

NO. 184 REFLECTION SPECTRA OF SOLIDS OF PLANETARY INTEREST

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ABSTRACT

This paper reproduces the spectra of solids which might be found on the surfaces of planetary bodies or as solid condensates in the upper planetary atmosphere. Among these are spectra of various iron compounds of interest in the study of the clouds of Venus. Other spectra are included of various sulfides, some at low temperature, relevant to the planet Jupiter. Meteorite and coal abstracts are also included, to illustrate dark carbon compounds.

1. Earlier Results; Method of Measurement

In his paper on the Venus cloud layers, G. P. Kuiper (1969) included a number of reflection spectra supplied by this author. These were obtained by means of a Zeiss Spectroreflectometer, courtesy of Dr. Robert Feltham of the University of Arizona Department of Chemistry. The instrument measures the reflection spectra of solids by illuminating the sample with monochromatic light at a 45° angle of incidence, and detecting the reflected light normal to the surface of the sample by an appropriate detector (PbS in the IR, photomultiplier in the visible and UV). In all cases, the radiation detected is normalized to 100% by setting the slit width of the monochromator such that the standard (finely-powdered optical LiF) registers 100% on the galvanometer. The spectrum was sampled every 100Å in the UV, every 200Å in the visible, and every 500Å in the IR. The sample and standard are mounted on the same movable holder. First the standard is placed in the beam, the galvanometer is set to 100, and then the sample moved into place and its reflection measured. The spectra in this paper and in *LPL Communication No. 101* are the smooth curves drawn through the measured values.

Occasionally, the sample reflects light better than the standard LiF. In some cases the sample reflects in a specular fashion off crystal surfaces, more so than does the standard. This is particularly true in the UV < 3000Å. At times the sample is drier than the LiF, so that the water absorption at 2.0µ may show as a positive feature. Some samples cooled to liquid-nitrogen temperature had liquid-nitrogen boiling on the surface of the sample and standard, both covered with quartz plates. This is particularly observed in Figure 1*l*. It is stressed that whenever the sample was covered with a protective sheet of polyethylene or 1 mm thick quartz, the standard was likewise covered.

2. The New Spectra

Figure 1 reproduces the absorption spectra of various sulfur compounds which might be possible constituents of the clouds of Jupiter and Saturn, or surface deposits of the satellites of the giant planets.

Figures 1*a*, *b*, and *c* are the reflection spectra of ammonium sulfide, produced by reacting the two gases H₂S and NH₃ in an air-free environment. Originally the ammonium sulfide is white in color. If air is introduced, the oxygen causes the decomposition of sulfide (S²⁻) or hydrogen sulfide (HS⁻) ions into polysulfide ions (S_x²⁻), where the length of the sulfur chain increases with continued oxidation, until the production of a long-enough chain, probably S₈²⁻, results in a cyclic molecule S₈, which is the molecule of elemental sulfur. Upon evacuating some yellow samples of ammonium sulfide, i.e., removing the NH₃ and H₂S decomposition gases, a yellow crust of elemental sulfur remains. It should be pointed out that exposure to ultraviolet radiation (principally Hg 2537Å) produced the same effect as exposure to oxygen. Solar UV should be capable of similarly oxidizing sulfide to polysulfide in the upper atmospheres of planets.

The hydrogen sulfide equivalent to the polysulfide is shown in Figure 1*d*. This compound, H₂S₅, is extremely labile and decomposes spontaneously into H₂S gas and S₈ at room temperature. At lower temperatures (-30°C) it can be stored for months in a sealed container.

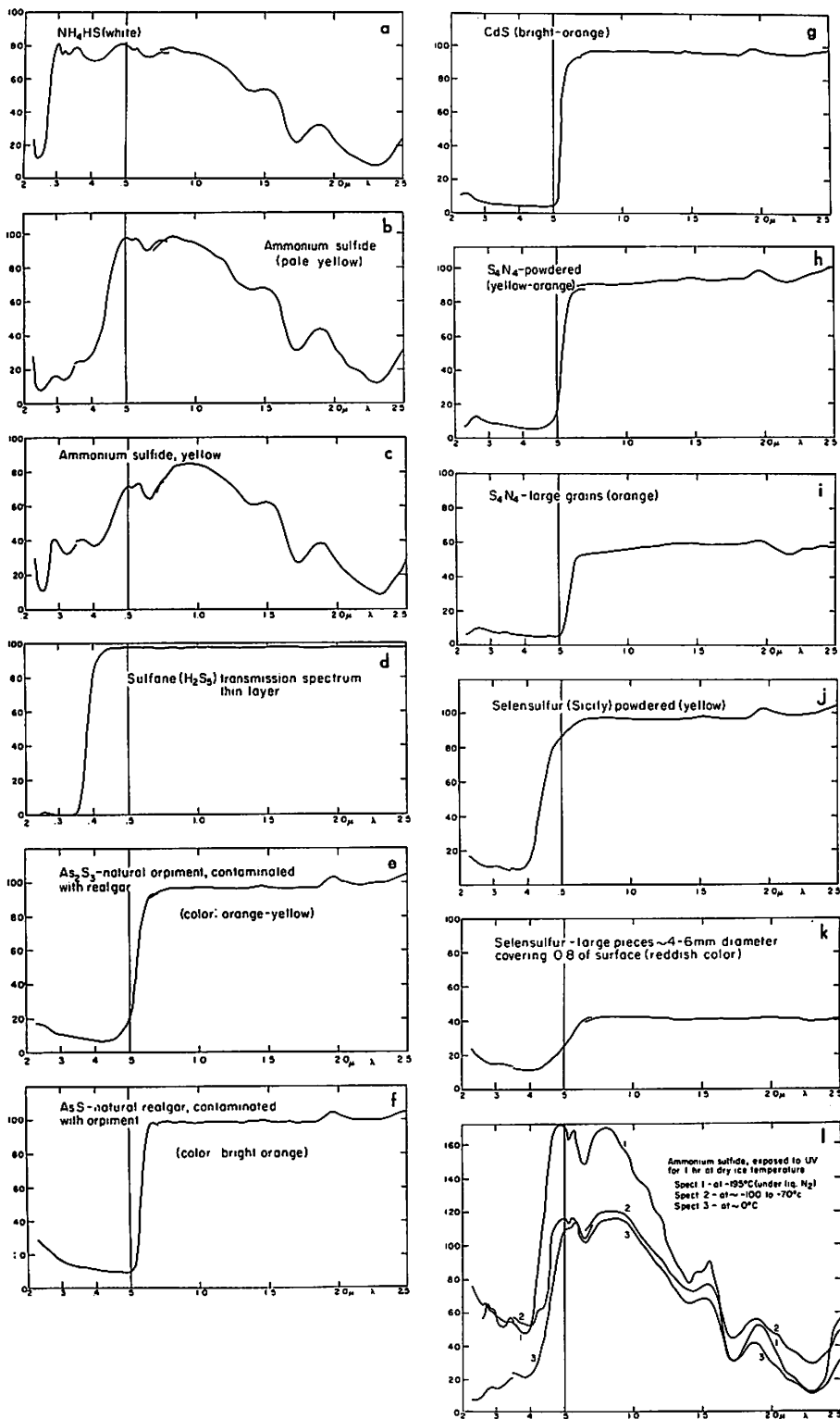


Figure 1

Ammonium sulfide cooled to liquid nitrogen temperature and intermediate temperatures is shown in Figure 1*l*. Problems with boiling liquid N₂ and the reflection off the polished surfaces of the protective quartz plates caused a reflectivity greater than the standard LiF. The positions of the absorptions are, however, accurate. It is interesting to observe the increase in absorption and the sharpness of the absorption caused by the lower temperatures in the features centered on 5350 and 6330A.

Cadmium and arsenic sulfides (Fig. 1*e, f, g*) are representative of possible satellite constituents. Both they and their elements are volatile, although the metals are not cosmically abundant. Tetranitrogen tetrasulfide, S₄N₄, (Fig. 1*h, i*) is a labile, even explosive, compound that can be formed by the reaction of ammonium sulfide in liquid ammonia. It is usually formed under highly selective laboratory conditions, and is added simply to show that various orange-colored sulfides are difficult to identify conclusively on the basis of their solid reflection spectra.

Selensulfur (sulfur contaminated with a few-percent selenium) shows a spectrum (Fig. 1*j, k*) similar to sulfur but with an absorption further into the visible than pure sulfur.

Figure 2*a-g* contain compounds of interest to the clouds of Venus, a continuation of the spectra produced in Kuiper's Venus paper (1969). Figure 1*a-d* show the spectra of ferrous chloride exposed to simulated Venus surface conditions. If ferrous chloride, hydrated to a small extent (about 1H₂O), is sublimed at 500°C under nitrogen gas, the spectrum is different from pure FeCl₂ (anhydrous) and FeCl₂ · 2H₂O. The coordinated Fe²⁺ ion absorption at 1.0μ, and the H₂O hydration at 2.0μ, are evident, as are the charge transfer bands in the UV. The same substance exposed to air for three days is seen in Figure 2*b*. The coordinated Fe²⁺ ion at 1.0μ is more intense, as are the charge transfer bands in the UV. Figure 2*c* shows the reddening (oxidizing) of FeCl₂ when sublimed in hot CO₂ (500°C). Upon exposure to air, the ferrous (or ferric) ion is coordinated by water, observed at 1.0μ, and the water of hydration, evident at 2.0μ.

Ferric sulfate with varying water of hydration is shown in Figure 2*e, f*. The addition of sulfuric acid to ferric sulfate produced a cream-colored paste whose spectrum is shown in Figure 2*g*. The liquid paste produced greater penetration and absorption in the IR observed longward of 1.5μ. It might be mentioned that the absorption characteristics of hydrated sulfates and sulfuric acid led the author to consider whether sulfuric acid itself might not be the main constituent of the Venus clouds (Sill 1972).

Figure 3*a* shows an iron compound, coordinated with ammonia instead of water. This can be compared with the equivalent aquo-complexed ferric chloride, Figure 6 (*c*) in *LPL Communication No. 101*. The ultraviolet is virtually identical, but the visible absorption is quite different, as is obvious from their colors: FeCl₃·6H₂O is bright yellow; and FeCl₃·6NH₃ is buff-colored. In the infrared, the coordinating NH₃ atom exhibits distinct ammonia-absorption bands versus the water bands of the aquo complex.

Some carbon compounds and the Orgueil carbonaceous chondrite are shown in Figure 3*b, c, d*. The Orgueil meteorite is a very dark specimen, darker than coal in the infrared. The overall dark-green color of the meteorite is due to the large

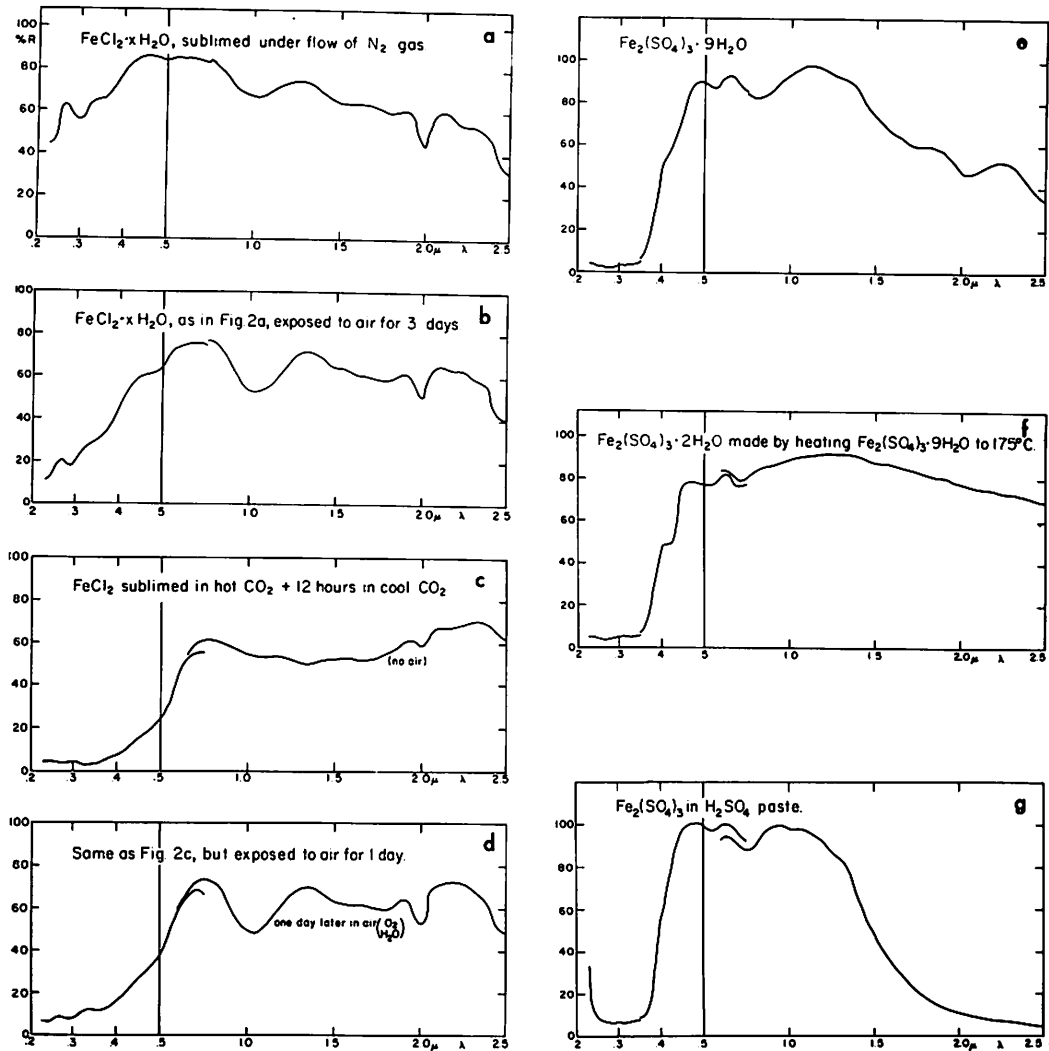


Figure 2

quantity of chlorite-type micaceous mineral present, an iron-bearing layer lattice silicate. Figure 3d is the spectrum of bituminous coal, not a likely object *per se* to be found on a planet, but illustrative of the chemical processes which have occurred in various carbon-bearing meteorites. Two extracts of bituminous coal are shown in Figure 3c. These have interesting IR reflection properties. They follow the overall IR brightening of bituminous coal, but show absorption features lacking in coal.

Figure 3e reproduces the spectra of elemental sulfur, both at room temperature and at about -160°C , cooled by nitrogen gas boiling off a reservoir of liquid nitrogen. The color of sulfur immersed in liquid nitrogen is *white* or, more exactly, a *faint pale green*. This is true even for large sulfur crystals a few mm thick. Liquid sulfane, H_2S_5 , whose transmission spectrum is seen in Figure 1d, behaves

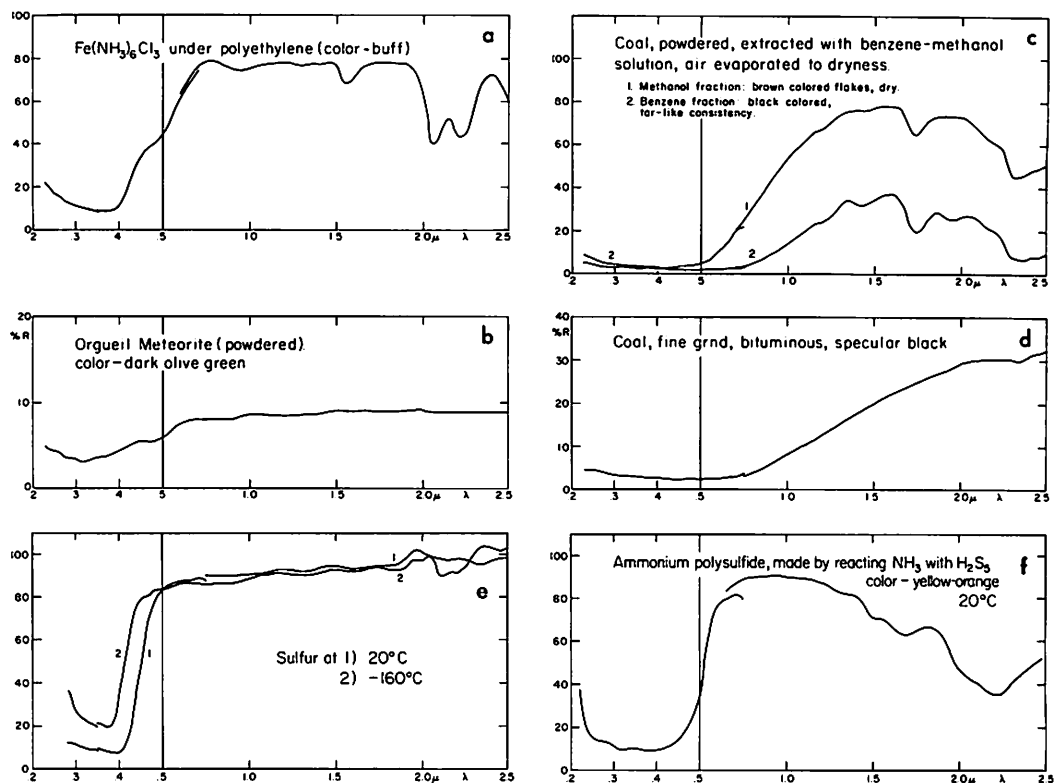


Figure 3

differently. When cooled to liquid-nitrogen temperature, sulfane still retains its *yellow* color, though not as intense as at room temperature. It should be noted that the transmission spectrum of Figure 1d is of a very thin layer, one drop squeezed between quartz plates, pale yellow in color. A thicker layer would cause the absorption wing to shift into the visible region of the spectrum.

Figure 3f shows the reflection spectrum of ammonium polysulfide at room temperature. The material was produced by reacting gaseous ammonia with liquid sulfane, H_2S_5 , cooled by powdered dry-ice. Some decomposition of sulfane occurred in the reaction, namely, bubbles of H_2S were observed. The ammonium polysulfide produced ranged in color from yellow to a red-brown, russet color. The material was ground in a mortar. Unfortunately, the grinding process resulted in the apparent destruction of the russet polysulfide, especially as the dry-ice sublimed and the material was warmed up. The final product was an orange-yellow powder at room temperature, apparently quite stable. In the spectrum of Figure 3f it is evident that the ultraviolet and visible absorptions of polysulfide have increased in intensity, such that the absorption at 0.65 μ has been lost in the long-wavelength wing of the polysulfide absorption. The ammonium ion absorptions in the IR are somewhat subdued versus the deeper absorptions of Figure 1. This is due to two sources: first, there is some elemental sulfur present with the polysulfide; second, the molar fraction of ammonium ion decreases as the polysulfide ion increases the length of the S chain.

3. Conclusions

The spectra here reproduced fill a need to identify constituents of planetary surfaces and cloud layers. Caution must be utilized in making unequivocal identifications of planetary materials on the basis of solid or particle spectra alone. As can be seen in the illustrations, solids of different chemical composition can exhibit similar reflection spectra. On the other hand, there are many features that are truly diagnostic and can indeed furnish tentative identifications. This is true especially for the bands of coordinating compounds in metal complexes, and for the peculiar absorptions of the ammonium polysulfides.

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REFERENCES

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