FINAL REPORT

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by

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This is the final report for NASA Grant NGR 05-002-116 and describes work carried out during the active period of this grant, January 16 1969 - November 31, 1969. By agreement of the investigators and Stephen Dwornik of NASA, this work was done by Hugh Kieffer. The principal investigator (B. C. Murray) was cognizant of this effort and concurs with the contents of this report.

The context of this study changed during the 8-month period between submission of the proposal and final authorization (May 1968 - January 1969) and in the first part of the grant period.

When the flight opportunity toward which the proposal was oriented did not materialize, it became apparent that the scientific questions about Mars which formed the basis of this study would be largely answered first by other types of investigations. The emphasis of this program was then shifted heavily toward laboratory and telescope observations. An outline of that fraction of the work accomplished on the flights instrument feasibility study is attached.

Toward the end of the grant period, effort was directed toward designing an experiment which reflected the current interests of NASA and which might shed some light on the basic scientific question of the proposal; the composition of martian frosts. This resulted in the proposal of an infrared radiometer experiment for the Viking mission.

Laboratory Program

The study of the spectral reflectance properties of simulated martian frosts was continued under this grant. The laboratory apparatus used has been described by Kieffer (1969). The new laboratory measurements included:

1. Semi-quantitative relation between frost grain size and absorption band widths based on computed line intensities.
2. Assignment of all absorption bands observed, including a suite of previously unreported forbidden transitions in solid CO_2.
3. Determination of the minimum amount of H_2O frost required for high reflectance as a function of wavelength.
4. Determination of the relation between absolute reflectance level and sample inclination and a study of band shape changes as related to theoretical predictions.

These results are published in "Spectral Reflectance of CO_2 - H_2O Frosts" Journal of Geophysical Research, 75, 501, 1970 and are included in Section II. Two laboratory results not included in that publication are described below.

Two absorptions reported over the martian polar cap by the Mariner 7 infrared spectrometer, and first attributed to atmospheric gases, occurred at wavelengths of forbidden transitions in CO_2; one which had been observed in the laboratory frosts. As the other was just longward of the spectral range covered by the laboratory measurements, this range was extended to include the reported position of the second feature. A strong absorption was observed in pure CO_2 solid at 3.33μ, the expected wavelength of the forbidden 011 transition. This result was communicated privately to the Mariner 7 investigators.

Spectra of methane and ammonia frost were obtained in the laboratory in order to check for trace contaminations of the CO_2 frost by these chemicals. A recent identification of ammonia in Saturn's rings was in strong disagreement with the laboratory ammonia frost spectrum. A note on this is in press in Science.

Instrument Development

Lead sulfide (PbS) and Indium Arsenide (InAs) cells were tested in the laboratory for optimum response and time constant. Though InAs has better specifications for defectivity and a shorter time constant, it was found that selected PbS cells, manufactured to be used at ambient temperatures, but used at liquid nitrogen temperature, had a better signal to noise ratio at the appropriate chopping frequency (10 to 30 Hz) than did InAs unless the InAs cells were cooled to liquid hydrogen temperature. As liquid hydrogen was not available at Cerra Tololo nor was 20°K thought to be a workable temperature for an orbiter experiment, PbS cells were used for the subsequent investigations. Following a basic design suggested by Jim Westphal,at Caltech,a set of improved dewars were built and one of these fitted into a double-beam photometer being used by

Tom McCord. This equipment was used for the observations at Cerro Tololo.

Telescope Observations

Observation of Mars were made at Cerro Tololo Observatory during March and May 1969. During both periods, the telescope time was shared between the observing programs of Kieffer, McCord, and Westphal. Two to three nights of both observing runs were allocated to observations of the polar cap. Observations during both periods were subject to a degradation of image quality on the 60-inch telescope due to an alignment difficulty which was not corrected until after our observing time. Observations of the polar cap were made on March 16 and 17 and May 23 and 28.

The method of measuring the polar cap reflectance was to scan at a fixed rate completely across Mars from pole to pole using a one second of arc aperature. A series of narrowband filters covering 0.32 to 2.5μ were used. In addition to spatial scans, some spectra of the north and south limb were obtained by guiding on those points. The south polar region is brighter than the equatorial deserts only shortward of 0.7 microns, as had been suggested by photographic surveys. In the preliminary analysis, the reflected intensity from the south polar cap does not show a minimum at 1.5μ when compared to either the north limb (no cap visible) or a solar type star. This contrasts to the 70% decrease reported at 1.5μ by Moroz (1964) and attributed to H_2O solid. This preliminary analysis suggests that the south polar cap was not covered by solid H_2O at this season (early spring, $L_s = 163°$)

Final reduction of this data is dependent on reduction of calibration observations made by McCord at the same time and not yet available. The support of this NASA grant will be acknowledged in any publication of this data.

An analysis of previous observations of the martian polar caps was continued under this grant. The results are published as "Interpretation of the Martian Polar Cap Spectra" Journal of Geophysical Research, 75, 510, 1970 and are included in Section III.

In the period following the initial proposal to the early phase of this grant, there was a significant decrease in the possibility of an experiment with the objectives described in the proposal being flown to Mars in the foreseeable future. As a result, the emphasis of this work was shifted away from a detailed spacecraft instrument specification. The results of the preliminary design are included in Section IV. The Science requirements and instrument specifications described are nominal. The experiment would be sufficient for identification of frost composition from a spacecraft. The simplest instrument adequate for this experiment is a small operature telescope and a 30 cm Ebert-Fastie fixed prism multi-detector spectrometer. However, it might be desirable to use a single experiment for both frost identification and study of the surface geologic materials, which have inherently the same type, through less intense, spectral features. The only major change in the instrument from the nominal design would be to increase the number of detectors.

IV. Spacecraft Experiment Requirements and Design

The prime constraints on the spacecraft instrument are the scientific requirements of spatial resolution, spectral resolution and intensity resolution. Nominal values of these parameters are developed and used to determine the required size and sensitivity of the instrument.

In the following discussion, clouds are not distinguished from frosts. There are no reliable differences between frost and solid cloud infrared spectra except that spectra indicating sufficiently large grain size would not be compatible with atmospheric suspension.

The major variations in frost spectra are likely to occur at the scale of the ground topography. Thus, in order to look for local frost features, ground resolution on the order of a few kilometers is required.

From the data presented in Section II and the calculated transmission of the martian atmosphere, a set of spectral channels has been selected which have the minimum cross correlation between CO_2 and H_2O from spectra, avoid strong martian atmospheric bands, and include reference channels which measure the reflected intensity adjacent to the CO_2 and H_2O absorptions. These spectral channels are listed in Table 1. Because of the correlation between CO_2 gas absorption in the martian atmosphere and the CO_2 solid absorption, a positive CO_2 solid feature can be detected only at 2.6 microns, correspondingly to a CO_2 lattice combination band. However, the absence of H_2O absorption features when the spectrometer was viewing a frost (indicated by TV coverage) would be strong evidence of a CO_2 frost.

The response of these channels to CO_2 and H_2O frosts for a range of grain size is shown in Figures 1 and 2. The most stringent requirement for intensity resolution is for mixed frosts (see Section II, Figures 3 and 4) where the intensity in the 2.6 and 1.5μ channels becomes critical. On the basis of the laboratory data, a 1% intensity resolution is minimal for this experiment.

The intensity of reflected solar radiation in a given wavelength interval can be expressed as

$$I \doteq \Omega_{\odot} \, w^{*}_{\odot} \, \frac{\mu_o}{\pi} \, \Delta\lambda \, \frac{w}{w^{*}_{\odot}} \, R$$

$\Omega_{\odot}$ = solid angle of the sun at Mars [3×10^{-5} str]

$w_{\odot}$ = flux per unit wavelength (w^{*} = maximum value of w for the source temperature [8000 watts str^{-1} cm^{-2} μ^{-1}])

μ_o = cosine of the angle of incidence

λ = wavelength interval

R = surface reflectance [assumed Lambert]

The values of I for the selected spectral channels with $\mu_o = 1$ and the average reflectance values for Mars are listed in Table 2.

The power incident on the detector will be

$$P = e \cdot A \cdot \Omega \cdot I$$

where e = optical efficiency

A = area
Ω = solid angle
} at any optical element or focus

The noise equivalent power for a photo conductor is

$$\text{N.E.P.} \quad = \quad \sqrt{aB/D}^{\,*}$$

where A = detector area

B = electronics detection bandwidth

D^* = detector detectivity

The noise due to amplification stages can be neglected for PbS detectors. For a spacecraft experiment, it is helpful to express B as a fraction q of the image scan frequency

$$B = q \frac{\omega}{\Omega_p}$$

where Ω_p = telescope solid angle (square)

ω = image angular velocity (determined by spacecraft orbit and altitude)

and to express a in terms of the collection optic parameters.

$$a \quad = \quad \Omega \ A \ f^2 \quad \text{where } f = \text{the } f \text{ ratio at the detector.}$$

Then the signal to noise ratio of the instrument is

$$\frac{S}{N} = \frac{P}{\text{N.E.P.}} = \frac{e \ A \ \Omega \downarrow}{aB/D^*} =$$

$$= \underbrace{W^*_{\odot} \ \Omega_{\odot}}_{\text{Sun}} \ \underbrace{\Delta\lambda \frac{w}{w^*}}_{\text{pass band}} \ \underbrace{\frac{\mu_o R}{\pi}}_{\text{Mars}} \ \underbrace{e \ A^{1/2} \ \Omega^{3/4} \ f^{-1} \ D^* \ q^{-1/2}}_{\text{Instrument}} \ \underbrace{\omega^{-1/2}}_{\text{Orbit}}$$

Representative values are

$\mu_o = .25$ (polar cap)

$R = .5$

$e = .2$ (4 mirrors, 1 window, 1 prism)

$q = .1/2$

$\omega = 4.6 \ \frac{\text{millirad}}{\text{sec}}$ (at 1000 km periapsis of 24-hour orbit)

$D^* = 10^{11}$ (typical for PbS at 195° K in the 1.5 - 3μ range)

$f = 4$ (near the practical limit for spectrometers)

$\Omega = 10^{-6}$ str (corresponds to 1 km surface resolution at periapsis)

$A = 20 \text{ cm}^2$ (5 cm diameter clear aperature)

These are equivalent to a detector area at $3.2 \times 10^{-4} \text{ cm}^2$ and a bandwith of 3.2 Hz. The calculated signal to noise ratio for the 3.1μ channel is 550; the others being greater by the ratio of reflected intensitites (Table 2).

For the observations at Cerro Tololo, the values of the instrumental parameters, apart from the collection optics, were similar to the nominal instrument.

$e = .2$ estimated for 4 mirrors (.9), one filter (.5) and 2 transmission optics (.8) and the atmosphere (.9)

$a = 2.5 \times 10^{-3} \text{ cm}^2$

$B = 1$ Hz

$D^* = 4 \times 10^{11}$

$\Delta\lambda = .05\mu$ at 1.3μ

$A = 1.5 \times 10^{4} \text{ cm}^2$

$\Omega = 2 \times 10^{-11}$ str

The calculated signal to noise ratio is 30. The value actually measured was 18, 60% of that calculated. Considering the uncertainty of the atmospheric and telescope transmission, this is good agreement.

The spectral resolution required could be achieved with a multi-channel Ebert-Fastie prism spectrometer. A 30 cm focal length instrument with a 30% half angle calcium fluoride prism would have a dispersion of .5 μ/mm at its minimum dispersion wavelength of 1.5μ. Assuming a triangular instrumental profile and using .1 mm slits, this would isolate channels .1μ apart as required. For an f-4 system, this requires a 4 cm prism. The data rate of the nominal experiment, assuming 10 bit digitization of the analog output, would be about 320 bits per second.

A detailed analysis of configuration and the corresponding weight volume and power requirements was not made. The instrumental requirements are, however, similar to other planned flight instruments (e.g. the 1975 orbiter water vapor mapping infrared spectrometer).

Table 1

Nominal Spectrometer Channels

Designation	Bandpass (microns)	Detection
1.3	1.25 - 1.35	reference
1.5	1.46 - 1.56	solid H_2O
1.8	1.74 - 1.84	reference
2.5	2.44 - 2.52	reference
2.6	2.58 - 2.64	solid CO_2, reference for H_2O
3.1	3.04 - 3.16	solid H_2O, reference for CO_2

Table 2

Reflected Intensity in the Spectral Channels

Channel	$\Delta\lambda$ microns	λT cm-°deg	$\frac{w}{w^*}$	R	I watt $str^{-1} cm^{-2}$
1.3	.1	.754	.2	.33	4.8×10^{-4}
1.5	.1	.876	.14	.38	3.0
1.8	.1	1.038	.085	.4	2.5
2.5	.08	1.438	.028	.4	.8
2.6	.06	1.512	.025	.4	.73
3.1	.12	1.800	.013	.4	.38

References

Kieffer, H. H., A Reflectance Spectrometer/Environmental Chamber for Frosts, Applied Optics, Vol. 8, No.12, 2497-2500, 1960

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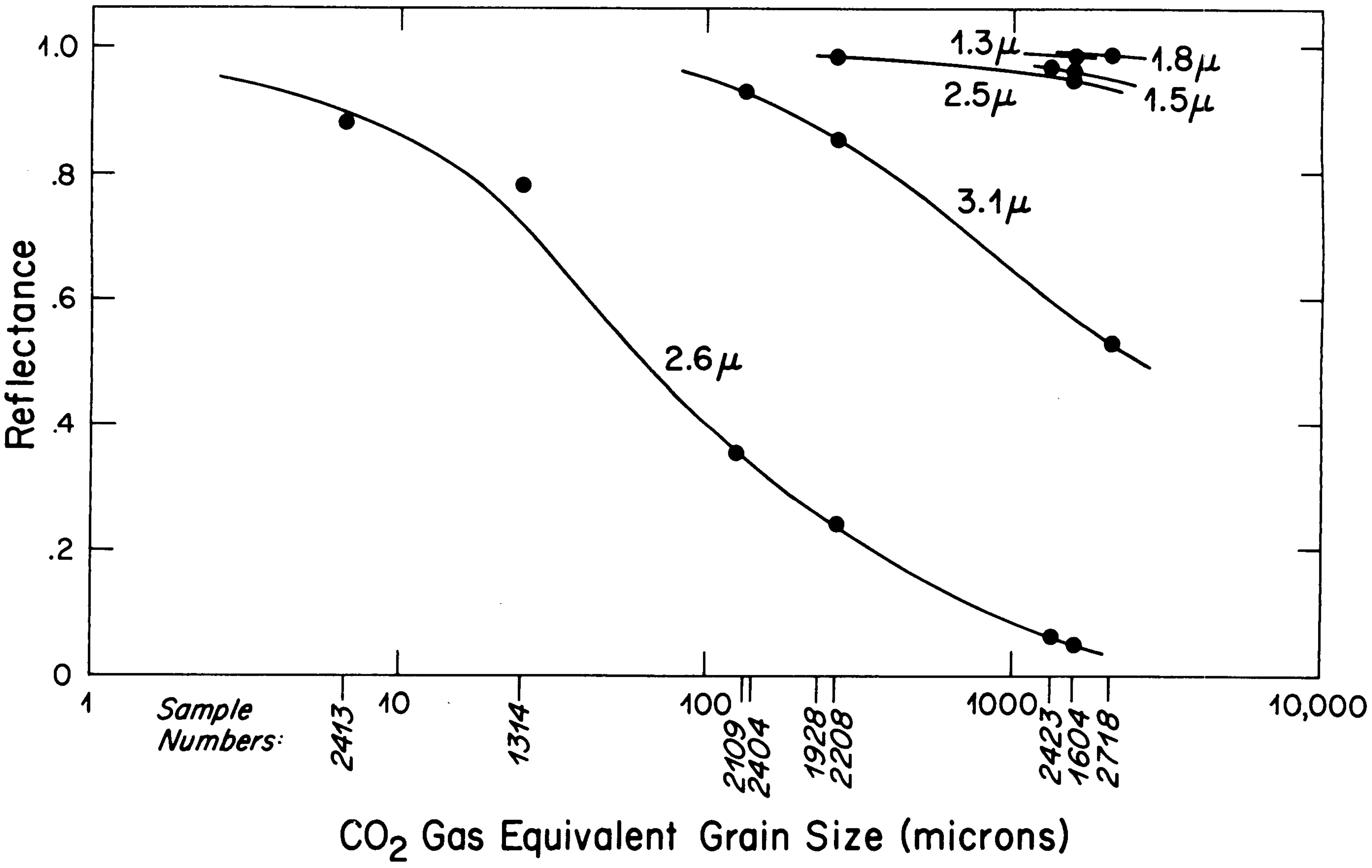

Figure 1. Reflectance versus grain size for CO_2 frosts for the nominal spectrometer channels.

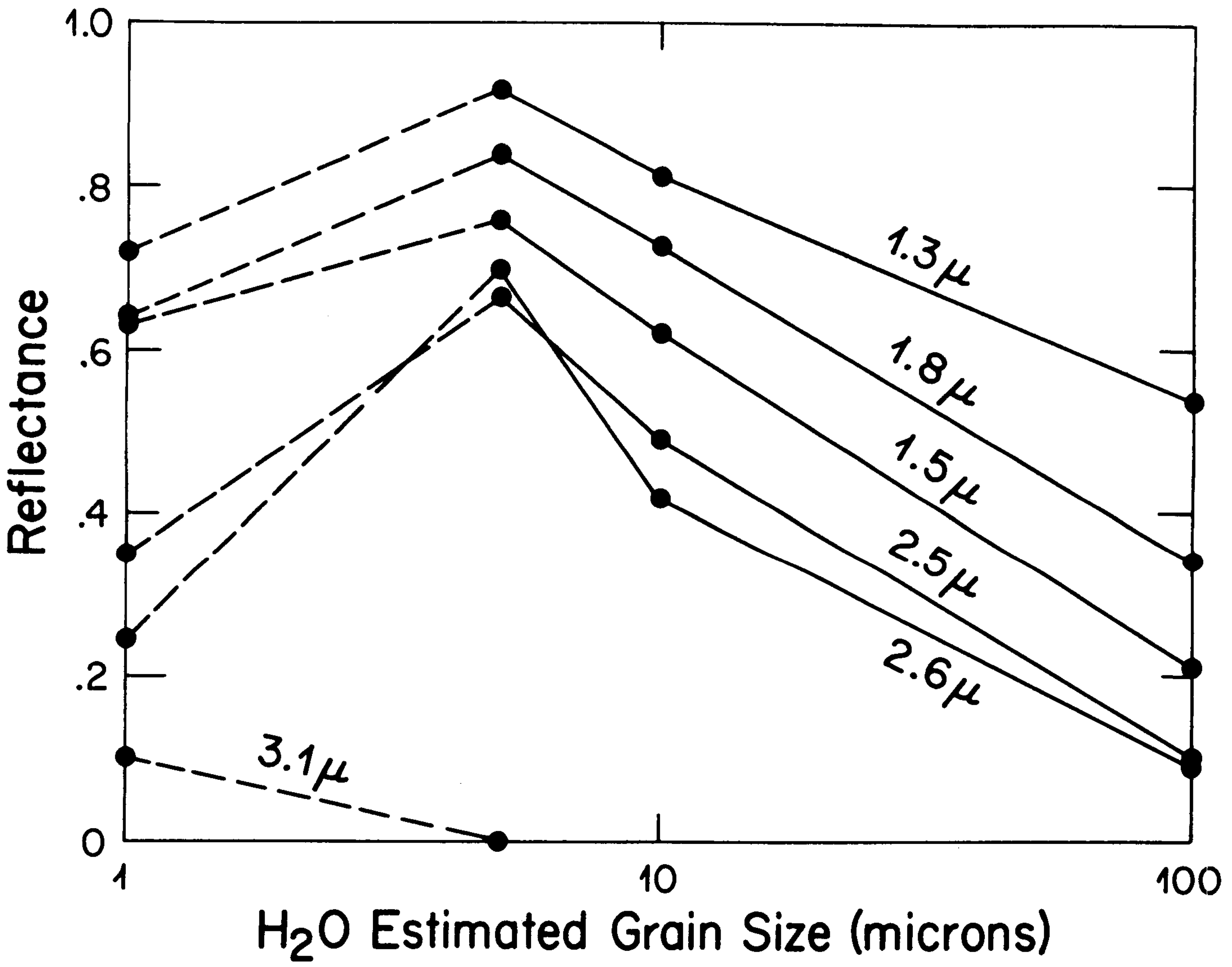

Figure 2. Reflectance versus grain size for H_2O frosts for the nominal spectrometer channels. The grain size of the finest sample (indicated as 1 micron) was below the resolution of the measuring equipment. This sample was probably not optically thick at most of the channel wavelengths.

Section II

SPECTRAL REFLECTANCE OF CO_2 - H_2O FROSTS

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Spectral Reflectance of CO_2-H_2O Frosts[1]

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The spectral reflectance of CO_2 and H_2O frosts grown individually, simultaneously, and sequentially have been measured from 0.8 to 3.2 μ. Contamination and metamorphism were minimized by growing the frosts from high-purity gases in a cold vacuum chamber. CO_2 frosts have generally high reflectance except for strong absorptions corresponding to those in the gas phase and several new absorptions unique to the solid. In contrast, H_2O frosts have overlapping broad absorption bands shifted longward from the gas absorption wavelengths. Small fractional additions of H_2O have pronounced effects on CO_2 frost spectra, but the reverse is not true. The apparent composition of mixed frosts depends on textural scale. A few milligrams per square centimeter of H_2O frost will mask an underlying thick CO_2 deposit.

INTRODUCTION

As part of a study of the Martian polar caps [*Kieffer*, 1968], reflectance spectra from 0.8 to 3.2 μ were measured for a variety of CO_2-H_2O frosts. Most spectral studies of solid CO_2 and H_2O have been of thin film transmission or slab reflectance. The only CO_2 frost spectrum [*Keegan and Weidner*, 1966] is apparently badly contaminated by H_2O. H_2O frost spectra have been obtained by *Plummer* [1969], and the spectral reflectance of laboratory H_2O ice clouds has been measured by *Zander* [1966, 1968]. There are no previous spectral investigations of two-component frosts. The main parameters affecting frost spectral reflectance are composition and textural scale. It was apparent early in the experimental work that the addition of small amounts of H_2O made appreciable changes in the CO_2 spectra, but not vice versa, and consequently, the low H_2O concentration range was studied most extensively. Even frosts grown from the purest CO_2 available in quantity show marked effects due to H_2O contamination.

Grain size (textural scale) is treated only semiquantitatively because of the difficulty in defining and measuring the appropriate size parameters for frosts. The primary interest was to establish the range of spectral variations that could be achieved by changing grain size.

Most spectra were measured with normal incidence and near-normal reflectance. Inclined backscatter, simulating Earth-Mars opposition geometry, was measured for some frosts. Because of the difficulty inherent in observing frosts without altering them, a reflectance spectrometer-environmental chamber was constructed which utilized extremely low incident flux for the spectral observations, allowed

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photography of the undisturbed samples, and allowed mechanical access to the cold frosts. The laboratory apparatus and procedure have been described in detail by *Kieffer* [1969].

METHOD

The samples were grown by allowing a regulated flow of very pure gases into a cold chamber, where frost formed on the interior walls. To attain uniformity of the frost across the area used for spectral measurements on the bottom of the chamber, a non-condensible buffer gas (nitrogen or helium, typically 3 torrs) was let into the chamber before frost growth started. The gases used in the experiments are given in Table 1. The small amount of H_2O in the CO_2 source gas was sufficient to cause major spectral changes near 3.1 μ. To obtain nearly pure CO_2 frosts, an extensive dry ice cold trap was put in the CO_2 gas line, which eliminated most or all of the effects of H_2O contamination. If it is assumed that the H_2O partial pressure was reduced to its equilibrium value in this trap, the resulting H_2O concentration was 0.8 ppm.

The textural scale of the laboratory frosts appears to be closely related to the relative concentration of the condensing gas at the frost surface. The complex dependence of uniformity and textural scale on the directly controlled parameters (substrate temperature, non-condensing gas pressure, condensing gas flow rates, inlet nozzle shape) was determined through considerable experimentation. A wide range of textural scale was achieved by varying these parameters.

Sample growth was usually continued until after the monitored reflected intensity became constant. Trapping of the buffer gas within the frost during growth apparently inhibits any significant size increase of the internal grains with time. A very thin layer of fine frost often occurred at the top of the deposit, representing the condensible gas remaining in the chamber when the gas flow was shut off. The samples were kept sufficiently cold after growth ceased to prevent any noticeable metamorphism.

The physical form and dimensions of the frost were determined by photography of the sample both in situ and on a microscope cold stage. The textural scale listed for the specimens is the dominant (or range of) path length through the grains visible with 5-μ resolution. The total heat and radiation load on the sample was about 4×10^{-3} watt cm^{-2} when the sample gas flow was turned off and typically 35×10^{-3} watt cm^{-2} during sample growth, due primarily to latent heat release. The radiation from the monochromator was negligible at all times.

TABLE 1. Source Gas Composition (ppm)

	CO_2	H_2O	N_2
Max. total impurities	100*	1	30
CO_2	...	0.2	
H_2O	17†	...	4
N_2	20.1	0.2	...
O_2	9.2	0.1	8
H_2	15*	<0.1	
CH_4	0.6		
NH_3	<0.2		
Total hydrocarbons	<1		

Notes

† Reduced to 0.8 by cold trap.

CO_2, J. T. Baker instrument grade, measured composition.

N_2, J. T. Baker pre-purified, stated maximum impurities.

H_2O, vacuum distillation at ambient temperature of triply distilled water, calculated limits.

* Stated maximum impurities.

Spectral reflectances were measured from 0.8 to 1.65 μ with a set of eighteen discrete interference filters spaced uniformly in wavelength (0.05 μ) and with bandwidth approximately equal to the separation (average 0.04 μ, range 0.016 to 0.074 μ). The measurements from 1.56 to 3.15 μ utilized a continuously variable interference filter with bandwidth 1½% of the wavelength. The response of the spectrometer was calibrated against a smoked MgO surface through a more stable intermediate reference surface, which was observed before or after each scan of a frost specimen. The error of the spectra vary with wavelength from approximately 1 to 5%, being greatest at 0.8 μ and at the extremes of the range of the continuous filter. Most observations were made with an incidence angle of 0° and a reflectance angle of 12°. The angle listed for the inclined measurements is the angle of incidence, the angle of reflectance being 12° less in the same plane.

Results

CO_2 frost reflection spectra. The major absorption features of CO_2 frost, the 2.0-μ triplet and the 2.7-μ doublet, correspond in wavelength and relative intensity to the molecular vibration frequencies observed for CO_2 gas (Figure 1). A pronounced new feature in the solid, the absorption at 2.62 μ, is stronger than the 2.0-μ bands and is easily observed in the finest samples. With increasing textural scale additional features at 1.87, 2.12, 2.85, and 2.90 μ become evident on the wings of the multiplets. Higher overtones, observed for the gas at 1.44 and 1.6 μ, appear only weakly in the coarsest frost samples. The features at 2.28, 2.34, and 3.03 μ are not associated with strong CO_2 vibration bands. The positions of the absorption features observed in CO_2 frosts are given in Table 2. The uncertainty listed is due to both the uncertainty of the wavelength calibration of the spectrometer and the difficulty of determining the position of a weak absorption on the wing of a stronger feature.

Samples of textural scale up to 3 mm were grown. Apart from the 2.0-μ bands, CO_2 frosts have greater than 90% reflectance below 2.5 μ. The lowest reflectance measured for the 2-μ band was 20%. The 2.7-μ band is saturated for frosts of textural scale greater than about 50 μ and has a minimum reflectance of 1%. The continuum level from 2.9 to 3.2 μ is strongly dependent on the amount of H_2O. For 17 ppm H_2O, the absorption at 3.1 μ is about the same as for the 2.62-μ band. For 1 ppm H_2O, the absorption in this region is similar to the strength of the 2.06-μ band. Spectra of commercial dry ice (1-mm round grains) are similar to the spectra of the coarsest frosts grown except for their apparent contamination by H_2O.

H_2O frost reflection spectra. The reflection spectra of H_2O frosts (Figure 2, top) with grain size larger than 5 μ are dominated by broad absorption features at 1.56, 2.04, and 3.0 μ, which correspond to transmission minima at 1.39, 1.88, and 2.69 μ in the gas phase. The 2.9- to 3.2-μ region is saturated for these frosts. Frosts grown in the chamber showed high re-

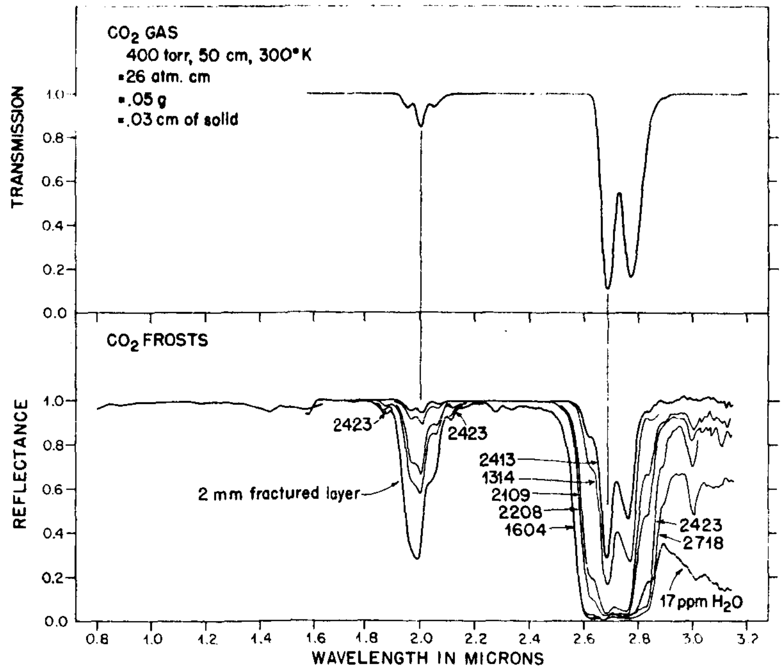

Fig. 1. Spectra of CO_2 gas and frosts. The finest sample precipitated from a cloud. The coarsest samples grew as closely packed columns. A typical example is shown of the low reflectance observed near 3.1 μ for commercial high-purity CO_2.

TABLE 2. CO_2 Frost Absorptions

Observed		Assignment		
λ, μ	ν, cm^{-1}		ν, cm^{-1}	$\Delta\nu$
3.030	3330 ± 15	130	3339	−9 ± 15
2.899	3450 ± 15	021-(Q_1Q_2)	3431	19 ± 15
2.848	3511 ± 15	021-Q_1	3499	12 ± 15
		021 $C^{13}O_2$	3528	−17 + 15
2.768	3613 ± 10	021	3613	0 ± 10
2.690	3717 ± 10	101	3715	2 ± 10
2.624	3810 ± 15	101 + Q_1	3829	−19 ± 15
2.336	4280 ± 15	300 f	4265	15 ± 15
		031 f	4249	31 ± 15
2.280	4387 ± 15	111 f	4391	−4 ± 15
2.121	4715 ± 20	041-Q_1	4740	−25 ± 20
		002 f	4743	−28 ± 20
2.065	4842 ± 20	041	4854	−12 ± 20
2.009	4978 ± 10	121	4978	0 ± 10
1.969	5079 ± 20	201	5100	−21 ± 20
1.872	5340 ± 20	012	5316	24 ± 20
		240 f	5330	10 ± 20
1.60	6250^{+120}_{-75}	141	6228	22^{+120}_{-75}
		221	6348	-98^{+120}_{-75}
1.44	6944 ± 150	003	6972	−28 ± 150

Notes.

f indicates forbidden.

$Q_1 = 114\ cm^{-1}$, $Q_2 = 68\ cm^{-1}$ [*Ron and Schnepp*, 1967].

flectance near 1.8 and 2.24 μ, but frosts with 100-μ texture, grown outside the chamber (see below) did not. The reflectance maximum at 2.24 μ is typically 90% of the value at 1.8 μ. The 2.2- to 2.7-μ region shows the greatest variation between samples. A small peak in reflectance at 2.64 μ occurred only for fine-grained samples.

Frost that had formed on the outside of the chamber was collected and heaped in the bottom of a clean cold chamber. This sample melted slightly while being transferred, removing the fine texture. It had considerably lower reflectance beyond 1.4 μ than did samples that were kept well below 0°C. The reflectance of undisturbed natural spring snow (Mt. Wilson, April 5, 1967, from storm of April 2) was less than 1% from 1.6 to 3.2 μ.

The reflectance of very fine frosts (grain size less than 5 μ) increases with deposit thickness most rapidly at short wavelengths (Figure 2, bottom). The 50% visual albedo can be obtained with only 0.1 mg cm^{-2}. The more rapid rise in reflectance with amount at short wavelengths for this series may be partially due to a corresponding increase in grain size, so that the transition from Rayleigh to the more efficient particulate scattering occurs at progressively greater wavelength.

CO_2-H_2O mixed frost reflection spectra. Frosts of several weight fractions of H_2O and various grain sizes were grown. Though the source gases were let simultaneously into a mixing manifold, some fractionation commonly occurred in the chamber, as evidenced by the formation of two zones of coarse crystals on the chamber wall. The H_2O weight fraction in the area viewed by the detector was measured after spectral observation.

Though the strength of the H_2O-CO_2 features depends on textural scale, H_2O has a much stronger effect on the reflection spectra (Figure 3) than does CO_2, and H_2O features predominate even at low concentrations. The sensitivity of the 3-μ region to H_2O is demonstrated by the spectrum of CO_2 frost grown without

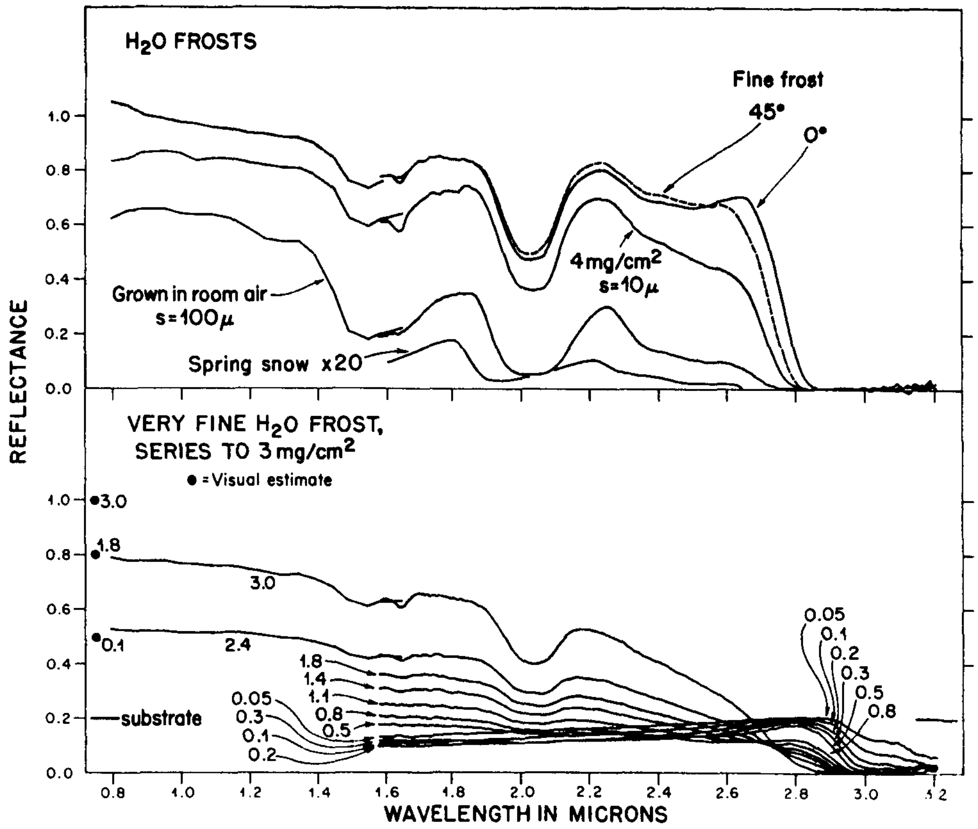

Fig. 2. Spectral reflectance of H_2O frosts. s is the textural scale. The snow and air temperatures were 0°C and 9°C for the undisturbed natural sample.

a cold trap in the gas source line, thus containing about 17 ppm H_2O (Figure 1).

At an H_2O weight fraction (h) of 0.008 all the features of H_2O spectra are present to some extent. There is about 5% absorption at 1.5 µ, the 2.0-µ band is broadened, the slope from 2.2 to 2.6 µ is increased, and the 3.1-µ region is saturated. As the weight fraction of H_2O is increased, the last distinguishable characteristics of CO_2 to disappear are the detail in the bottom of the 2.0-µ band and the high reflectance (greater than 80%) near 2.5 µ. For coarse-grained frosts with $h \leq 0.05$ the presence of CO_2 is discernible only as small detail at 2.7 and 2.0 µ. There is some evidence of the 2.7-µ CO_2 band in the spectra of all mixed samples.

The 2.0-µ detail is due to strong CO_2 absorption and is most marked in the spectra of strongly absorbing, i.e. coarse-grained, frosts. In contrast, the high reflectance at 2.5 µ is most evident in the spectra of fine-grained frosts. The effect of the increasing strength of the absorption features on the apparent composition is illustrated by the spectra of $h = 0.2$ and $h = 0.23$. The coarse-grained sample at $h = 0.2$ shows no indication at all of CO_2 except for a small feature at 2.7 µ, whereas the very fine-grained sample of $h = 0.23$ deviates only slightly from a pure CO_2 spectrum except near 3.1 µ.

The effects of surface concentrations were determined by letting the gases in sequentially. Complex changes in the spectra can occur owing to the additional variables (relative grain size and thickness of the surface deposit). The spectra (Figure 4) show that 0.5 to 1 mg cm^{-2} surface layer of H_2O can subdue CO_2 features and 7 mg cm^{-2} H_2O will completely disguise a CO_2 frost. A sample of CO_2 on H_2O indicated that about 50 mg cm^{-2} is required to disguise

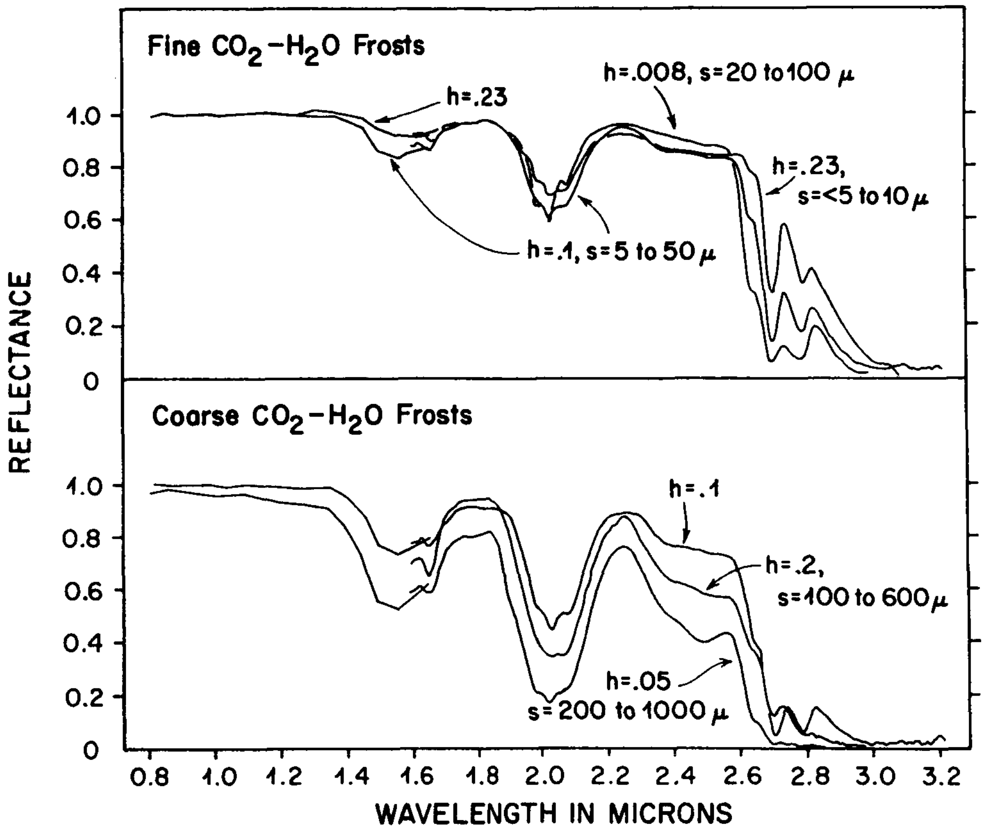

Fig. 3. Spectral reflectance of CO_2-H_2O mixed frosts. *h* is the weight fraction of H_2O. *s* is the textural scale. The reflectance of the coarse frosts has been normalized slightly.

the H_2O spectrum, but H_2O vapor may have transferred into the CO_2 surface layer of this sample.

Discussion

The fundamental molecular vibration frequencies change only slightly between phases for CO_2 [*Osberg and Hornig,* 1952], in contrast to H_2O. No difference in positions of the strong CO_2 overtones between gas and solid phases were detected with this equipment. The new assignments made here are based solely on the agreement of frequency (Table 2). The calculated wave numbers are taken from the extensive tables of *Stull et al.* [1963]. Features similar to the features observed here on the wings of the 2.0- and 2.7-μ multiplets have been observed in thin film transmission spectra in association with the ν_2 and ν_3 fundamentals. They have been attributed to combinations of molecular and lattice vibrations [*Dows,* 1959; *Jacox and Milligan,* 1961] and some to reflection peaks [*Osberg and Hornig,* 1952]. The absorptions at 2.12, 2.62, 2.85, and 2.90 μ are attributed to sum and difference transitions of the lattice fundamentals (Q1 at 114 cm^{-1} and Q2 at 68 cm^{-1} [*Ron and Schnepp,* 1967]) and the strong molecular vibrations. The 2.85-μ band is attributed to the unresolved combination of the 021(0)-000(Q1) transition of $C^{12}O_2^{16}$ and the 021-000 transition of the isotope $C^{13}O_2^{16}$ (1.1% abundance). Several new features agree best with the calculated positions of forbidden combination and overtone bands. The absorption features at 2.28 and 2.34 μ are assigned entirely to forbidden transitions, and the forbidden transition 002-000 may contribute to the 2.12-μ feature. Lattice defects, crystal edge effects, or impurities could negate the center of symmetry selection rule. The crystal structure of CO_2 is T_h^6(Pa 3) and a pair of nearest neighbor molecules does not have a

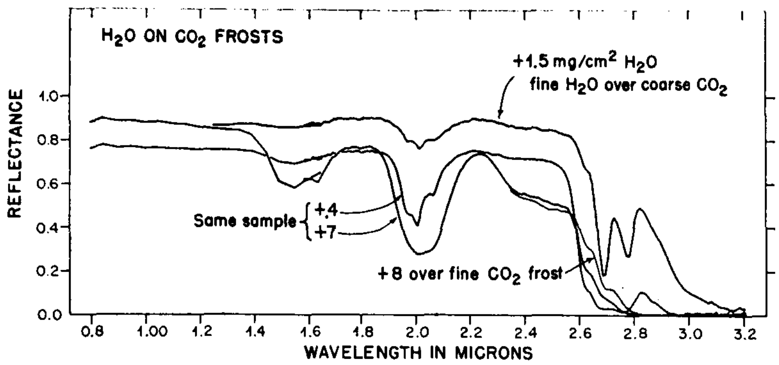

Fig. 4. Spectral reflectance of CO_2 frost with surface layers of H_2O frost. Samples were formed by allowing H_2O gas into a chamber containing a thick CO_2 frost.

center of symmetry [*Wyckhoff*, 1963, p. 368] so that pair transitions are not forbidden.

Though the CO_2 fundamental intensities differ by less than 40% between the gas and solid phases [*Yamada and Person*, 1964], the equivalent widths for frosts are considerably larger than for the amount of gas (STP) equivalent to the textural scale. This effect is due to line broadening, the additional features on the wings of the multiplets that occur only in the solid phase, and to multiple scattering, which is increasingly important for fine frosts. The equivalent widths of the 2.0- and 2.7-μ multiplets of several representative samples are shown in Figure 5. Most frosts exhibit a range of textural scale, and so they are not adequately described by one size parameter and do not follow a single curve of growth. For a slightly fractured 2.5-mm-thick layer over a bright substrate (5-mm path length, sample 1604), the solid equivalent widths are approximately twice those of the equivalent amount of gas.

The H_2O frosts were presumably vitreous as they formed and were maintained well below 110°K [*Dowell and Rinfert*, 1960]. However, there are only slight spectral differences between vitreous and cubic or hexagonal ice [*Ikawa and Maeda*, 1968; *Bertie and Whalley*, 1964]. The

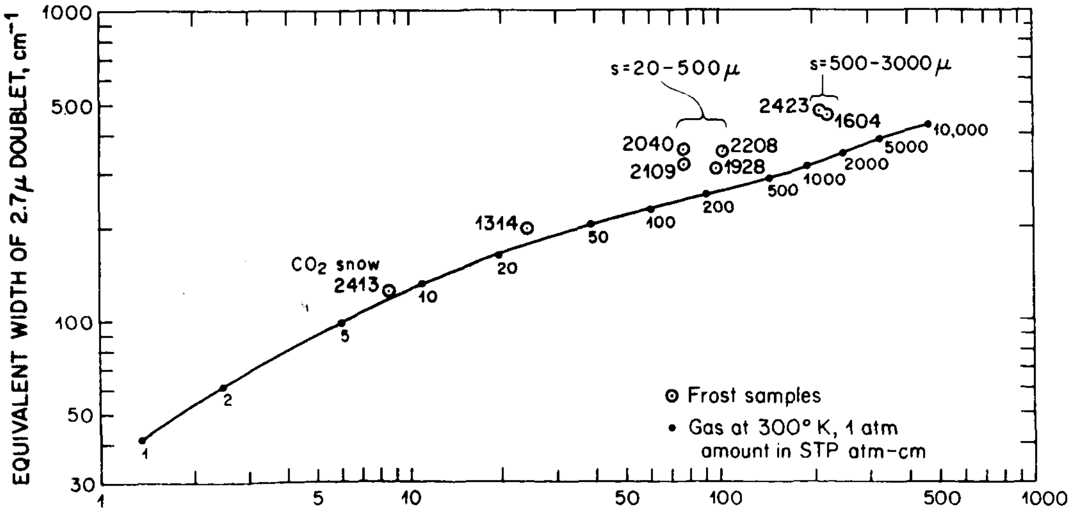

Fig. 5. The 2.0- and 2.7-μ multiplet equivalent widths for CO_2 frost and gas. The values for the gas were computed from the tables of *Stull et al.* [1964]. The mass of 1.2 atm cm equals 1 μ of the solid.

H_2O frost spectra are generally similar to the spectra obtained for frosts grown in a cold nitrogen gas stream [*Plummer*, 1969] and to the spectra of laboratory ice clouds [*Zander*, 1966, 1968]. However, a greater reflectance at 2.2 μ than at 1.8 μ, as reported by Plummer, was never observed. The saturation of the 3.1-μ band for very thin samples and the sensitivity of CO_2 spectra to contamination by H_2O at that wavelength result from the extreme intensity of the H_2O stretching modes in the solid phase (140,000 cm^2/millimole [*Ikawa and Maeda*, 1968]), 30 times greater than for water vapor.

The relatively large effect of H_2O on the mixed frost spectra is in accord with the ratio of band intensities for CO_2 and H_2O. For the 21 samples of CO_2-H_2O mixed frosts studied, the effects of textural scale are too great to allow any simple quantitative relation between reflection spectra and composition. The indication of composition least dependent on textural scale is the amount of detail from the CO_2 triplet at 2.0 μ, where the strengths of the CO_2 and H_2O features are comparable. The effect of H_2O, the more absorbing molecule, increases with textural scale. The textural scale can be determined approximately by the depth of the 2.62- and 2.7-μCO_2 absorption bands, where the H_2O intensity is relatively weak. There was no spectroscopic evidence of a CO_2-H_2O complex in the mixed frosts, in agreement with a study of CO_2-H_2O thick films [*Jacox and Milligan*, 1961]. Some hexagonal crystal forms were observed, however, in 80% CO_2 (cubic) samples.

The spectral contrast of inclined samples indicates that scattering by fine frosts is more nearly Lambert (no change in spectral contrast) than diffuse (normalized reflectance increases with inclination). The largest measured changes in spectral contrast for the five samples studied

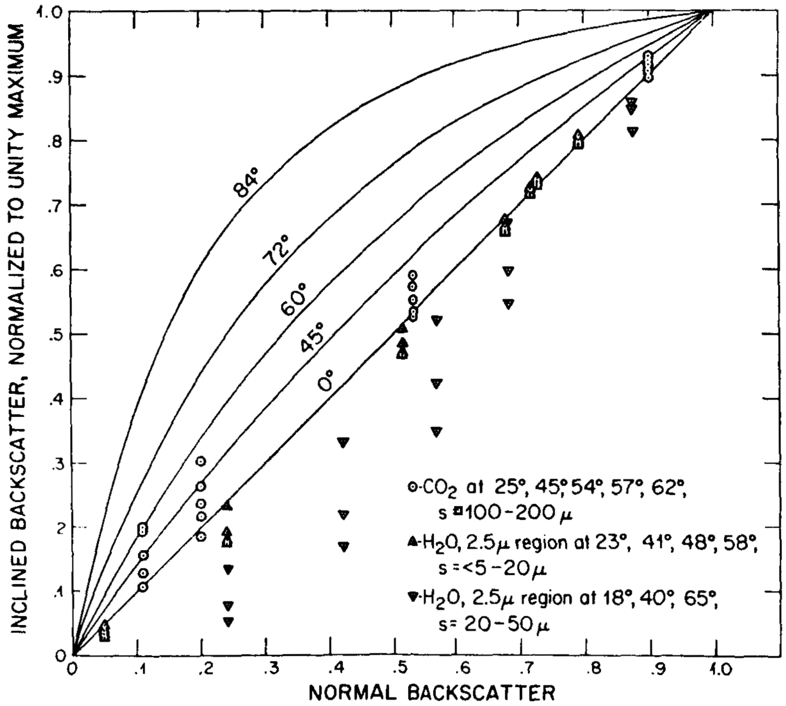

Fig. 6. The dependence of backscatter spectral contrast (spectral reflectance normalized to unity for pure scattering) on inclination. The curves show the theoretical relation for diffuse isotropic scattering (computed from the tables of *Chandrashekar* [1960, p. 125]). Spectral contrast is independent of inclination for Lambert scattering. The angle listed for the frost samples is the angle of incidence, the angle of reflectance being 12° less in the same plane.

are shown in Figure 6. The other changes measured were from zero to one-half that predicted for diffuse isotropic reflectance. The edge of the H_2O stretching band at 2.5 μ appears anomalous in that contrast decreases with inclination. The absolute reflectance outside the absorption bands for these samples followed within 10% of the Lambert (cosine) law.

SUMMARY

The spectral reflectance of frosts is dependent on their textural scale. The strength of absorption features increases with textural scale, though a single size parameter is not adequate to describe the texture of a frost deposit. From 0.8 to 3.2 μ, CO_2 frosts have high reflectance except near 2.0 and 2.7 μ and H_2O frosts have overlapping strong absorption bands. CO_2 frosts have additional features not observed in the gas phase. They are much more sensitive to contamination by H_2O than is indicated by gas transmission calculation, because of the increased intensity of the H_2O stretching modes (3.1 μ) in the solid. Small weight fractions of H_2O in mixed samples will yield spectra similar to the spectra of pure H_2O frost, and the sensitivity of CO_2-H_2O concentration increases with grain size. This dependence on textural scale prevents the forming of a simple quantitative relation between spectral reflectance and composition. A few milligrams per square centimeters of H_2O frost on the surface of a CO_2 frost will largely disguise the CO_2 deposit. Scattering by fine frosts follows the cosine law approximately, whereas variations of band shape with inclination are observed for coarser frosts.

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INTERPRETATION OF THE MARTIAN POLAR CAP SPECTRA

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Interpretation of the Martian Polar Cap Spectra[1]

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Laboratory measurements of CO_2-H_2O frost spectral reflectance are applied to spectral observations of the Martian polar caps. There is some discrepancy between the 1.5-μ absorption feature reported for the polar cap and the spectra of either H_2O or CO_2 frost. Even if the original interpretation of absorption due to H_2O frost is accepted, the predominantly CO_2 polar cap model cannot be excluded. Similar spectra could result from the concentration of H_2O expected on a CO_2 cap during the late spring, the season the Martian cap spectra were taken. Thus the existing observations of the polar cap are inconclusive and do not demonstrate that the Martian polar caps are composed primarily of H_2O.

INTRODUCTION

Infrared spectral [*Kuiper*, 1952, pp. 361–362; *Moroz*, 1964, p. 279] and visible polarization [*Dollfus*, 1961, pp. 381–382] observations of the Martian polar caps have been interpreted to mean that the caps are composed of H_2O frost. Theoretical discussions [*Leighton and Murray*, 1966] based on recent determinations of the composition and pressure of the Martian atmosphere suggest that H_2O caps would require an extreme planetary circulation system, whereas a model of CO_2 frost caps does not require exceptional meteorology and is compatible with all information about Mars except the interpretations just mentioned.

The purpose of this work is to compare the telescope observations with laboratory spectra for simulated Martian frosts and to examine the possible role of H_2O in a predominantly CO_2 polar cap model. This study includes only CO_2 and H_2O as they are the only likely chemicals with the required physical properties that have not had prohibitively low limits placed on their abundance by spectroscopic observations.

OBSERVATIONS OF MARTIAN POLAR CAPS

The only infrared spectral observations of the Martian polar cap reported are those of *Kuiper* [1952] and *Moroz* [1964]. Both authors reduced the spectral resolution of their equipment to one-ninth the wavelength in order to have the sensitivity required to detect light reflected from the polar cap alone. The apparent sizes of the polar cap when Kuiper and Moroz made their measurements were about 2 and 1.5 square seconds of arc, respectively.

Kuiper observed natural snows and water frost formed on dry ice and found the spectra to be equivalent to the spectra of water absorption cells of different thickness. He made no mention of the marked frequency shifts between H_2O gas, liquid, and solid absorption features. He found terrestrial snow 'nearly black beyond 1.5 μ and almost fully black beyond 2.0 μ.' Measurements with CO_2 snow showed it to remain 'white' up to 2.5 μ except for the 2-μ absorption band. The reflection spectrum of the Martian polar cap was similar to terrestrial snow 'though the drop at 1.5 μ is less steep.' No data or spectra of Martian caps, H_2O or CO_2 frosts were published. The implied date of this observation is February 1948 (early northern summer). He concludes that 'the Martian polar caps are not composed of CO_2 and are almost certainly composed of H_2O frost at low temperature (much below 0°C).'

Moroz observed the polar cap spectrum in the region of 1 to 2 μ and found in the 1.5- to 1.8-μ region the cap intensity was relatively lower than that of the central portion of the disk. He published averaged spectra of the north polar cap (late spring) and the center of the

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planet. Moroz interpreted the polar cap spectrum as being similar to the spectra of snow and hoar frost which he had observed, concurring with Kuiper's interpretation.

Visual polarization measurements of the polar cap have been interpreted as evidence of the presence of H_2O frost and clouds [*Dollfus*, 1961, p. 382]. Dollfus made no measurements of CO_2 frost or clouds. Polarization is so highly dependent on texture (see, for instance, the laboratory measurements by *Dollfus* [1961, pp. 361–366]) that it is not likely to yield reliable diagnostic results as to composition in any event.

The above measurements constitute the direct observational evidence for the composition of the Martian polar caps. The rate of spring regression of the polar caps constitutes indirect evidence of the polar cap composition. However, the relations of composition, quantity of frost, and details of the daily thermal balance and planetary circulation are complex and the observational data have been used in support of both CO_2 [*Leighton and Murray*, 1966] and H_2O [*Miyamoto and Hattori*, 1968] polar caps.

LABORATORY MEASUREMENTS

The spectral reflectances of pure CO_2, pure H_2O, mixed CO_2-H_2O, and H_2O on CO_2 frosts were measured from 0.8 to 3.2 μ [*Kieffer*, 1970]. The results of the laboratory spectral measurements relevant to Mars are summarized below:

1. Spectral contrast is strongly affected by grain size (dominant textural scale).
2. CO_2 frosts have high reflectance outside the 2.0- and 2.7-μ bands for grain sizes up to at least 3 mm.
3. H_2O frosts have appreciable absorptance near 1.5 and 2.0 μ and longward of 2.3 μ for grain size larger than 10 μ. For grain size larger than 100 μ, reflectance is high only at wavelengths less than 1.4 μ.
4. Small relative concentrations of H_2O have a major effect on the spectra of mixed frosts. This effect increases with grain size. Identification of CO_2 when the weight fraction of H_2O is greater than 10% is difficult except at 2.7 to 2.8 μ.
5. Surface additions of small amounts of H_2O on CO_2 frosts will result in H_2O reflection spectra. The alteration is noticeable at 0.4 mg cm^{-2} and complete at less than 7 mg cm^{-2} for fine frosts.
6. The intensity of oblique backscatter (sun-Mars-earth geometry) between absorption bands for the fine frosts approximately follows the cosine of the incident angle. Spectral contrast of fine frosts does not change appreciably with inclinations (measured to 65°) for small phase angles. The scattering from strong bands in coarse frosts behaves more like diffuse isotropic reflectance except for anomalous widening of the extremely strong 3-μ H_2O band.
7. High visible reflectance can be obtained with as little as 0.5 mg cm^{-2} of fine H_2O frost.
8. Thin, very fine H_2O frosts have a general decrease in reflectance from 0.8 to 3 μ.

APPLICATION TO MARS

Though there is to date no evidence that Martian frosts have anomalous scattering properties, the possibility that they have 'unusual' grain shape, size distribution, or packing resulting in an anisotropic phase function or possibly some spectral effect must be remembered. The measured spectral contrast for backscatter from fine laboratory frosts did not vary significantly for inclination up to 65°. This is greater than the inclination of the edge of the Martian cap at the time of both Moroz' and Kuiper's observations. Thus it appears that the spectral contrasts of laboratory frosts measured at normal backscatter are directly applicable to the geometry of Martian observations.

The atmospheric H_2O mixing ratio on Mars is observed to be about 10^{-4} [*Kaplan et al.*, 1964; *Spinrad et al.*, 1966; *Schorn et al.*, 1967]. As this is similar to the mixing ratio for terrestrial polar conditions (saturated air at −40°C), the behavior and form of H_2O frosts on Mars might be much the same as on earth. However, the condensation of CO_2 on Mars has no terrestrial analogy as it would involve freezing of a nearly pure gas with the latent heat released being lost by radiation. This process does not occur naturally on earth, and possibly cannot be produced in the laboratory [*Kieffer*, 1968, p. 21]. Though a dense layer can form by this process, the visual albedo of the Martian caps (0.5) implies that they have a scattering, and therefore probably permeable, surface layer. This albedo is lower than the albedo for any laboratory sample. It could, however, be caused by large (minimum size unknown) textural scale, anisotropic scattering, incomplete frost coverage, or contamination by Martian dust or dirt.

INTERPRETATION OF EXISTING MARTIAN POLAR CAP SPECTRA

Moroz [1964] reported that the spectrum of the polar cap in the 1.5- to 1.8-μ interval was less intense than the spectrum of the central region of Mars. An estimate of the spectral reflectance of the polar cap can be obtained from his data [*Moroz*, 1964, Figure 6] by dividing the cap spectrum by the spectrum of the center of the planet. *McCord and Adams* [1969] show the reflectance of Mars as approximately 0.3 in the 0.8- to 1.1-μ region and then increasing smoothly to about 0.4 at 1.6 μ, though they present only two data points beyond 1.33 μ. Recent observations with 0.05-μ resolution (T. B. McCord, personal communication, 1969) do not indicate appreciable detailed structure on this general trend for either light or dark areas on Mars. Thus the major features in the cap to center ratio should be attributed to the polar cap. The resulting spectrum is compared with representative laboratory results in Figure 1. Moroz' cap spectrum represents the average of three selected tracings so that detailed analysis may not be warranted. The peak at 1.3 μ in the cap to center ratio does not correspond to any H_2O or CO_2 feature and the minimum is clearly at shorter wavelength than for H_2O frosts. These discrepancies may reflect changes in the transparency of the terrestrial 1.4-μ water vapor band. These difficulties aside, the strength of the absorption feature observed for the cap is comparable to that for H_2O frosts with textural scale from 20 to 100 μ. An absorption of this strength due to CO_2 would require a textural scale larger than 10 cm. Apart from these uncertainties, if one accepts the original interpretation that the absorption in the cap spectrum is due to H_2O frost, then the common inference that this interpretation excludes the CO_2 cap model must be examined.

There is as yet no quantitative treatment of the role of H_2O in a carbon dioxide cap. By treating the total condensation budget of the polar cap, however, a simple limiting model can be derived. The observed H_2O mixing ratio, 10^{-4}, is the minimum likely weight fraction of H_2O in the material condensed in the polar regions. The model of a pure CO_2 cap [*Leighton and Murray*, 1966] predicts about 80 g cm^{-2} average annual CO_2 deposition, though the computed rates may be in error [*Kieffer*, 1968, pp. 67–72].[3] This implies that at least about 10 mg cm^{-2} of H_2O is deposited on the cap in the winter. During CO_2 sublimation in the spring at the saturation temperature of 145°K, however, the H_2O mixing ratio is 10^{-6} at most, so that only 1% of the condensed H_2O can have sublimed where any CO_2 remains. Any atmospheric circulation would increase the efficiency of the polar cold trap, yielding a larger spring residual of condensed H_2O than derived by this simple approach. It is likely that during the spring a surface concentration of H_2O frost would grow locally in proportion to the fraction of CO_2 sublimed.

This total budget model omits the details of many relevant possibilities (cloud formation and snowfall, formation of a cap fringe of pure H_2O frost, daily enrichment of H_2O on equatorial facing slopes, and the increase of grain size through the spring). It exhibits, however, the basic principles of the CO_2 polar cap cold trap and time lag of H_2O sublimation that constitute a plausible case for a surface accumulation of H_2O frost in the spring.

The laboratory results indicate that a 5-mg cm^{-2} H_2O surficial layer is sufficient to disguise a CO_2 frost. As the amount of H_2O that would be trapped in a conservative CO_2 cap model is

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[3] This discussion is summarized here. Leighton and Murray assume the effective emissivity of solid CO_2 through the Martian atmosphere to be 0.85. However, low reflectance is observed for CO_2 frosts in the near infrared only near frequencies of strong CO_2 gas absorption, except for some weak and medium strength transitions that are forbidden in the gas phase. The longest-wavelength forbidden transition, though not yet observed for the solid, would be at 7.8 μ. No other bands associated only with the solid are known or expected at wavelengths less than the 88- and 146-μ lattice vibrations. Thus, from 8 to 80 μ the region containing 94.3% of the thermal radiation for a blackbody at 150°K, the spectral emissivity of CO_2 frost is expected to correlate with the absorptance of the Martian atmosphere and the effective emissivity of Martian CO_2 frosts, though dependent on grain size, could be quite low. Measurements of the spectral emissivity of CO_2 frosts in this wavelength region do not exist but would be very helpful.

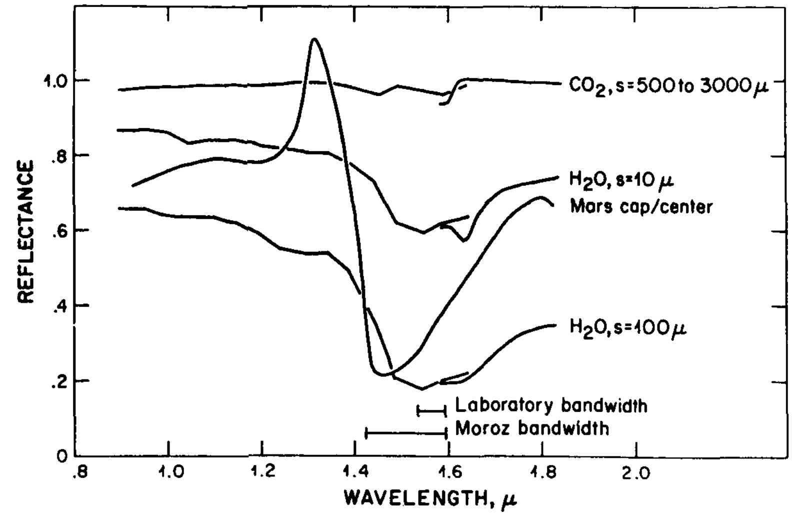

Fig. 1. The spectral reflectance of the Martian polar cap and laboratory frosts. The Mars curve is the unnormalized ratio of the polar cap and equatorial region spectra presented by *Moroz* [1964] as Figure 6. *s* is the textural scale.

about 10 mg cm^{-2}, it appears that Martian polar caps composed primarily of CO_2 could exhibit water frost reflection features at least during the latter half of the sublimation phase. Thus the infrared spectral observations of Moroz and Kuiper, taken in the Martian late spring, do not indicate that the polar caps are composed of H_2O, but only that water frost may be present, which is to be expected whether the polar caps are H_2O or CO_2. Observations during the Martian winter or early spring, before a surface concentration of H_2O would form, would be more diagnostic of bulk composition as the presence of H_2O spectral features would then be strong evidence against the CO_2 cap model.

SUMMARY

Spectral observations of the Martian polar caps were originally interpreted as indicating the presence of H_2O frost. Comparison of the one published spectrum with the spectra of frosts grown under controlled conditions reveals some discrepancies though the strength of the 1.5-μ absorption suggests a frost textural scale of 20 to 100 μ. However, similar spectra can result from small surface concentrations of H_2O frost on CO_2 frost. The amount of H_2O required is compatible with the quantity expected during the late sublimation phase of a predominately CO_2 polar cap, just the time of the existing observations. Thus the conclusion that the Martian caps are composed primarily of H_2O is not warranted. Measurements of the winter or early spring cap would be more definitive, though more difficult because of the unfavorable geometry.

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