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Spectral Reflectance (0.4 - 5.0 μm) of Sulfur Related Compounds and Mixtures

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ABSTRACT

The objectives of this study were to study and to quantify (1) the spectral properties of sulfur-related compounds and materials, (2) the effects of thermal history, temperature and mixing ratios on the spectral properties of these materials, and (3) the application of these results to the Jovian system, in particular, the surfaces of Io, Europa and Amalthea, and the chromophores in the Jovian atmosphere.

This study was originally intended as a 24-month study but on the advice of NASA was reduced in objective and funding to cover only 12 months at only half the funding.

Major results of this study include: (1) a study of how sulfur deposition affects the band strengths in various silicates, (2) a study of how the ultraviolet absorption band of sulfur is affected by dilution in ice, and (3) the application of these two sets of experimental studies to Io, in the case of silicate band strengths, and Europa, as in the case of sulfur dilution in ices.

1. INTRODUCTION

Sulfur is ubiquitous in the inner Jovian system. The source of this sulfur is the Jovian satellite Io. This fact, in combination with the peculiar spectral properties of the satellite, argues for a sulfur-rich Ionian surface. Some of this sulfur spreads outward to Europa, perhaps coating the surface with a thin veneer of sulfur or, perhaps, combining with the water molecules in the surface to form a sulfur or sulfur dioxide impregnated ice layer.

This report covers the two major areas of research that have been covered under this grant. First I describe the research results of experiments done with sulfur coatings on silicates with application to Io. Second I describe the results of experiments performed to determine the effects of sulfur concentration in ice on the strength of the ultraviolet absorption band.

2. SULFUR DEPOSITION ON SILICATE

The surface of Io is certainly sulfur-rich but the form that the sulfur takes on the surface, pure sulfur, sulfur silicate mixtures or sulfur compounds has not been determined. Furthermore, it is not clear which surface morphological units, i.e. flow-like features, can be ascribed to silicate or sulfur volcanism. On the basis of comparisons with the spectral properties of cooled sulfur and the morphology expected for sulfur flows Pieri, et al. (1985) argue for the presence of pure sulfur flows particularly near Ra Patera. Others argue on the basis of morphology and the physical strengths of rock and sulfur that many of the morphological features must be silicates.

One of the few methods available for resolving the controversy is the spectral reflectance properties of the flow-C like features. It has been suggested that the spectral reflectance (0.4 to 5.0 microns) may be able top resolve this issue since sulfur is relatively featureless at wavelengths greater than 0.5 microns whereas mafic silicates can have charge transfer absorptions between 1 and 5 microns. Also, silicate flows tend to be much darker ($r_N < 0.1$) at wavelengths > 0.5 microns than sulfur and most sulfur compounds. It seems reasonable that silicate flows could be identified by either low reflectance or silicate absorptions. The spectral properties of mixtures of silicates and sulfur have been investigated by Gradie and Moses (1985). These studies have shown that under certain conditions of thermal history and silicate to sulfur ratios that the spectral properties of some regions on Io can be matched with the results of Voyager imaging.

An important problem that must be addressed is the effect that the predicted, relatively large resurfacing rate (0.1 to 10 cm/yr) will have on the spectral properties of basalt and sulfur since blanketing by pyroclastics from local vents may be a very effective method of masking or modifying the spectral characteristics while maintaining the morphological identity of the surface. If sulfur is ejected from vents and fumaroles, then sulfur could cover and mask the spectral properties of a basalt flow. Likewise, silicate ash ejected from silicate volcanism can cover and spectrally mask sulfur deposits and flows. This situation is analogous in many respects to the problem of contrast reversal on the Martian surface caused by windblown dust (Wells, et al., 1984).

One measure of the effectiveness of blanketing by sulfur dust is the degree to which a layer (gm/cm^2) can degrade the spectral contrast in mineral absorption bands. Laboratory experiments were made to examine this issue in some detail. In these particular experiments, Hawaiian basalt and the spectrally active mafic minerals olivine and pyroxene observed over a wavelength rang of 0.7 to 2.5 microns were covered with layers of sulfur (particle size < 10 microns) of varying thickness.

Figure 1 illustrates the results for the experiments with olivine. In this case a sulfur layer of only 200 $milligrams/cm^2$ is sufficient to mask completely the spectral contrast in the 1 micron band (spectral contrast is defined as the reflectance at 1.8 microns relative to the reflectance at 1.1 microns). From these experiments and experiments with other substrate materials, it is apparent that for the suggested Ionian resurfacing rates and the implied upper regolith density of 0.3 gm/cm^3 (Nash, et al., 1985), a silicate surface can be spectrally masked in as little as 30 days. The actual time needed to spectrally mask the surface will depend upon the proximity to and the activity of the vent or fumarole. Given the ubiquitous and constant nature of Ionian volcanism it seems unlikely that a silicate spectral signature will be seen on Io except in the freshest, most active flows.

3. SULFUR DISSOLVED IN ICE

Spectral unit maps of Europa show a marked hemispherical asymmetry in the ultraviolet (Johnson, et al., 1983); Nelson, et al., 1986. The cause of this asymmetry is thought to be ion bombardment effects, perhaps involving S or SO_2 as well as the effects of micrometeorites. To test this theory, samples of water ice were irradiated with SO^{++} ions at the University of Virginia KeV Ion Accelerator Facility under separate funding. The spectral (0.25 to 4.5 microns) properties of these samples were then measured at the Planetary Geosciences Division to be compared with the physical properties observed for Europa. It was found to be difficult to implant enough sulfur to be seen in the reflectance spectrum in a reasonable time by the irradiation technique without physically altering the sample. Experiments with physical mixtures of sulfur and water-ice produced in our laboratory were then attempted to bracket the range of sulfur concentration that could be detectable in the reflectance spectrum before doing more irradiation experiments.

A study of the ultraviolet spectral reflectance of sulfur dissolved in water-ice and a water-ice analog, frozen at 77 K, was completed using an ultraviolet spectrometer and a vacuum environmental chamber. Water-ice/sulfur mixtures (Figure 2) suffer from the inability of water to dissolve large quantities of sulfur on the molecular level due to the strong "polar" (electronic) nature of the water molecule. The water-ice study was limited to determining the spectral detectability of micron- sized sulfur grains in water-ice. It appears that micron-sized sulfur grains become spectrally visible at a concentration of 0.1 milligrams/^{3} (see Figure 4).

To study the spectral detectability of sulfur molecules dissolved in an ice, a water-ice analog, a 1:2 mixture of pentane and cyclohexane (PcH), was used. This mixture has the advantage of being spectrally similar (but not identical) to water-ice at 77 K, i.e., highly transparent to light in the spectral region 0.25 to 0.6 microns and the advantage that it can dissolve sulfur as dispersed S_8 rings (Meyer, et al., 1971). Samples were prepared by dissolving a measured amount of sulfur in PcH solvent, freezing the mixture in liquid nitrogen, grinding the ice to a particle size < 1 millimeter, and then measuring the sample under vacuum at 77 K in an environmental chamber.

The spectral reflectances of these PcH-sulfur mixtures are shown in Figure 3 where the reflectances (normalized to at a wavelength of 0.6 microns) are plotted with respect to the UV channels measured. The spectral reflectance of the solvent (PcH) alone shows an absorption at 0.29 microns which is not present in the water-ice but this feature does not affect the interpretation of the overall effect caused by varying the concentration of sulfur.

Figure 4 illustrates how the band strength [measured as r(0.60)/r(0.30)] of the broad sulfur ultraviolet absorption (two centers at 0.26 and 0.28 microns corresponding to the $E_1 <- A_1$ electronic transition) changes with varying concentration of sulfur. Also, we show in Figure 4 the effects of micron-sized sulfur crystals suspended in water-ice as a function of sulfur concentration.

Several conclusions have been reached from these ultraviolet spectral studies. First, the large changes in the spectral contrast found in and around strong absorption bands such as in sulfur can affect the interpretation of the presence or absence of the absorbing material. This effect occurs for both micron- sized crystals of sulfur as well as sulfur dissolved as S8 molecules. Interpretation of spectral reflectance measurements of Europa, Ganymede, and even Io should take this effect into account.

A second important conclusion deals with the interpretation of the nature of the 3% ultraviolet absorption reported by Lane, et al. (1981) for Europa (see below). This absorption, seen in the ratioed IUE spectra of the leading and trailing hemispheres of Europa is interpreted as S-O bands in a water-ice matrix originating from sulfur ion implantation. A concentration of 2 x 10^{16} molecule of SO_2 per cm^2 is required to produce a 3% absorption. Based upon the experiments described above, it is estimated that a concentration of 10^{15} to 10^{16} sulfur atoms as S8 rings dissolved in water-ice would produce the same 3% absorption. This latter point brings into question the uniqueness of the conclusion of Lane, et al. (1981) concerning the form but not necessarily the presence of sulfur in the water-ice on Europa.

Finally, sulfur/water-ice mixtures and sulfur/PcH-ice mixtures have been shown to provide important constraints on the spectral reflectance properties of materials relevant to the study of the icy Jovian satellites. These materials can be studied easily in the laboratory and can provide a sound basis for more complex studies of sulfur ion implantation.

4. SULFUR IN THE JOVIAN SYSTEM: PLASMA BOMBARDMENT

Reflectance spectra of the icy satellites of the outer planets have been interpreted as exhibiting features produced by magnetospheric ion and or/dust bombardment. One striking confirmation of the magnetospheric ion modification is the observation of a UV band detected by IUE on the trailing hemisphere of Europa which Lane, et al. (1981) identified as an SO band produced by sulfur ions from the Io plasma torus. In addition, Clark, et al. (1983) showed that the average ice grain size in the regolith is determined, in part, by magnetospheric ion sputtering, as indicated by the 1.04 micron water band on the inner Saturnian and icy Jovian satellites. In fact, the very source of the heavy ions in the inner solar Saturnian magnetosphere is determined by sputter removal of material from the satellite surfaces (Johnson, et al., 1986) indicating that this bombardment must remove the reflecting layer in times which are short on geologic scale.

Morrison and Burns (1976) originally ascribed the well- observed hemispherical asymmetry in the visible reflectance spectra of Europa to magnetospheric ion bombardment and this interpretation was re-enforced by the Voyager images (Johnson, et al., 1983). However, the estimate of the UV band depth by Lane, et al. (1981) and the analysis by Clarke, et al. (1983) of comparative ice grain size were the first quantitative tests of this hypothesis. Recently, Nelson, et al. (1986) analyzed the spatial dependence of the normal albedos obtained from the Voyager reflectance data on EUropa in the 0.35 micron (UV), 0.41 micron (VI), 0.48 micron (BL), and 0.59 micron (OR) bands each having a width of about 0.03 microns. These albedos appeared to exhibit a striking, nearly cosine dependence on latitude related to the fact that Europa is rotationally phased-locked to Jupiter. The minimum normal albedo in every band in the Voyager reflectance measurements occurs on the trailing hemisphere, consistent with the maximum in the magnetospheric ion bombardment (Sieveka and Johnson, 1981). By contrast the maximum in the dust flux would be on the leading hemisphere (Shoemaker and Wolfe, 1982). However, Nelson, et al. (1986) noted that the latitudinal variations could not be compared to the magnetospheric ion flux in any simple quantitative way. In addition, the observed latitudinal variations suggested to both authors that more than one ice contaminant affected the spectra.

We have studied the possibility that the exogenic effects are predominantly caused by the plasma bombardment and have shown that an absorption band occurs at 0.35 microns which is closely connected with ion implantation distribution (Johnson, et al., 1987). This quantitative comparison with the latitudinal variation in the ion flux is the first to confirm the hypothesis that magnetospheric bombardment determines the occurrence of this spectral feature. Implanted co-rotating sulfur ions have very small penetration depths, about 0.01 micron, with a distribution in range of equivalent size (Cheng, et al., 1986). These depths are much smaller than the grain diameters estimated by Clark, et al. (1983). Such ions will, therefore, tend to build-up a layer of implanted sulfur atoms on the outer surface on the ice grains. The less frequent, but more penetrating ions might produce a distinct effect (Sieveka and Johnson, 1982) as individual distributed S atoms in an ice matrix. However, the gyroradii are relatively small compared to the radius of Europa for these ions also, the implantation distribution is not very distinct from that for the co-rotating ions. Detailed modelling of the implantation flux now required as the UV absorption results in Figure 5 indicate that the absorbing impurity occurs on the leading hemisphere also even allowing for uncertainties in the subtraction above. This may be due to the plasma inflow to this hemisphere or to sputter transport of the UV absorbing species (Sieveka and Johnson, 1982). The ratio of the leading to trailing, disc-averaged band depths of the implantation feature, obtained using the dependence in Figure 5, is about 0.08. This ratio is consistent with the limits placed by Lane, et al. (1981).

In addition to implantation, water ice is effectively sputtered by the incident plasma. Clarke, et al. (1983) attribute grain size differences on the trailing and leading hemispheres to preferential sputter erosion of the smaller grains. In the process of sputtering water ice H_2 and O_2 are created efficiently. The H_2 so formed predominately escapes Europa's gravitational field whereas the O_2 may form a tenuous atmosphere or recondense on the surface, depending upon the local temperature (Johnson, et al., 1982) giving an O2 contribution to the UV. In addition, net loss of H would imply that the plasma ions are implanted in a slightly oxidizing surface, hence, implanted S is likely to predominantly form S-O bonds (SO, HSO, SO_2) rather than, for instance, H_2S, although the latter can occur by a direct insertion.

If sulfur continues to be implanted in the surface layer of the grain, the sulfur containing molecules can accumulate. Therefore, if the grains are not altered or mixed with underlying fresh ice, in a time scale fast compared to the molecular segregation, S-S bonds can also form (i.e., S_2O or S_2) due to incident ion bond alteration and thermal agitation.

Analysis of the Espat (Effective Single Particle Thickness) allows for a very rough estimate of the effect of impurity absorption and grain size. Although the analysis of the spectra versus latitude presented by Johnson, et al. (1987) is not unique, it is self consistent, to first order, and consistent with constraint obtained from other observations such as grain size, ion implantation distribution, and coloration (reddening) of species typically found in the outer solar system. The UV absorption band occurs in a wavelength region having a number of plausible molecular species but as definite identification is not possible.

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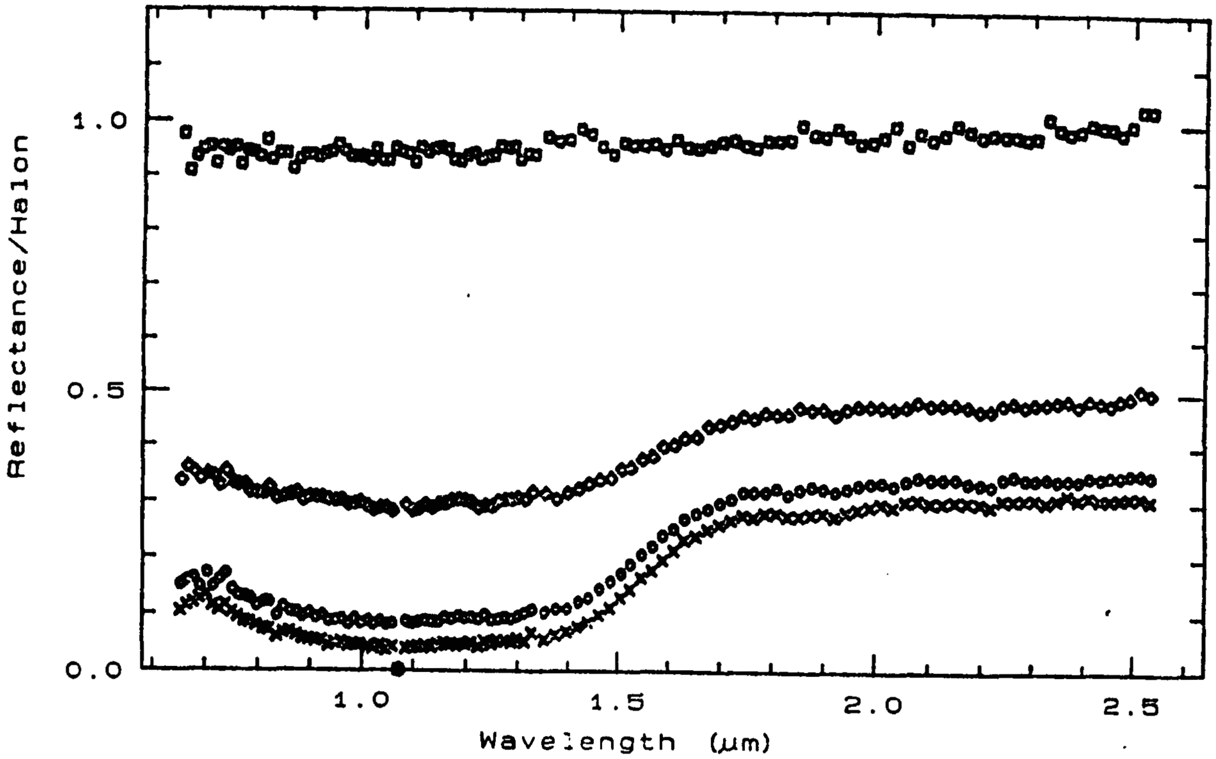

FIGURE 1. The spectral reflectance of olivine (particle size <1 mm) for several coatings of sulfur dust of different thicknesses. The lower curve is pure olivine (washed, Green Sand Beach, Hawaii), the upper curve is pure sulfur dust.

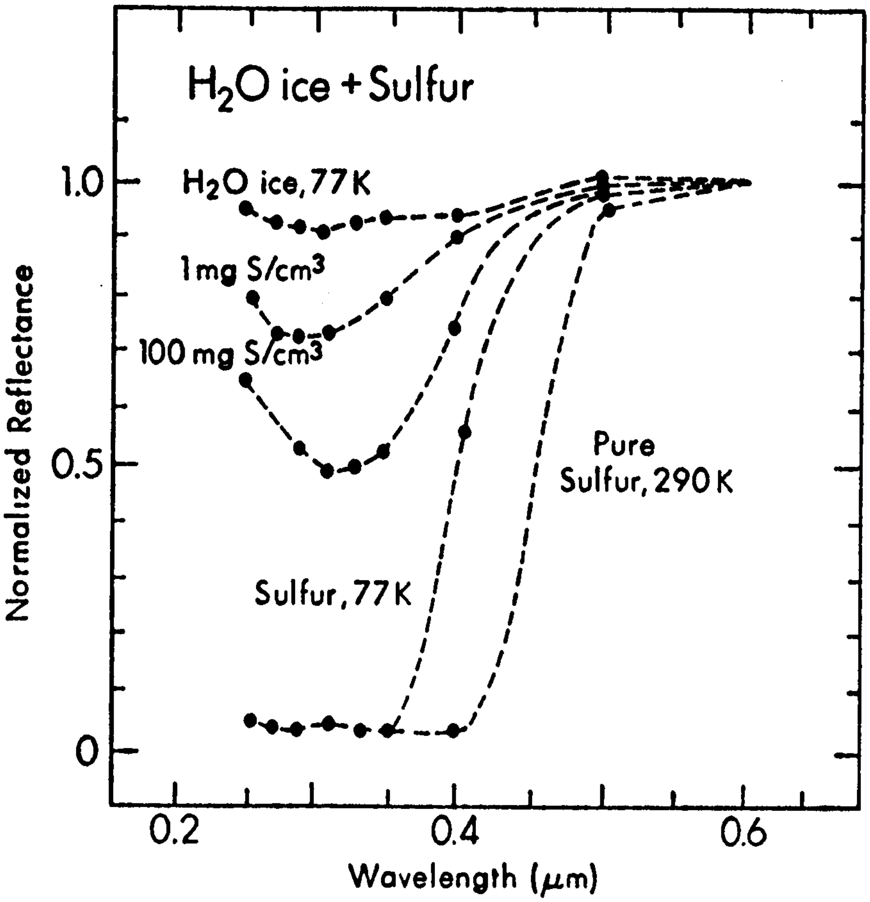

FIGURE 2. The normalized spectral reflectance of water-ice/sulfur mixtures. Samples were prepared by crushing frozen mixtures. Each sample (except for pure S at 290 K) was measured at 77 K under vacuum.

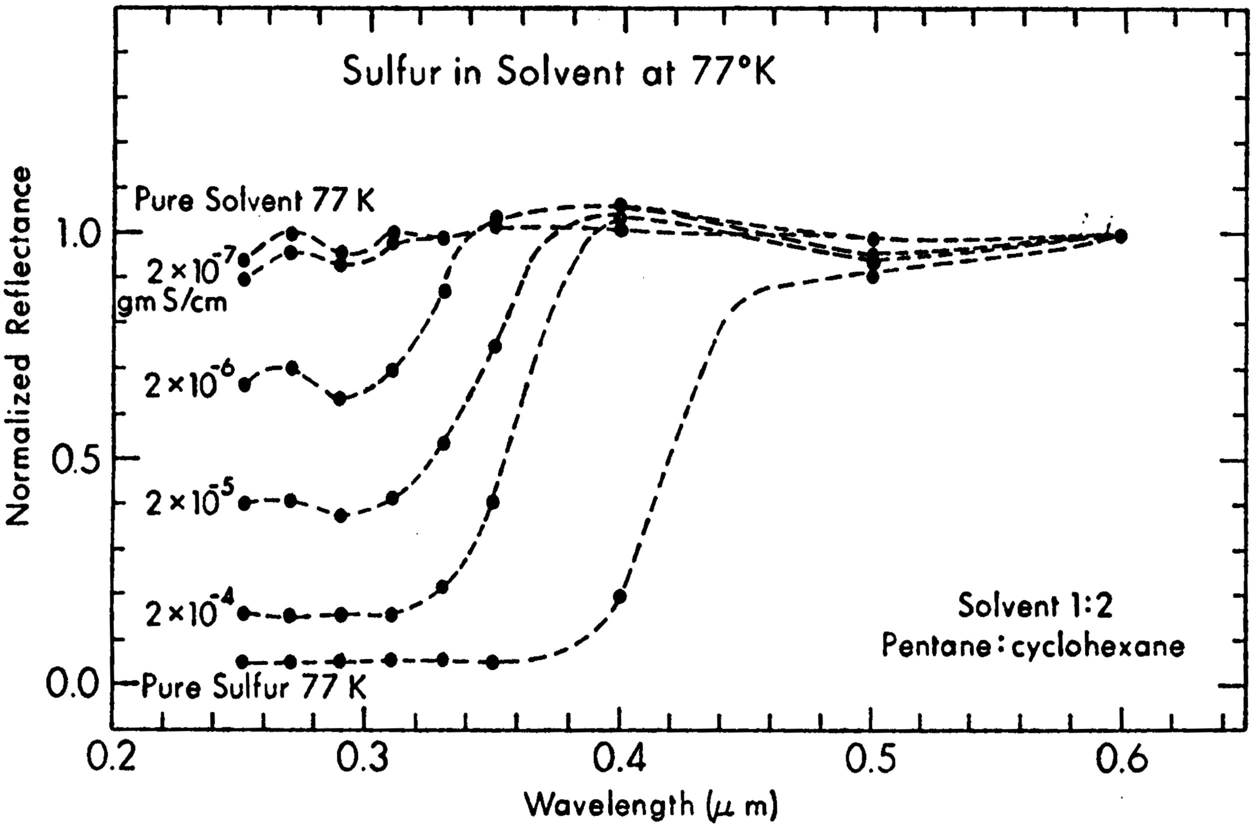

FIGURE 3. The normalized spectral reflectance of various concentrations of sulfur dissolved in a 1:2 mixture of pentane and cyclohexane. All samples were prepared by crushing the ice mixture and measured at 77 K under vacuum.

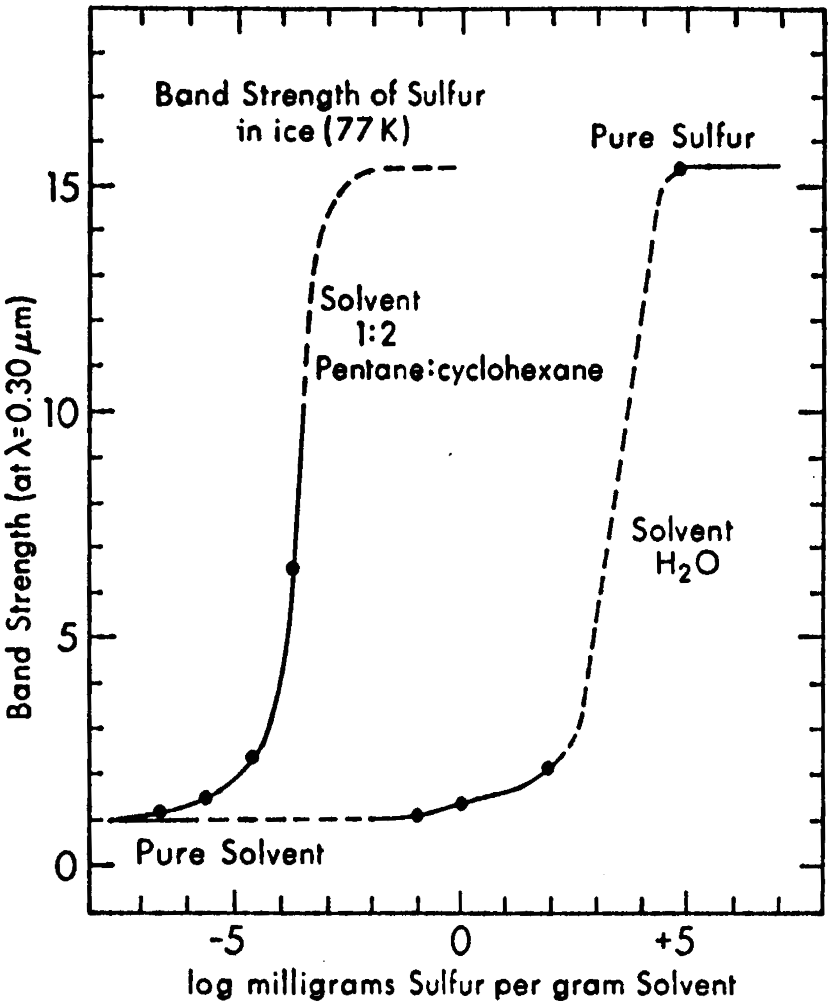

FIGURE 4. The "band strength" of the 0.28 micron absorption of sulfur dissolved in pentane-cyclohexane-ice or suspended as micron-sized grains in water-ice.

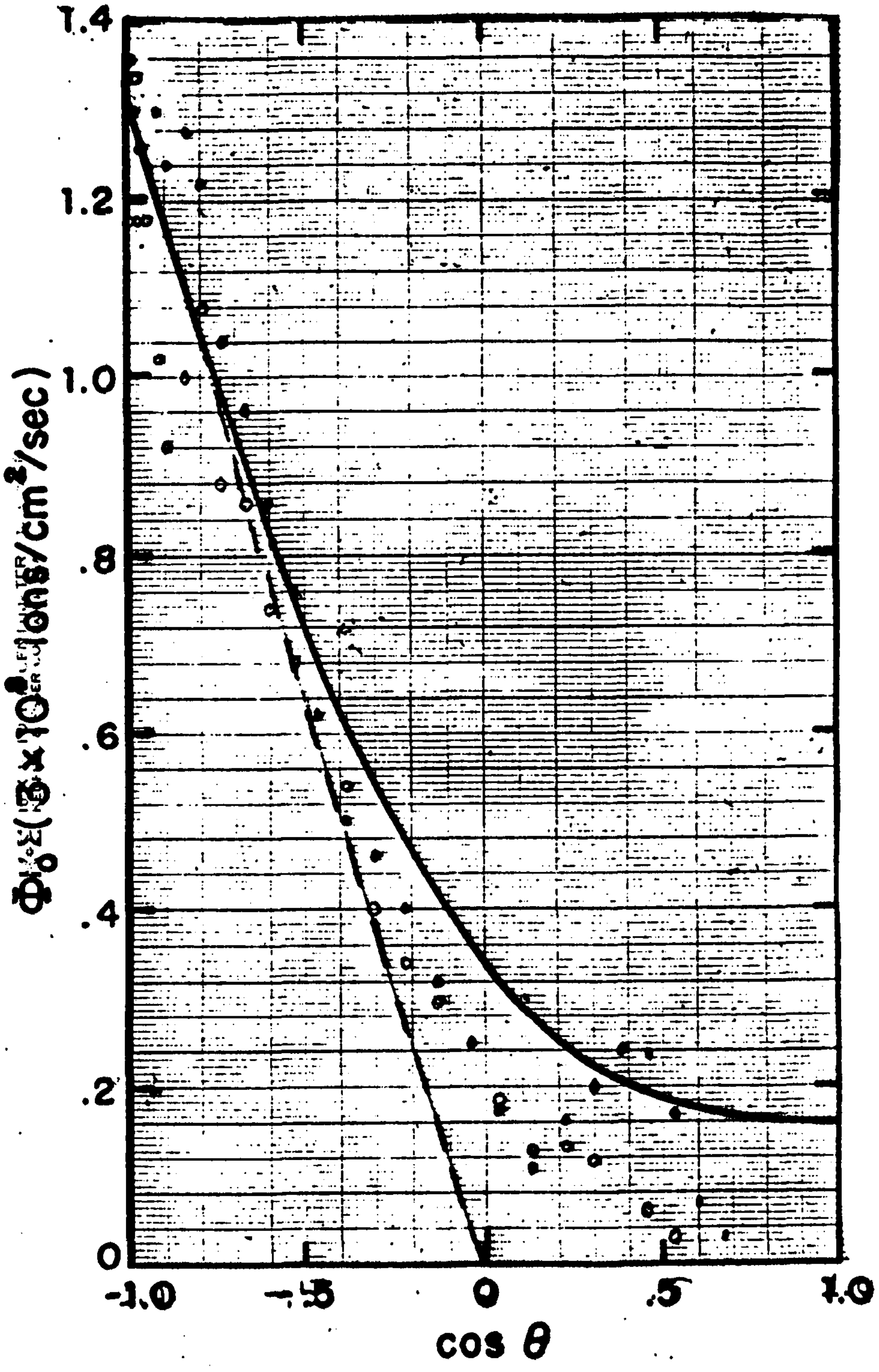

FIGURE 5. Solid line: flux of sulfur ions to the surface of Europa versus cos(theta); plasma treated as a co-rotating gas (10 S ions/cm3) at a temperature 100 eV and (1 S ion/cm^3) at a temperature of 30 keV. Dashed line: simple cos(theta) dependence on the trailing hemisphere (i.e. small gyroradius, no inflow limit, normalizing anti-apex to the above). Open circle: UV/OR ratio of W (single particle scattering albedo) for bright terrain with average value near cos(theta) = 1 (about 3.28) subtracted at each theta. Dark circles: same as above for dark terrain (about 3.81).