

GEORGETOWN COLLEGE OBSERVATORY  
 GEORGETOWN UNIVERSITY  
 WASHINGTON, D. C. 20007

SEMI-ANNUAL STATUS REPORT NO. 6 ON SPECTROSCOPIC STUDY  
OF SOLAR AND PLANETARY ATMOSPHERES

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PREPARED BY:

Francis J. Heyden, S. J.  
 Director

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SEMI-ANNUAL STATUS REPORT NO. 6 TO THE NATIONAL AERONAUTICS  
AND SPACE ADMINISTRATION

"SPECTROSCOPIC STUDY OF SOLAR AND PLANETARY ATMOSPHERES"

NAME AND ADDRESS OF INSTITUTION: GEORGETOWN UNIVERSITY  
WASHINGTON, D. C. 20007

PROJECT DIRECTOR: Dr. Francis J. Heyden, S. J.

ASSISTANT SCIENTIFIC DIRECTOR: Dr. Carl C. Kless

Work Performed. This report is divided into four areas, the first area is the Observations of the Planets, the second is the Simulation of the Martian Atmosphere and analysis in the photographic region, the third is the Simulation of the Martian Atmosphere and analysis in the infrared region, and the last includes other work which does not fall under the first three categories.

Area 1. Observations of the Planets.

Venus was at greatest eastern elongation on November 15, 1965, and Jupiter was at opposition on December 18, 1965. Initially we attempted to obtain exposures using our 50 foot focal length mirror and our 30,000 line per inch original grating ruled by Professor E. H. Wood at Johns Hopkins University for the National Bureau of Standards. This grating has a six inch aperture, and is faster in the infrared and has lower ghost intensities than our 30,000 line per inch original grating ruled by H. G. Gale at the University of Chicago.

The fifty foot focal length mirror was employed in order to obtain a larger image of the planets, and therefore reduce the amount of vertical trailing of the image. Vertical trailing of the image tends to broaden the spectral lines of planets and to wash out the fainter absorption features. This vertical trailing also tends to give unevenness in the exposures in the vertical direction when used with a stigmatic optical system. It has

another disadvantage in that the exposure times are necessarily longer.

The 30,000 line per inch Wood grating gives a reciprocal dispersion of about  $2\text{\AA}/\text{mm}$ . Initially we attempted to obtain spectra of Venus and Jupiter in the photographic infrared. It was immediately found that Venus rose behind Healy tower of Georgetown University which is the highest building on the Georgetown Campus. This unfortunate circumstance limited our exposure times to about one hour before sunrise. Our initial spectrograms of Venus were underexposed and neither hypersensitizing the plates nor increasing the slit width were sufficient to obtain proper exposures.

Because of the unfortunate position of Venus, we had to use a 15,000 line per inch grating and observe only in the visible portion of the spectrum. These alterations enabled us to obtain good exposures of Venus.

Since the focusing of the Wadsworth mounting is very critical, it is not possible to change any of the optical alignment during the night. Therefore once the alignment is set for the night both Jupiter and Venus have to be photographed in the same wavelength region. We were faced with the decision of either obtaining only Jupiter in the photographic infrared, or both Venus and Jupiter in the visible. We chose the latter knowing that we have many more opportunities for obtaining the spectra of Jupiter in the infrared.

The purpose in obtaining high dispersion spectrograms in the infrared of Jupiter is described by Kiess, Corliss and Kiess in Ap. J. 132, 221, 1960. In these spectrograms the features of the ammonia bands at 6450A and 7900A and the methane bands at 6200A, 7250A, 8420A and 8620A were identified. In addition four lines attributable to molecular hydrogen were found at 8497.52A, 8272.60A, 8150.60A and 8046.44A. Finally, general absorption was found in Jupiter's spectrum. This absorption begins longward of 4200A and gains in strength with decreasing wavelength until it blots out the planet's spectrum a little shortward of 3800A. The brightness of Jupiter is reduced by one-half relative to that of the moon for every decrease of 135A in wavelength.

At present we have one graduate student investigating the spectral plates of Jupiter in the long wavelength region. This program is intended to confirm the previously reported absorption features, to look for new absorption features, and to look for variations of these absorption features as a function of time. We have many excellent plates which were obtained under this grant, and this particular graduate student's time is being contributed to the grant.

Area 2. Simulation of the Martian Atmosphere and Analysis in the Photographic Region.

As yet we have not definitely proved or disproved the existence of the oxides of nitrogen in the Martian atmosphere. In order to prove the existence of the oxides of nitrogen, it is considered necessary to positively identify spectral bands or lines in the planet's spectrum. The main stumbling blocks to positive identification are as follows.

1. The oxides of nitrogen exist in the earth's atmosphere. In order to reduce the possibility that the  $\text{NO}_2$  appearing in the Martian plates is atmospheric, the moon's spectra is taken juxtaposed to the spectrum of Mars, and as near in time and altitude as the planet.

2. The spectrum of nitrogen dioxide is very complex and has not been analyzed in the visible region. Tables of laboratory spectra made by Miss Carwyle for her doctorate dissertation at the University of Virginia in 1927 do not correlate very well with tables obtained by Corliss at the Bureau of Standards in 1961 (unpublished data). The evidence of  $\text{NO}_2$  in the Martian spectrograms that were taken in the opposition of 1956, 1960 and 1963 has been based on this data with some degree of uncertainty because of this lack of agreement. The absorption spectrum of the peroxide in the visible region is due almost entirely to the dioxide  $\text{NO}_2$ . It consists of myriads of fine, closely-spaced lines representing the rotational structure of unidentified vibrational bands of the molecule. Even the rotational lines are fuzzy under the highest dispersion, and no

sharp band heads appear. Therefore we are not attempting under this present study to determine the energy levels leading to the transitions in the photographic region.

3. The photographic densities of the lines and bands of  $\text{NO}_2$  are strongly effected by path length and exposure time. Only a small portion of discrete lines or bands of  $\text{NO}_2$  are visible in any one exposure. This fact has been overlooked by many investigators in searching for  $\text{NO}_2$  in the visible spectrum of Mars.

4. There is much blending between the  $\text{NO}_2$  lines in the Martian spectrum and the Fraunhofer lines of the solar spectrum. Because of this fact the solar lines would be deepened, or distorted when overlaid by the very numerous  $\text{NO}_2$  features, and consequently many of the  $\text{NO}_2$  features will not be evident.

In order to circumvent these difficulties the following procedures are followed.

a. The spectrum of Mars is always obtained with the moon juxtaposed to the spectrum of Mars. The two exposures are taken as close in time as feasible in order to minimize any atmospheric changes in the earth's atmosphere. The altitude of Mars and the moon are taken as close in altitude as is feasible in order that the same air mass is used. In addition the length of exposure is regulated so that the photographic densities of the two bodies match at  $H\alpha$ . The length of the lunar exposure can vary from 15 minutes at full moon to about 2 hours at one quarter phase. The ideal would be to have the planetary exposure time the same length as the lunar exposure time and meet all the other conditions. This however is seldom possible. Therefore we take exposures on every clear night and try to meet the conditions as well as possible. We now have many sets of excellent plates for Mars, Venus and Jupiter.

b. Since the spectrum of  $\text{NO}_2$  is so complex that no attempt can be made under the present study to determine the energy levels leading to

the transitions in the photographic region, descriptive methods must be used in order to identify  $\text{NO}_2$ . These descriptive methods include the wavelength of the feature and an estimate of its intensity. Of particular interest are sharp features in the  $\text{NO}_2$  spectrum. We have found quite a few sharp  $\text{NO}_2$  features which also appear on Martian plates, however, we need more identifications to be sure of our findings. Some of the sharp features cannot be used as they are blended with strong Fraunhofer lines in the solar spectrum. From the converse point of view all the peculiar Martian features seem to have corresponding  $\text{NO}_2$  features.

c. The fact that the photographic densities of the lines and features of  $\text{NO}_2$  are strongly effected by path length and exposure time may be to our advantage. If the sun's light is sent through the optical tube, and the pressure of the peroxide is varied, then the relative intensities of the  $\text{NO}_2$  and Fraunhofer absorption lines should vary correspondingly. We then can compare the relative intensities of the lines in the Martian spectra. We have investigated pressures which so far give path lengths which are too long for the amount of  $\text{NO}_2$  in the Martian atmosphere. We are planning to reduce this pressure to a point which will match our exposure of December 30, 1960. This exposure was taken very near to the time of zero radial velocity between the earth and Mars. The actual point of zero radial velocity occurred on December 25, 1960. However, the actual doppler shift on December 30, 1960 was approximately 0.04A at 5000A and should not adversely effect our results.

d. In general the blending of  $\text{NO}_2$  features and Fraunhofer features causes considerable difficulty. There are two methods for sorting out these two features. First we can look in areas where there are few Fraunhofer lines, secondly one can integrate under the microphotometric tracings of the two spectra and calculate the differences. The latter method is much more satisfactory and our procedures are quite accurate, however, the method even though it is completely mechanized is quite time consuming. We are therefore at present confining our efforts with

the nearly zero radial velocity plate of December 30, 1960 in order to make our positive identifications. If we then can positively identify  $\text{NO}_2$  on this plate, then we will investigate the other plates for redundancy, and for variations of the amount of  $\text{NO}_2$  with time.

Area 3. Simulation of the Martian Atmosphere and Analysis in the Infrared Region.

In conjunction with the National Bureau of Standards the following infrared spectral reflectance measurements have been made.

Wavelength region 2.5 to 22.2  $\mu$

1.  $\text{H}_2\text{O}$  frost on Brass.
2.  $\text{H}_2\text{O}$  frost on black electrical tape.
3.  $\text{CO}_2$  frost.
4. Mixture of  $\text{N}_2\text{O}_4$  frost and  $\text{H}_2\text{O}$  frost.
5. Mixture of  $\text{N}_2\text{O}_4$  frost and  $\text{CO}_2$  frost.
6. Mixture of  $\text{CO}_2$  frost and  $\text{H}_2\text{O}$  frost.
7.  $\text{N}_2\text{O}_4$  frost.

Wavelength region 0.6 to 2.5  $\mu$

1.  $\text{N}_2\text{O}_3$  frost blue area viewed.
2.  $\text{N}_2\text{O}_3$  frost white area viewed.

A. Measurements in Wavelength Region 2.5 to 22.2  $\mu$ .

Dr. Sebastian Karrer, consultant to Georgetown Observatory, assisted in the handling and safeguarding the instrumentation and personnel from damage of nitrogen peroxide. The nitrogen peroxide was furnished by Georgetown College Observatory. The National Bureau of Standards financed the tests. The instrumentation used in making the measurements was provided under the "Infrared Optical Measurements" program financed by the Advanced Research Projects Agency.

The results are presented by the National Bureau of Standards in NBS Test No. 212.11P-20/66 entitled "Infrared Spectral Reflectance of Frost 4000 to 450 Wavenumbers (2.5 to 22.2  $\mu$ ) Formed at Temperatures Below Approximately Minus 100° C." The purpose of the test was to

measure the spectral directional reflectance of nitrogen tetroxide ( $N_2O_4$ ) frost,  $H_2O$  frost,  $CO_2$  frost, and mixtures of these frost samples.

Measurements of spectral directional reflectance of the samples were made by means of a Cary-White Model 90 recording spectrophotometer. The measurements were made for total hemispherical illumination by using a nichrome helix source operating at 45 watts and a thermocouple detector.

The frost samples were collected and measured on a specially prepared sample holder consisting of a polystyrene foam liquid-nitrogen container having a 50mm cube cavity. The frost was formed on a 50mm square brass plate 1mm thick. Brass machine screws silver soldered to the brass plate projected from its base into the liquid nitrogen reservoir. Liquid nitrogen was added to the reservoir, as needed, through an opening connected to the reservoir. In this way the brass plate and frost formation on its upper surface were maintained at a low temperature throughout a period of approximately 15 minutes necessary for making the measurements of spectral directional reflectance. The thickness of the frost formations were approximately 2mm.

A sample of  $N_2O_4$  frost was prepared by covering the brass plate with a Saran Wrap envelope and allowing the evaporating liquid nitrogen to purge the space between the brass plate and the envelope. A tubing from the compressed gas cylinder containing nitrogen peroxide was inserted into the purged envelope and nitrogen peroxide was released at a slow rate until a layer of  $N_2O_4$  frost approximately 2mm in depth was formed on the brass plate. The Saran Wrap envelope was removed after the sample holder was placed in the closed dry-air-purged reflectance attachment of the instrument. To protect the optical system of the instrument from possible damage in the event of release of nitrogen peroxide gas due to the sublimation of the frost, an exhaust line was employed to remove such gas, however, no such sublimation was observed.

A sample of  $H_2O$  frost was prepared by placing the same holder in a closed container with warm water. The container was first purged of



$\text{CO}_2$  by allowing liquid nitrogen to evaporate in it for a few minutes before exposing the brass plate to the vapor from the warm water. The container with the  $\text{H}_2\text{O}$  frost sample was then placed in position for measurement in the dry-air-purged reflectance attachment of the instrument. A second sample of  $\text{H}_2\text{O}$  frost was prepared with the brass plate covered with black electrical tape to determine the influence that the backing material had on the reflectance measurement. This comparison was made only for the  $\text{H}_2\text{O}$  frost. As it was found that the brass backed frost sample was only slightly higher in reflectance than the black tape sample, it is assumed that a 2mm layer of frost is sufficient to give a representative reflectance curve for the frost.

A sample of  $\text{CO}_2$  frost was prepared in a manner similar to that used in the preparation of the  $\text{H}_2\text{O}$  frost. Crushed dry ice was placed in a closed container with the liquid nitrogen cooled sample holder and a layer of  $\text{CO}_2$  frost was deposited on the brass plate.

The other samples of frost prepared and measured consisted of mixtures of  $\text{N}_2\text{O}_4$  frost and  $\text{H}_2\text{O}$  frost,  $\text{N}_2\text{O}_4$  frost and  $\text{CO}_2$  frost, and  $\text{H}_2\text{O}$  frost and  $\text{CO}_2$  frost.

Although the measurements of spectral directional reflectance of  $\text{N}_2\text{O}_4$  frost,  $\text{H}_2\text{O}$  frost, and  $\text{CO}_2$  frost were believed to be of nearly pure samples, there is a possibility of some contamination. No attempt was made to determine the ratio of one frost to another in the mixed samples.

#### B. Measurements in Wavelength Region 0.6 to 2.5 $\mu$ .

Dr. Sebastian Karrer, consultant to Georgetown Observatory, designed a special flask in which solid  $\text{N}_2\text{O}_3$  was formed. The flask was filled with an equivalent amount of  $\text{NO}$  and  $\text{NO}_2$ . These two molecules chemically react to form  $\text{N}_2\text{O}_3$  which is almost complete at low temperatures. The reaction is not instantaneous but requires time for completion. The flask was constructed of an 8-inch diameter round bottom beaker. The neck of the flask was sealed to a vacuum jacketed cold finger which projected into the flask to within approximately 1/4 inch

of the bottom of the flask. The bottom of the cold finger was not vacuum jacketed but was treated to provide a roughened surface upon which the cryogenic deposits could adhere. The observations of  $N_2O_3$  are much more difficult than those of  $N_2O_4$  frost,  $CO_2$  frost, and  $H_2O$  frost because the  $N_2O_3$  disassociates into  $NO$  and  $NO_2$  except at very low temperatures, and also, if exposed to dry air it will become contaminated and disassociates.

The measurements of  $N_2O_3$  were made at the National Bureau of Standards and are presented in NBS Test No. 212. 11P-46/66 entitled "Spectral Directional Hemispherical Reflectance Relative to  $MgO$  of Cryogenic Deposits of  $N_2O_3$ ." The measurements were made by means of a Cary Model 14 recording spectrophotometer, equipped with a Cary Model 1411 reflectance attachment.

#### C. Results of Infrared Experiments.

The study of the infrared spectrum of the oxides of nitrogen was initiated by the article in the American Scientist of December 1963 by Robert M. Danielson entitled "The first Flight of Stratoscope II." Even though only one half of an hour was devoted to tracing the Martian infrared spectrum, reference was made to two features in the Martian spectrum near 2.0 and 2.7 microns. In this article Dr. Danielson states that these features are almost entirely due to Martian carbon dioxide.

In the reflectance experiments conducted at the NBS indeed a  $CO_2$  band at approximately 2.7  $\mu$  appears. However  $N_2O_4$  frost also has a band beginning at 2.6  $\mu$  which is quite wide and extends to about 3.0  $\mu$ . The combination of  $CO_2$  frost and  $N_2O_4$  frost gives a spectrum which fits Danielson's 2.7  $\mu$  band as well as the pure  $CO_2$  band. The  $N_2O_4$  frost begins to absorb just in the region where Danielson indicates the presence of 10 microns of water vapor in the Martian atmosphere.

The  $N_2O_3$  spectrum shows features at approximately 1.37  $\mu$  which is weak, at approximately 1.72  $\mu$  which is weak, at approximately 1.81  $\mu$

which is strong, at 1.89  $\mu$  which is weak, at 1.95  $\mu$  which is weak, at 2.0  $\mu$  which is weak, at 2.14  $\mu$  which is strong, and a strong absorption feature starting at approximately 2.24  $\mu$  and continuing out to 2.5  $\mu$  (the end of the tracing) with slight undulations.

At first glance and without better Martian data we can conclude the following

1. That Danielson's data does not negate the presence of the oxides of nitrogen on Mars.
2. That the absorption which he attributes to water vapor on Mars could be equally well attributed to either  $N_2O_3$  or  $N_2O_4$ .
3. That a combination of  $N_2O_4$  frost and  $CO_2$  frost fits his 2.7  $\mu$  band as well as  $CO_2$  frost by itself, but that pure  $N_2O_4$  would not fit Danielson's data because its absorption feature extends to longer wavelengths than Danielson's absorption band does.
4. That the scatter in points starting at 2.1  $\mu$  and continuing to 2.5  $\mu$  can be attributed to  $N_2O_3$  absorption.
5. Better Martian data is needed in order to unambiguously fit the laboratory data.

#### Area 4. Other Work.

1. A note was published entitled "Faint Terrestrial Lines in the Solar Spectrum Near 8200 $\text{\AA}$ " in the Astrophysical Journal, Volume 143, page 595, February 1966. This article in answer to two articles published by Kaplan, Spinrad, and Munch concerning the evidence of water vapor on Mars.
2. The correlation studies of Martian phenomena will be compiled and finished this summer when the assistant who is performing this project returns to Washington.
3. A Masters thesis is being completed which is aimed at determining the variations of  $NO_2$  in the earth's atmosphere from studies of the lunar spectrum at various times and altitudes.

4. Additional motion pictures have been taken of laboratory experiments exhibiting the characteristics of the oxides of nitrogen.

Personnel in Grant.

Dr. Francis J. Heyden, S. J., Research Director

Dr. Carl C. Kiess, Assistant Project Director

Dr. Sebastian Karrer, Consultant

Dr. Whiting R. Willauer, Project Head

Dr. Ahmad Kiasatpoor, Project Assistant

Dr. Harvey W. Banks, Project Assistant

Graduate Student Assistants.

Mr. Rong-an Lin

Mr. Robert E. Murphy

Mr. Marvin B. Mullenix

Mr. Carl S. Brown

Undergraduate Assistants.

Mr. Pasquale A. Alberico

Mr. Robert T. Staron

Financial Report.

C. f. University Nonprofit Institutional Management Report  
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