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Semi-Annual Report on

REFLECTION SPECTRA AS A BASIS FOR STUDYING EXTRATERRESTRIAL LIFE

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Principal Investigators: Professors Melvin Calvin and Harold F. Weaver

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PLANETARY SPECTROSCOPY

Accomplishments During the Past Semi-Annual Period and Current Status

1. Instrumentation to obtain planetary infrared spectra. Work on the Michelson interferometer has been held in abeyance until the successful application of a grating monochromator currently on order.

2. Calculations of the effect of re-radiation in lunar craters on apparent brightness temperatures. There are two parts to the study of the effects of re-radiation on the apparent brightness temperature. The first part is related to the hot spots observed by Shorthill and Saari of Boeing. We have programed craters of various depths on the computer, and found that they cool more slowly than the surrounding area during an eclipse or lunation. A comparison of our results with the observations suggests that certain areas of the lunar surface, particularly in the large rayed craters, are covered with small craters with depths approximately equal to the diameter and dimensions of the order of 1 cm or greater.

The second part of our investigation is concerned with the anomalous daytime radiation patterns observed by Pettit and Nicholson. The Moon's surface is known to have a pronounced back-scattering lobe from the observation of the high visual brightness at full moon. What is not as well known is that the Moon's surface is also a thermal backscatterer. Backscattering can be produced by various roughness models. However, our study shows that the radiation patterns observed can only be explained by a surface covered with hemispherical shaped craters, whose dimensions may be as small as 1 mm. The study has been completed and forms the Ph. D. thesis of Mr. D. Buhl of the Department of Electrical Engineering. The research was codirected by W. J. Welch and was supported in part by NASA Grant NsG 243.

3. The search for a halo effect on Venus. At Kitt Peak National Observatory, B. T. O'Leary performed photometry of Venus in three colors (B, V, and R) between phase angles 153° and 165°, before and after inferior conjunction of 1966. These results, along with an interpretive study of the photometric, colorimetric, and polarimetric characteristics of Venus as it passes through these phase angles, suggest a halo effect of brightness amplitude 0.05 magnitude. The most common terrestrial halo phenomenon is a luminous ring located 22° from the Sun or Moon, and is due to the presence of hexagonal ice crystals in the atmosphere. Although the existence of a Venus halo effect cannot now be definitely established, it is suggested by many types of observations and is not inconsistent with any observations. A halo effect would indicate definite proof of ice as a constituent of the Venus cloud layer because of the uniqueness of the angle and brightness, color, and polarization curves corresponding to an index of refraction of 1.31 and a hexagonal shape. The amplitude of the effect shows that, at most, a small fraction (a few percent) of the tops of the Venus clouds would consist of these halo-producing crystals. The Kitt Peak observations also indicated that Venus was a tenth of a magnitude redder in B-R color index after inferior conjunction than before inferior conjunction at phase angles around 160°. The interpretation of this phenomenon might depend on a change in the scattering properties of the cloud tops from the Venus morning to afternoon, or on local differences between the clouds near each limb during the times of observation. Details will be presented in an article to appear in Astrophysical Journal (December, 1966).

4. The construction of a photometer-polarimeter for laboratory reflection studies of powdered samples. A photometer-polarimeter has been designed and is being constructed for the purpose of measuring reflectivities and polarizations of various possible Martian surface materials. A light source, with a narrow collimated beam, can be set at any angle of incidence, and the photometer-polarimeter can be set at any zenith and azimuth angle of viewing. The phase angle, i.e. the angle at the surface sample between the light beam and direction of observation, can be made as small as $3/4^{\circ}$, so that conditions near Martian opposition

can be simulated. Two detectors, S-1 and S-11 photomultiplier tubes, will enable us to measure values of the polarization and reflectivity at wavelengths between 0.35 and 1.1 μ.

5. The design and construction of a high-vacuum system for studying the interaction of mineral powders with an H_2O and CO_2 – atmosphere in the presence of ultraviolet radiation. One of the most intriguing phenomena on Mars is the darkening wave which moves with the seasons across the planet. Several explanations of this phenomenon have been proposed, but none has been accepted unanimously by the scientific community. One interesting possibility is a reversible reaction of the surface materials with the seasonally-varying atmospheric water vapor in the presence of CO_2 and a high ultraviolet solar flux. To explore this possibility we have designed an all-metal high-vacuum system which will enable us to expose materials of interest to an H_2O and CO_2 atmosphere in the presence of a high UV flux. Analytical techniques available are sufficiently sensitive that we will be able to detect reactions which have proceeded to only very limited degrees. The results should be of value not only for considerations of the darkening wave but also of weathering processes on Mars in general. This information is particularly important when considering Martian landers, since the weathering processes acting on Mars and shaping the surface materials are markedly different from anything on Earth with which we are familiar. The equipment to carry out this study has been partially ordered, and it is anticipated that the remainder of the equipment will be ordered shortly.

6. A re-examination of the polarimetric evidence for an atmosphere on Mercury. B. T. O'Leary and D. G. Rea have submitted a paper to Nature on the polarimetric evidence for an atmosphere on Mercury. Dollfus interpreted polarization differences between green and red wavelengths, and between the Mercurian cusps and center, as being due to the presence of a molecular atmosphere of surface pressure $p_s \sim$ 1 mb. However, O'Leary and Rea found that Dollfus' assumptions were incorrect. Such polarization differences occur in the laboratory and on the Moon, and can be explained best by the surface of Mercury alone. An upper limit of $p_s \sim$ 1 mb was deduced. This result conflicts with the only other evidence for a Mercurian atmosphere, where

$p_s > 3.3$ mb was inferred from observations of CO_2 absorption at 1.6 μ by Moroz. Moroz' observations were very marginal, so it is suggested that his results are spurious. Thus, Mercury might have been conditioned by similar mechanisms as the Moon, so that $p_s < 10^{-5}$ mb for solar protons to reach the Mercurian surface.

Proposed Program for the Next Semi-Annual Period

1. Debugging of the interferometer has been postponed until a more modest instrumentation program, now initiated, is well underway. This is the application of a 0.5 meter McPherson monochromator to the 120" telescope to obtain near infrared planetary spectra. The monochromator, together with several diffraction gratings, has been ordered and optics have been designed to couple it to the telescope. The instrument will be used initially as part of our site evaluation work for a planetary telescope in the White Mountains of eastern California, and will later be put in use on the 120" telescope. When it is producing good planetary data, we will then return to the interferometer and debug it.

2. The photometer-polarimeter will be used for measurements on a variety of mineralogical samples pertinent to the nature of the Martian surface. Measurements of suspended particles will also be carried out. Dollfus' extensive polarimetric work on Mars, much of it unpublished, will then be re-examined in the light of our laboratory data. Calculations of the scattering properties of a variety of atmospheres, containing various amounts of particulate matter, will also be incorporated in the re-evaluation, It is expected that this will result in a significant improvement in our knowledge of the Martian atmosphere and surface. In addition, photometry and polarimetry of Mars in the April 1967 opposition will be performed by B. T. O'Leary at Kitt Peak. This laboratory and observational photometry and polarimetry constitutes the research for O'Leary's Ph. D. thesis in Astronomy.

3. The high-vacuum all-metal system for studying the weathering of putative Martian minerals will be constructed and put into operation. A variety of solid-atmosphere-radiation systems will be tested to obtain information pertinent to weathering processes on Mars and to the darkening wave.

4. A principal shortcoming in planetary studies is the lack of detail in photographs of the planets taken from ground-based observatories. This is a result of the atmospheric turbulence, which restricts the resolution to no better than approximately 0.3" at best, and 0.5" as a general rule. This contrasts with resolution approaching 0.1" achieved by visual observations at the telescope. The improvement for the latter is due to the ability of the eye-brain system to freeze the image for those rare moments when the "seeing" is particularly good. Visual observations have invariably resulted in drawings of the planets showing much finer detail than the corresponding photographs. However, they are beset with the subjectivity of the observer which decreases their value considerably and makes them almost useless for quantitative studies of brightness variations. Attempts have been made to improve the photographic pictures by superposing several selective photographs. We believe that the superposition procedure can be significantly improved by the use of equipment developed for a government agency and to be used for terrestrial surveillance. The procedure will be to take a large number of very short exposure pictures, scan each of them with a flying spot scanner and evaluate the image quality electronically, select those images of the highest quality, and then superpose them using electronic correlation techniques to form a final image. It is believed that we can obtain access to the equipment to evaluate the photographs and to superpose them, at least to the extent that we can evaluate the technique. This approach should produce photographs approaching the 0.1" theoretical resolution of the 36" refractor at Lick Observatory.

Personnel:

Dr. Donald G. Rea - Associate Research Chemist;

David Buhl, Norriss Hetherington, Robert Mifflin, James Nicholls, and Brian O'Leary - Graduate Students; and

Dawn Nyman - Principal Clerk.

Electronics technicians and machinists have been employed at various stages of this work.

Publications and Lectures:

Rea, D. G. The Atmosphere and Surface of Mars--A Selective Review, Proceedings of the Cal. Tech. -JPL Lunar and Planetary Conference, JPL Technical Memorandum No. 33-266 (1966).

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Rea, D. G. Remote Sensing of Planetary Environments from the Microwave to the Infrared, Space Technology Seminar, Stanford University, Stanford, California, July 28, 1966.

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O'Leary, B. T., and Rea, D. G. On the Polarimetric Evidence of an Atmosphere on Mercury. Nature. (Submitted for publication.)

DEVELOPMENT OF MASS SPECTROMETRIC AND ANALYTIC TECHNIQUES and ANALYSIS OF ORGANIC MATTER IN ANCIENT SEDIMENTS AND METEORITES

Accomplishments During Past Semi-Annual Period and Current Status:

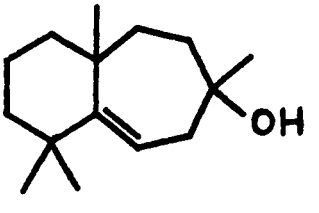
Introduction

In May and June the relocation of equipment from Leuschner Observatory and the College of Chemistry in the new Space Sciences Laboratory on Grizzly Peak Boulevard was completed. These new facilities, located on the first floor of the Space Sciences Laboratory, permitted the mass spectrometry laboratory to be concentrated in one physical location for the first time and brought to the members of the group of chemists, graduate students, engineers, programmers, and technicians an esprit de corps that carried the rebuilding and modification of our high resolution mass spectrometer to an unprecedentedly high level of performance which was achieved during the month of June. Our new location permitted a rational reorganization of research activities in addition to the considerable improvement in our instrumental capabilities, particularly with respect to the quantity and quality of data output that previously had been hampered considerably by difficulties due primarily to inadequate physical arrangements. It should

be mentioned also here that enthusiasm and productivity during the beginning of the summer, which has carried along at a high level, was enhanced by the funding of our Apollo Mission Proposal for the upgrading of our analytical mass spectrometric facilities and the closed-loop computer control of the high resolution mass spectrometer system under NASA Grant NGR-05-003-134. This occurred in June at an opportune time to provide the funds for badly-needed new equipment and, most of all, personnel, in the research area, but primarily in the engineering and computer-programming areas necessary to initiate the proposed sophisticated approach to data acquisition, processing, and computer-aided interpretation of mass spectral data. This aspect will be reported in a separate report on the Apollo grant. The research efforts of the group during the last period generally continued to center around the application of mass spectrometry to the solution of molecular structure problems and can be divided into the following categories: Natural Products, Chemistry, Mechanistic Studies of Fragmentation Reactions occurring on Electron Impact in the Ion Source of a Mass Spectrometer, and Organic Geochemistry.

1. Mechanistic Mass Spectrometry.

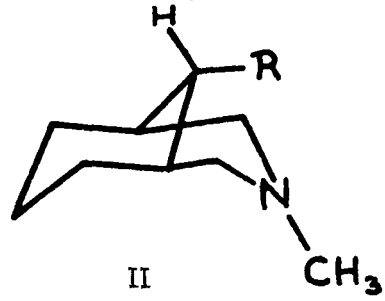
a. Sesquiterpenes. Several mass spectrometric investigations have been undertaken with the aim of elucidating the detailed mechanism of the ionic decomposition pathways. The systems studied include the sesquiterpenes widdrol I and thujopsene, where high resolution mass spectrometry, together with isotopic labeling, led to a complete delineation of fragmentation sequences.



I

b. Azabicycloalkanes. A second class of compounds investigated is represented by the azabicyclic system II, whereby it proved of particular interest to establish the effect of stereochemistry of the bridgehead substituents on the fragmentation pattern of these compounds. It could be shown that the bridgehead stereochemistry can lead to qualitative

differences in the fragmentation sequences. In continuation of these studies, the effect of stereochemistry on mass spectrometric elimination reactions in dicyclic bases of type III has been initiated. The study of these compounds,



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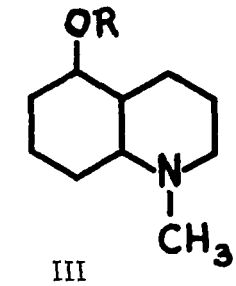


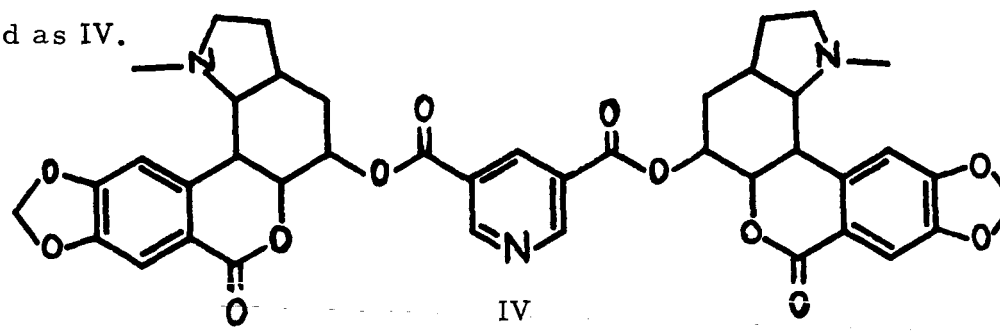
III

where organic chemical behavior is well investigated, will provide an interesting basis for comparison of mechanisms operative in solution chemistry with those responsible for the fragmentation of ionized excited systems in the gas phase.

c. Diketones. The mechanisms of fragmentation of aliphatic diketones have been studied in detail by high resolution mass spectrometry and isotopic labeling techniques. Since the mass spectrometric behavior of simple monoketones is reasonably well understood, the study of a diketone system encompassing the simple carbon backbone provided the opportunity to investigate the effect of the introduction of a second functional (and fragmentation directing) grouping. It could be demonstrated that the fragmentation pattern and underlying mechanism of these diketones differed in several important points from those of monoketonic compounds. Thus, β-cleavages were much more prevalent in diketones than in monoketones and some complex decompositions involving hydrogen rearrangement were incurred for diketones which either do not occur or are of minor importance in monoketone systems.

2. Natural Products

a. Clivimine (dimeric alkaloid of the Amaryllidaceae). In collaboration with others the structure of the alkaloid clivimine could be established as IV.



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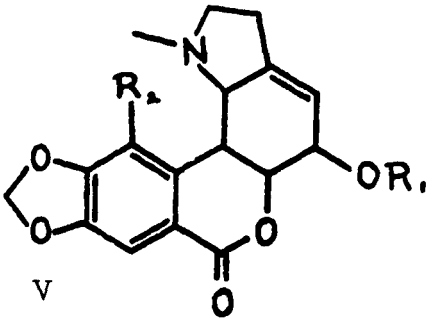

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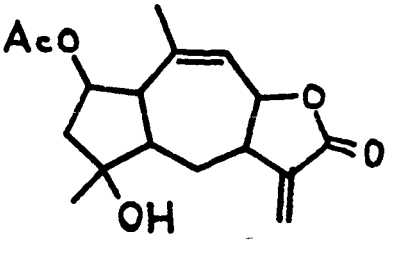
In connection with this work a thorough investigation of the mass spectrometric behavior of lactone alkaloids of type V was undertaken. The ionic decomposition pathways of these substances could be delineated.

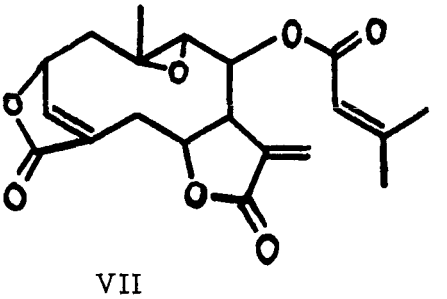
b. Sesquiterpenoid and steroidal lactones (Gaillardin, elephantopin and withaferin A). The collaboration with Professor Kupchan's group (University of Wisconsin) has been continued and resulted in the structural elucidation of several sesquiterpenoid lactones and one steroidal lactone. High resolution mass spectrometry played an important role in these investigations.

For gaillardin structure VI could be established; the mass spectra of a number of derivatives of VI have been investigated.

Elephantopin, a tumor inhibitor, could be shown to possess gross structure VII, whereas for withaferin A the interesting steroidal skeleton was derived.



VI



VII

Structural studies on several other compounds of this type are in progress.

3. Organic Geochemistry. Work on the isolation and characterization of organic materials and oils has continued along the general lines of our previous efforts. Areas under investigation during the last period include:

a. Moonie Oil. An analysis of the hydrocarbon constituents of the Moonie Oil from Australia (ca. 200 million years in age) has been completed. Utilization of chromatographic techniques and mass spectrometry led to the isolation and identification of several series of hydrocarbons. These comprise the C_{15}, C_{16}, C_{18}, C_{19}, C_{20} and C_{21} isoprenoids; a C_{15} iso-alkane, as well as the C_{18} anteiso-alkane; and two members of the cyclohexyl alkane series (C_{15} and C_{16}). Several other hydrocarbons could be isolated but not unambiguously identified by our present techniques. The analysis of the Moonie Oil derives some significance from the fact that it provides a comparison of the constituents present in an oil from the Australian continent with those from other sediments and oils analyzed in this laboratory and elsewhere.

b. Occurrence of a C_{17}-isoprenoid alkane. In a continuation of our hydrocarbon analysis, it has now been possible to demonstrate the presence (in very small amounts) of the C_{17}-isoprenoid hydrocarbon in extracts from the Antrim Shale (Michigan, Devonian Age, 265×10^6 years) by a combination of GLC coinjection experiments and mass spectrometric analysis. The C_{17}-isoprenoid had thus far not been found in any shale or oil investigated, and its presence is of significance in relation to the question of possible precursors of the isoprenoid alkane material found in geologic formations. In the course of this work several isoprenoid-type hydrocarbons were synthesized (including 2,6,10-trimethyl hexadecane; 2,6,10,13-tetramethyl pentadecane; 2,6,10,14-tetramethyl heptadecane; 2,6,10,15-tetramethyl heptadecane) to serve as reference standards for comparison with compounds isolated from geologic source materials.

c. Acidic and Basic Materials from the Green River Shale, Rifle, Colorado. From the Green River Shale small quantities of both acidic and basic compounds have been obtained by extraction techniques. Chromatographic separation (absorption and GLC techniques) of individual

substances is in progress and structural studies on several components already isolated in small amounts is being carried out, relying most heavily on mass spectrometric and other physical methods. It is intended to extend the investigations to include the phenolic materials, as well as the carboxylic acids.

d. Steranes. Further work on the characterization of the sterane fraction from the Green River Shale is in progress. For this purpose fairly large quantities of rock material have been extracted and the separation of individual steroid hydrocarbons is now to be carried out.

Projected Program for the Ensuing Semi-Annual Period

The mass spectrometry and organic geochemistry groups will continue to concentrate their efforts on the three areas mentioned in this report.

Heavy emphasis on the broad scope of molecular structure studies both in the natural products field and more in organic geochemistry will continue to provide the challenge to our current understanding of the nature of molecular fragmentation and its correlation with the detailed features of molecular architecture. Such a forefront of chemical and geochemical studies on ever decreasing amounts of organic sample must be balanced by vigorous research effort into the mechanistic nature of electron-impact induced decomposition of organic molecules both involving the rearrangement of hydrogen atoms and either functionality or carbon skeleton. For these reasons, it is necessary to gain experience on three research fronts which will yield an iterative body of knowledge upon which a group such as ours can attack the formidable problems of the composition of ancient sediments and their organic precursors.

Personnel:

Under the supervision of Professors Calvin and Burlingame the following people were engaged in the research results described.

Dr. Catherine C. Fenselau (A. A. U. W. Fellow, 1966/67), Dr. Heinrich K. Schnoes - Research Associates;

Pat Haug, Eugene McCarthy, William Van Hoeven - Graduate Students;

Fred C. Walls - Spectroscopist;

Patricia Murphy, Sandra Noton - Clerical Workers.

Dr. Pierre Longevialle (NATO Fellow) and Mr. Dennis H. Smith (NASA Trainee, 1966/67; 1967/68) have also been associated with these researches.

Additional supporting staff are associated with NASA Grant NGR 05-003-134.

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