Optical Properties of Venusian Clouds

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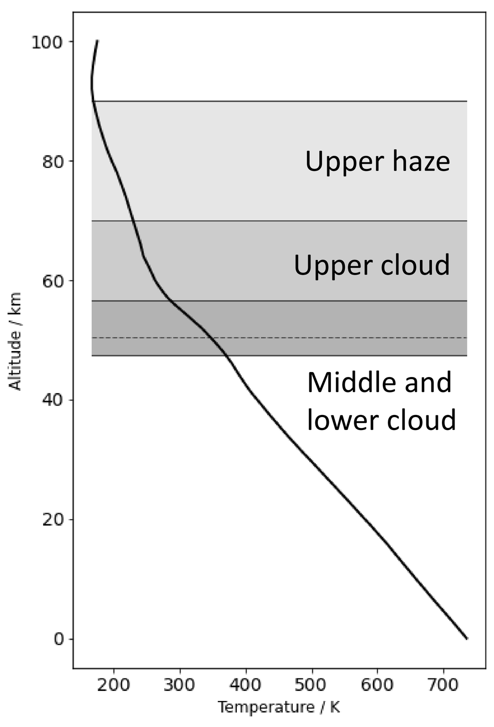
1 Venus and the unknown absorber

Venus has a complex and highly stratified cloud system. The clouds have three distinct main layers, and a thinner "haze" above. The main clouds are formed of highly reflective ~2 µm diameter spherical aqueous sulphuric acid droplets (mode 2), and smaller, submicron particles (mode 1). [1]



Cloud structure on Venus, with VIRA temperature profile.[2]

Absorption centred at 365 nm is well established, but unexplained. The absorber is located within the upper cloud, but its altitude profile is not known. Both gaseous and particulate absorbers have been proposed and either model can reproduce the observed spectrum equally well.

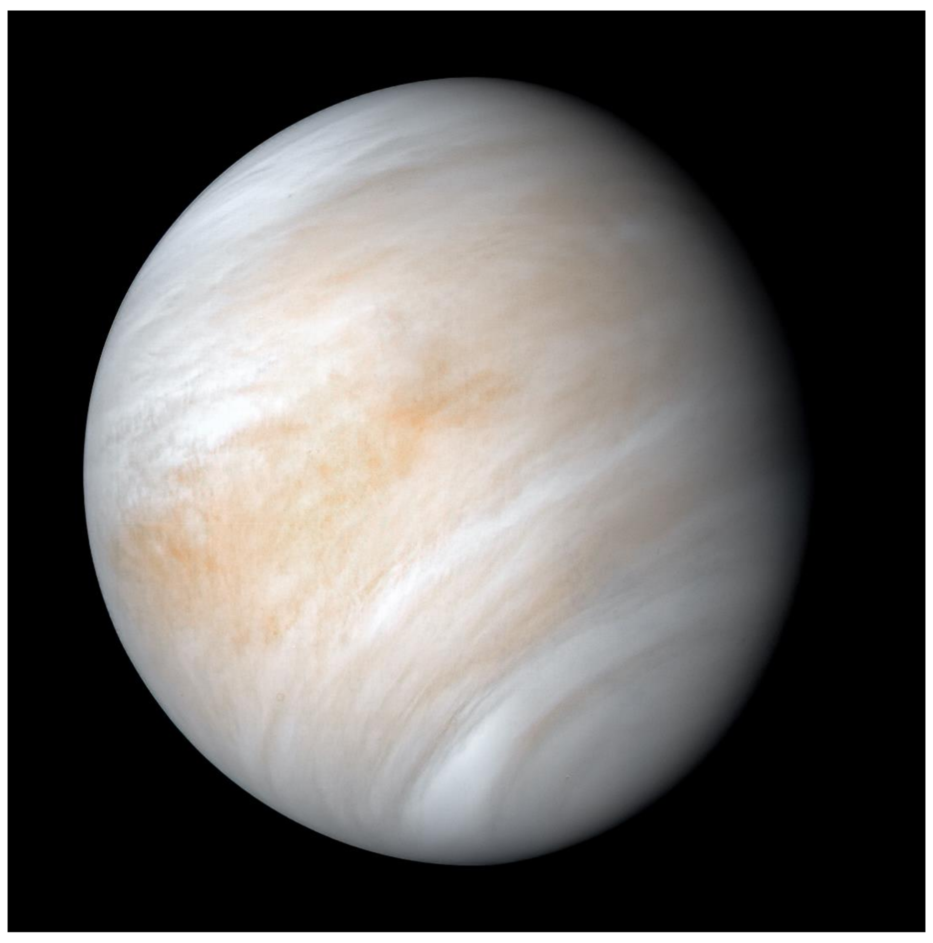
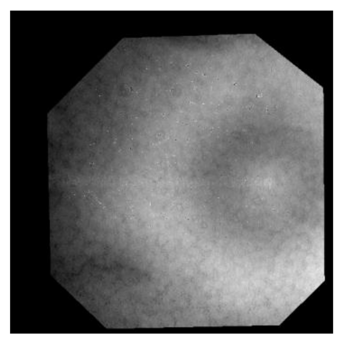


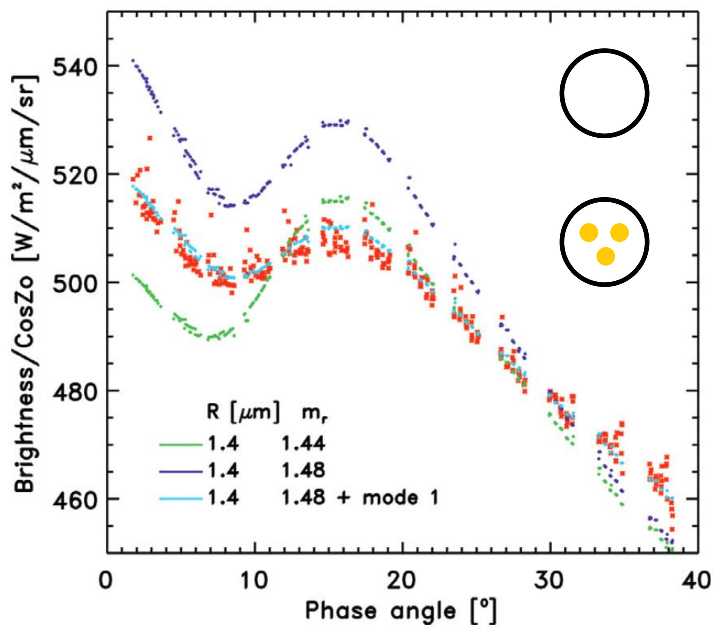
Image: NASA/JPL-Caltech. Contrast-enhanced false colour composite image of the unknown absorber on Venus, using Mariner 10 images.

Particulate absorbers which act as cloud condensation nuclei for sulphuric acid may also be able to explain the shape of glories on Venus.[3] This work focuses on one such candidate: ferric chloride ($FeCl_3$).

However, $FeCl_3$ is highly deliquescent, birefringent, and poorly understood under Venusian conditions, so the available absorption spectra may not be representative of $FeCl_3$ on Venus.

Example glory pattern at 365 nm (right) and 965 nm (below). Pure sulphuric acid cannot be responsible for the shape of the glory observed.[3,4]





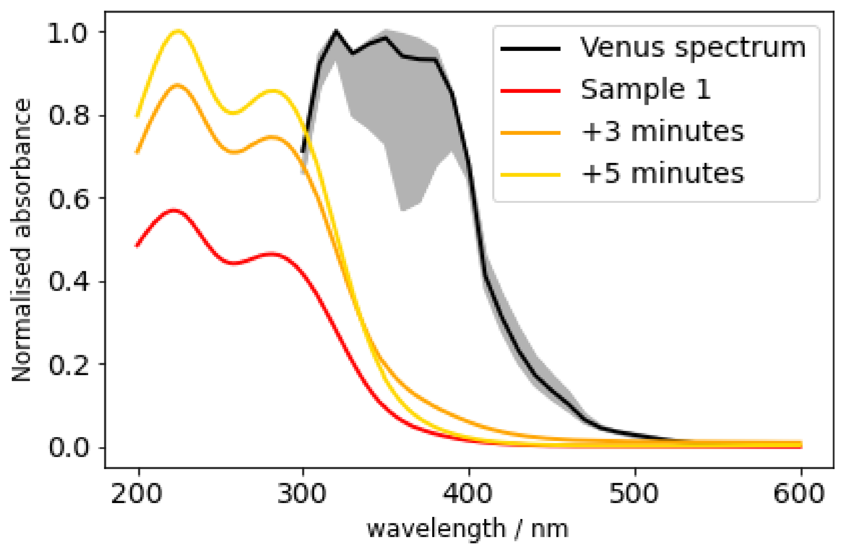
2 UV-Vis absorption spectroscopy

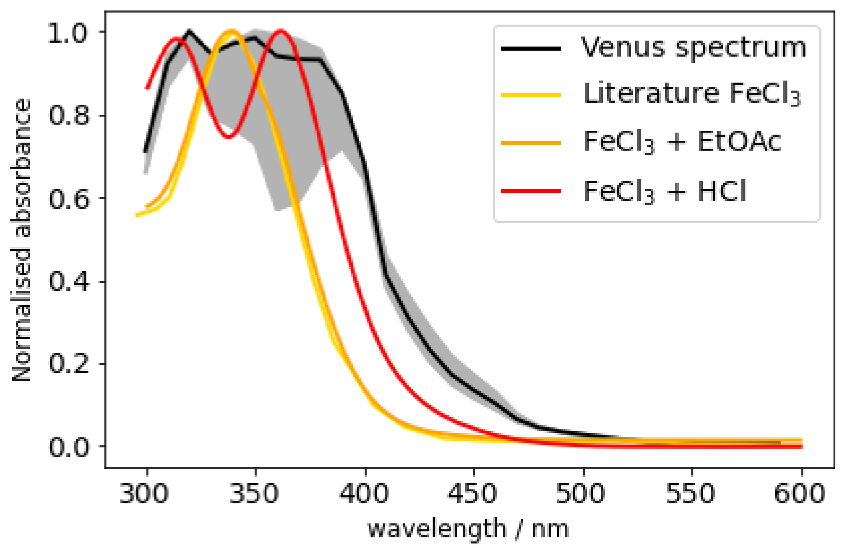
$FeCl_3$ particles in H_2SO_4.

If mode 1 particles exist as impurities within mode 2 cloud droplets, their absorbance should be considered in a sulphuric acid solution.

When added to cool (12.5 °C) 80 wt% sulphuric acid (consistent with the upper clouds on Venus), $FeCl_3$ slowly dissociated, and formed ferric sulphate complex ions. Particulates of $FeCl_3$ were visible in the sample, but not apparent in the spectrum.

The literature spectrum of $FeCl_3$ is measured in ethyl acetate. As $FeCl_3$ can react with ethyl acetate, the spectrum cannot be assumed to be correct.[5] Comparison with a mixture of $FeCl_3$ and aqueous HCl (37%), where $FeCl_4^-$ is formed, suggests the complex ion formed in ethyl acetate is not $FeCl_4^-$ and some reaction may have occurred.





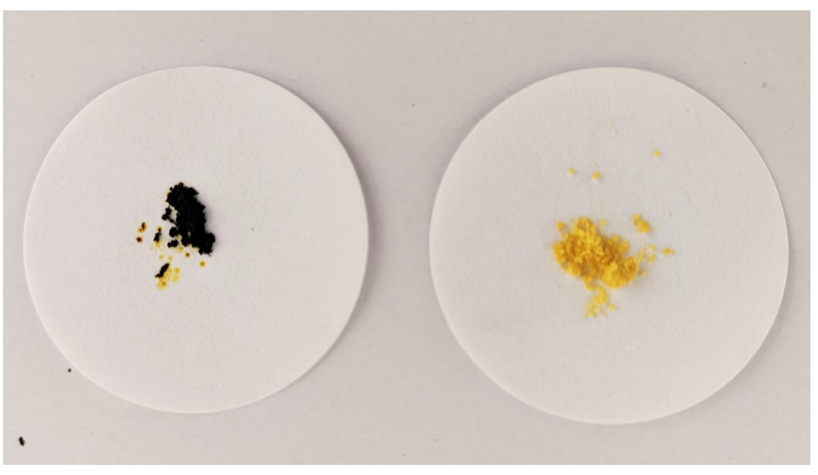
UV-vis (Agilent Cary 100) normalised spectra of $FeCl_3$ in 80 wt% sulphuric acid (left) and ethyl acetate (EtOAc) and 37% HCl (right), with MESSENGER Venus spectrum for comparison.[6]

The spectrum of $FeCl_3$ is strongly variable with its environment, so further work is needed to identify the species present in the literature spectrum, and to measure the refractive indices of the $FeCl_3$ particles present in sulphuric acid.

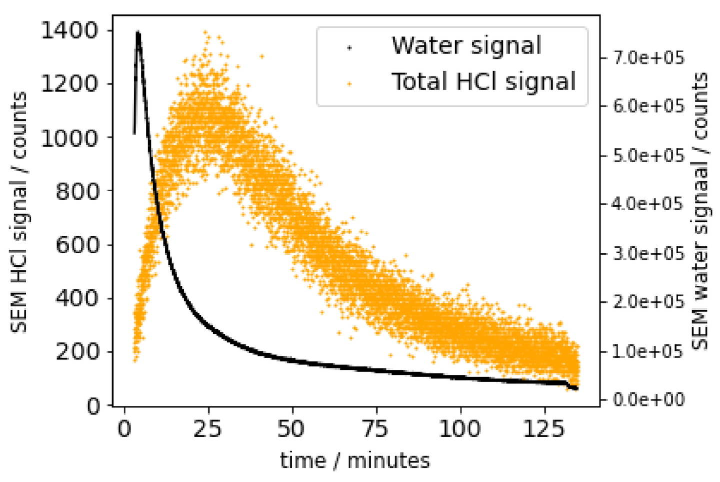
3 Forms and reactions of $FeCl_3$

Ferric chloride can exist in different forms. Its anhydrous form is dark red or green, while the hexahydrate ($FeCl_3.6H_2O$) is yellow. The anhydrous form is highly deliquescent, reacting with ambient water vapour and turning yellow .

When heated to even slightly above room temperature, or when under vacuum, the hexahydrate produces HCl and a dark red solid. Literature suggests this could be ferric oxychloride (FeOCl), but I have not been able to identify it experimentally.



Anhydrous (left) and hexahydrate (right) forms of $FeCl_3$. The anhydrous powder has begun to absorb water.



Above: Mass spectrometer signal for water and HCl (sum of all relevant masses) at 45 °C with time.

Below: $FeCl_3.6H_2O$ before the experiment, and the red solid after.

It has been proposed that anhydrous $FeCl_3$ could be emitted from the surface of Venus and react with atmospheric water vapour in the lower clouds to form $FeCl_3.6H_2O$.[1] If this happens, the temperatures are high enough for it to decompose, producing HCl and, presumably, FeOCl, which could also be a suitable candidate for the absorber, and requires study.

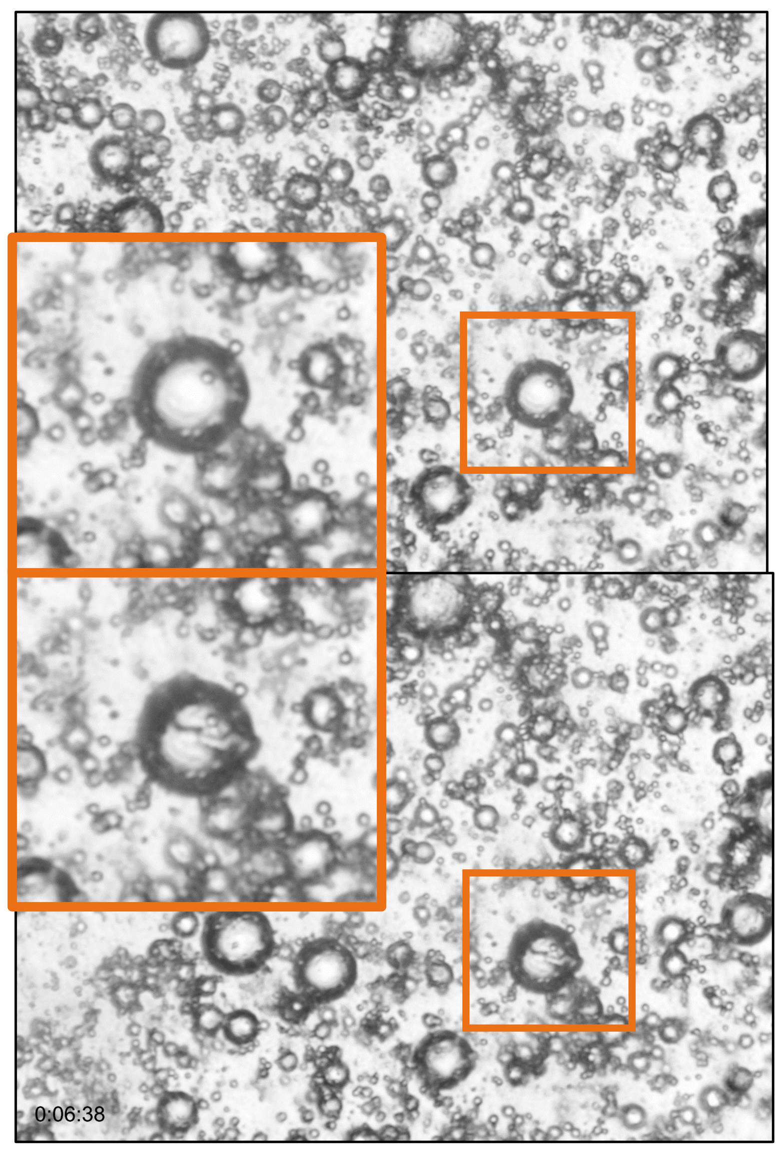
The kinetics of the reaction are being studied by flowing dry nitrogen over a sample of $FeCl_3.6H_2O$ in a water bath and monitoring the production of water and HCl.

4 Emulsion freezing

The temperature change at the boundary between the upper and middle clouds could indicate a phase change. This change occurs at the melting point of 80 wt% sulphuric acid.[7] High concentrations of sulphuric acid have never been observed to freeze homogeneously in lab experiments, even after significant supercooling.

To study this, an emulsion will be formed by mixing sulphuric acid, oil, and surfactant and pushing the mixture through a filter to produce droplets. The emulsion is spread on a slide and the temperature decreased using liquid nitrogen. Viewed through a microscope, freezing of individual droplets can be seen and the temperature recorded.

These experiments will be carried out with aqueous sulphuric acid emulsions of varying concentrations, and with mixtures of sulphuric acid and absorber candidates. If the presence of the impurities changes the freezing behaviour of the emulsion, comparison with the measured behaviour and observations will reveal information about the composition of the mode 2 cloud droplets.



A freezing event in a water/mineral oil/lanolin emulsion. The droplet instantly becomes darker and non-circular.

So far, only preliminary tests with pure water have been carried out.

5 Conclusions and future work

This work considers just one of the most promising candidates for Venus's unknown absorber.

- At low temperatures, **$FeCl_3$ particles do not dissolve instantly** in concentrated sulphuric acid, but UV-Vis spectrometry is not well suited to the study of particles and suspensions, so other methods will be required.
- The behaviour of $FeCl_3$ in different solutes varies, making it **unlikely that the use of other solutes will provide relevant data**.
- The suspended particles in the sulphuric acid need to be identified and studied.

- **$FeCl_3.6H_2O$ produces HCl and presumably FeOCl**, at Venusian temperatures.
- **FeOCl is another promising candidate for the absorber** if its production is feasible.
- Studies of the kinetics of this reaction are ongoing.

- A cold stage microscope is capable of seeing **individual freezing events** in an emulsion.
- The experiments need to be carried out with **increasing concentrations of sulphuric acid**.
- Different **impurities will then be added** to the emulsions to observe the change in freezing behaviour.

References and acknowledgements

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