

MINOR CONSTITUENTS IN PLANETARY ATMOSPHERES:

ULTRAVIOLET SPECTROSCOPY FROM THE

ORBITING ASTRONOMICAL OBSERVATORY

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ABSTRACT

Orbiting Astronomical Observatory data between 2000 Å and 3600 Å, obtained by the Wisconsin Experimental Package objective grating scanning spectrometer, are used to set upper limits to the abundances of many minor constituents in the atmospheres of Mars, Jupiter, Saturn, and Venus.

I. INTRODUCTION

Because of the large absorption cross-section of electronic transitions, ultraviolet spectroscopy has considerable appeal for the study of planetary atmospheres, providing an opportunity to search for trace constituents with abundances of one ppm or less. On the other hand, because of the increase of Rayleigh scattering towards short wavelengths, the effective penetration of ultraviolet photons into the planetary atmosphere may not be very deep, resulting in ultraviolet sampling of only the outer parts of the planetary atmospheres. In the present paper we present the results of a search for such trace constituents in the atmospheres of Mars, Jupiter, Saturn and Venus from observations carried out for this purpose by the Wisconsin Experimental Package (WEP) of the Orbiting Astronomical Observatory OAO-2.

The data were obtained with an objective grating scanning spectrometer, providing usable data between 2000 and 3600 Å.

A description of the instrumentation has been published by Code *et al.* (1970). A treatment of the planetary observations and their reduction, used in the following analysis, has been presented and discussed in general terms by Wallace, Caldwell and Savage (1972). Our analysis takes their results and derives specific upper limits on atmospheric constituents and some further interpretation of the observations in terms of simple atmosphere models, a division of labor agreed upon during our association as guest investigators on OAO/WEP. The albedo curves are reproduced here as Figures 1 and 2 for Mars at two different phase angles; Figure 3 for Jupiter; Figure 4 for Saturn (this is a brightness ratio of Saturn to the Sun rather than a geometric albedo); and Figure 5 for Venus. The reliability of this observational material is discussed in the above-cited article. The resolution achieved by the WEP scanner between 2000 and 3500 Å was slightly better than 25 Å. Wallace *et al.* (1972) describe the necessary modifications of this resolution required in cases where there were gaps in the data resulting from non-overlapping scans. Most of the gases in which we are interested exhibit continuous rather than discrete absorptions, in which case such refinements are unnecessary. We assume throughout that a 20% deviation from the continuum would be readily detectable ($\tau \approx 0.1$). Accordingly any gas producing an absorption with a total equivalent width ~ 3 Å should be easily detectable at these wavelengths. Under these assumptions, abundance upper limits are readily derived with an absorption model and a systematic culling of the literature on absorption cross-sections. In all cases we have adopted a simple reflecting layer formalism. We feel that greater sophistication is unjustified and unnecessary at present (Regas and Sagan 1970a, 1970b; Sagan and Regas 1970).

II. MARS

In Figures 1 and 2 are displayed the OAO data on the Martian geometric albedo as a function of wavelength for two phase angles, with representative probable errors also shown. The spectra seem to be in good agreement with the ground-based photometry of Irvine, Higdon and Ehrlich (1971). The results of two measurements made by the WEP broad band photometers are also indicated. While there is a bare hint of structure in the 3200 to 3600 Å region, there is no convincing evidence of absorption anywhere in the spectrum. The data are consistent with a pure Rayleigh atmosphere of carbon dioxide at a surface pressure of about 5.5 mb — or somewhat lower pressures if there is a significant aerosol component to the scattering. However, the Rayleigh component alone does not provide useful compositional information. An earlier indication (Wallace 1970) of a 2600 Å OAO absorption feature, ascribed to ozone,

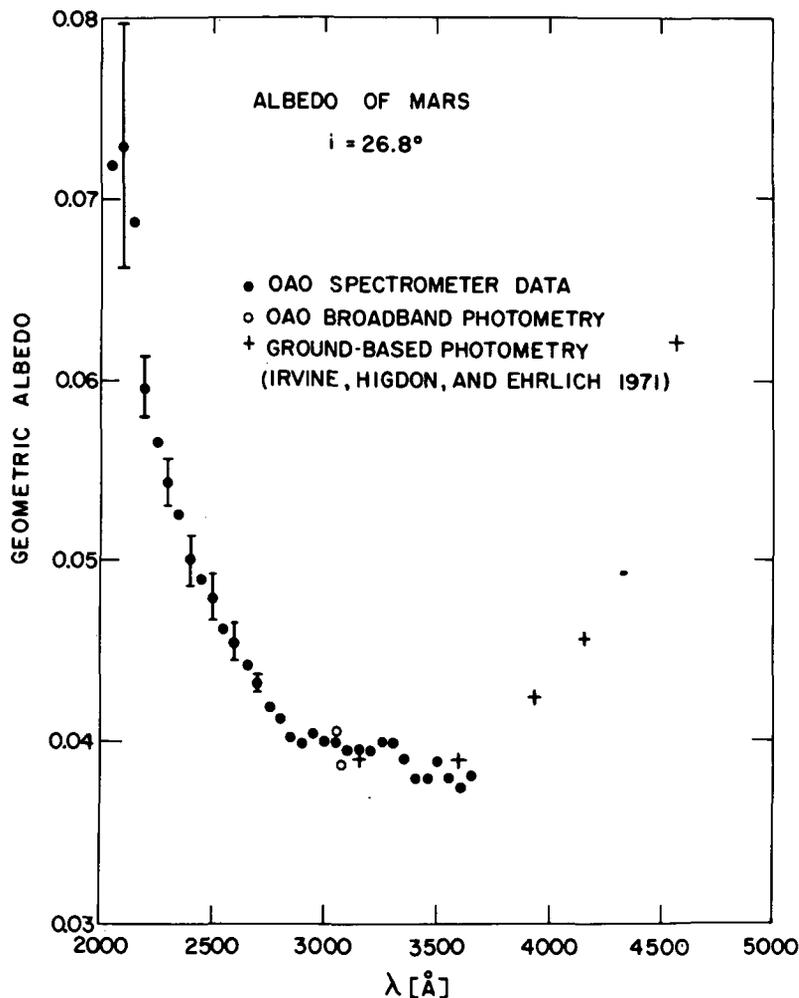


Figure 1.—Geometric albedo of Mars as a function of wavelength, at phase angle 26.8° , as determined by the Wisconsin Experimental Package of OAO-2. The large increase in reflectivity to short wavelengths is consistent with Rayleigh scattering by a CO_2 atmosphere of 5.5 mb surface pressure. Observational details of this and the following figures are discussed by Wallace, Caldwell & Savage (1972).

has disappeared in the present photometric reduction. Since the OAO observations are made of the integrated planetary disc the present observations neither confirm nor deny the report by Barth and Hord (1971) that ozone absorption is present preferentially over the south polar cap.

Upper limits in cm-atm to the abundances of a number of gases of interest are shown in Table 1. Our OAO upper limits,

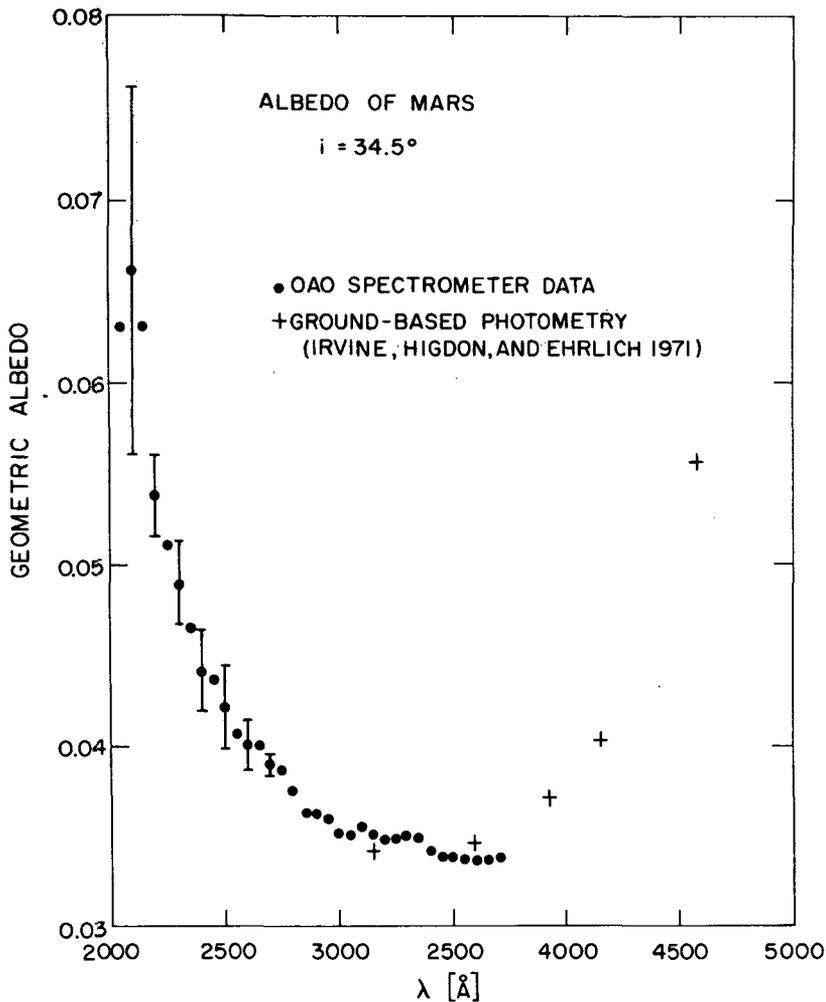


Figure 2.—Geometric albedo vs. wavelength of Mars at 34.5° phase angle.

based on a model atmosphere composed entirely of 80 m-atm of CO_2 , are there compared with limits set by other techniques. The last column is our best estimate on abundance upper limits from all methods. We stress that values we report here are very conservative, corresponding to a 20% deviation from continuum reflectivities. For some materials such as H_2S the ultraviolet upper limits are much below infrared upper limits because of the large ultraviolet absorption coefficient. In other cases, for example HCl and especially O_2 , our ultraviolet wavelength range does not extend to short enough wavelengths, and infrared results are more sensitive.

As in the case of the Earth, the low upper limits on such

Table 1. Upper Limits on Minor Constituents in the Martian Atmosphere

Molecule	OAQ	Other Methods	Best Limit
O ₃	2×10^{-4} cm-atm	3×10^{-3} cm-atm	(1) (2) 0.025 ppm
O ₂	500	20	(3) 2500
C ₃ O ₂ monomer	1×10^{-2}	3×10^{-3}	(1) 0.5
		2×10^{-2}	(4)
COS	1×10^{-2}	4×10^{-3}	(1) 0.6
		2×10^{-1}	(4)
SO ₂	1×10^{-3}	4×10^{-3}	(1) 0.1
H ₂ S	1×10^{-3}	27	(1) 0.1
		3	(4)
NO	1×10^{-1}	5×10^{-3}	(1) 0.7
NO ₂	1×10^{-3}	2×10^{-3}	(1) 0.1
		2×10^{-2}	(4)
		8×10^{-4}	(5)
N ₂ O ₄	3×10^{-3}	4×10^{-2}	(4) 0.4
N ₂ O		1×10^{-2}	(1) 18
NH ₃	1×10^{-3}	3×10^{-3}	(1) 0.1
HCN		4×10^{-1}	(1) 50
CH ₄		3×10^{-2}	(1) 4
C ₂ H ₂		4×10^{-1}	(1) 50
		2	(4)
C ₂ H ₄ , C ₂ H ₆		4×10^{-2}	(1) 6
Benzene and its derivatives	1×10^{-3}	4×10^{-2}	(1) 0.1
HCHO	1×10^{-1}	5×10^{-3}	(4) 0.6
CH ₃ CHO and higher aldehydes	1×10^{-1}	7×10^{-2}	(4) 0.8
(C ₂ H ₅) ₂ S ₂ etc.	1×10^{-1}		12
CH ₃ COCH ₃ and higher ketones	1×10^{-1}		12
Purines, pyrimidines and their derivatives	3×10^{-4}		0.03
HCl	1×10^{-1}	4	(1) 0.1
		1×10^{-3}	(4)

Upper limits for other gases, largely halides, are set in Ref. (1).

References for Table 1

- (1) Horn, McAfee, Winer, Herr, and Pimentel (1972)
- (2) Barth and Hord (1971)
- (3) Margolis, Schorn, and Young (1971)
- (4) Beer, Norton, and Martonchik (1971)
- (5) Marshall (1964)

potential volcanic effluents as H₂S and SO₂ might be particularly interesting in view of the extent of geologically recent volcanic activity reported by Mariner 9 (Masursky *et al.* 1972). However, the rate of ultraviolet photodissociation of H₂S and SO₂ on Mars is such that these results place no useful limits on the possibility of a few sites of contemporary volcanism on the planet. The Mariner 9 ultraviolet spectrometer (Barth *et al.* 1972), which is able to obtain comparable ultraviolet spectra, but in the vicinity of the observed calderas, may be able to shed more light on the problem. Somewhat more stringent upper limits than shown in Table 1 on the abundance of oxides of nitrogen on Mars can be set from the photochemistry (Sagan, Hanst and Young 1965).

The upper limits on formaldehyde, acetaldehyde and other aldehydes are of some interest. Such materials were first suspected on Mars from infrared spectroscopy in the 3.5 μ region (Sinton 1957, 1961; Colthup 1961), but subsequent investigations show that the reported absorption features are almost certainly spurious (Rea, O'Leary and Sinton 1965; Beer, Norton and Martonchik 1971). However, Hubbard, Hardy and Horowitz (1971) have found formaldehyde and acetaldehyde to be among the products synthesized by long wavelength ultraviolet irradiation of simulated Martian atmospheres above a silicate substratum. From the results reported by Hubbard *et al.* (also Hubbard 1971, private communication), a quantum yield of several times 10^{-6} results. The ultraviolet photon flux at Mars, capable of synthesizing aldehydes in this way, is very roughly $5 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$, implying a production rate $\sim 10^{10}$ molecules $\text{cm}^{-2} \text{ sec}^{-1}$. The photolytic photon flux is approximately the same with an absorption cross-section for photolysis of the order of $3 \times 10^{-20} \text{ cm}^2$. The mean time to photolysis of an aldehyde molecule is then $\sim 10^4$ sec, or a few hours. The expected steady state concentration is therefore $\sim 10^{15}$ molecules cm^{-2} , several orders of magnitude below the OAO limit exhibited in Table 1. With even the OAO upper limit on aldehyde abundance, the ultraviolet optical depth of these molecules is less than 0.1, implying no self protection against ultraviolet photolysis. The short aldehyde lifetime in the Martian solar ultraviolet radiation flux implies that,

like H_2S , it cannot be found very far from its site of production. The quantum yields, while large by ordinary photochemical standards, are still so small that there does not appear to be any prospect for an immediate ultraviolet test of the production of aldehydes on Mars by the mechanism of Hubbard et al. (1971). However, the possibility of large quantities of aldehydes in the Martian surface material does seem to be excluded: each time a molecule leaves the surface it is photolyzed, producing a situation not unlike evaporation into a vacuum. We have also listed in Table 1 abundance upper limits on some other organic molecules, such as alkyl sulfides and acetone, materials much less likely than aldehydes on a priori ground to be present on Mars.

Our upper limits on the abundances of the carbon suboxide monomer permits us to comment on the suggestion by Plummer and Carson (1969) that the carbon suboxide polymer $(C_3O_2)_n$ may be a principal coloring material of the Martian surface. The monomer vapor has been studied in the ultraviolet by Bell et al. (1966), who found that an effective path of the order of 0.25 cm-atm led to detectable absorption at 2600-2700 Å. The results of Smith et al. (1963) suggest ~0.4 cm-atm. The absence of this feature in our OAO data suggests an upper limit of 30 ppm for the monomer. A more sensitive upper limit of 200 μ -atm (2.5 ppm with our model) has been set by Beer et al. (1971) from their infrared interferometry and of 30 μ -atm by Horn et al. (1972) from the Mariner 1969 infrared spectrometer. This independent confirmation of the low upper limit on the abundance of the monomer unfortunately has little direct bearing on the fundamental question of whether the polymer is present in large abundance on the Martian surface. The molecular structure of the polymer is not a simple repetition of the monomer. Accordingly the vapor pressure of monomer above polymer should be very low and may follow a temperature dependence different from the usual reciprocal exponential law. From our literature survey, no definite detection of the monomer above the polymer could be found, but recent experiments place an upper limit to the C_3O_2 mixing ratio above ultraviolet-irradiated polymer under Martian conditions at $\sim 10^{-5}$ (Khare, Khare and Sagan 1972), or $\sim 10^{-4}$ mb. The upper limits on the monomer abundance found by Beer et al. (1971) correspond to a partial pressure $\sim 2 \times 10^{-5}$ mb, and by Horn et al. (1972) $\sim 3 \times 10^{-6}$ mb. We must conclude that the vapor pressure above the polymer on Mars will be below the observational limits given. Accordingly spectroscopic searches for the monomer are poor indices of the existence of the polymer. Such tests also must take account of the ultraviolet photolysis of the monomer, following arguments similar to those presented above for the aldehydes. The residual reflection spectrum of the planet in the ultraviolet, after the contribu-

tion of the atmosphere is removed, could also be used to provide information on surface materials. However, many samples of $(C_3O_2)_n$ do not show the characteristic 2600 Å absorption feature of the monomer, and the ultraviolet reflectivity of the polymer appears to be strongly dependent on its mode of formation (Smith *et al.* 1963, Khare *et al.* 1972). The absence of an absorption feature in these wavelength regions is not a convincing demonstration of the absence of carbon suboxide polymer on the surface. The monomer absorption at 2600 Å mimics moderately closely the absorption in the same wavelength region of ozone; accordingly it is barely possible that the results of Barth and Hord (1971) apply to C_3O_2 , and not to O_3 .

Another gas of some interest is HCl. Here again (Table 1), our data complement those of Beer *et al.* (1971) who find an equivalent upper limit of 0.1 ppm, an order of magnitude more sensitive than our results. These limits are of significance because HCl has been detected on Venus (Connes *et al.* 1967) where the mixing ratio is quoted as 0.6 ppm. Thus the present detection threshold for this gas in the Martian atmosphere is comparable to the abundance which is identified in the atmosphere of Venus, especially because of the chance that substantial quantities of CO_2 reside in the north polar cap of Mars. The Martian atmosphere may be deficient in HCl relative to Venus. However, because of the possibility of the preferential trapping of HCl and its compounds both as condensates and as clathrates in the Martian polar caps, and as chlorides in the epilith, such a discrepancy cannot yet be considered established. Since both atmospheres were presumably formed by an outgassing process similar to that which occurred on Earth, real differences in composition provide clues to differential planetary atmospheric evolution. For this reason it seems especially worthwhile to attempt an improvement in the HCl detectivity.

III. JUPITER

The OAO Jupiter spectrum is displayed in Figure 3 where the spectrophotometric and broad band photometric results are compared with the ground-based spectroscopy of Younkin and Münch (1963), and the ground-based photometry of Hopkins and Irvine (1971). The decline from long to short visible wavelengths, corresponding to the generally reddish or yellowish coloration of Jupiter, is reversed at about 3000 Å. The spectrum exhibits a slight rise to about 2500 Å and a falloff towards shorter wavelengths. The general decline from long visible wavelengths to 3000 Å is due to chromophores, probably not in the gas phase, whose identification is still under discussion (see, e.g., Sagan 1971a). The general rise from 3000

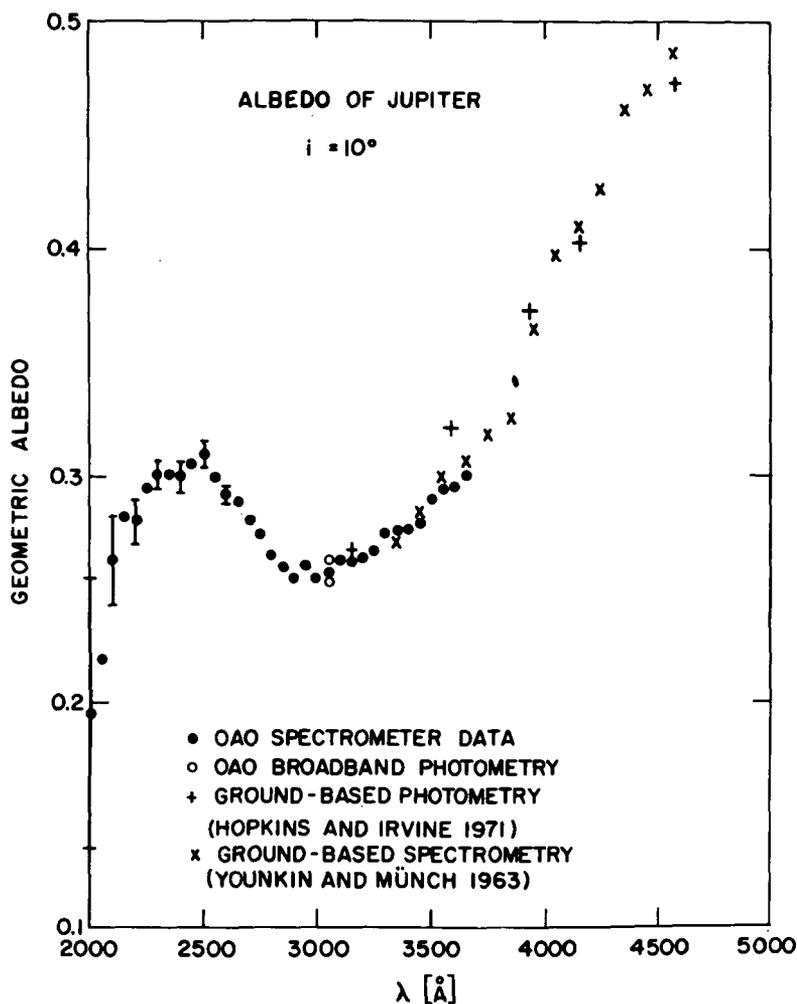


Figure 3.—Geometric albedo vs. wavelength of Jupiter at phase angle 10° . The increase in reflectivity short of 3000 \AA is attributed to 5 km-atm of H_2 ; the decline shortward of 2500 \AA to $\sim 50 \text{ } \mu\text{-atm}$ of NH_3 .

to 2500 \AA is consistent with Rayleigh scattering by $\sim 5 \text{ km-atm}$ of H_2 . The decline shortward of 2500 \AA is consistent with absorption by $\sim 50 \text{ } \mu\text{-atm}$ of NH_3 . But these quantitative estimates must be regarded as quite uncertain, and even such qualitative attributions as the decline at short wavelengths to absorption by ammonia must be regarded as conjectural. What seems quite well established, however, is that the solar radiation reflected in the near ultraviolet from Jupiter arises from a much higher atmospheric level than the radiation observed at long visible and infrared wavelengths, a conclusion in agreement with previous interpretations of such spec-

tra (see, e.g., Greenspan and Owen 1967; Anderson *et al.* 1969).

Vapor pressure limitations furnish our principal reason for attributing the 2100 Å absorption feature to NH₃, other than the fact that we know this gas to exist on Jupiter. We still lack the spectral resolution to distinguish NH₃ from H₂S absorption at these wavelengths, and we cannot be completely certain of the relative importance of solid and gaseous NH₃ in causing the observed absorption, the solid being especially likely to contribute at the shorter wavelengths (Dressler and Schnepf 1960).

A conceivable alternative interpretation of this spectrum is that, superposed on a broad general decline in reflectivity from visible to ultraviolet wavelengths, is a broad absorption feature centered at 2900 Å. In this interpretation we look so high in the atmosphere in the ultraviolet that the Rayleigh scattering contribution is dominated by the broad absorption feature. But this model runs into serious difficulties precisely because at such high altitudes and therefore low temperatures there are no likely candidate absorbers to produce the broad absorption feature. The most successful category of such absorbers would be the aldehydes; roughly 1 mm-atm of formaldehyde, plus the same quantity of acetaldehyde, could produce a broad absorption feature of this sort, but the vapor pressure and ultraviolet photolysis time scale, as presented above for Mars, as well as the absence of the aldehyde precursor molecule, water, at these altitudes, makes this hypothesis quite unlikely. Accordingly, we opt for an explanation in terms of Rayleigh scattering and short wavelength absorption.

Except for the short wavelength decline, here attributed to ammonia, no other absorption features are in evidence. In Table 2 are compared the OAO ultraviolet upper limits on constituents, relative to 5 km-atm of H₂, with ground-based infrared upper limits on a number of molecules, based on the work of Owen (1969) and Cruikshank and Binder (1969), as related to 80 km-atm of H₂ by Sagan (1971a). The differences in ammonia mixing ratios, like the differences in H₂ abundances, reflect the smaller depth of penetration of ultraviolet compared to infrared photons into the Jovian atmosphere. Alkyl sulfides are produced in simulated Jovian environments if initial H₂S is present (Sagan and Khare 1971). The upper limits for benzene and its derivatives derived here are of the same order as the abundance of benzene predicted under conditions of quenched thermodynamic equilibrium in the Jovian atmosphere (Lippincott *et al.* 1967). Since the molecules are expected to be produced under non-equilibrium conditions, it is not implausible that they should be secularly variable with abundances hovering around 10⁻⁸ - 10⁻⁹. A similar remark probably applies to purines and pyrimidines. Because many of these constituents are readily photolyzed in the ultraviolet

Table 2. Mixing Ratios for Minor Constituents on Jupiter

Molecule	OAO UV	Ground-Based IR
CH ₄		$\sim 6 \times 10^{-4}$
NH ₃	$\sim 1 \times 10^{-8}$	1.2×10^{-4}
H ₂ O		6×10^{-7}
H ₂ S	$< 6 \times 10^{-9}$	$< 3 \times 10^{-6}$
C ₂ H ₂		$< 5 \times 10^{-7}$
C ₂ H ₄		$< 2 \times 10^{-5}$
C ₂ H ₆		$< 3 \times 10^{-5}$
HCN		$< 6 \times 10^{-7}$
HCHO	$< 2 \times 10^{-7}$	
CH ₃ CHO and higher aldehydes (C ₂ H ₅) ₂ S ₂ , etc.	$< 2 \times 10^{-7}$	
CH ₃ COCH ₃ and higher ketones	$< 2 \times 10^{-7}$	
Benzene and its derivatives	$< 5 \times 10^{-10}$	
Purines, pyrimidines and their derivatives	$< 2 \times 10^{-10}$	
HCl	$< 6 \times 10^{-8}$	

we would not expect to see them in significant abundance at these high altitudes. In addition, simple atmospheric models suggest temperatures on the order of 115°K or less at the base of the atmospheric region probed in these ultraviolet wavelengths. Such low temperatures place serious constraints on the presence of vapor phase complex molecular constituents. Studies of the constituents expected at thermodynamic equilibrium (Greenspan and Owen 1966; Lippincott *et al.* 1967; Lewis 1969) show no molecules other than hydrogen, helium, methane and ammonia expected in this region of the atmosphere. Likely non-equilibrium products, such as simple hydrocarbons and nitriles (Sagan and Miller 1960; Lippincott *et al.* 1967; Woeller and Ponnamparuma 1969; Sagan and Khare 1971) do not absorb at these ultraviolet wavelengths. When water vapor is introduced into such experiments, aldehydes are produced (Sagan and Miller 1960; Sagan and Khare 1971), but no water vapor is expected at the altitudes probed at these ultraviolet frequencies. The upper limits on aldehyde abundances ~several ppb are consistent with these expectations.

The best hope of more useful ultraviolet spectroscopic determinations of minor constituents in the Jovian atmosphere is from a flyby or orbiter ultraviolet spectrometer able to resolve the disc of Jupiter. The non-uniform distribution of optical frequency chromophores across the Jovian disc should continue to be characteristic of the planet in the ultraviolet. A variety of evidence suggests that the disturbance re-

sponsible for the Great Red Spot propagates very high into the Jovian atmosphere and that the chromophores responsible for its characteristic coloration may be located at least in part at high altitudes (Sagan 1962; Owen and Mason 1969; Sagan 1971b). It would be most interesting to determine whether characteristic ultraviolet absorption features are associated with the GRS, but a firm test of this hypothesis requires good spatial resolution. It is a remarkable curiosity that none of the ultraviolet spectra of the integrated disc of Jupiter to date have been obtained when the GRS is near the planet's central meridian. Our best hope in detecting disequilibrium products and simple organic molecules at the low temperatures which apply to the ultraviolet is when they are entrained in solid particles — presumably ammonia — circulating up from greater depth. The fact that we do not see a very large increase in reflectivity towards shorter wavelengths, as expected from the near infrared abundances of hydrogen, indicates that the ultraviolet reflectivity is indeed dominated by such cloud particles. It is exactly such a situation which may be responsible for the color of the GRS.

The absence of absorption features other than the general decline short of 2500 Å is consistent with other recent data (Kondo 1971; Anderson *et al.* 1969), and inconsistent with the early reports of a discrete absorption feature near 2600 Å in rocket spectra by Stecher (1965) and by Evans (1965). This absorption is of particular interest because the two categories of molecules proposed to explain it — benzene and its derivatives (Greenspan and Owen 1966; Owen and Greenspan 1968) and purines and pyrimidines and their derivatives (Sagan 1968) — are organic molecules whose presence in the Jovian atmosphere would have important implications. The difference in results of the 1965 work from that of more recent workers may be due to problems with the solar spectral calibrations employed, but it is at least barely possible that all observations are valid and that the feature is a true secular variable (Sagan 1971b).

IV. SATURN

Here again a significant degradation of the data occurs because of the limited angular resolution of the OAO spectrometers. For Saturn we are forced to observe the rings and the disc together. Because of the difficulty in separating these two components we do not learn much about either. This is a special pity since we know that the Equatorial Belt darkens in the near ultraviolet, and limb brightening along the belt also occurs at these wavelengths (Marin 1968). Furthermore, extension of observations of the rings to shorter wavelengths might help to better define the composition of its constituent par-

ticles. We already have evidence that at least two components (of which water ice is certainly one) are present (Lebofsky et al. 1970).

Unresolved ultraviolet observations of Saturn have been reported by Bless et al. (1968). Three filters were used to isolate 300 Å bandpasses centered at 2800, 2500 and 2100 Å. If the rings are black in the ultraviolet, an upper limit of 25 km-atm for the H₂ abundance in the planetary atmosphere was obtained. The present OAO data are consistent with this interpretation, and the general pattern of the Saturnian ultraviolet spectrum is very reminiscent of that of Jupiter. There is some hint of absorption features at 3000, 3200 and 3400 Å, but we do not believe the reliability of the data warrants any attempt to search for candidate absorbers. If we accept 25 km-atm of H₂, the resulting upper limits are those listed in Table 2 for Jupiter, but with upper limits on mixing ratios reduced by a factor of 5.

The increase of reflectivity short of about 3600 Å is very likely due to Rayleigh scattering; a similar feature appears in the ground-based spectrometry of Younkin and Münch (1963), where the contribution from the ring was very small. The alternative explanation in terms of increased ultraviolet reflectivity by the rings towards short wavelengths seems unlikely, in view of the results of Lebofsky et al. (1970) which indicate a sharp decrease in reflectivity towards the blue and the ultraviolet. While the error bars are large, there does seem to be a marginally significant decrease in reflectivity below 2500 Å. By analogy with Jupiter, we might again anticipate the presence of ammonia absorption. While equivocal results have been obtained, the best recent evidence suggests that ammonia is not detectable on Saturn in the near infrared (Owen 1965). The near infrared upper limit would be ~1-2 m-atm. The amount of ammonia required to account for our ultraviolet absorption is extremely small — 10 to 20 μ-atm, an amount not inconsistent with the vapor pressure curve of ammonia if the relevant regions of the upper atmosphere of Saturn are not below 100°K. In the lower atmosphere of Saturn, ammonia is expected on cosmic abundance grounds, and indeed the microwave spectrum gives a rather clear indication of ammonia absorption (Gulkis et al. 1960; Wrixon and Welch 1970). Uniform mixing ratios ~10⁻⁴ NH₃ in the lower atmosphere, implied by the microwave data, would also be consistent with abundances of a few tens of μ-atm of ammonia in the upper atmosphere under the temperature boundary conditions mentioned above.

Concerning the ring spectrum, pure ammonia ice is, from observations in the 1 to 2.5 μ region (Pilcher et al. 1970), not a significant constituent of the ring particles. Water ice does not significantly absorb in the 2000 to 2500 Å region

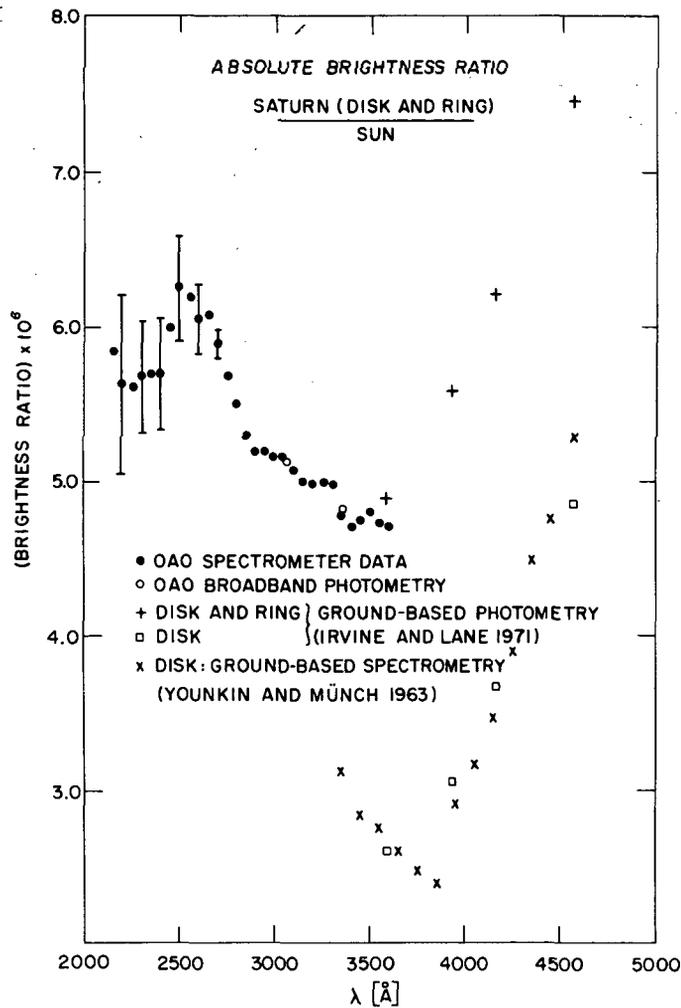


Figure 4.—Absolute brightness ratio of disc plus rings of Saturn as a function of wavelength. The increase in reflectivity shortward of 3500 Å is consistent with Rayleigh scattering by several tens of km-atm of H₂; the decline shortward of 2500 Å is consistent with absorption by a few tens of μ -atm of ammonia.

(Dressler and Schnepf 1960). Other conceivable components of the ring such as NH₄OH might absorb in this region, but the atmosphere will dominate the ring spectrum below 2500 Å; accordingly, ring absorption features should have little effect on the overall spectrum. Separate ultraviolet spectra of the disc and rings — as, for example, obtained by a Saturn flyby — would be of considerable interest.

V. VENUS

Of the OAO data presented in the present paper those for Venus are most uncertain. They have been presented as geometric albedo vs. wavelength in Figure 5 where they have been made to join smoothly to the ground-based photometric results of Irvine (1968). The general character of the spectrum is again similar to that of Jupiter and Saturn. The general decline from long visible wavelengths to 3000 Å is a quantita-

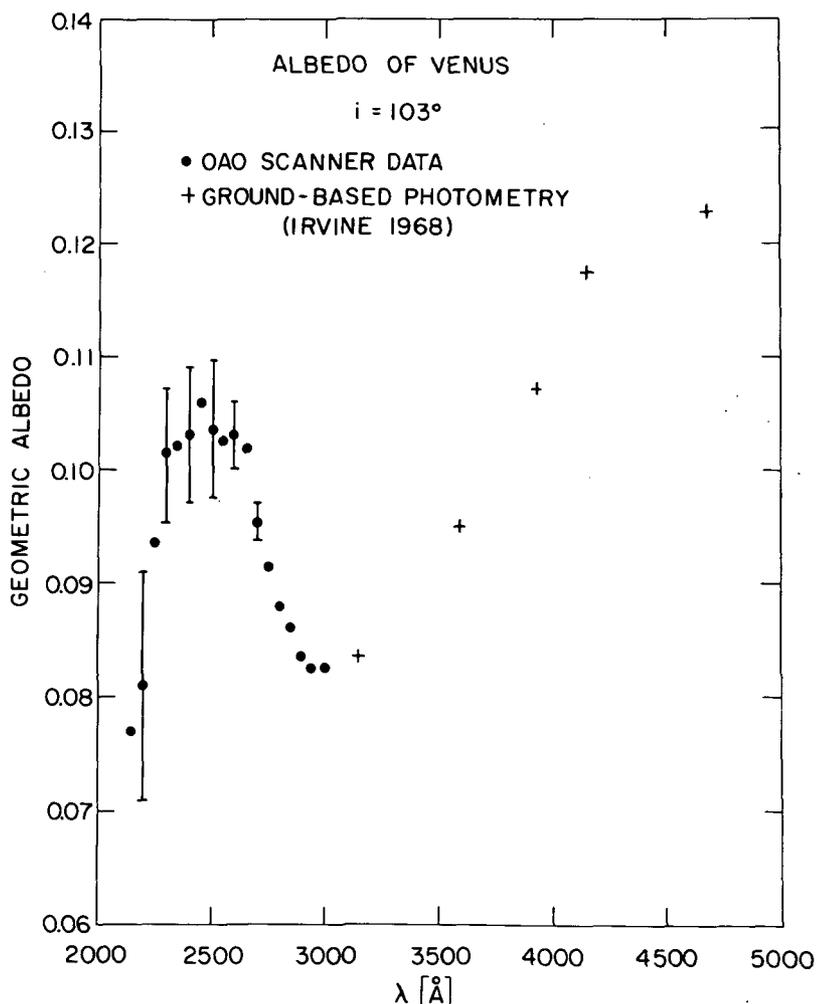


Figure 5.—Geometric albedo of Venus as a function of wavelength at phase angle 103° . The increase in reflectivity short of 3000 Å is consistent with ~ 1 km-atm of CO_2 Rayleigh scattering. The decline in reflectivity shortward of 2500 Å is due to an as yet unidentified absorber.

tive indication of the pale lemon yellow color of Venus. The nature of the chromophores — probably in the Venus clouds — responsible for this absorption remains in dispute. The most natural explanation of the increase in reflectivity between 3000 and 2500 Å is Rayleigh scattering by atmospheric carbon dioxide. Very roughly several km-atm of CO₂ would be required — the correct order of magnitude of the effective amount above the visible clouds. In this interpretation, an additional absorber, operating at wavelengths shortward of 2500 Å would be required.

In the case of Jupiter, we have discussed an alternative explanation, namely, that, in the ultraviolet spectrum, we are looking sufficiently high that no strong Rayleigh component remains. A similar alternative exists for Venus, where we would be observing a broad absorption feature centered at about 2950 Å. Sulfur dioxide has an absorption spectrum of this sort; $\sim 5 \times 10^{-3}$ cm-atm would produce a dip of approximately the observed extent. In some models of atmospheric chemistry decoupled from gas-mineral equilibria (Lippincott *et al.* 1967), SO₂ is expected to be the principal sulfur-containing molecule. But again because of the ultraviolet lability of this molecule (and vapor pressure problems?) we believe the Rayleigh scattering interpretation is more likely to be correct.

In this case upper abundance limits on a number of constituents can be set from the OAO scanner data and are displayed in Table 3. As in the case of Mars, the low upper limits found on the monomer of carbon suboxide and on the aldehydes may again have little to do with the possible presence of carbon suboxide polymer or paraformaldehyde, this time as significant constituents of the Venus clouds. It is of interest that the upper limit for the HCl abundance set by OAO is of the same order as the abundance detected by Connes *et al.* (1967) in the near infrared. However, again because of the vapor pressure and ultraviolet photolysis arguments, it is likely that the HCl mixing ratio as observed in the ultraviolet will be less than that observed in the infrared.

The short wavelength decline in geometric albedo begins in the OAO spectra several hundred Å longward of that implied by the rocket ultraviolet spectrum of Anderson *et al.* (1969). But whether the difference is due to the 27° difference in phase angles between the two observations, to a secular variation in cloud reflectivity, or to undiagnosed observational errors is not known at the present time. Observations at an intermediate phase angle by Jenkins *et al.* (1969) also show the cut-off at shorter wavelengths, thereby weakening the first alternative. Anderson *et al.* attribute their short wavelength absorption edge to CO₂ and HCl. If the OAO data are accurate, CO₂ cannot be responsible for an absorption beginning at 2500 Å although it can play a role in diminishing

Table 3. Upper Limits on Minor Constituents in the
Cytherean Atmosphere
(OAO Estimates Based on ~ 1 km-atm CO_2)

Molecule	OAO Upper Limit	Previous Estimates (1)
O_3	0.003 ppm	0.03 ppm
C_3O_2	0.1	1.
COS	0.1	0.2
SO_2	0.01	0.05
H_2S	0.1	0.3
NO	1.	
NO_2	0.01	0.8
N_2O_4	0.04	
HCHO	1.	
CH_3CHO and higher aldehydes	1.	
CH_3COCH_3 and higher ketones	1.	
HCl	1.	1.
NH_3	0.1	

(1) Tabulated by Anderson *et al.* (1969)
Further upper abundance limits are tabulated by Marov (1972).

the reflectivity at the shortest wavelengths we observe. Possible time-variable contributors to the short wave cut-off include Cl_3^- and HOCl , complexes suggested by Lewis (1972) as likely constituents in an $\text{HCl-H}_2\text{O}$ cloud system. Further integrated-disc ultraviolet spectroscopy of Venus would clearly be a great help in checking these points.

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