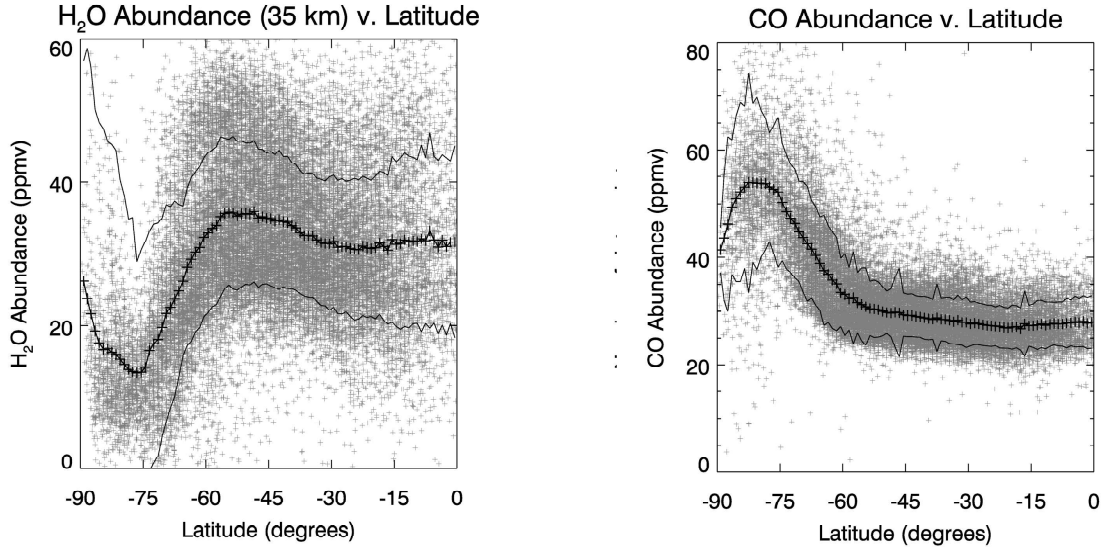


Figure 7.9: Results for H_2O and CO abundances as a function of latitude (as Figure 5.2).

is drier, this could also explain the decrease in water vapour abundance. The anti-correlation observed here is robust and directly attributable to latitudinal variation; in the low latitude regions, no such anti-correlation is observed between these two variables.

This enhancement of CO and depletion of H_2O is possible at these latitudes as the atmosphere below 50 km is no longer convectively stable, facilitating transport of species into the deep atmosphere. This explains why the opposite result is not observed at the equator in the upwelling branch of the Hadley cell. Along the returning branch of the circulation, the atmosphere becomes mixed again and the enhancement/depletion is no longer observed.

7.3 Local solar time variation

Figure 7.10 may show the existence of trends in acid concentration, H_2O abundance and CO abundance as a function of local solar time, but the large scatter on the

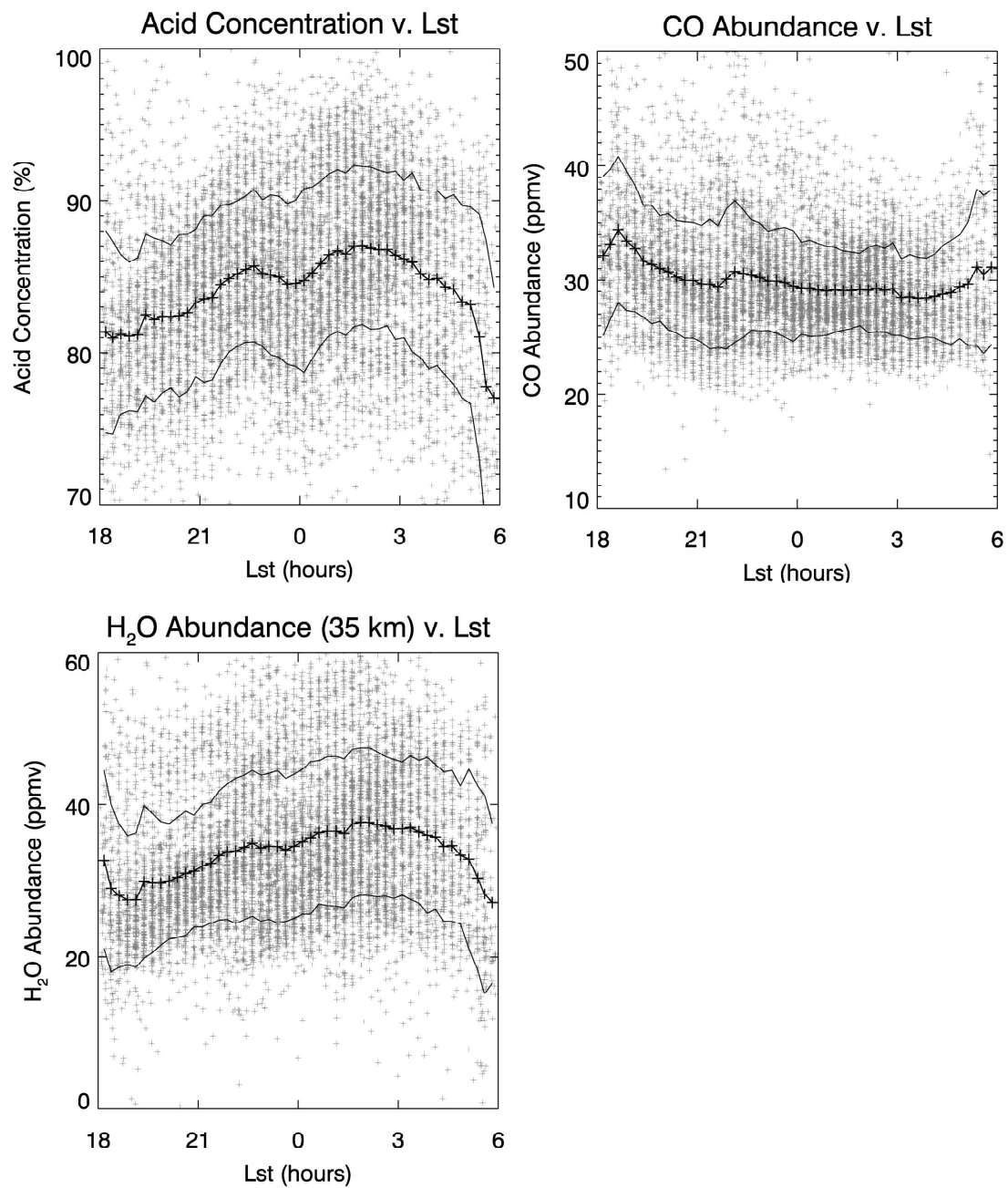


Figure 7.10: Results for acid concentration, CO and H₂O abundances as a function of local solar time (as Figure 5.3).

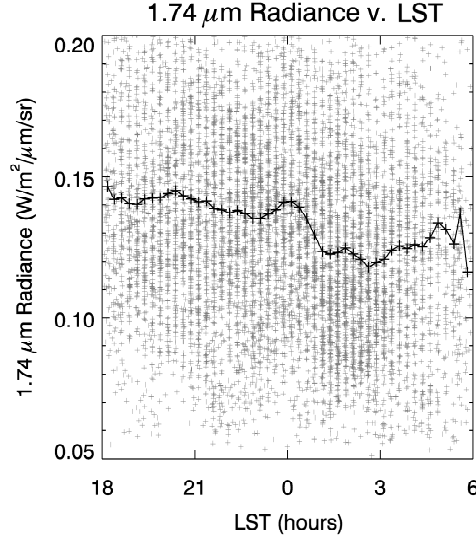


Figure 7.11: 1.74 μm radiance as a function of local solar time.

results makes all of these somewhat tentative. Tsang et al. (2008) report a similar variation in CO abundance to that observed here, and postulate that this is due to transport of CO by the zonal superrotation from the subsolar regions where it is produced. As the flow is from evening to morning on the nightside, this may explain the enhancement in the evening. A similar mechanism cannot explain the acid concentration variation, as an enhancement in sulphuric acid vapour would be expected in the evening since this is also a photochemical product. The slight decrease in radiance towards the morning terminator (Figure 7.11) may partially explain the increase in acid concentration. There is also a potential discrepancy in the response of the VIRTIS instrument along the slit direction, possibly a change in the spectral width of the instrument function (Bézard et al. 2009), and due to the orbit geometry the slit is usually orientated in the same direction with respect to the local solar time, with one side always observing more towards the morning side than the other, and this could introduce a bias. Schofield and Taylor (1983) observe some diurnal variation in the cloud top altitude with the Pioneer Venus orbiter infrared radiometer, but Ignatiev et al. (2009) see little evidence of this, although they

observe a slight increase in cloud top altitude in the afternoon which may corroborate the results of Schofield and Taylor (1983). These respective cloud top altitudes were measured at different wavelengths, 11.5 μm (Schofield and Taylor 1983) and 1.63 μm (Ignatiev et al. 2009), so features seen at one wavelength would not necessarily be present at the other, which may explain the different results. There is insufficient evidence to suggest very significant variation in the cloud properties or gaseous abundances as a function of local solar time, which is not unexpected as the tropospheric temperature variations in the zonal direction are much smaller than those that occur as a function of latitude.

7.4 Longitudinal variation

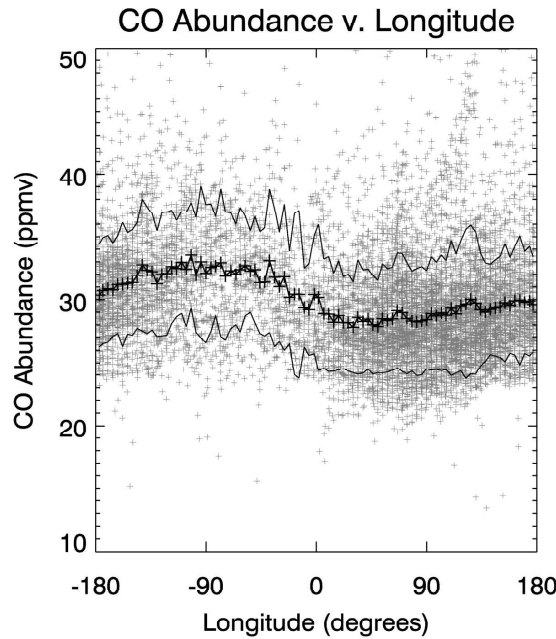


Figure 7.12: Results for CO abundance as a function of longitude (as Figure 5.4).

There is very little variation in any of the retrieved quantities as a function of planetocentric longitude, as expected (Figure 5.4). The slight apparent increase in CO around -90° longitude (Figure 7.12) is attributed to a combination of observational

bias in longitude-local time space and a relative lack of data at this longitude. This indicates that topographical features are sufficiently removed from the cloud deck that they do not affect the thermodynamics of cloud formation.

7.5 Temporal variation

There is very tentative evidence of secular change in some retrieved quantities as a function of orbit number (Figure 7.13). Acid concentration in the cloud droplets, water vapour abundance and CO abundance have all decreased over the duration of the mission. As mentioned in Section 6.1, the large scatter on these results, and the fact that the possibility of long-term instrumental drift is unaccounted for in this analysis, mean that further observational evidence is required before the presence of these secular trends can be confidently asserted. The exploration of potential scenarios is however still of use. There are two potential sources for sulphuric acid vapour that might vary over these timescales; one is active volcanism, and the other is photochemistry. The components of sulphuric acid, water and SO₂, are likely components of volcanic gas, and a decrease in volcanic activity over the lifetime of the VIRTIS-M-IR instrument could result in the observed behaviour as these are necessary for the formation of sulphuric acid. This could also explain the decrease in water vapour abundance. A corresponding decrease in SO₂, such as that observed by Esposito et al. (1988), would corroborate this finding. Marcq et al. (2011) present measurements of SO₂ at the cloud tops using the SPICAV instrument on Venus Express, and they in fact observe an increase in SO₂ in early 2007 (orbit 310) compared with previous retrieved values from SPICAV. The data examined do not extend beyond mid-2007, but they appear to preclude a steady decrease in SO₂ throughout the lifetime of VIRTIS-M-IR, and if the SO₂ abundance variations above the cloud are volcanically driven there cannot have been a decrease in the rate of

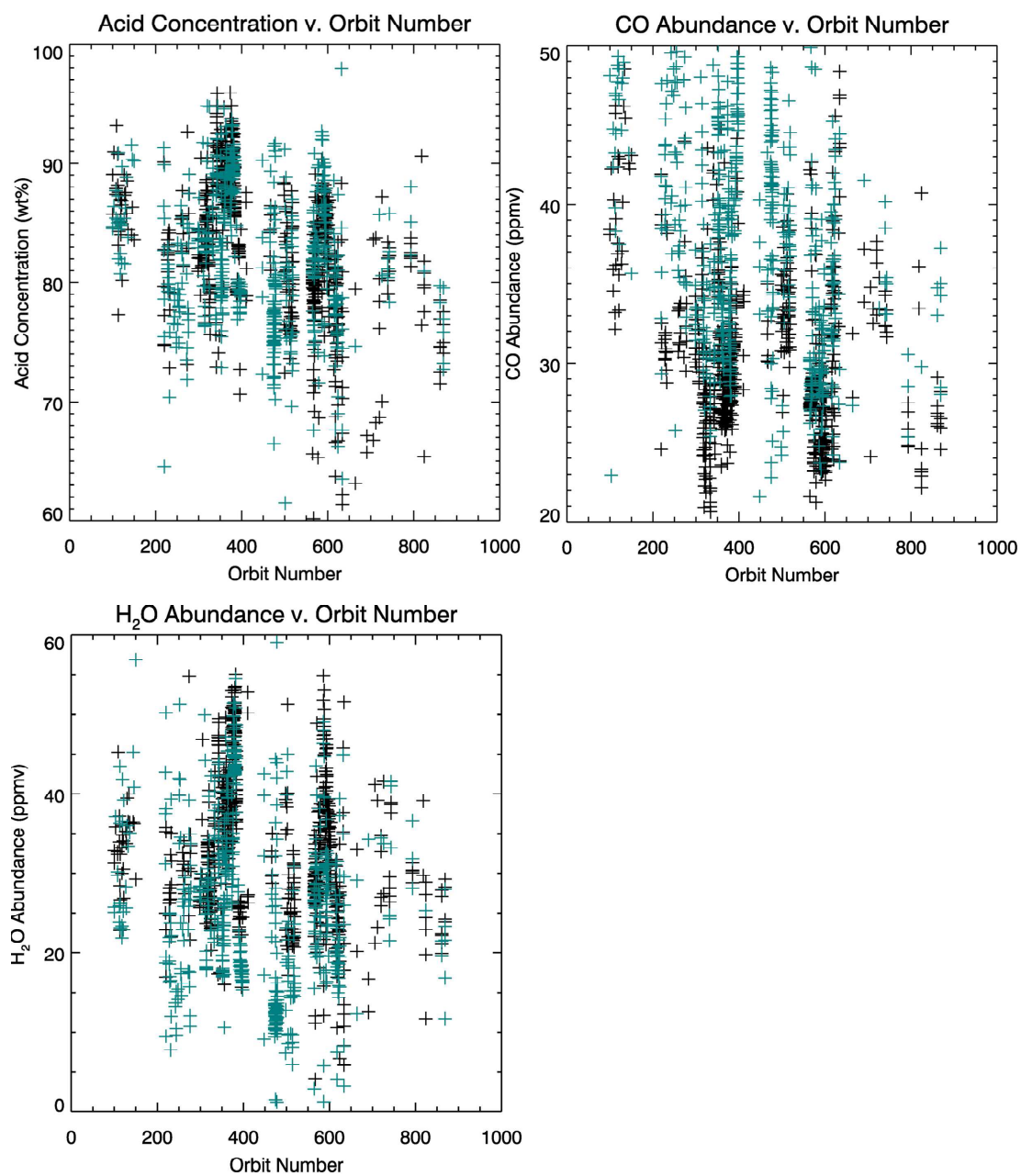


Figure 7.13: Results for acid concentration, CO and H₂O abundances as a function of orbit number (as Figure 5.5).

volcanism.

CO and sulphuric acid are photochemically produced above the clouds, CO from photodissociation of CO₂ and sulphuric acid from photolysis of SO₂ and subsequent reaction with water vapour. The rate of these photochemical processes depends on the amount of solar photons incident on the planet, so variations in the level of solar activity may drive alterations in the abundances of these chemical species. Solar cycle 23 was ending and sunspot activity was decreasing from early 2006 to late 2008, so potentially this could also provide an explanation for lower abundances of photochemical species. This does not, however, explain the observed decrease in water vapour abundance, as if less is being converted into H₂SO₄ due to reduced photochemistry the abundance would be expected to increase. The SO₂ measurements by Marcq et al. (2011) do not appear to corroborate this hypothesis either, as the only observed variation up to orbit 400 is the sudden increase in SO₂ abundance in orbit 310. If the rate of photochemical production of H₂SO₄ was to decrease as a result of weakening solar radiation, one would expect the abundance of SO₂ to demonstrate a corresponding increase as less is converted to H₂SO₄. The observed secular decrease in acid concentration and CO abundance in this work is much steadier than the SO₂ increase observed by Marcq et al. (2011), so it is unlikely that both phenomena are a consequence of the same process.

The apparent discrepancies between these results and those of Marcq et al. do not rule out either of the above hypotheses altogether; the mechanism for variation in SO₂ above the cloud tops has been heavily debated, and the observed variation may be unconnected with volcanic or radiative phenomena. There may be alternative sinks and sources of SO₂ which have not been considered here. Yung et al. (2009) suggest that variation in SO₂ and H₂O above the clouds is linked to the clouds themselves, and also that abundances of these two gases are mutually controlled.

They argue that this mutual control could smooth out shorter-term variations due to dynamical change, creating instead the kind of secular variation discussed here. It is however unlikely that above-cloud H₂O variation would be correlated with any observed variation below the cloud, due to the vapour sink provided by the cloud.

7.6 Summary

The figure above (Figure 7.6) summarises the key findings related to the latitudinal cloud variations on Venus; the acid concentration, cloud base altitude and H₂O abundance all peak in the mid-latitudes and are decreased in the polar region. The decrease in cloud base altitude is attributed to decreased temperatures at ~ 50 km (Tellmann et al. 2009) towards the pole, resulting in a lower altitude of condensation; a reduced supply of sulphuric acid vapour and an increase in cloud-top H₂O abundance (Cottini et al. 2012) may be responsible for the decreased acid concentration in this region. The decrease in H₂O abundance below the cloud is anticorrelated with an increase in CO abundance in the polar collar, suggesting that both results are due to the presence of the descending branch of the Hadley cell. The findings of Wilson et al. (2008) of large cloud particles at the south pole are corroborated, and it is suggested that a lack of cloud condensation nuclei could be responsible for the observed increase.

The other major findings are the increase in acid concentration from 70 ± 6 wt% in bright regions to 87 ± 6 wt% in dark regions, and a possible secular decrease in cloud acid concentration, CO and H₂O abundances during the lifetime of VIRTIS-M-IR. The increased acid concentration is likely to be due to combination of local temperature change and variation in the sulphuric acid vapour abundance below the cloud; the secular changes could be attributed either to variation in rates of volcanic

outgassing, or a decrease in the number of sufficiently energetic solar photons due to the solar cycle. All of these findings have been discussed in context with each other and established dynamical and microphysical constraints.

Chapter 8

Conclusions and Further Work

8.1 Conclusions

This work has provided an insight into the variable and complex nature of the Venusian convective cloud. The VIRTIS dataset, with its unprecedented global coverage of the near-infrared window regions, has been exploited to provide the first global remote sensing study of the lower cloud. A detailed sensitivity analysis of the atmospheric window regions provided a basis for a computationally-efficient and transparent method to retrieve properties of the cloud using data from VIRTIS. Consideration of cloud parameterisations presented in the existing literature for use in radiative transfer models led to the implementation of a new parameterisation that allowed me to study variation in the cloud particle size and acidity, and the altitude of the cloud base, whilst keeping the number of variable parameters to a minimum. A detailed error analysis, with careful consideration of the assumptions made and possible alternatives, provided a demonstration of the robustness of the results and the extent to which they can be trusted. It was generally found that the results did not vary outside the stated errors when the assumptions were altered,

suggesting a high degree of insensitivity to the *a priori* assumptions made.

The acid concentration in the cloud droplets is observed to vary as a function of cloud optical depth, with the highest values of $\sim 87 \pm 6$ wt% occurring in regions of dark cloud, and low values of $\sim 70 \pm 6$ wt% in the brightest regions. This variation is likely to be a result of local variations in temperature and H_2SO_4 vapour abundance. CO and H_2O average abundances are found to be 28 ± 5 ppmv (at 39 km) and 32 ± 8 ppmv (between 28 and 50 km) respectively, values which are in excellent agreement with previous results (Bézard and de Bergh 2007, Marcq et al. 2008). The water vapour abundance below the cloud is tentatively found to be decreased in the very darkest regions, which supports the results of Tsang et al. (2010), although a constant water vapour abundance is also consistent within the error.

Larger particles are present in regions of low cloud optical depth, which may provide evidence for a different composition for the largest particles. The average cloud base altitude is found to be between 47 and 52 ± 2 km, which agrees very well with the results of the Pioneer Venus descent probes, and is also largely consistent with the findings of Tellmann et al. (2009) that the convectively unstable region within the cloud extends down to approximately 50 km. The retrieved base altitude has some sensitivity to assumptions about the spectral variation of the refractive indices of sulphuric acid for different concentrations, but I find that it is $47\text{--}48 \pm 2$ km in the darkest regions, with a somewhat broader possible range of $47\text{--}52 \pm$ km in the brightest regions. This indicates that the base altitude may be higher in regions of low cloud optical depth, suggesting that particles are preferentially removed from the lowest few km of the cloud when holes in the cloud form.

The acid concentration, cloud base altitude and H_2O abundance display correlated behaviour as a function of latitude, which is clearly linked to the planetary-scale dynamics. All peak in the mid-latitudes, with respective values of 85 ± 6 wt%, 51 ± 3

km and 35 ± 10 ppmv, and they have minima in the polar region of 75 ± 6 wt%, 42 ± 2 km and 15 ± 20 ppmv. The acid concentration and cloud base altitude minima are due to cooler temperatures within the cloud at the poles, and the extension of the convectively-unstable region to lower altitudes (Tellmann et al. 2009). The decreased acid concentration at the pole is likely to also be due to low H_2SO_4 vapour abundance; H_2SO_4 is photochemically produced, preferentially in equatorial latitudes, and this reduction may also contribute to the increased brightness in the polar regions due to low cloud optical depth.

The CO abundance peaks at $\sim 75^\circ$, with a maximum value of 55 ± 15 ppmv, occurring at the same latitude as the minimum in H_2O abundance. This is in the region of the downwelling branch of the Hadley cell; the maximum and minimum are attributed to convergence above the cloud, followed by downward transport of relatively CO-rich and H_2O -poor air to regions below the cloud. The increased H_2O abundance at the cloud top found by Cottini et al. (2012) is likely also to be a result of this convergence.

The particle size parameter is increased in the polar region, which if all cloud particles are assumed to be H_2SO_4 is attributed to a relative lack of cloud condensation nuclei in the polar regions. The origin of the cloud condensation nuclei (CCN) on Venus is unknown; if they are photochemically produced, they would be least abundant in the polar regions. Alternatively, this may be evidence that the largest particles on Venus are a different chemical substance to the other particles; since they are more abundant at the poles, where the atmosphere is unstable to convection over a much greater altitude range, they could plausibly be dust or volcanic ash particles, which would reach the cloud level more easily in polar regions.

Some tentative evidence for long-term secular change is also presented, in the form of a steady decrease in acid concentration, CO abundance and H_2O abundance as a

function of orbit number, from $\sim 85\text{--}75$ wt%, $\sim 40\text{--}30$ ppmv and $\sim 35\text{--}25$ ppmv respectively, although the scatter on the results is very large. Since H_2SO_4 and H_2O are constituents of volcanic gas, this may indicate a decrease in volcanic outgassing over the duration of the mission. The decreases in acid concentration and CO could also be linked to the solar cycle as they are both photochemically produced, and sunspot activity was decreasing during the time period in question; however, H_2O would not necessarily be expected to decrease also, as less H_2O would be removed during photochemical production of H_2SO_4 .

These results demonstrate a strong link between dynamical and chemical processes on Venus and the structure of the cloud. They provide a basis for improved representation of the cloud in radiative transfer and general circulation models, and further insight in particular into the latitudinally-varying dynamics and atmospheric structure. Of especial interest is the cloud structure observed in the polar regions compared with the low latitudes, which indicates the presence of a very different regime at the pole; this could be evidence for the presence of a mixing barrier in the polar vortex region, as observed on Titan by Teanby et al. (2008), which would result in different chemical abundances and thereby a different cloud structure in the vortex eye. The upwelling and downwelling structures in the vortex eye which best explain the observed gaseous abundance gradients are similar to structures seen in terrestrial hurricanes (Figure 7.6), as suggested by Limaye et al. (2009). Study of the cloud is shown to be a potential means of eliciting new information, and corroborating previous findings, about the Venusian atmospheric structure and dynamics as well as providing an insight into the cloud structure itself.

8.2 Future work

The work presented in this thesis provides opportunities for further study using the method that has been developed, and for microphysical and dynamical modelling based on the results. Here, I outline some suggestions for future work that could be usefully undertaken. I have mentioned several times during this thesis, mostly in Section 6.3, properties of the cloud or atmosphere that cannot be retrieved using the method presented here, nor in my opinion by other remote sensing methods; I therefore also suggest what I consider to be some key measurements that should be if possible incorporated into future missions to Venus.

8.2.1 Retrieval algorithm

Further refinement of the retrieval algorithm is possible, in particular based on results of the Venus Express mission which have only recently become available. Some possible changes have already been discussed in Section 6.3. Others are briefly described below.

Global temperature structure variation

The known latitudinal variation in temperature structure has been taken into account in the work presented here, but using only four profiles provided by the VeRa instrument team as described in Section 2.2.5 (Tellmann et al. 2009). The number of publicly available profiles has been increased subsequently, and in the future a more detailed correction for temperature structure variations could be implemented, although it is unlikely that much difference would be made to the results (see Figure 6.6). Also, temperature structure variation as a function of local solar time has not been considered here, and this could be a useful exercise for the future as it may

shed some light on the robustness of the weak trends observed in Figure 5.3. Further investigation into the effect of temperature variation in the deep atmosphere would also be an important step, although this is more challenging as the VeRa instrument cannot observe temperature variation in the region below the clouds and so there are no recent constraints. There is no global data at these altitudes at all, as the only previous information comes from the Venera and Pioneer Venus descent probes which can provide only local information. Deep atmospheric temperature retrieval must be left to future missions.

Limb darkening

A recent empirical investigation into the limb darkening effect as observed by VIRTIS has been undertaken by Longobardo et al. (2010). The corrections obtained differ slightly from the model-based correction used in this work at $2.3\ \mu\text{m}$, as the results found by Longobardo et al. (2010) are close to the results originally presented by Carlson et al. (1993) (see Section 4.1.3 for the correction used in this work). In addition, they find that there is very little limb darkening in the polar regions at any wavelength, which they postulate may indicate a reduction in the cloud scale height near the cloud top. There is however a geometrical bias, as the equatorial regions are observed by VIRTIS at high emission angles and the poles at low emission angles, therefore the possibility that latitudinal variation in the cloud opacity affects the empirically-derived limb darkening correction would need to be carefully considered and this result does not seem to be reliable.

An investigation into the effects of different limb darkening corrections may be fruitful, and may shed further light on processes at the poles, although since a large majority of the polar observations are at low emission angle the limb darkening effect here would always be small.

8.2.2 Analysis and applications

There are several possible extensions of this work, and the results presented make it apparent that understanding the cloud layer on Venus is an important prerequisite for studying other aspects of the planet. In particular, studies of the surface using the near-infrared window region are sensitive to assumptions made about the cloud, as the cloud attenuates the radiation coming from the surface, and so a reliable cloud parameterisation is necessary for near-infrared surface studies, in particular for declouding images. The new results presented here also provide a dataset that can be usefully compared with results from microphysical models to gain greater insight into the cloud formation process.

Surface window studies

VIRTIS has provided a preliminary opportunity to study surface emissivity properties, and thereby to infer the composition of the Venusian surface in different regions. Atmospheric windows at 1.02, 1.1 and 1.18 μm have large radiance contributions from the surface, but there is still attenuation by the cloud. Currently, the 1.31 μm window is used in conjunction with the surface windows to separate effects due to the atmosphere and cloud layer from those attributable to the surface (Helbert et al. 2008, Mueller et al. 2008). However, this process does not take into account possible variations in the spectral response of the cloud between 1.02 and 1.31 μm , and this work has shown that the acid concentration in particular significantly alters the spectral properties of the cloud in the near-infrared. Such variations may be very important for declouding the surface windows correctly. A study of the impacts of variable cloud properties in this region of the spectrum would be invaluable for future surface study, and the method presented in this work could be used to formulate a new declouding procedure with the potential to account for variations

in the cloud properties.

Global microphysical modelling

The results of this work provide an opportunity for comparison with microphysical modelling results. In particular, the observed presence of anomalously large particles at the poles (after Carlson et al. (1993) and Wilson et al. (2008)) bears further investigation. Microphysical modelling could be used to study the effects on the lower cloud of removing both soluble cloud condensation nuclei and particles from the upper cloud in the polar region, and whether or not this does, as suggested in Section 7.2.3, result in the formation of larger particles. An insight into the formation mechanisms of these larger cloud particles could be gained. Detailed investigations into acid concentration equilibria over spherical surfaces would also complement the work presented here, and could suggest a more detailed mechanism for the significant variations in acid concentration as a function of cloud optical depth and of latitude. The hypothesis that the convective cloud base should occur several kilometres lower at the poles due to the tropopause temperature decrease can also be tested.

8.2.3 Future missions and measurements

In-situ cloud studies

The *a priori* assumptions made in this work that have potentially the largest effect on the results obtained are the mode 3 size distribution and the identification of mode 3 as liquid sulphuric acid (Section 6.3.2). These assumptions are certainly the best that can be made with the available information, but they are based on very few data. Measurements of the size and shape of the cloud particles on Venus

can only be made by an instrument similar to the Large Probe cloud particle size spectrometer (LCPS), as part of an in-situ mission. Nephelometers do not provide such detailed information as did the LCPS about the exact sizes and aspect ratios of the particles measured. Further direct measurements of the atmospheric composition in the cloud deck, and if possible the composition of the cloud particles, would also be invaluable in settling the debate about the composition of the mode 3 particles. In-situ information about local cloud base altitude variability would also be useful.

Two proposed missions that have the potential to make some of these valuable measurements are EVE, the European Venus Explorer (Chassefière et al. 2009), and VALOR, Venus Aerostatic-Lift Observatories for in-situ Research (Balint and Baines 2008). Both teams proposed a long-duration balloon flight at approximately 55 km altitude on Venus, within the convective cloud deck, which would provide an unprecedented opportunity for direct measurement of cloud properties over a large expanse of the planet. The balloon would be transported by the zonal winds, circling the planet once every 4—5 days, and if originally located in the mid-latitudes would gradually move towards the pole during the mission due to the poleward meridional circulation. The dynamical environment would also be monitored, as the balloon would act as a passive tracer; data on its location would enable measurement of wind speeds in three dimensions. Such a mission would be very well placed to perform studies of the cloud layer, if selected for flight in the future.

Global deep atmospheric temperature measurements

As discussed in Section 6.3.5, temperature variations in the deep atmosphere play a significant role in infrared thermal emissions and therefore accurate *a priori* temperature profiles are important for infrared spectroscopic studies of Venus. There are however very few data available for altitudes below 45 km, and there are no data

below this altitude for any region polewards of $\pm 60^\circ$ latitude. The deep atmosphere temperature structure cannot easily be measured by remote sensing techniques due to inadequate altitude resolution in nadir observations (limb observations cannot penetrate the cloud layer) and degeneracy with other variables in a retrieval. As with further direct measurements of the cloud properties, a new in-situ mission seems to be the only option for this study. A balloon mission such as those mentioned in the previous section could, if situated slightly below the cloud deck, provide valuable information about the temperature structure over a narrow altitude range but covering a large region of the planet; small drop sondes could conversely provide vertical profiles down to the surface, but only for specific localities. A compromise between the two mission designs (for example, a balloon with small drop sondes for ballast that are released periodically as the mission progresses) would maximise the information obtained.

Laboratory measurements of CO₂ collision-induced absorption

As mentioned in Section 2.2.4, the amount of collision-induced absorption due to CO₂ at the high temperatures experienced on Venus is not well constrained by observations, and the attempts at quantifying it based on measurement in the laboratory have so far failed to improve upon the empirical estimates by such authors as de Bergh et al. (1995). As collision-induced absorption is a continuum effect, this lack of constraint adds uncertainty to infrared remote sensing studies. Laboratory measurements of this property at Venus conditions would therefore be of great value for future studies.

8.3 Summary

This chapter has summarised the conclusions drawn from this work, and suggested possible future applications and extensions to the method. It is apparent that, whilst much can be gained from global remote sensing studies of the cloud, future in-situ data is needed to definitively confirm or reject the hypotheses presented here. Nonetheless, this work represents an advance in the understanding of the Venusian cloud, and as such can inform future study and investigation.

Chapter 9

Appendix

9.1 Formulae for calculating cloud parameters based on branching ratios

The equations used in the retrieval process described in Section 4.2.1 are listed below, to aid reproduction of the work described in this thesis. Corrections for latitudinal temperature variation are given in Equations 9.1—9.4. θ is latitude in degrees, and I_λ are radiances at wavelength λ . Quantities with a suffix l are corrected for latitude variation.

$$I_{1.74l} = I_{1.74} / (0.9918 - 0.0044 \times \theta) \quad (9.1)$$

$$\begin{aligned}
I_{2.2l} = I_{2.2} &- (79.717 \times \theta^3 + 9.8108 \times 10^3 \times \theta^2 + 1.7459 \times 10^5 \times \theta) \times I_{1.74}^3 \\
&- (-4.5344 \times 10^{-3} \times \theta^3 - 5.8297 \times 10^{-1} \times \theta^2 - 9.1464 \times \theta) \times I_{1.74}^2 \\
&- (7.536 \times 10^{-8} \times \theta^3 + 8.981 \times 10^{-6} \times \theta^2 + 2.1791 \times 10^{-4} \times \theta) \times I_{1.74} \\
&- (-2.1941 \times 10^{-12} \times \theta^2 + 3.8898 \times 10^{-11} \times \theta)
\end{aligned} \tag{9.2}$$

$$\begin{aligned}
I_{2.3l} = I_{2.3} &- (-3.1136 \times 10^2 \times \theta^3 - 6.226 \times 10^4 \times \theta^2 - \\
&4.9794 \times 10^6 \times \theta - 8.873 \times 10^7) \times I_{1.74}^3 \\
&- (1.0348 \times 10^2 \times \theta + 1.638 \times 10^3) \times I_{1.74}^2 \\
&- (-1.9826 \times 10^{-7} \times \theta^3 - 2.8947 \times 10^{-5} \times \theta^2 - \\
&1.6226 \times 10^{-3} \times \theta - 1.8066 \times 10^{-2}) \times I_{1.74} \\
&- (9.4971 \times 10^{-13} \times \theta^3 + 1.1589 \times 10^{-10} \times \theta^2 + \\
&5.2528 \times 10^{-9} \times \theta + 4.1133 \times 10^{-8})
\end{aligned} \tag{9.3}$$

$$\begin{aligned}
I_{2.53l} = I_{2.53} &- (0.1265 \times \theta^2 + 6.5114 \times \theta) \times I_{2.4}^2 \\
&- (-5.9692 \times 10^{-6} \times \theta^2 - 3.9994 \times 10^{-4} \times \theta) \times I_{2.4} \\
&- (-1.4489 \times 10^{-11} \times \theta^2 - 6.9254 \times 10^{-10} \times \theta)
\end{aligned} \tag{9.4}$$

The retrieval calculation follows in Equations 9.5—9.15. Radiances with a prime (ν) are adjusted to take into account an already-determined variable. Some radiances are adjusted for several different variables, and these have multiple primes.

Calculation of acid concentration from $I_{2.2l}$ v. $I_{1.74}$:

$$\begin{aligned} \text{acid} = & (I_{2.2l} - 1.2148 \times 10^8 \times I_{1.74}^3 + 2.2806 \times 10^3 \times I_{1.74}^2 \\ & + 9.7857 \times 10^{-2} \times I_{1.74} - 7.5307 \times 10^{-8}) \\ & / (-1.4514 \times 10^6 \times I_{1.74}^3 + 66.1 \times I_{1.74}^2 \\ & + 1.2659 \times 10^{-3} \times I_{1.74} - 8.4054 \times 10^{-10}) \end{aligned} \quad (9.5)$$

Calculation of CO abundance from $I_{2.32}$ v. $I_{2.29}$:

$$\begin{aligned} \text{co} = & 35 \times EXP((I_{2.32} - 738.57 \times I_{2.3}^2 - 0.31681 \times I_{2.3} - 9.8043 \times 10^{-9}) \\ & / (-417.62 \times I_{2.3}^2 - 0.22764 \times I_{2.3} + 8.9506 \times 10^{-9})) \end{aligned} \quad (9.6)$$

Adjustment of $I_{2.29l}$ v. $I_{1.74l}$ to take into account acid concentration:

$$\begin{aligned} I'_{2.3} = & I_{2.3l} - 240.42 \times (\text{acid} - 96.0) \times I_{1.74}^2 \\ & - 1.0073 \times 10^{-2} \times (\text{acid} - 96.0) \times I_{1.74} + 1.4765 \times 10^{-8} \times (\text{acid} - 96.0) \end{aligned} \quad (9.7)$$

$$I'_{1.74l} = I_{1.74l} / (0.004377 \times \text{acid} - 0.41911 + 1) \quad (9.8)$$

Calculation of $\ln(\text{mode 3:mode 2'})$ relative abundance from $I'_{2.29l}$ v. $I'_{1.74l}$:

$$\begin{aligned} \ln(\text{m3} : \text{m2}') = & (\ln((I'_{2.29l} - 26454 \times I_{1.74}^2 - 0.16538 \times I_{1.74} + 2.2443 \times 10^{-7}) \\ & / (-2966.4 \times I_{1.74}^2 - 0.062417 \times I_{1.74} + 1.5648 \times 10^{-7})) \\ & - 7.1862 \times 10^8 \times I_{1.74l}^2 + 78317 \times I'_{1.74l} - 1.1143) \\ & / (1.7735 \times 10^9 \times I_{1.74l}^2 - 51472 \times I'_{1.74l} + 0.56111) \end{aligned} \quad (9.9)$$

Adjustment of $I_{2.4}$ v. $I_{2.29}$ to take into account acid concentration and CO abundance:

$$I'_{2.4} = I_{2.4} + 240.93 \times (\text{acid} - 96.0) \times I_{2.3}^2 - 0.010248 \times (\text{acid} - 96.0) \times I_{2.3} + 1.9745 \times 10^{-9} \times (\text{acid} - 96.0) \quad (9.10)$$

$$I''_{2.4} = I'_{2.4} - (0.020244 \times (\text{co}^2 - 30.0^2) - 29.89 \times (\text{co} - 30.0)) \times I_{2.3}^2 - (5.5622 \times 10^{-5} \times (\text{co}^2 - 30.0^2) - 8.213 \times 10^{-3} \times (\text{co} - 30.0)) \times I_{2.3} - (-1.4067 \times 10^{-11} \times (\text{co}^2 - 30.0^2) + 2.157 \times 10^{-9} \times (\text{co} - 30.0)) \quad (9.11)$$

Calculation of H_2O abundance (35 km) from $I''_{2.4}$ v. $I_{2.29}$:

$$\begin{aligned} \text{h}_2\text{o} = & ((I''_{2.4} - 4984 \times I_{2.3}^2 - 0.98855 \times I_{2.3} + 1.1496 \times 10^{-7}) \\ & / (-0.36425 \times I_{2.3}^2 - 7.2255 \times 10^{-3} \times I_{2.3} + 1.3968 \times 10^{-9}) \\ & + \text{EXP}((I''_{2.4} - 1.6114 \times I_{2.3} + 5.2334 \times 10^{-7}) \\ & / (-0.2281 \times I_{2.3} + 8.6888 \times 10^{-8}))) / 2 \end{aligned} \quad (9.12)$$

Adjustment of $I_{2.53l}$ v. $I_{2.4}$ to take into account acid concentration and CO abundance:

$$I'_{2.53} = I_{2.53l} + 4.04045455 \times 10^6 \times (\text{acid} - 96.0) \times I_{2.4}^3 - 93.95 \times (\text{acid} - 96.0) \times I_{2.4}^2 + 2.84454545 \times 10^{-4} \times (\text{acid} - 96.0) \times I_{2.4} - 2.45109091 \times 10^{-9} \times (\text{acid} - 96.0) \quad (9.13)$$

$$\begin{aligned}
I''_{2.53} = & I'_{2.53} - (3.1207 \times 10^{-1} \times (\text{co}^2 - 30.0^2) - 22.657 \times (\text{co} - 30.0)) \times I_{2.4}^2 \\
& - (-4.0562 \times 10^{-6} \times (\text{co}^2 - 30.0^2) + 4.7997 \times 10^{-4} \times (\text{co} - 30.0)) \times I_{2.4} \\
& - (4.7725 \times 10^{-12} \times (\text{co}^2 - 30.0^2) - 3.1018 \times 10^{-10} \times (\text{co} - 30.0)) \quad (9.14)
\end{aligned}$$

Calculation of cloud base altitude from $I''_{2.53l}$ v. $I_{2.4}$:

$$\begin{aligned}
\text{base} = & ((I''_{2.53} + 4.32 \times 10^7 \times I_{2.4}^3 - 2403.9 \times I_{2.4}^2 \\
& + 1.0103 \times 10^{-2} \times I_{2.4} + 9.9477 \times 10^{-8}) / (3.0594 \times 10^{14} \times I_{2.4}^3 \\
& - 1.61 \times 10^{10} \times I_{2.4}^2 + 2.655 \times 10^5 \times I_{2.4} + 1.0215))^{-0.25} \quad (9.15)
\end{aligned}$$

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