Venus’s ultraviolet absorber: Cyclo-octal ($S_8$) and polymeric sulfur ($S_x$) and their latitudinal behavior.

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Some suggested Venus UV absorbers:

Formaldehyde CH₂O
Carbon suboxide C₃O₂
Nitrosylsulfuric acid NOHSO₄
Nitrogen dioxide NO₂ and nitrogen tetroxide N₂O₄
Ammonium nitrite NH₃NO₂
Ammonium sulfate (NH₄)₂SO₄
Ammonium pyrosulfate (NH₄)S₂O₅
Ammonium chloride NH₄Cl
Amides
Chlorine Cl₂
Sulfur dichloride, SCl₂
Iron chloride FeCl₂•2H₂O, FeCl₃
Perchloric acid HClO₄
Disulfur monoxide S₂O

Sulfur
Ferric chloride at Venus?

FeCl₃

The (uncommon) mineral Molysite

Associated with terrestrial fumaroles

Considered by Kuiper (1969)

Resurrected by Zasova, Krasnopolosky, & Moroz (1981)

Computed profile matches Mode-1 particles in lower and middle clouds (Krasnopolosky, 2006)

FeCl₃ in plume

Molysite (FeCl₃) deposits

Forms sulfuric acid cloud droplets with FeCl₃ in solution

Ferric chloride, a salt, is deliquescent and FeCl₃ aerosols can act as a condensation nuclei

Dimer condenses at 315 K (54 km)

(FeCl₃)₂ gas formed at 400 K (42 km)

FeCl₃ gas from plume and sublimation
Spectroscopy of FeCl₃ solutions

Transmission spectra by Mark Anderson

Obtain absorption coefficient and imaginary index

In sulfuric acid solution,

get mainly Fe³⁺, FeSO₄⁺⁺, FeHSO₄²⁺

Fe³⁺ absorption bands at 194 nm and 245 nm (Brown & Kester, 1980)

FeSO₄⁺⁺ and FeHSO₄²⁺ bands at about 290 and 360 nm.

Extends into visible region
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Extends into visible region

Very little absorption > 500 nm
Expected FeCl₃ signature at Venus

Cloud droplets of FeCl₃ in sulfuric acid

Mie scattering for single scattering albedo, asymmetry factor

Radiative transfer a la Hapke

Geometric albedo

FeCl₃ at Venus? Normalized geometric albedo spectra for various concentrations.

FeCl₃ in 80% H₂SO₄ at various percentage concentrations

Spherical grains, 1-µm radius, log-normal distribution

Mie scattering calculations using experimental indices of refraction
Elemental sulfur

Elemental sulfur is one component of Venus’s sulfur cycle

$H_2SO_4, SO_2, SO, OCS, SO_3, S_x$

$SO_2 + h\nu \rightarrow SO + O,$  \hspace{1em}  $SO + h\nu \rightarrow S + O$

$OCS + h\nu \rightarrow CO + S$

$(SO)_2 + OCS \rightarrow CO + SO_2 + S_2$

Sublimation from surface

Mills, Esposito, & Yung 2007
Spectral properties of $S_8$ and $S_x$

The stable form of sulfur is cyclo-octal $S_8$ which has absorption bands at $\sim 220$, $260$, and $280$ nm, and a gaussian tail that extends to $\sim 450$ nm. Similar to FeCl$_3$, little absorption $> 500$ nm.

BUT

Absorption in these bands breaks the $S_8$ ring. Forms amorphous sulfur a-S. Similar structure to polymeric sulfur $S_x$ produced in liquid sulfur (long chains, large rings). New bands at longer wavelengths, so...

Polymeric sulfur $S_x$ and FeCl$_3$ compared

Computed to match observed UV absorber band depth

Can discriminate using the long-wave region > 500 nm
**Venus Express VIRTIS hyperspectral image cube**

VV0459_03, MTP016

Image uses 380 to 400-nm UV bands and is illumination-corrected and stretched

Black denotes UV absorption

Scanning mirror moves slit in ~ N - S scan

Use Vega calibrated sample (126)

60 spectra, each for 1 sample × 4 lines

Spectra normalized to “white” polar cloud
Absorption extending to 640 nm and well beyond!

So not predominately FeCl$_3$ nor pure S$_8$.

Polymeric sulfur implicated

(but may be consistent with Krasnopolsky’s lower and middle cloud FeCl$_3$/H$_2$SO$_4$ aerosols)

As south latitude increases, slope increases
Two examples

**VV0436_03:** Barker’s ground-based spectra

To investigate further:

Take ratio of 500 – 700 nm slope to band depth at 350 nm

Venus albedo
Barker et al., *J. Atmos. Sci.* 32, 1205 (1975)
Somewhat polymeric at -45°

Polymeric content increases with south latitude...

...and time in Hadley cell

Decrease in amount of sulfur and relative slope starting at ~ -65° where....

...cloud top descends in cold collar...

...and overlying hazes provide complications.

Bright white polar hazes here
Summary

Provides good evidence for polymeric sulfur as Venus’s UV absorber

Supports Hapke & Nelson’s 1975 suggestion

Consistent with the UV absorber brought up from depth in low latitudes as suggested by Titov et al. 2008.

Polymerization appears to proceed as sulfur aerosols move poleward

Curious and unexplained behavior at high latitudes
  (annealing, mixing effect, temperature effect, stratification?)

Lots more data available for further analysis

Also need photolysis measurements of micron-size $S_8$ grains!

  Rate of polymerization as function of excitation wavelength

  Absorption spectra changes with temperature

  Annealing rate at various temperatures
Backup Material
(Previous work and notes)
Wavelength, nm

I/F ratio

- Virtis VV0459_03
- FeCl₃ (0.25%) in sulfuric acid
- S₈ + S₄ (0.4:0.6) grains + sulfuric acid droplets
## In-situ & orbital measurements inferring sulfur

<table>
<thead>
<tr>
<th>Method</th>
<th>Details</th>
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</thead>
<tbody>
<tr>
<td>S elemental X-ray fluorescence</td>
<td>(Andreichikov et al. 1987; see Krasnopolsky 1989 for review of Vega cloud results)</td>
</tr>
<tr>
<td>S elemental Gas chromatography</td>
<td>Porshnev et al. 1987; Surkov et al. 1987</td>
</tr>
<tr>
<td>$S_2, S_3$ Descent spectra</td>
<td>$S_2 \sim 2 \times 10^{-8}$, $S_3 \sim 3 \times 10^{-11}$ to $10 \times 10^{-11}$ (Moroz, 1979; Sanko 1980; Moshkin 1983; Krasnopolsky 1987, Malorov et al. 2004)</td>
</tr>
<tr>
<td>$S_{2-8}, S_8$ Descent active absorption spectroscopy</td>
<td>25 ppm at 45 km, 5 ppm at 25 km (Bertaux et al. 1986) But see Bertaux et al., 1996.</td>
</tr>
<tr>
<td>$S_{12}$ Venera 15 infrared spectroscopy</td>
<td>(Spankuch &amp; Schuster 1990)</td>
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Sulfur Models and Thoughts

$S_8 + S_\mu$  Hapke & Nelson 1974, 1975  One 10-µm $S_x$ grain per 670 H$_2$SO$_4$ droplets. (sulfur mass > H$_2$SO$_4$ mass!)

$S_{2n}$  Prinn 1975  Simultaneously suggested sulfur as the absorber from photochemical S$_2$

$S_8$  Young 1977  Can be $S_8$ if concentration increases with depth

Not $S_8$  Pollack et al., 1979; Tomasko et al. 1979  $S_8$ band edge too sharp, and shifts on cooling. (but UV irradiation shifts in opposite direction)

$S_8+S_3+S_4$  Toon et al. 1982  Sulfur grains act as condensation nuclii, forming cores with H$_2$SO$_4$ mantles. But $S_3$ and $S_4$ are unstable.

Young 1983  Sulfur doesn’t “wet” sulfuric acid, so can’t form cores. suggests “Gumdrop” Model

James et al. 1997  H$_2$SO$_4$ cloud model seems to require soluble condensation nucleii
Two-component cloud

$S_8:S_\mu \sim 1:1$

S grain sizes ~ $\frac{1}{2} \mu m$

Relative number ~ 3%

Elemental $S/H_2SO_4$ ~ 1%

Venus 2-component cloud
Sulfuric acid & sulfur

$S_8:S_\mu = 0.4:0.6$, $r = 0.6 \mu m$, $f = 0.032$

Barker et al. 1975
Composite particle

If one assumes that all cloud particles are nucleated with monodisperse soluble sulfur grains (e.g. thionates), then

The models don’t match observations!

Inclusion of smaller sulfur grains may help. Probably would require a bi-modal distribution.

Or allow the presence of non-nucleated droplets.
Gumdrop Model

Droplets “decorated” with many small sulfur grains does not work (too much absorption).

OK for low grain/droplet ratio, with some fraction “decorated” with one S grain, most not.

Elemental $S/H_2SO_4 \sim 1\%$

Results preliminary; more work needed for very small S grains.