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SATURN AND JUPITER: A STUDY OF
ATMOSPHERIC CONSTITUENTS

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION
OF THE UNIVERSITY OF HAWAII IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
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IN ASTRONOMY
MAY 1975

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ABSTRACT

An explication is given of the optical technique known as sky subtraction, applicable in astronomical Michelson interferometry. Cancellation of the sky background is possible if background radiation is introduced in both arms of the interferometer. The method imposes stringent requirements upon the beamsplitter. We discuss an astronomical photometer incorporating sky subtraction whose design permits object measurement 100% of the time and tailoring of the spectral response by controlled oscillation of one mirror. The photometer may be especially valuable in the submillimeter region.

The operation of a Digilab sky-subtracting Fourier-transform spectrometer is described; the instrument was employed for much of the planetary studies presented in this work. Advantages of the system include: elimination of low-frequency noise problems through rapid scanning, real-time co-adding of interferograms under computer control, and great flexibility in manipulation of data after acquisition.

We describe a search for H₂O in Jupiter's atmosphere. Image-tube spectra of the N. Equatorial Belt in the 8200-A region in September 1973 show no more than 10 precipitable micrometers of H₂O. We attempt to detect the 6190-A band of CH₄ in 50 A/mm spectrograms of Pluto and Triton;
upper limits of 7 and 6 meter-atmospheres are found respectively.

Features due to NH$_3$ gas are sought in 1-3 $\mu$m spectra of Saturn having resolution 0.5 cm$^{-1}$. A search in the 1.6-$\mu$m region (6400 cm$^{-1}$), where absorption by CH$_4$ is weak, yields an upper limit of 1 cm-atm for the columnar NH$_3$ abundance. No absorption is found from NH$_3$ in the 2-$\mu$m band (5000 cm$^{-1}$) or even in the vicinity of the strong 3-$\mu$m band (3325 cm$^{-1}$), which gives the most stringent test: an upper limit of 0.5 cm-atm results.

We search in the 1.6-$\mu$m Saturn spectrum for evidence of C$_2$H$_2$ and H$_2$S. Neither molecule is detected, but improved upper limits result: 1.5 cm-atm for C$_2$H$_2$ and 15 cm-atm for H$_2$S.

The S(1) line of the pressure-induced fundamental band of H$_2$ is measured in the spectra of Saturn and Jupiter. The broad line at 4750 cm$^{-1}$ lies in a region free from absorption by CH$_4$ and NH$_3$. The line is about 99% absorbing in the core; the high-frequency wing extends to at least 5100 cm$^{-1}$. We compare the observed line shape to the predictions of both a reflecting-layer model (RLM) and a homogeneous scattering model (HSM). The RLM provides a good fit to the Saturn profile for temperatures near 150 K; the derived base-level density is 0.52 (+0.26, -0.17) amagat and the H$_2$ abundance is 25 (+10, -9) km-amagat, assuming a scale height 48 km. The Jupiter profile
is fit by the RLM for a temperature near 248 K, implying either that the line is formed below the upper cloud level or that there is (unidentified) continuum absorption at 5000 cm$^{-1}$. The HSM does not fit the data of either planet for reasonable assumptions of atmospheric temperature. Derived RLM densities and abundances for both planets are substantially lower than those resulting from RLM analyses of the H$_2$ quadrupole lines, the $3\nu_3$ band of CH$_4$, and from other sources.
INTRODUCTION

"Seized in thought,
On Fancy's wild and roving wing I sail,
From the green borders of the peopled EARTH,
And the pale MOON, her duteous fair attendant,
From solitary MARS, from the vast orb
Of JUPITER, whose huge gigantic bulk
Dances in ether like the lightest leaf,
To the dim verge, the suburbs of the system,
Where cheerless SATURN, 'midst his watery moons,
Girt with a livid zone, majestic sits,
In gloomy grandeur, like an exiled queen
Amongst her weeping handmaids."

Barbauld

Fourier transform spectroscopy has come of age as a technique for studying planets. Most of the known molecular constituents of the major planets have been discovered with a Michelson interferometer. In the past four years we have seen the number of compounds rise from three (H₂, CH₄, and NH₃) to at least nine, with C₂H₂, C₂H₆, CH₃D, C¹³H₄, and H₂O recently discovered. Helium is virtually certain to exist, and there is evidence for PH₃. C₂H₄ may be detected on Saturn (Encrenaz et al 1975). Through the use of interferometers, there now exist for Jupiter excellent spectra in the 1-5 micrometer region (2000-10000 cm⁻¹) with a resolution element of about 0.2 cm⁻¹. There are good spectra in the 10-μm atmospheric window (1000 cm⁻¹) at 1.3-cm⁻¹ resolution,
and the first submillimeter spectra (10-30 cm\(^{-1}\)).* The data existing for Saturn are typically of poorer quality or lower resolution, and there are no published spectra of Uranus and Neptune at all in the infrared. As detectors and amplification methods improve, however, the quality and breadth of spectroscopic information from the major planets will surely increase.

There are many sections of the 1-3 \(\mu\)m spectra of Jupiter and Saturn that have not received detailed study. This circumstance is due partly to the complexity of methane band absorption that dominates both spectra. Also, there are presently few research groups able to perform spectroscopy beyond 1.1 \(\mu\)m, where photographic plates and photomultipliers become insensitive. The \(3\nu_3\) band of methane at 1.1 \(\mu\)m (9100 cm\(^{-1}\)) has been widely studied by both interferometric and dispersive spectroscopy. Atmospheric temperatures in the range 120-140 K and methane abundances between 40 and 140 meter-amagats have been derived for Jupiter and Saturn (see for example de Bergh et al 1973). At longer wavelengths, there has been no spectroscopic feature of comparable usefulness. The purpose of this work is to examine the 1-3 \(\mu\)m spectrum of Saturn particularly, and of Jupiter also, to detect new

*At 1-cm\(^{-1}\) resolution. Martin, Sinton, and Wood 1971, unpublished.
atmospheric constituents if possible and to extract new pressure, temperature, and abundance information from known spectral features. We employ spectra obtained for these general purposes at Mauna Kea Observatory as part of a continuing NASA-sponsored investigation of the planets undertaken at the Institute for Astronomy (grant NGL 12-001-057). The observations were made by the author in close cooperation with Institute staff members William M. Sinton, Dale P. Cruikshank, Carl B. Pilcher, and graduate student Nancy D. Morrison.

We have also performed a search for water on Jupiter (prior to the above-mentioned discovery) and methane on Triton and Pluto, using image-tube techniques, because the goals are similar to those in our interferometric work. The latter two objects are far too faint to seek the strong infrared methane bands by use of the interferometer, and the Jupiter water search was not instrumentally possible in the most desirable infrared wavelength band: the 5-μm atmospheric window.

The optical scheme known as sky-subtraction does not appear to have been treated in astronomical literature, although (perhaps because) the principles involved are basic. The first part of this work attempts to present the ideas needed to comprehend the technique and problems relevant to its use.

The writer's experience in submillimeter Fourier-
transform spectroscopy prompted an inquiry into the potential employment in that region of sky-subtraction techniques currently used in the near infrared. Filter design has been a difficult problem at submillimeter wavelengths; the photometer discussed in part II of the first section of this dissertation contains an inherent filtering characteristic, derived from the sky-subtraction technique.
Instrumental Concerns

I. An Explication of Sky Subtraction

A. Introduction

In astronomical photometry and spectroscopy it is generally desirable to separate the contributions to a detected quantity which arise from the object from those which arise from the background. Scattering of light near bright sources is commonly a problem in the visible part of the spectrum. Thermal radiation from the air and telescope is a difficulty affecting the design of ground-based infrared experiments. Cancellation of the effects of the sky is best achieved if the sky radiation near the object of interest is sampled and compared with the radiation from the object plus sky; this technique varies as few as possible of the instrumental parameters, and therefore is most likely to provide an accurate accounting of the degree of sky-induced contamination.

In the infrared region, techniques which effect a cancellation of background contributions by changing the detector's field of view, so that temporally close signal levels are compared, are known as "chopping" schemes. Typically, a mirror in the telescope-instrument optical train is oscillated to alter the radiation field impinging on a single detector. Associated electronic components subtract the amplified detector signal levels for object
and comparison beam positions of the mirror motion; the difference signal contains the desired contribution of the object itself. If two detectors are employed, it is theoretically possible to view the object 100% of the time. The gain in signal-to-noise ratio (SNR) in the presence of detector noise is limited to $\sqrt{2}$. This gain of 41% is seldom considered to be worth the effort; detectors are often an expensive part of the experiment, and it is difficult to obtain both high sensitivity and matched noise performance. Mismatches in detectivity result in a SNR gain that is less than $\sqrt{2}$.

When a Michelson interferometer is used for spectroscopy (or photometry, as will be described later), it is possible to obtain a continuous optical subtraction of the background radiation by use of a particular characteristic of the instrument. We intend here to describe "sky subtraction" in interferometry, present the origins of the effect, and compare the benefits with those of chopping techniques. Section II will deal with the concept of photometry with a Michelson interferometer, and Section III will present details of the operation of a sky-subtracting interferometric spectrometer that was used to obtain much of the data discussed later in this work.

B. The Idea of Sky Subtraction

The heart of the Michelson interferometer is the beamsplitter, which divides the amplitude of an incoming
light wave's electric field, and permits subsequent superposition of the beams returning from the interferometer mirrors. Phase shifts are introduced by reflections from the beamsplitter and the mirrors, and also by transmission through the beamsplitter. Beams leave the interferometer in both arms, with amplitudes equal to the superposed amplitudes of the various waves that exit the instrument in the same direction. The resultant amplitude may be squared to give the output intensity, the quantity sensed by any detector. Detailed mathematical treatment of the wave relationships has been presented by Bell (1972) and by Pilcher (1973).

Sky subtraction arises from, and depends upon, the phase shifts induced by the beamsplitter in entering light waves. Let us consider an interferometer in which the moving mirror has been positioned so that there is zero difference in optical path between the two central-axis distances from the mirrors to the beamsplitter. We call this condition zero OPD (optical path difference). A single monochromatic beam, which we call beam A, enters one arm of the instrument, also labeled A, and is divided into four components (figure 1). These are labeled by the order and nature of their interactions with the beamsplitter: \( A_{TT}, A_{RR}, A_{RT}, \) and \( A_{TR} \). Here T stands for transmission and R reflection. Beams \( A_{TT} \) and \( A_{RR} \) exit along the same axis that they entered. For the ideal
Fig. 1. Relative phases of interferometer output-beam components.
beamsplitter, which is a free-standing dielectric film with no absorptive losses, beams $A_T$ and $A_R$ will differ in phase by $\pi/2$ (Tescher, 1971), and thus beams $A_{TT}$ and $A_{RR}$ will differ by $\pi$. This result will be explained in detail later. If the reflectance $R$ and transmittance $T$ of the beamsplitter are equal (which is not true in general), then beams $A_{TT}$ and $A_{RR}$ will superpose to give zero amplitude, and zero intensity will be detectable in the output at arm A.

The output in arm B will consist of beams $A_{RT}$ and $A_{TR}$; they will not differ in phase, and therefore produce constructive interference. The full intensity of beam A is the output at arm B.

We now introduce beam B in arm B. For the condition of zero OPD, symmetry dictates that beam B must produce no intensity in arm B and full intensity in arm A. A detector placed in arm A will see no radiation from beam A, and all of the intensity of beam B. A detector in arm B will see all of beam A and none of B. We assume here no physical blockage of beams by detectors and also $R = T$.

At mirror positions other than that for zero OPD the situation changes. For a mirror displacement of $\lambda/4$ ($\lambda$ = wavelength of incident radiation), beams $A_{RT}$ and $A_{RR}$ (for example) will have an additional path difference of $\lambda/2$, relative to beams $A_{TR}$ and $A_{TT}$. Thus, the phase difference between $A_{TT}$ and $A_{RR}$ becomes 0, and between
ART and A_TR, π. Constructive interference will occur where it was destructive at zero OPD, and vice-versa. As the moving mirror sweeps through successively larger path differences, a detector in either arm will see alternately radiation from beam A and beam B, with the intensity of each beam varying as $\sin^2 (\omega t)$, but with the two being out of phase.

Since the detector is sampling radiation from both beams, a kind of "chopping" occurs. Consider input beams of intensity $I_A$ and $I_B$ entering the interferometer in the two arms. A detector in arm A or B will see the intensity

$$I_1 = I_A \sin^2 \omega t + I_B \sin^2 (\omega t + \pi/2) \text{ (arm A)}$$

$$I_2 = I_A \cos^2 \omega t + I_B \cos^2 (\omega t + \pi/2) \text{ (arm B)}$$

where $\omega = 2\pi \sqrt{v}$, $v$ is the speed in cm/sec. at which the OPD is changing, $\nu$ is the wavenumber of the radiation, and $t = 0$ when OPD = 0. If $I_A = I_B$, then $I_1 = I_2 = I_A = A_B$, and there is no sensible interferogram (infrared detectors are normally AC-coupled and therefore have low response to the DC component of input radiation).

Usually, the object of interest is present in one beam, creating a difference in intensity $I_A - I_B$. Then, the intensity in arm A is

$$I_1 = I_B + (I_A - I_B) \sin^2 \omega t$$

[3]

The variable component is detected. There may well be variations in $I_A - I_B$ due to factors other than the object, such as spatial inhomogeneities in sky emission, attenu-
ation, or scattering. The effect of these variations, insofar as they are random in space and time, is reduced by the coherent addition of a large number of interferograms (see description of instrument in Section III). With chopping techniques the same problems may occur and are likewise solved by the expenditure of observing time.

We note that in sky subtraction, the use of two detectors is natural. The symmetric layout of an interferometer makes this procedure physically more convenient than it would be in most photometric systems, but the problems mentioned earlier regarding detectivity are not overcome, and commonly only one detector is employed. The object of interest is then viewed with a duty cycle determined by equation [1], which applies to each frequency of the input radiation.

We now derive a useful relationship between the phases of beams that are passed through and reflected from a freestanding dielectric beamsplitter. The result, which was used above, is necessary and sufficient for sky subtraction to function as we have described.

The following Fresnel formulae give the reflection coefficients for incidence from medium 1 onto medium 2, with refractive indices $n_1$ and $n_2$ respectively, and angles of incidence $\theta_1$ and refraction $\theta_2$ (measured to the normal):

$$
\hat{n}_{12} = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2}
$$

[4]
for the electric vector perpendicular to the plane of incidence;

\[
\lambda_{12} = \frac{n_1 \cos \Theta_1 - n_2 \cos \Theta_2}{n_1 \cos \Theta_1 + n_2 \cos \Theta_2}
\]  \hspace{1cm} [5]

for the electric vector parallel.

The corresponding values of the transmission coefficients are:

\[
t_{12} = \frac{2 n_1 \cos \Theta_1}{n_1 \cos \Theta_1 + n_2 \cos \Theta_2}
\]  \hspace{1cm} [6]

\[
t_{12} = \frac{2 n_1 \cos \Theta_1}{n_1 \cos \Theta_1 + n_1 \cos \Theta_2}
\]  \hspace{1cm} [7]

Following the treatment given by Born and Wolf (1964, p. 61), the total reflection coefficient for incidence upon a slab of index \( n_2 \) and thickness \( h \) is:

\[
\rho = \frac{\lambda_{12} (1 + e^{2i\beta})}{1 + \lambda_{12}^2 e^{2i\beta}}
\]  \hspace{1cm} [8]

\[
t = \frac{t_{12}^2 e^{i\beta}}{1 + \lambda_{12}^2 e^{2i\beta}}
\]  \hspace{1cm} [9]

where \( \beta = \frac{2\pi}{\lambda} n_2 h \cos \Theta_2 \) and we assume \( n = n_1 \) on both sides of the slab. Tescher (1971) has shown that the reflected and transmitted beams differ in phase by \( \pi / 2 \). We reproduce here his derivation. If the complex numbers \( \lambda \) and \( t \) are expressed in polar representation:

\[
\lambda = n_0 e^{i\delta_{\lambda}} \quad t = t_0 e^{i\delta_t}
\]
then $\delta_r$ and $\delta_t$ are the phase changes undergone by the reflected and transmitted beams. In cartesian representation,

$$\lambda = \kappa + i\gamma \quad \text{so} \quad \tan \delta_\lambda = \frac{\gamma}{\kappa}.$$ 

Thus we get, using [8] and [9]:

$$\tan \delta_\lambda = \frac{-n_{12} (1 - n_{12}^2) \sin 2\beta}{n_{12} (1 + n_{12}^2) (1 - \cos 2\beta)}$$ \hspace{1cm} [10]

$$\tan \delta_t = \frac{1 + n_{12}^2}{1 - n_{12}^2} \tan \beta$$ \hspace{1cm} [11]

The signs in these expressions are appropriate for $n_{12}$ negative at the first interface and positive at the second interface. We form now the product

$$\tan \delta_\lambda \tan \delta_t = \frac{-\sin 2\beta \tan \beta}{1 - \cos 2\beta}$$

$$= \frac{-2 \sin \beta \cos \beta \sin \beta}{\cos \beta (1 - 1 + 2 \sin^2 \beta)}$$

$$= \frac{-2 \sin^2 \beta}{2 \sin^2 \beta} = -1.$$ 

Therefore, $\tan (\delta_\lambda - \delta_t) = \frac{\tan \delta_\lambda - \tan \delta_t}{1 + \tan \delta_\lambda \tan \delta_t} = \infty$

from which $\delta_\lambda - \delta_t = \pi/2$. \hspace{1cm} [12]

This result applies for incident light of either polarisation, and therefore also for the general case of unpolarised light. In figure 1, we show schematically the consequences of [12] in an interferometer with a non-absorbing dielectric beamsplitter. Let the phase shift $\delta_t$ be equal to $\infty$ for the particular material, thickness, and wavelength chosen.
The reflected beam then has phase $\alpha + \pi/2$. Phase shifts of $\pi$ occur at the reflections from the two metal interferometer mirrors. The beams return to the beamsplitter, where beam TT acquires a total phase shift $2 \alpha + \pi$. Beam RR has phase $2 \alpha + 2\pi$, and we note the relative shift of $\pi$ between these two beams leaving in the same arm. Beams RT and TR both acquire phase shifts $2 \alpha + \frac{3\pi}{2}$; these two combine constructively, as stated near the beginning of this section.

It is important to realize that for this simple case, the effectiveness of sky subtraction does not depend on the value $\alpha$. However, the distribution of amplitude between reflected and transmitted beams does depend on the material, thickness, and wavelength of concern. To maximize the efficiency of the instrument, we may therefore adjust $n_2$ and $h$.

Ideally, a beamsplitter will be characterised by a reflectance $R$ and transmittance $\gamma$ each equal to 0.5. In the absence of absorption, $R = 1 - \gamma$. Output beams of an interferometer are the result of both reflections and transmissions at the beamsplitter, so to maximize modulated intensity, $R$ and $\gamma$ must both be high. The $R\gamma$ product is proportional to beamsplitter efficiency and is often expressed to describe them. The maximum value of the product is clearly 0.25.

We calculate the reflectance of a freestanding
silicon film at 2 μm wavelength to provide a realistic example of the values of $R$ which may be obtained with high-index materials. Silicon is in fact the beamsplitter material used in the interferometer described in Section III. At normal incidence,

$$R = \left( \frac{1 - 3.45^2}{1 + 3.45^2} \right)^2 = 0.715$$

This value is the maximum that occurs when the optical thickness $n_2 h = m \lambda / 4, m = 1, 3, 5, \ldots$. The silicon film cannot be freestanding for small $m$, and a thick plate would have noticeable absorption and undesirable dispersive effects. Consequently, the silicon is deposited in the desired thickness onto a substrate such as CaF$_2$ ($n = 1.42$ at 2 μm). In this case, the maximum reflectivity at the CaF$_2$/Si interface becomes

$$R = \left( \frac{1.42 - 3.45^2}{1.42 + 3.45^2} \right)^2 = 0.616$$

To ensure a high $R \cdot \tau$ product over a fairly wide wavelength band, the thickness $h$ is carefully chosen, as well as the choice and thickness of substrate. The results of thin film deposition research are presented in the context of beamsplitters by Tescher (1971).

There are numerous complications over the simple
dielectric case that arise in the design of near-infrared beamsplitters for astronomical use. The two polarisations of light have different reflection-transmission properties. The substrate plate, supporting the beamsplitter, and the compensating plate both have finite surface reflections. The dielectric material may have a non-zero absorption coefficient, which alters the simple relationship between $\delta_r$ and $\delta_t$. This last effect is crucial. Inspection of figure 1 will show that modification of the phase relationships between, for example, beams $A_{TT}$ and $A_{RR}$ will result in incomplete interference for any position of the moving mirror. The amplitude of the variable component in [3] decreases, and detection of the factor $I_A - I_B$ is hindered.

To deal with these problems, we present a specific beamsplitter-substrate-compensator example and investigate numerically the magnitudes of the first and second complications. The problem of beamsplitter absorption will then be discussed, as a pathological variant of the simple dielectric film.

In figure 2 we show a schematic beamsplitter in its full complexity. A Si coating of thickness $S$ is deposited on a CaF2 substrate of thickness $L$. A compensating plate of thickness $L$ is separated (in general) from the coating by a small air gap of width $H$. The compensating plate is tilted slightly with respect to the coating to reduce the amplitude of "channeling" modulation in the interferogram produced by multiple reflections in the gap.
Fig. 2. Intensities of beams produced by interaction of a polarized beam with a CaF$_2$/Si beamsplitter.
region. The tilt will not affect our calculations, since we shall not be assigning particular values to $H$.

We take the refractive index of CaF$_2$ to be 1.42 at 2 $\mu$m, and that of silicon, 3.45. The angle of incidence on the system is 45$^\circ$ in all cases. Reflection coefficients are calculated from equations [4] and [5], and reflectances are taken to be $|\eta|^2$. The transmitted intensities are given by $1 - R$ if no absorption occurs.

For an incident wave with the electric vector perpendicular to the plane of incidence, the reflected and transmitted intensities are shown for incidence from either side of the system (figure 2). It can be seen that for incidence through the substrate, two nearly equal reflected components occur, which will differ in phase by

$$\phi = \left( \frac{2\pi}{\lambda} \right) \cdot \text{OPD} + \pi = \frac{2\pi}{\lambda} \left[ S \cdot \sqrt{\left( \frac{n(Si)}{n(CaF_2)} \right)^2 - \frac{1}{2}} + \frac{1}{4} \right]$$

(Bell 1972, p. 113). Here we recognise that a phase shift of $\pi$ occurs at every reflection from a surface of higher index, and no shift occurs when incidence is on a lower index medium. Both beams have the same optical path length through the CaF$_2$. We get

$$\phi = (8.09 \times 10^4) \cdot S \text{ cm}^{-1}.$$  

Now the minimum phase shift which will give constructive interference for a finite $S$ is $2\pi$. This minimum $S$ will also give the widest range of $\lambda$ between successive minima.
in reflected intensity. We set $\varphi = 2\pi$ and get $S = 0.776\mu m$. With this value, the reflected intensity of the two components is 0.411.

Clearly there will be interference between the beams mentioned above and the first surface reflection from the CaF$_2$, having intensity 0.0732. It is possible to tailor also the value $L$ to obtain constructive combination of this small component with the other two.

The thickness of the compensating plate is made equal to that of the substrate. In such a case, we see that the transmitted beam and the two major reflected components have traversed equal optical paths in CaF$_2$. Thus, whatever $\delta_r$ and $\delta_t$ happen to be, we can subtract from both the contributions from the CaF$_2$, so that we are left with the Si coating as the only source of differences between $\delta_r$ and $\delta_t$. But we have found that for an isolated dielectric film, $\delta_r - \delta_t = \pi/2$, so that the results obtained above for a dielectric film that is freestanding apply to the complex beamsplitter, provided that the substrate and compensator are precisely equal in thickness, or differ by precisely

$$\Delta L = \frac{m \lambda \cos \Theta_2}{n_2} \quad m = 1, 2, 3, \ldots$$

We keep the thicknesses nearly equal rather than allow $m$ to be very large because the substrate material has dispersion. By providing a compensator at virtually the same
angle to the beams as the beamsplitter, we ensure that the dispersion is effectively equal in both reflected and transmitted beams.

If the incident beam is polarised with the electric vector parallel to the plane of incidence, the reflected and transmitted intensities are different from those given above. Much less light is reflected; for the materials and wave-length used above, nearly 70% of the incident intensity is transmitted (see figure 3). We again find two nearly equal reflected components for incidence through the substrate, and a single major component for incidence through the compensating plate.

If a completely unpolarised beam is incident on the system described above, the resultant reflected and transmitted intensities will be the same as for an incident beam consisting of two equal intensity beams, one polarised parallel and one perpendicular to the plane of incidence. We assume that the substrate, coating, and compensator thicknesses have been tailored to maximize the constructive interference of the reflected components, as described above. Then we find that for incidence through the substrate, the mean reflected intensity is

$$R = \sqrt{0.48^2 + 0.27^2} / 2 = 0.39 \text{ times the mean intensity of the input beam.}$$

The transmitted intensity is 0.55, and the missing 6% in the sum of $R$ and $T$ is due to neglecting
Fig. 3. Intensities of beams produced by interaction of a polarized beam with a CaF$_2$/Si beamsplitter.
very low-intensity reflections in the ray-tracing diagram. For incidence of unpolarised light on the compensating plate, we find

\[ R = \sqrt{\frac{0.27^2 + 0.45^2}{2}} = 0.37 \quad \text{and} \]

\[ T = \sqrt{\frac{0.70^2 + 0.357^2}{2}} = 0.55 \]

The product \( R T \) is about 0.21 for this beamsplitter system and the chosen wavelength \( 2 \mu m \). Relative to the ideal product \( R T = 0.25 \), the system's efficiency is 84%.

Any real beamsplitter will have some absorption in the wavelength band of interest. The very small thicknesses of the beamsplitting material itself mean that absorptive losses are small. The amount of absorption is given by

\[ \frac{I}{I_0} = \exp(-\alpha t), \text{ where } \alpha \text{ is the absorption coefficient and } t \text{ the material thickness.} \]

The absorptive losses for transmission of a 2 \( \mu m \) beam through a Si film of thickness 0.776 \( \mu m \) amount to 0.38% for incidence at 45° (\( \alpha = 35 \text{ cm}^{-1} \), from Becker and Fan, 1949). We are concerned more with the effect of a non-zero absorption coefficient on the phase changes that occur on reflection and transmission. If the net phase differences described
earlier for emerging beams differ from precisely $\pi$ or 0, as the case may be, there will result incomplete cancel-
lation of beams that should be subtracted, and only partial addition of the beams that should constructively interfere.

Precise formulae have been developed by Born and Wolf (1964, p. 627) for the phase changes on reflection and transmission, for either polarisation, of light interacting with an absorbing film. We consider now, as we did earlier, the case of a freestanding film, and inquire what the difference is between the phase of the reflected wave, $\delta_r$, and the transmitted wave, $\delta_t$. The difference was $\pi/2$ without absorption in the film. Because the formulae are complicated, we investigate a specific case, where the film is silicon, the wavelength is 2 $\mu$m, and the wave incident at 45° has the electric vector perpendicular to the plane of incidence. The surrounding medium is presumed to be a vacuum. Following the terminology of Born and Wolf, the complex refractive index is

$$\hat{n}_2 = n_2 \left(1 + i\kappa_2 \right), \quad \kappa_2 = \frac{\alpha \lambda}{4\pi n_2}$$

where $\alpha$ is the absorption coefficient and $n_2$ the real refractive index.

We set

$$\hat{n}_2 \cot \Theta_2 = u_2 + i\sqrt{2}$$

All subscript 2's refer to the values within the silicon film. The angle of refraction $\Theta_2$ is 11.84°, so

$$u_2 = \cot (11.84°) \cdot n_2 = 3.38$$
The following expressions give the amplitudes and phases of the first- and second-interface reflection coefficients (subscripts 12 refer to the first and 23 to the second interface):

\[
\phi_{12}^2 = \frac{(\cos 45^\circ - \mu_2)^2 + \nu_2^2}{(\cos 45^\circ + \mu_2)^2 + \nu_2^2} = 0.42769
\]

\[
\tan \phi_{12} = \frac{2\nu_2 \cos 45^\circ}{\mu_2^2 + \nu_2^2 - \cos^2 45^\circ} = 0.00007055
\]

\[
\phi_{12} = 0.00007055 \text{ rad}
\]

\[
\phi_{23}^2 = \phi_{12}^2 \text{ so } \phi_{23} = \phi_{12} = 0.65398
\]

\[
\tan \phi_{23} = \tan \phi_{12}, \phi_{23} \text{ in third quadrant}
\]

\[
\phi_{23} = \pi + 0.00007055 \text{ rad}
\]

Transmission coefficient phases are given by:

\[
\tan \chi_{12} = -\frac{\nu_2}{\cos 45^\circ + \mu_2} = -0.0001333
\]

\[
\chi_{12} = -0.0001333 \text{ rad}
\]

\[
\tan \chi_{23} = \frac{\nu_2 \cos 45^\circ}{\mu_2^2 + \nu_2^2 + \mu_2 \cos 45^\circ} = 0.0000279
\]

\[
\chi_{23} = 0.0000279 \text{ rad}
\]

We introduce the quantity \( \eta = \frac{2\pi t}{\lambda} = 2.44 \)

where \( t = 0.776 \mu \text{m} \) is taken to agree with the thickness
found earlier to give maximum reflection. The expression for the phase of the wave reflected from the silicon sheet, considering both interfaces, is (Born and Wolf, p. 630): 

\[
\tan \delta_{t} = \frac{\rho_{23} \left(1 - \rho_{12}\right) \sin \left(\omega_{+} + \phi_{12}\right) + \rho_{12} \left[ e^{2 \nu_{1} \gamma} - \rho_{23}^{2} e^{-2 \nu_{1} \gamma} \right] \sin \phi_{12}}{ho_{23} \left(1 + \rho_{12}\right) \cos \left(\omega_{+} + \phi_{21}\right) + \rho_{12} \left[ e^{2 \nu_{1} \gamma} + \rho_{23}^{2} e^{-2 \nu_{1} \gamma} \right] \cos \phi_{12}}
\]

\[
= 0.166216 \quad \text{so} \quad \delta_{t} = 9.4372
\]

The phase of the transmitted wave, referred to the second interface, is given by: 

\[
\tan \left(\delta_{t} - \delta_{r} - \chi_{12} + \omega_{-}\right) = \frac{e^{2 \nu_{1} \gamma} \sin \left(\chi_{12} + \omega_{-}\right) - \rho_{12} \rho_{23} \sin \left(\phi_{12} + \phi_{21}\right)}{e^{2 \nu_{1} \gamma} \cos \left(\chi_{12} + \omega_{-}\right) + \rho_{12} \rho_{23} \cos \left(\phi_{12} + \phi_{21}\right)}
\]

in which we desire \(\delta_{t}\). We have 

\[
\tan \left(\delta_{t} + 8.2473\right) = 0.624736
\]

\[
\delta_{t} = -7.68889 \quad \text{rad} = -80.541
\]

so that \(\delta_{r} - \delta_{t} = 89.978\)

This result indicates that the absorption in silicon at 2 \(\mu_{m}\) produces a negligible effect on the phase difference \(\delta_{r} - \delta_{t}\) for the freestanding thin film we have considered.

Other materials, particularly metals, may have very much higher absorption coefficients (\(\alpha = 5.5 \times 10^{5} \text{ cm}^{-1}\) for silver at 2.25 \(\mu_{m}\)). In such a case, the difference \(\delta_{r} - \delta_{t}\) will depart significantly from 90°, and the operation of a sky subtraction system will be hindered.

We have had practical experience with such a beamsplitter, nominally \(\text{Fe}_{2}\text{O}_{3}\) deposited on a quartz substrate. Testing
by the manufacturer revealed that, to some extent, Fe had been deposited rather than the dielectric oxide. This conclusion explained the total failure of the beamsplitter to produce a sky subtraction effect; in fact, signal from the comparison beam was fractionally added to that in the sample beam.

Sky subtraction can be an effective technique in interferometric spectroscopy. It is successful because of the convenient way that the object and comparison beams are alternately presented to the detector. Chopping techniques are also applicable to Michelson interferometry. In the simplest form of the step-and-integrate mode, the moving mirror is successively halted at increasing values of the path difference, while the detector receives radiation alternately from the object and comparison beams. However, the advantage of rapid scanning is then lost; the resulting interferograms may contain greater low-frequency noise than can occur with the rapid-scanning technique. In the next section we explore the application of sky subtraction technique to an area where chopping schemes have been dominant.
II. A Scheme for Astronomical Photometry with Sky Subtraction

The principle of sky subtraction is inherent in the design of the Michelson interferometer, but there is no reason to restrict use of the principle to interferometric spectroscopy. It is possible to build a double-beam photometer in which the object of interest is viewed 100% of the time, and in which sky subtraction is continuous. Essentially equivalent results can be achieved using "chopping" schemes; however, the Michelson photometer has a unique capability in terms of built-in spectral filtering that is particularly advantageous in the far infrared.

We consider an interferometer exactly as in Section I, with the moving mirror fixed at the position for zero OPD. The arguments of Section I apply completely, so that, with a beamsplitter appropriate for sky subtraction, a detector placed in either arm will sense the full intensity of the beam entering in the other arm. With two detectors employed, the object of interest will be sensed by one detector, and the comparison beam by the other.

Now we displace one mirror so that the OPD becomes \( \lambda_o/4 \), where \( \lambda_o \) is some wavelength in the detector passband. The phase change will be \( \pi \) in the arm containing that mirror, for all rays entering that arm and having wavelength \( \lambda_o \). As we noted in Section I, the detectors now receive the full intensity at \( \lambda_o \) of the other beam.
than was detected for zero OPD. The detector originally sensing the comparison beam will now sense the object beam, and vice-versa.

The mirror can be made to oscillate in a square-wave fashion between the position of zero OPD and the displacement $\lambda_o/4$. If the electrical output of the two detectors is differenced, and the resulting signal fed to a phase-sensitive detection system locked to the oscillation frequency, the DC output of the synchronous-detection amplifier will be proportional to the time-averaged value of (object signal - comparison signal). This difference signal level is dependent on the object's emission spectrum, modified by the particular transmission properties of the atmosphere, detector optics, etc. There is also an instrumental filtering function affecting the value of the signal level; we now investigate the nature of this function.

Since the mirror motion is accurately $\lambda_o/4$ for only one particular $\lambda_o$, there will be wavelengths at which the phase difference is a multiple of $2\pi$. For those wavelengths, the mirror motion will produce no modulation of the radiation, and the AC-coupled detectors will not respond to the radiation. The spectral response of the system goes to zero at $\lambda_o/2$, $\lambda_o/4$, etc. The maximum response occurs at $\lambda_o$ and $\lambda_o/3$, $\lambda_o/5$, etc. (see figure 4). The system acts like a conventional photometer.
Fig. 4. Sky-subtracting photometer response function.
equipped with a unique wavelength-dependent chopper mechanism (perhaps a rotating blade made from a simple interference filter). At very long wavelengths, the mirror displacement becomes negligible, and the phase difference goes to zero. Therefore, the system response decreases monotonically at wavelengths longer than $\lambda_0$.

Filter design in the far infrared (100 - 2000 $\mu$m) can be a fairly severe problem, because the absorption edges in most solid materials are not as sharp as the wings of the water lines that define the atmospheric windows. Multiple-element filters made from metallic grids have good characteristics but are difficult to manufacture and to adjust. In the Michelson photometer described here, the peak system response can be selected to occur at the center frequency of an atmospheric window by adjusting the amplitude of oscillation of one interferometer mirror. The slope of the filter cut-off can be chosen by changing the order number; this is 1 plus the number of response-function peaks occurring at frequencies below the one of interest. As the mirror amplitude is increased beyond $\lambda_0/4$, additional lobes of the response function appear at $\lambda > \lambda_0$. This behavior is best seen in the response function itself:

$$R(\sigma) = \frac{1}{2} (1 - \cos 2\pi \sigma x)$$

$$= \frac{1}{2} (1 - \cos \frac{2\pi x}{\lambda})$$
where $\sigma$ is optical frequency in $\text{cm}^{-1}$ and $x$ is the OPD in $\text{cm}$ between the two mirror position extremes. The expression applies for a collimated beam in the interferometer. For a given frequency $\sigma$, there is a minimum value of $x$, equal to $(2\sigma)^{-1}$, for which $R(\sigma) = 1$. For larger $x$, the cosine term becomes a faster function of $\sigma$, meaning that maxima of $R$ are more closely spaced in $\sigma$, and the function is steeper between the maxima. Clearly, the steepness of the filter response must be traded off against proximity of the next response lobe.

As an example, consider a system operating for peak response at 29 $\text{cm}^{-1}$, the frequency of highest transmission in the 345–$\mu\text{m}$ window. Response peaks will occur at 5.7, 17.4, and 40.6 $\text{cm}^{-1}$, as well as other higher frequencies, if the system is operated in the third order (see figure 5). For observations of blackbody astronomical sources, the system response provides very effective attenuation of signal in the neighboring 450–$\mu\text{m}$ window (atmospheric transmission is taken from Nolt et al 1971). The maximum monochromatic signal in that window would be about 12% of the peak signal at 29 $\text{cm}^{-1}$. While response will rise in the 13–17 $\text{cm}^{-1}$ region, the signal there, amounting to about 30% of the peak value, can easily be reduced with a simple screen filter to negligible values.

It is not physically possible to drive a mirror of finite mass in a pure square-wave motion. Consequently,
Fig. 5. Sky-subtracting photometer response function tailored for the 27-32 cm\(^{-1}\) atmospheric window.
the mirror will spend a certain amount of time at positions other than zero OPD and the desired displacement. The effect of departure from square-wave motion is a "washing out" of the response function, so that it does not equal zero at the minima.

The response function is the Fourier transform of the mirror motion. A square-wave motion may be represented in position space by two delta functions, one located at the origin (zero displacement) and the other at the value \( x \) corresponding to the alternate mirror position. The transform of the displacement function will be a function in \( \text{cm}^{-1} \) space. The transform has the shape of a sinusoid, and may be envisioned as the "beating" of the two delta functions. As \( x \) increases, the spacing of the lobes in frequency space decreases. We are led to wonder if an arbitrarily-shaped response function can be created by the appropriate selection of a mirror motion. The answer is affirmative in general. However, inspection of a table of Fourier-transform pairs (Bracewell 1965) shows that certain functions, such as a high-frequency pass filter, will require very complex mirror drive motions. It is not clear that it is worthwhile to attempt generation of the required motions in a fashion that is compatible with synchronous detection systems.

Oscillation of the normally-fixed mirror in an interferometric spectrometer has been performed for some
years (Chamberlain 1971). The spectral filtering characteristics of the technique, known as phase modulation, were noted but not specifically employed by these investigators, perhaps because of the absence of the submillimeter atmospheric windows and consequently the need to isolate them. The advantages of the Michelson photometer may be considerable for work at sites where the 345 and 450-μm windows are usable.
III. Instrumental Parameters

In this section are presented the details of the interferometric observations. The experiments involving other equipment will be described along with the results of that work.

The Digilab Model 496 Fourier Transform Spectrometer is a commercial instrument built for, and primarily used in, laboratories performing chemical analysis. As such, the FTS, with a maximum moving mirror travel of 5 cm, provides rapid and efficient spectroscopy of sample materials with a resolution up to 0.0625 cm\(^{-1}\).* The spectral range is limited only by the detector and beam-splitter efficiencies.

The optical elements of the system are tied to a sophisticated data-acquisition and control unit, consisting of a Nova 1200 mini-computer, 128 K (16-bit word) disk storage, hard-wired multiply/divide electronics, and other devices which service the optical system or handle data. The computer, controlled by the operator through a teletype, supervises the collection of data, storage and

*In this work we shall consider the instrumental resolution to be the full width at half maximum of the instrument function, \(\text{sinc}\ 2\sigma x = \frac{\sin 2\pi \sigma x}{2\pi \sigma x}\). This width is given very nearly by \(\Delta \sigma = 1/2x\), where \(x\) is the maximum optical path difference, in cm, characterizing the raw interferogram. The particular value 0.0625 cm\(^{-1}\) arises from the digital specification of resolution choices varying by convenient factors of 2.
manipulation of data, and Fourier transformation. A disk-resident software package allows considerable flexibility in the way data is handled. A magnetic-tape unit is used to store data in its raw form and data which has been transformed or modified in other ways. Interferograms and spectra can be displayed in a wide variety of formats on a digital plotter.

For astronomical purposes, the basic interferometer is separated from the source lamps and double-beam apparatus used in chemistry, and is coupled (in this case) to foreoptics which perform sky subtraction as described earlier. The assembly is housed, together with the detector, in a box which is strong enough to prevent misalignment of the optical parts under the various gravitational forces placed on a device used at the Cassegrain focus of a telescope. A long cable supplies control signals to the instrument from the electronics in another room of the observatory, and conducts the detector output and feedback information in the opposite direction.

The interferometer moving mirror is driven electromagnetically, and rides on a linear air bearing. The back side of the mirror is also aluminized. Part of it serves as the moving mirror in a "reference" cube interferometer, which has two optical channels: a helium-neon 6328-A laser, and a white light. Fringes in the laser interferogram are counted to provide velocity and position informa-
tion to the drive control electronics. The peak of the white light interferogram is detected to provide a fiducial mark in the mirror travel. Digital sampling of the main interferometer detector output in synchronism with the laser fringes is commenced after sensing the white-light fiducial; the mirror has attained a fairly constant velocity by this time. Data acquisition is performed in one travel direction only. The mirror is driven only as far as necessary to obtain spectra of the desired resolution; it then is driven rapidly back to begin another run.

The advantages of rapid scanning in astronomical interferometry have been discussed at length elsewhere (Mertz 1965, Bell 1972). The principal advantage arises from the fact that flux variations which occur at frequencies lower than the scan repetition frequency are not manifested in the spectrum; with a high repetition rate typical of rapid-scanning instruments, a considerable band of sky or detector noise frequencies is excluded. For example, a typical repetition rate of one scan per second excludes noise frequencies below 1 hz. The lowest spectral frequency of use in this work is about 2800 cm\(^{-1}\); at the scan speed of 0.316 cm/sec, the corresponding temporal frequency is 890 hz. Noise components below this frequency will not affect the spectral range of interest unless their amplitude is so great that the linearity of the detector or
subsequent electronics is affected.

The detector used in the Saturn observations is a photovoltaic indium-arsenide cell, manufactured by Barnes Eng. Co. and cooled to 77 K by liquid nitrogen. Its dewar incorporates a sapphire window and a cooled silicon meniscus lens which is designed to image the telescope primary onto the detector element. The lens is coated to reduce reflective losses in the 1-3 \( \mu \)m region. In our instrument, the lens was not supplied mounted at the correct distance from the detector, so that an appreciable amount of light is probably lost at the detector. The effect is readily noted by measuring the angular response of the device to a distant point source. As much as a factor of two in detectivity may have been lost from this problem, but due to the difficulty and risk of modifying components in the glass dewar, the detector was employed in its existing state.

The spectral response of these detectors peaks at 3.1 \( \mu \)m, and is down by about a factor of five at 1.3 \( \mu \)m. The response falls quite rapidly below 1.3 \( \mu \)m, due to absorption by the silicon field lens. The overall response is well suited to broadband planetary and stellar studies, since the flux from these objects is falling where the detector's response is rising, so that the plotted spectra show good signal-to-noise ratio over a wide band. However, for studies below 1.3 \( \mu \)m, such as spectroscopy of the
The interferometric Jupiter spectra were obtained with an InSb detector that was made available to us only after the completion of the Saturn investigations. The InSb detector was supplied with a cooled filter excluding radiation beyond about 3 μm; in the 1-3 μm region, its detectivity was better than that of the InAs cell by a factor of approximately 2.

A schematic drawing of the optical system is shown in figure 6. Radiation enters the system along the optical axis of the telescope, which passes between plane mirrors M1 and M2 and is perpendicular to the drawing. M1 and M2 lie in the focal plane of the telescope; they define the field stops of the sample beam and the sky comparison beam. The diameters of the mirrors are 1.8 mm, corresponding to 18 arcsec in the sky. The f/10 radiation from M1 is reflected to collimator M3 and from M2 to M4. M3 and M4 are off-axis paraboloids, which produce 5 cm diameter beams directed at plane mirrors M5 and M6. These feed directly into opposite arms of the interferometer. The emergent beams strike M5 and M6 at a slightly lower position than the incoming beams, because the mirrors M1 and M2 lie just above the extension of the central axes of the interferometer. Consequently, when the emerging beams are refocused by M3 and M4, the images of the

3 ν3 methane band, it is advisable to employ detectors selected for those wavelengths (Smith et al 1968).
Fig. 6. Optical layout of interferometer with sky-subtraction fore-optics.
entrance field stops are displaced below the field stops themselves. Mirrors M9 and M10 pick off the emerging beams about 2 cm before the focus point, and deflect them to positions where detectors can be placed.

If two matched detectors are employed, all the radiation from the object can be used, and a gain of $\sqrt{2}$ in sensitivity is possible over the use of one detector. For this work, however, only one detector was available.

In operation of the system, one observer is located at the telescope, monitoring the position of the planetary image with respect to the two entrance "apertures." An eyepiece, mounted below the glass plate upon which mirrors M1, M2, M9, and M10 are located, allows the image to be seen. Another observer, in the telescope control room, gives instructions to the computer for data acquisition, stores completed runs on tape, and keeps the observing log. Both observers have an oscilloscope display of the individual interferograms as they are collected, so that assessment can be made of signal-to-noise ratio and transient problems.

All data mentioned here were recorded with sampling of the detector output performed every half-wave of the laser interferogram. This sampling rate produces a folding frequency* equal to the laser frequency, 15800 cm$^{-1}$. Since

---

*When analog waveforms are to be digitized, it is necessary for accurate representation to sample the wave-
the detector response is very low above this frequency, we expect negligible contribution to the signal levels in our spectra from radiation folded into this band. Noise at higher frequencies, however, is not negligible and can contribute to the noise level in the 3000-10,000 cm\(^{-1}\) band. We have suppressed this noise by employing an electronic filter in series with the final amplification stage, before analog-to-digital conversion. We typically used a cutoff frequency (50% reduction) of 3200 hz. The filter slope is such that the lowest frequency that could fold into our bandpass, namely 6800 hz, is reduced in amplitude by a factor of 250 relative to the signal in the passband.

The sky-subtraction system performed flawlessly during the Saturn observations. There is no evidence in the spectra of sky emission, which produces signal below 3000 cm\(^{-1}\) in single-beam spectra of weak sources. An estimate of the degree of subtraction can be obtained. If a uniform source such as a laboratory hotplate is placed in the beam so as to fill both foreoptics beams, a certain amplitude is found for the interferogram center burst. This represents the detected difference signal. If one form at least twice per shortest wavelength of interest. If higher frequencies are present, they will modify the reconstruction by appearing as lower frequencies than the one which is just adequately sampled. Frequencies higher than the just-correctly sampled "folding frequency" contribute to a spectrum in the frequency domain below the folding frequency.
beam is now blocked, the amplitude increases greatly. The ratio of amplitudes in these two cases is typically 20, so that the degree of sky subtraction in the passband, weighted by the spectral distribution of the hotplate emission, is about 95%.

During the collection of the best Saturn data, the peak-to-peak amplitude of a single interferogram center burst was typically 1.5 volts; the noise level was approximately 0.12 volts. Thus, the signal-to-noise ratio in a single interferogram was about 12, with the entire ball of Saturn detected. For Jupiter, the single interferogram SNR was approximately 35 for the data from the summer of 1974.
Study of Molecular Atmospheric Constituents

I. A Search for water on Jupiter

Water has been suspected for some time to be a component of the atmospheres of the major planets. The elements carbon and nitrogen apparently exist in their fully reduced states in these atmospheres as CH$_4$ and NH$_3$. The clearly high abundance of hydrogen and the high cosmic abundance of oxygen make it likely that oxygen will be fully reduced also, as H$_2$O, if the conditions for stability of the molecule are met.

Extensive theoretical studies of the requirements of cloud formation by Lewis (1969) and Weidenschilling and Lewis (1973) have shown what vertical distributions of condensates are likely on the major planets. For Jupiter, it is expected that ice clouds will form in the temperature region between 280 and about 220 K. An increased relative oxygen abundance would tend to increase the depth and base-level density of the cloud, but would leave the upper layers unaffected. The ice is mixed in the upper regions with the base of a cloud of NH$_4$SH, existing in the 200-180 K range. Above this, a clear space exists, but still another cloud deck, of NH$_3$, is above with a base near 150 K and 1 bar pressure. Thus H$_2$O, if significant amounts of the vapor are present in the ice cloud, is still effectively hidden by two distinct cloud decks above.
The appropriate wavelength region for a ground-based spectroscopic water search will be one where the following conditions are met:

1. Narrow, strong water vapor absorption lines exist. It is necessary that the lines be narrow so that they may be separated easily from telluric features by Doppler shifting.
2. No strong absorptions due to overlying constituents occur.
3. Scattering of light is at a minimum.

The best spectral region for Jupiter for 2. and 3. seems to be the 5 μm window, which exists in both the earth and Jovian atmospheres. Here are several isolated water lines, noted in the solar atlas of Migeotte et al (1957), which have half-widths on the order of 0.1 cm⁻¹. A list of suitable lines is given in Table 1. In this region, Jupiter has been found to emit very strongly, indicating that lower-lying parts of the atmosphere are being exposed to view, either by the process of convective upwelling or, more likely, the production of holes in the upper clouds. Neither CH₄, NH₃, nor H₂ have strong absorption features in the 5 μm region, and certainly Rayleigh scattering for a given particle size distribution will be less important here than in the visible; the mean particle size of 0.1 μm determined by Tomasko (1974) from Pioneer 10 data supports the conjecture that the upper clouds are Rayleigh
<table>
<thead>
<tr>
<th>Vacuum Frequency</th>
<th>Number in Migeotte Atlas</th>
<th>Depth</th>
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scattering at 5 \( \mu \)m wavelength. Tomasko (1975) reports, however, that analysis of Pioneer 11 results does not support the simple model employed earlier, and conclusions regarding particle size are now weakened.

Enhanced 5-\( \mu \)m emission from Jupiter appears to be concentrated in, but not restricted to, the dark equatorial belts. Indeed, Westphal et al. (1974) found the brightness temperature at no point on the disk to be below 190 K in his remarkable high-resolution 5-\( \mu \)m images of Jupiter. We note that 190 K corresponds, in the Weidenschilling and Lewis model, to a level just above the \( \text{NH}_4\text{SH} \) cloud, and that Westphal's highest temperatures, near 300 K, actually correspond to levels well below the ice cloud base.

Searches for water should obviously be directed to areas where the material is most likely detectable. Ideally, one might combine 5-\( \mu \)m photometry of Jupiter with a spectroscopic study, so that "hot spots" could be followed with the aperture of the spectrometer, thereby increasing the spectral contrast of any Jovian water lines.

At present, the problem of obtaining sufficiently high-resolution spectra of Jupiter at 5 \( \mu \)m is a severe one. The planet must be observed near quadrature to insure a large Doppler shift. This requirement tends to restrict observing hours, since many observatories do not operate into daylight. But a more severe obstacle to be overcome is the inadequate sensitivity of existing detector-
pre-amplifier combinations. These limit the SNR of data obtained with spectrometers presently in use. The highest resolution of published Jovian 5-κm spectra is 0.5 cm⁻¹; at this resolution, Beer et al (1972) discovered CH₃D with whole-planet data. Good spectra with a resolution of 0.1 cm⁻¹ will probably be obtained within the next year; if whole-planet spectra do not reveal H₂O, an additional step will be necessary to seek the molecule in regions of anomalously high temperature.

During the time this work was in progress at the Institute for Astronomy, no capability existed for performing spectroscopy at 5 μm. We have tried, therefore, to seek Jovian water vapor in the region employed for H₂O searches on Mars, Venus, and Jupiter in the past: the 8200-A band. Here, the spectral resolution achievable with a high-dispersion coude spectrograph allows ready separation of the Doppler-shifted Jovian lines from their telluric counterparts. The lines are also sharp and plentiful (sharp at least in the telluric spectrum if the abundance is low, as it is above Mauna Kea Observatory). The observed penetration of ultraviolet and infrared radiation into the Jovian atmosphere is consistent with an increasing mean particle size with depth, and a dominance of Rayleigh scattering even to several micrometers wavelength (McElroy 1969). In such a model, it is less likely at 0.82 μm than at 5 μm that an incoming or exiting
photon will survive transit through the scattering layer and thus be able to interact with the lower-lying H$_2$O or to escape the atmosphere after interaction. Nevertheless, it is possible that 0.82 $\mu$m radiation does penetrate sufficiently deep that water lines will impress themselves into the spectrum. Rayleigh scattering by H$_2$ alone is entirely negligible even to levels in the atmosphere near 10-bar pressure. The Jovian atmospheric structure is not well enough known to preclude searches of this kind.

Water on Jupiter has been sought previously in the 8200-A region by Fink and Belton (1969) and also by Traub and Carleton (1973). The former group obtained an upper limit of 40 $\mu$m precipitable H$_2$O from observation of the 8189-A line by photoelectric means. Their imageslicing optics accepted "between 10 and 15% of the total area of the disk of the planet centered on the sub-earth point." Therefore, it is probable that the equatorial belts were included in their observations; the upper limit is quite low. Traub and Carleton employed a Fabry-Perot spectrometer to get high-resolution spectra of the 8197-A line. By tilting the spectrometer mirrors, they were able to compensate for the planetary-rotation Doppler effect, so that all portions of the disk would appear to absorb that line at the same wavelength. However, this procedure also distorted the shape of the strong telluric
line which was very close to the wavelength of the expected Jovian line near opposition when Traub and Carleton observed. They were able to assert that no Jovian water line appeared with a depth greater than 2 per cent, giving an upper limit on the equivalent width of 2 mA, assuming a pressure-broadened line width of 102 mA. This equivalent width is lower than Fink and Belton's by a factor of 5, and implies a precipitable water content no more than about 5 µm, if we consider the expected line strength at 150 K and an airmass factor of 4 (only the limb of the planet was measured, certainly a poor choice for an H₂O search).

The problem was approached somewhat differently in our work. To get the highest possible spectral resolution, the #1 camera (focal length 488 cm) of the coude spectrograph at the Mauna Kea Observatory 224-cm telescope was used. This instrument has a dispersion of 3.4 Å/mm when the 600 l/mm grating, blazed for 8400 Å, is used in first order. Although this dispersion is probably adequate for the experiment, the spectrograph was used in double-pass mode, giving a dispersion of 1.7 Å/mm. Because the system had been used earlier with a Varo image tube by Sinton and Carson (1972) to study the same H₂O band on Mars it was relatively easy to prepare the equipment for the Jupiter search.

The intensity of Jupiter at 8200 Å is down considerably from that of Mars, so that long exposures were
necessary. In fact, the best plate was one exposed for 7 hours—the longest exposure made with the spectrograph up to that time. IIa-D plates were exposed with the Varo tube's fiber-optic faceplate in optical contact with the emulsion. The plates have a sensitivity matching the green color of the tube output. With a plate resolution of 30 micrometers, the spectral resolution is 0.05 Å at 8200 Å (resolving power = 164,000). The two best plates are presented in figure 7.

Because of the characteristically dry atmosphere above Mauna Kea, the telluric H₂O lines in the Jovian spectra are narrow; the region where the tilted and shifted Jovian lines are expected is free from contamination. The central-meridian Doppler shift amounted to 0.49 to 0.64 Å for the plates. We expect the vertical penetration of solar photons into the atmosphere to be greatest near the sub-earth (sub-solar) point. The plates represent a longitudinally-averaged sample of the atmosphere; the slit was maintained along the North Equatorial Belt for the exposures.

Several strong telluric H₂O lines occur in the 37-Å band covered by the plates. However, no Jovian absorptions are noted with the expected shift and tilt. Therefore, we derive the abundance of water vapor that could exist above the effective reflecting layer for 0.82-μm photons. To do this, we compare the equivalent
Fig. 7. Spectra of the N. Equatorial Belt of Jupiter in the 8200-A band of H₂O. Dispersion = 1.7 A/mm. All tilted lines are of solar origin.
widths of solar lines in the planet spectra with the widths of features representing the noise level at the expected Jovian H₂O-line wavelength. Knowing the strengths of the lines at the temperature of the reflecting layer, we can compute an abundance upper limit from the upper limit to the equivalent width.

Equivalent widths of the three solar lines at 8187, 8195, 8199 Å were measured in the solar atlases of Minnaert et al (1940), and of Delbouille and Roland (1963). The average values obtained were 50, 299, and 111 mA respectively.

The two best Jupiter plates were examined on a Grant measuring engine, which has an oscilloscope display of plate density versus wavelength. In the range of densities considered, the dependence of intensity on density is sufficiently linear that this display can be used to yield reasonably accurate equivalent widths. The measuring slit, 4 mm long by 50 micrometers wide, was centered on the spectrum, so that 12 arc-sec of the NEB nearest the sub-earth point are included in the actual upper-limit measurement. The slit width was chosen to smooth slightly the plate graininess, and match the expected Jovian H₂O line width. This was calculated to be about 75 mA, assuming an STP width of 0.08 cm⁻¹, a reflecting layer pressure of one bar, and a square-root temperature correction to 150 K.
The 8189-A line was found to have the greatest spectral contrast; it therefore gave the most stringent limits for both plates. Using the nearby 8187-A solar line for comparison, it was determined that the equivalent widths of noise features near the expected H$_2$O line positions were about 3.6 mA for plate KE-1111 and 1.6 mA for KE-1207. Jovian lines having the expected width would need to have greater equivalent widths than these to produce a detectable line. Thus the derived upper limits for the water abundance are 20 $\mu$m ppt for KE-1111 and 10 $\mu$m ppt for KE-1207. (The strengths were taken from Farmer [1971].)

These limits are comparable with those given by Traub and Carleton and are a better test for H$_2$O in the NEB. It is important to know if there were appreciable 5-$\mu$m emission from the NEB when these observations were made--we expect that the best time to observe would be when high 5-$\mu$m emission exists. Fortunately, 5-$\mu$m pictures of Jupiter were obtained by Westphal et al (1974) on September 13 and 20, 1973 UT, which dates are between our two best observations of the water-band region, on September 8 and 26. The pictures show that the NEB region was indeed a very strong source of 5-$\mu$m radiation in September, at all longitudes. Therefore, the test for H$_2$O was fairly stringent. The eventual detection of water vapor will, in all probability, be made in the 5-$\mu$m
Note: A report has been received (Treffers et al., January 1975) that 14 H₂O lines have been detected in a 5-μm spectrum of Jupiter obtained from an aircraft. The preliminary abundance estimate is 100 μm of precipitable H₂O. The lines are strong and apparently arise from deep layers. Evidently the 5-μm opacity of the Jovian atmosphere is indeed lower than that at 8200 Å, since 100 μm of H₂O would have been readily detectable in our photographic spectra. Photons at the longer wavelength are emitted in the atmosphere, of course, and need only escape, while the 8200-Å photons must both penetrate and emerge from the atmosphere. Westphal (1975) has indicated that the NEB and other belts may be dark simply because little solar radiation is reflected from regions where clouds have not formed. The often-mentioned "purple" color of 5-μm hot spots may be Rayleigh-scattered light from the very thin hazes remaining over holes in the clouds. Our result implies that at 8200 Å there is considerable scattering in the longitudinally-integrated light of the N. Equatorial Belt.
II. A Search for ammonia on Saturn

A. Introduction

Ammonia is a highly probable component of Saturn's atmosphere. Neither Jupiter nor Saturn is likely to have lost ammonia during the protoplanet stage of condensation from the primeval "solar nebula." Indeed, NH$_3$ may be enriched relative to H$_2$ for Saturn (Lewis 1973). The evidence available from the visible bands of NH$_3$ for Jupiter and the microwave thermal emission for both planets indicates that the ammonia abundances are nearly in keeping with a solar H:N ratio (Gulkis 1973 and Lewis 1973). This ratio is $1.2 \times 10^4$ for the sun and $1.6 \times 10^4$ for Jupiter (Hunt 1974).

Most of the tests for NH$_3$ on Saturn have been made in the very accessible $5\nu_3$ band at 6450 Å, which is prominent in the spectrum of Jupiter. Early spectra were obtained by Dunham and reported in 1952. His Saturn spectrum, at a dispersion of 12 Å/mm, was not shown. He made the statement, "The amount of ammonia present is considerably less [than for Jupiter], probably not more than 2 meters at atmospheric pressure." However, Dunham did publish his spectra of Jupiter, Saturn, and a 40 m-atm NH$_3$ path in the range 7700-8100 Å. Here, he claims, "All the same ammonia lines [39] are present, but fainter, in the spectrum of Saturn." It is difficult to see that this is true in the published plate. In the region near 7850 Å there are perhaps 10 coincidences that are convincing, but
without a comparison spectrum with a high abundance of methane, these data are not very useful. There are strong methane lines throughout this region, and if in fact one sees deep enough into the Saturn atmosphere to probe regions where ammonia may be detectable, it is probable that vast quantities of methane have been traversed, so that very weak methane lines may produce unusually strong absorption.

Kuiper (1952) obtained numerous medium-dispersion spectra of Saturn and Jupiter in the 6450-A region and set an upper limit of 2.5 m-atm for the Saturn NH$_3$ abundance.

Spinrad (1964) obtained high-dispersion plates of Saturn in 1962 and was unable to find lines of the 6450-A band. He reported that low atmospheric rotational temperatures measured from the relative strengths of lines in the 4-0 H$_2$ quadrupole band near the date of his spectroscopy were consistent with the non-observability of NH$_3$, and said that the observability may well be variable because of the changing altitude of the reflecting layer.

Giver and Spinrad (1966), and Giver (1965), reported detection of the Saturn 6450-A band in 1964, with a strength of 0.15 ± 0.06 that of the Jovian band. Temperatures derived from relative strengths of the H$_2$ quadrupole lines were relatively high at this time, suggesting that the reflecting layer was at a lower altitude. Ammonia may thus be detectable when the visible cloud layers are low and warm enough that the vapor pressure of ammonia at the cloud level
is appreciable.

Cruikshank (1971) reported the absence of a detectable 6450-A band in 5.5 A/mm Saturn spectra obtained in 1970; his upper limit was 7 m-atm. He also reported results of a study of the 1.5-\(\mu\)m (6450 cm\(^{-1}\)) region in interferometric spectra of resolution 10 cm\(^{-1}\) obtained by Kuiper, Cruikshank, and Fink (reproduced in part in Fink and Larson 1971). Comparison with laboratory spectra (Cruikshank and Binder 1968) gave an upper limit of 20 cm-atm to the Saturn abundance of NH\(_3\). Because of the strength of the 1.5-\(\mu\)m band Cruikshank's upper limit was the most stringent set to that date.

With increased spectral resolution, the 1.5-\(\mu\)m NH\(_3\) band rotational structure can be resolved. Since the individual lines are narrow, their spectral contrast increases with greater resolution, and the sensitivity for detection of the molecule improves. The Saturn spectrum between 3000 and 10000 cm\(^{-1}\) has a pronounced peak in intensity near 6400 cm\(^{-1}\). The close similarity with the lunar spectrum between 6250 and 6360 cm\(^{-1}\) indicates a very high relative transparency of Saturn's atmosphere, at least to the level of some cloud or continuous-opacity source. Where the atmosphere is transparent, presumably the deepest layers not obscured by the cloud will be traversed. It is in such regions we expect NH\(_3\) to be detected.
B. The 1-3 $\mu$m Saturn Spectrum (10000-3300 cm$^{-1}$)

At this point, it is instructive to consider the overall features of the Saturn spectrum in the region sensed by the interferometer. We shall also present here some descriptive details of the observations.

Our first spectra of Saturn at 1-cm$^{-1}$ resolution were obtained in January 1974. During 3 nights, 18 separate interferogram averages were collected (each the co-added result of many individual scans), representing a total integration time of 326 m. Airmasses ranged from 1.00 to 1.83, with a mean of 1.21 (see Table 2). A single interferogram was computed from the 18 component data sets, with weights assigned to de-emphasize particularly noisy data.

The 1 cm$^{-1}$ spectrum is shown in figure 8 in a somewhat compressed form, to allow judging of the signal-to-noise ratio in various regions. Portions of the 0.5 cm$^{-1}$ data will be shown later in connection with particular problems.

Figure 8 shows clearly the 3- $\mu$m window in the Saturn atmosphere. The region of atmospheric transparency most likely extends beyond the telluric window, since CH$_4$ lines are not particularly plentiful at the high-frequency cutoff near 3600 cm$^{-1}$. At low frequencies, there is probably strong absorption in the R branch of the CH$_4$ $\nu_3$ fundamental band, extending to about 3100 cm$^{-1}$. The Saturn spectrum mimics that of the moon quite closely over much of
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Details of Telescopic Observations

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<td>1.11</td>
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Fig. 8. Spectra of the moon (top) and Saturn, 3000 - 10000 cm$^{-1}$. Resolution = 0.5 and 1.0 cm$^{-1}$ respectively.
Fig. 8. Spectra of the Moon (top) and Saturn, 3000 - 10000 cm⁻¹. Resolution = 0.5 and 1.0 cm⁻¹ respectively.
the 3200-3600 cm\(^{-1}\) range; most of the discrepancies are due to relatively isolated methane lines. The high-frequency side of the window is cut off by the telluric 2.7-\(\mu m\) (3800 cm\(^{-1}\)) \(H_2O\) band. Probably the Saturn spectrum is fairly intense in the region obscured by this telluric feature.

Several strong \(CH_4\) bands absorb in the region 4100-4600 cm\(^{-1}\), together with the broad pressure-induced vibrational fundamental of \(H_2\). The \(S(1)\) line of this 1-0 \(H_2\) band creates the broad but discrete feature centered at 4750 cm\(^{-1}\) and extending well beyond 5000 cm\(^{-1}\) (see discussion in section VI). There is a small window centered at perhaps 5300 cm\(^{-1}\), which is mostly obscured by the telluric 1.9-\(\mu m\) \(H_2O\) band. Methane depresses the spectrum again from 5500-5900 cm\(^{-1}\), with three separate combination bands. The regular and theoretically well-studied 2 \(\nu_3\) band, at 6000 cm\(^{-1}\), is so saturated that determinations of temperature and abundance are unlikely to be very accurate, compared with parameters found from the weaker 3 \(\nu_3\) band at 9050 cm\(^{-1}\). Due to the large abundance of \(CH_4\) on Saturn, numerous weaker lines contribute very tangibly to the absorption in the neighborhood of the saturated J-manifolds, and the effects of weak lines cannot be readily accounted for, making analysis presently difficult.

Between 6100 and 7000 cm\(^{-1}\), the Saturn spectrum becomes quite intense. The high-frequency end of this re-
gion is determined by the telluric 1.4-\mum H_2O band and another strong, broad band of CH_4. At 7550 there is a regular but little-studied methane band, called \( \nu_2 + 2 \nu_3 \) by Herzberg (1945), which is not so strong as to obliterate the structure in the P and R branches. The spectrum is then clear to 10000 cm\(^{-1} \) except for another strong methane band between 7950 and 9000 cm\(^{-1} \), and the aforementioned 3 \( \nu_3 \) band at 9050 cm\(^{-1} \).

We obtained spectra of Saturn at 0.5-cm\(^{-1} \) resolution starting in February, 1974. It was possible to obtain sufficient data to equal the quality of our 1-cm\(^{-1} \) data before the planet was lost for the season (Table 2). Between February 7 and March 12, on five nights, 25 runs were made, representing 627m of integration time. Air-masses at the conclusion of the runs ranged between 1.00 and 2.08, with a mean of 1.23. The data were combined, as before, into one grand average interferogram, which was then transformed with no apodization to yield the spectrum that will be discussed in all the work that follows.

C. Laboratory Spectra

Comparison spectra of minor-constituent compounds expected in the Saturn spectra were obtained by using short-path gas cells and the same interferometer used for the astronomical observations. In this way we ensured that any systematic errors in the frequency scale of the
spectra were the same for the planetary and comparison data. It is very difficult to attempt comparisons with wavelength-scaled data, or spectra plotted at arbitrary expansions, especially when planetary absorption intensities are modified by temperature, are weak, or are absent.

For NH$_3$, we used a galvanised pipe, 161 cm long, having glass windows. The light from an incandescent lamp was condensed to f/6 after passing through the cell, and focused onto one of the sky subtraction system input beam posts of the interferometer. Spectra of anhydrous NH$_3$ were obtained at four pressures: 4, 12, 40, and 60 cm Hg, giving abundances of 8.5, 25.4, 85, and 127.5 cm-atm. A resolution of 0.5 cm$^{-1}$ was used to match the best Saturn data.

NH$_3$ spectra in the 3300-cm$^{-1}$ region were obtained with a shorter cell of 14.3 cm path length to avoid oversaturating the strong 3335-cm$^{-1}$ fundamental. To simplify the experimental arrangement, NH$_3$ gas was used in equilibrium with a strong NH$_4$OH solution sitting in the bottom of the cell. At the ambient temperature, about -3 C, the gas pressure was about 132 torr, so that the abundance was 2.5 cm-atm.

Spectra of C$_2$H$_2$ from a welding tank were also obtained with the 14.3-cm cell. The gas was admitted at atmospheric pressure (Mauna Kea), 46 cm Hg, yielding 8.6 cm-atm.
It was not possible to obtain sufficiently large path lengths of CH\textsubscript{4} in the laboratory experiments to match the spectrum of Saturn. Consequently, we have relied for the identification of CH\textsubscript{4} features in the 6400 cm\textsuperscript{-1} region upon spectra obtained with a grating spectrometer and very kindly loaned to us by J. Margolis. These data have a spectral resolution of 0.3 cm\textsuperscript{-1} and a methane abundance of 75 m-atm. Without high-abundance methane spectra that show very weak features appearing in supposedly "clear" parts of the spectrum it is difficult to be certain what features in the planetary data may be assigned to other minor constituents, such as NH\textsubscript{3}.

D. The 1.6-\mu m Region (6000-7100 cm\textsuperscript{-1})

In figure 9 we present the 0.5-cm\textsuperscript{-1} resolution spectrum of Saturn, from 5850 to 7100 cm\textsuperscript{-1}. The figure covers the entire 1.6-\mu m window, the 2\nu\textsubscript{3} band of methane near 6000 cm\textsuperscript{-1}, and part of the strongly absorbed 7200-cm\textsuperscript{-1} methane and water band. The noise level of the trace may be judged from the appearance between 5800 cm\textsuperscript{-1} and about 5900 cm\textsuperscript{-1}, where there begins to be appreciable transmittance between the individual J-manifolds in the P branch of the 2\nu\textsubscript{3} band. Near 6300 cm\textsuperscript{-1}, where the signal is largest, the signal-to-noise ratio is about 70.

The upper trace in figure 9 is a lunar spectrum at the same resolution, chosen to show a similar degree of
Fig. 9. Spectra of Saturn and the Moon, 5850-7100 cm$^{-1}$. Resolution = 0.5 cm$^{-1}$. Lines of CH$_4$ are indicated in the region of expected NH$_3$ absorption.
absorption in the H₂O lines. Direct examination of this spectrum is the most reliable way to determine if a particular Saturn spectrum feature is telluric. A comparison of Saturn and the Moon is especially valuable in the 6250-6360 cm⁻¹ interval; here we can establish how noise-free the Saturn data are, by the excellent match of the two traces.

Tick marks have been placed in figure 9 at the positions of CH₄ absorptions that might confuse the search for NH₃ in its 6450-cm⁻¹ band. These have been taken from the 75 m-atm laboratory spectrum of CH₄. In the most intense part of the Saturn spectrum, the methane lines are stronger than in the reference spectrum, indicating that a more complete accounting for the planetary spectrum would be achieved by a comparison with a greater abundance spectrum of methane, perhaps 200 m-atm.

The test for ammonia proceeded as follows. A region of inspection was defined. The low-frequency cut-off, 6360 cm⁻¹, was chosen by the apparent absence of significant Saturn absorptions shortward of this frequency (the region of detailed matching to the lunar spectrum extends from 6250 to 6360 cm⁻¹). The high end of the search band was chosen by the onset of methane domination of the spectrum. Very few features above 6550 cm⁻¹ were not readily accounted for by comparison with the spectrum of methane.
It was necessary to apply a correction to the Saturn wavenumber scale to allow comparison with the vacuum-wavenumber scale of the methane laboratory data. The shift arises from several sources, which are:

1. **Doppler shift.** The relative motion of the Earth and Saturn produced a Doppler (red) shift, ranging between 0.47 and 0.61 cm\(^{-1}\) over the dates of data collection. The rotational motion of Saturn broadens lines but does not shift them; the entire ball was detected, so this effect applies to our data. An infinitely-narrow line would acquire a semicircular profile with a FWHM of 0.38 cm\(^{-1}\).

The Earth's rotation also broadens spectral lines, if observations made before and after meridian transit are averaged together. The emphasis on observing near transit ensures that this effect is very small. The shift is given by

\[ v = v \cdot (V/c) \cos I \cos \delta \sin z \]

where \(V\) is the Earth's equatorial rotational speed, \(I\) is the observatory latitude, \(\delta\) is the planet declination, and \(z\) the zenith distance. The extreme case of Saturn in February 1974 at \(z = 60^\circ\) gives \(v = 0.0074\) cm\(^{-1}\).

2. **Interferometer beam obliquity.** The signal beam does not traverse the interferometer optics on-axis, because of the need to have the output beam emerge where it can be detected (a perfectly symmetric geometry would re-
turn the output beam to space). The interferometer does not distinguish between a monochromatic input of frequency $\nu$ entering normally and an input of frequency $\nu \cos \theta$ entering at an angle $\theta$ from the normal. The non-normal rays have a longer wavelength but the same effective wavelength for interference purposes as the rays of frequency $\nu$. A spectral line entering at angle $\theta$ and occurring at true frequency $\nu$ will be interpreted by the interferometer as occurring at $\nu \sec \theta$; we must multiply the wavenumber scale by a factor $\cos \theta$ to restore the correct values. In our case, $\theta$ is half the angle between the input and output beams as seen from the collimator, 0.00197 rad; the correction factor is 0.012 cm$^{-1}$ at 6400 cm$^{-1}$, quite negligible for this work.

3. **Vacuum correction.** The Digilab interferometer control software assumes that the wavenumber of the He-Ne laser used to control sampling is 15800.8233 cm$^{-1}$. That is different from the vacuum wavenumber of the laser, 15798.00 cm$^{-1}$ (Hanes and Baird 1969). Consequently, the wavenumber scale applied to the spectra is in error; it will be corrected by a multiplicative factor equal to 15798/15800.82. At 6400 cm$^{-1}$, the magnitude of the error is 1.14 cm$^{-1}$.

The dispersion of air creates a slight change in the relative frequencies of the laser and features in the band of interest. The correction is, however, only 0.02
cm$^{-1}$ at 6400 cm$^{-1}$.

4. **Reference laser tilt.** Since the frequency scale of the spectra is derived from the frequency of the laser used as a mirror-travel reference, any change in the apparent frequency of the laser caused by its being tilted will be directly applied to the spectra. If the laser beam is not normal to the reference interferometer elements, it will have a shorter effective wavelength for interference, and a higher effective frequency. Features in the spectra will therefore appear at higher frequencies than the correct ones. The correction to be applied is again multiplicative, and is just \( \cos \varphi \), where \( \varphi \) is the angle from the normal at which the laser beam enters the reference cube. Unfortunately, this angle \( \varphi \) was not measured during the Saturn data acquisition, but the angle was certainly substantial. The amplitude of the laser reference interferogram revealed considerable optical apodization as the traveling mirror was allowed to move over its full 5 cm path. Also, the return beam from the reference cube did not coincide with the emergent laser beam, but produced a visible spot on the laser endplate. A tilt of just 1°, which is entirely possible, would produce an error at 6400 cm$^{-1}$ of 0.96 cm$^{-1}$, a very substantial shift.

We expect that most of the unassigned wavenumber discrepancy between the Saturn data and vacuum frequencies is in fact due to the effect of laser tilt. The total dis-
crepancy was assessed by comparing the plotted frequencies of six telluric H$_2$O lines which appear in the clear part of the Saturn spectrum, between 6250 cm$^{-1}$ and 6350 cm$^{-1}$, with the vacuum wavenumbers of these lines given in Hall's atlas of the infrared solar photosphere spectrum (1970). The net calculated correction is $-0.60$ cm$^{-1}$, and the measured correction for telluric lines $-1.78$ cm$^{-1}$, leaving an unassigned discrepancy for the Doppler-shifted Saturn lines of $-0.64$ cm$^{-1}$.

In the search band, all 57 features in the Saturn spectrum were marked which were possibly non-telluric. Of these, 48 were considered to be definitely or possibly due to methane by comparison with the laboratory spectrum. Some of these assignments arose from very weak features in the laboratory data, just above the noise level, making the identification less certain than for stronger lines.

In order to assess the likelihood that the unassigned lines in the search band were due to NH$_3$, we followed the statistical procedure employed by Russell and Bowen (1928) in their discussion of the solar coronal lines. They determined, from a universe of laboratory lines, how many of these would be expected to coincide with a collection of candidate lines in a spectrum of unknown origin, given a certain coincidence criterion. If the number of actual coincidences in the comparison of laboratory and unknown spectra exceeds the number of expected chance coin-
cidences, the detection is relatively certain, to the extent of the excess.

Let $M$ be the number of NH$_3$ laboratory lines in the search band which we suppose are sufficiently strong to appear if a small quantity of ammonia is present in the Saturn spectrum. The conservative approach is to make $M$ equal to the total number of lines in the laboratory spectrum. However, we have chosen to set $M$ equal to the number of laboratory lines that appear in the spectrum of Jupiter. The Jovian atmospheric conditions are a good approximation to a low-temperature laboratory sample of NH$_3$. If a line is weak in the laboratory sample and does not appear in the Jovian spectrum, there is virtually no hope of finding it in the Saturn spectrum, which has certainly less abundance, and probably still lower temperature. We have taken $M = 80$. If $X$ is the band width, 190 cm$^{-1}$, then $I = X/M = 2.38$ cm$^{-1}$ is the average interval between NH$_3$ lines in the laboratory spectrum.

Our criterion for coincidence is that a suspect feature lies within $\pm 0.4$ cm$^{-1}$ of the position of a line in the laboratory spectrum. Coincidence was tested visually, and the criterion measured from trials in which lines were matched repeatedly at various frequency separations, with judgments made in each trial of the coincidence. The value 0.4 cm$^{-1}$ is roughly appropriate for spectra of 0.5 cm$^{-1}$ resolution. Let us call $2x = 0.8$ cm$^{-1}$. 
The probability that an arbitrary line in the Saturn spectrum will lie within $x \text{ cm}^{-1}$ of a particular NH$_3$ line in the search band is just $2x/X$. The probability this will not happen is $1 - 2x/X$. The probability of coincidence failing for $M$ lines is $(1 - 2x/X)^M$, and the probability of getting coincidence for all $M$ lines is

$$p = 1 - (1 - 2x/X)^M.$$ 

Now consider the $N$ lines in the Saturn spectrum that are actual candidates for ammonia; that is, all non-telluric lines which are neither due to methane nor "possibly methane." The probability $p$ will be the same for each of these. The number of chance coincidences to be expected in a large number of trials with random lines would be $C = pN$, so


In individual cases the number of coincidences will fluctuate about the mean value $pN$. The standard deviation for this distribution of values of $C$ is given by

$$\sigma^2 = pN(1 - p).$$

The number $N$ for the Saturn 0.5-cm$^{-1}$ spectrum is 9. From equation 13, we get

$$C = 9 (1 - [1 - 0.8/190]^{80}) = 3.03$$

so that 3 coincidences are expected by chance. The standard deviation is $\sigma = 1.42$. We actually find 5 coincidences. This implies detection, but with a certainty of only $1.4\sigma$, which is not statistically significant. On Saturn, there
are few chemicals known to exist in the atmosphere, so that if a feature is definitely not due to CH$_4$, NH$_3$ or H$_2$, that fact is important. In this case, however, the lack of a sufficiently high abundance CH$_4$ lab spectrum prevents us from categorically assigning the nine lines to a new chemical species.

We proceed to inquire if the upper limit for the NH$_3$ abundance can be improved by the general absence of lines in our search band. Models of Saturn's atmosphere due to Weidenschilling and Lewis (1973) and Palluconi (1972), indicate that the expected NH$_3$ cloud would lie at a pressure level of 1-2 bars. Lines formed in this region would have widths similar to those of our laboratory data, if not greater. Thus we may claim that an abundance somewhat less than that in our comparison data would indeed have produced a detectable line in the Saturn data. The smallest abundance in the comparison spectra is 8.5 cm-atm. If central line depth is proportional to abundance, 2 cm-atm, we estimate, would have been readily detectable placed in series in the optical path while the Saturn observations were made. The implication for the Saturn atmosphere is that during the time covered by this spectroscopy, the total path in the atmosphere traversed by photons which contribute to the 6400 cm$^{-1}$ brightness of Saturn can contain no more than 2 cm-atm of NH$_3$ gas. Probably such photons traverse a considerable path of methane, since the nearby
methane lines are of a strength typical of perhaps 150-200 m-atm of the gas.

It is not certain whether the opacity at 6400 cm\(^{-1}\) is due to an abrupt cloud deck, an extended haze permeating the traversed methane, or absorption of a broad nature arising from the wings of distant H\(_2\) lines or from some condensed species. A clue to the answer would be provided by a study of the center-to-limb variation of the equivalent widths of weak methane lines, in the region of high apparent reflectivity. Previous studies of Saturn in the region of the 3\(\nu_3\) band, by Trafton (1973) and others, have shown that the reflecting-layer model satisfactorily describes the observed line shapes. If we adopt it, then our upper limit translates into a column-abundance upper limit for NH\(_3\) of about 1 cm-atm. In this calculation we have ignored the increased mean air mass due to full-disk observation, since the size of the correction is at most about 30%.

Our upper limit contrasts sharply with the observations of Owen (1974), in which the 6450-A band of NH\(_3\) was reportedly detected on Saturn. In order to observe that band at all, about 1 m-atm of the gas is necessary, or about 100 times as much as our columnar abundance upper limit. It is difficult to believe that the atmosphere is more deeply probed at 6450 A than in the infrared, where Rayleigh scattering due to submicron-sized particles is
certainly less important. Rather than invoke time variation of the above-cloud deck abundance by such large values, it may be necessary to postulate the existence of a broad absorption in the infrared which prevents viewing to levels as deep as in the visible. However, we have already mentioned the large (150-200 m-atm) apparent CH₄ abundance implied by the weak infrared lines. These values are in reasonable accord with the large abundances found by Kuiper (1952) to match the Saturn 6190-A band, which is fairly close to the wavelength of the visible NH₃ band. Recent estimates of the abundance from the 6190-A band have been lower than Kuiper's, so that, on the evidence given by CH₄, it is unlikely that a new absorber is present which can explain the non-appearance of NH₃ at 6400 cm⁻¹. We are left with a dilemma; we feel that a valuable new piece of evidence will be a high-abundance laboratory spectrum of CH₄ in the 6450-A region, which would establish if CH₄ is truly responsible for lines attributed recently to NH₃.

E. The 2.0-μm region (4900-5200 cm⁻¹)

The moderately strong ν₃ + ν₄ band of NH₃ occurs near 5050 cm⁻¹, and consists primarily of a regular series of J-manifolds which extend, in laboratory data, from roughly 4920 to 5150 cm⁻¹. This is a region of relatively low reflectivity in the spectra of both Jupiter and Saturn,
where we might expect to see the NH$_3$ band due to gas lying above whatever reflecting level is effective at this frequency. The telluric spectrum is marked by both CO$_2$ and H$_2$O absorption throughout this range. Fortunately, at Mauna Kea Observatory the 1.9-$\mu$m H$_2$O band is often sufficiently weak to allow useful planetary spectra to be obtained up to 5200 cm$^{-1}$.

The 0.5-cm$^{-1}$ spectrum of Jupiter reveals the NH$_3$ band in question with very high contrast; at least 14 of the individual manifolds can be recognized (see figure 10). Unfortunately, the band has received little attention from molecular spectroscopists, so that the assignment of quantum numbers to individual manifolds, and the prediction of temperature dependence, is still awaited. We already have rotational temperatures for Jupiter derived from the hydrogen and methane spectral features. It would be of considerable interest to compare these temperatures with one obtained from ammonia, which is probably much more localized in the atmospheric vertical structure than CH$_4$ or H$_2$. It is not, of course, strictly necessary that a full quantum number description of the band be performed; laboratory spectroscopy at various low temperatures would allow an empirical determination to be made of the temperature dependence of the relative manifold strengths.

Now we consider the question of the upper limit for NH$_3$ derived from data at 5000 cm$^{-1}$. Here we know there
Fig. 10. Spectra of Jupiter and Saturn, 4400 - 5100 cm\(^{-1}\). Resolution = 0.5 cm\(^{-1}\). Lines of the 5050 - cm\(^{-1}\) Jovian NH\(_3\) band are indicated.
is considerable absorption taking place in the wing of the $H_2$ band, which fact prevents us from clearly seeing to the level of the cloud tops. At 5025 cm$^{-1}$, the intensity is only one-third of the intensity at 6320 cm$^{-1}$. Therefore, it is unlikely that a good NH$_3$ upper limit could be obtained near 5025 cm$^{-1}$, unless the ammonia band were much stronger than it is.

A comparison of our laboratory spectrum of 25 cm-atm of NH$_3$ and the Saturn data shows a general absence of the NH$_3$ lines. The laboratory cell pressure was 158 mb. In Weidenschilling and Lewis' (1973) model of Saturn's cloud structure, the ammonia cloud has a base pressure of about 2 bars. It is likely, therefore, that the width of NH$_3$ lines in the laboratory spectra does not exceed the expected width of possible Saturn lines. About 10 cm-atm of NH$_3$ would be readily apparent if it were present in our Saturn data, and this is the upper limit we place on the total path abundance deduced from the 5000-cm$^{-1}$ band.

F. The 3.0-$\mu$m region (3200-3600 cm$^{-1}$)

The strong $\nu_1$ band of NH$_3$ and the regular structure of the $\nu_3$ band fall in the region 3200-3600 cm$^{-1}$, where the Saturn atmosphere is sufficiently non-absorbing that the spectrum resembles that of the moon in some detail. Although telluric H$_2$O lines are very frequent in this range,
it is apparent that Saturnian CH$_4$ lines do not dominate the spectrum, so that there are numerous frequencies where we might expect penetration to a cloud level.

We have attempted to determine the relative reflectivity of the Saturn atmosphere at 3325 cm$^{-1}$, one of the clear spaces, compared to the very clear region around 6320 cm$^{-1}$. In order to eliminate the effect of the lunar reflectivity on the Saturn/moon ratios calculated at those frequencies, we have extrapolated the data of McCord and Johnson (1970) from 2.5 to 3.0 $\mu$m. Specifically, we assumed a value of 4.1 for the ratio $R(3.0 \mu m)/R(0.56 \mu m)$. Then, the ratio of the lunar reflectivity at 3325 cm$^{-1}$ to 6320 cm$^{-1}$ is 1.63.

There is considerable variation between our various Saturn data sets in the relative intensities at 3325 cm$^{-1}$ and 6320 cm$^{-1}$. The ratio we have chosen, 1:5.8, may be in error by 50%. The errors presumably arise from small misalignments occurring in the co-adding of the data; the effect would tend to depress the high-frequency end of the spectra resulting from the adding process. The effect is appreciable here because the frequencies of interest differ by nearly a factor of two.

We derive a value of 0.83 for the reflectivity at 3325 cm$^{-1}$ relative to that at 6320 cm$^{-1}$. We conclude that the continuum has comparable intensity at both frequencies, and that we might expect a good upper limit to the NH$_3$
abundance to be derived in the 3-\textmu m region.

We now consider the appearance in our spectra of ammonia features in this region. The $\nu_1$ band at 3335 cm$^{-1}$ is by far the strongest of the bands we have employed to obtain upper limits. Our laboratory spectrum shows the band to be saturated at an abundance of only 2.5 cm-atm. The central feature has a width (FWHM) of 6.8 cm$^{-1}$ in our 0.5-cm$^{-1}$ resolution data. Other strong manifolds appear from the $\nu_3$ band near 3440 cm$^{-1}$ and the $2\nu_4$ band near 3240 cm$^{-1}$, which regions are also accessible in the Saturn spectrum.

The spectra of Saturn and the moon are shown in figure 11 for the frequency interval 3200-3600 cm$^{-1}$. Features which are clearly not of telluric origin are indicated by vertical lines. It can be seen that the region of the NH$_3$ $\nu_1$ band is remarkably similar to the lunar spectrum, except for a feature about 25% deep occurring at 3332 cm$^{-1}$. That is within the bounds of the wide absorption in the laboratory NH$_3$ spectrum, but not at the expected position for a very low abundance sample. Moreover, there is a general absence of non-telluric features at the frequencies of other lines of NH$_3$. Probably the feature at 3332 cm$^{-1}$ and most of the other absorptions noted in figure 11 are due to methane. As we mentioned, there is no available large abundance comparison spectrum of CH$_4$ for this region.
Fig. 11. Spectra of Saturn and the Moon, 3200-3650 cm\(^{-1}\). Resolution = 0.5 cm\(^{-1}\).
Clearly non-telluric absorptions in the Saturn spectrum are indicated.
We estimate conservatively that 1 cm-atm of NH₃ gas would produce a 50% deep absorption in the υ₁ band. Such an absorption would easily be noted in the Saturn spectrum, and other features nearby would be detectable also. With the conservative airmass factor of two, we arrive at the most stringent upper limit for NH₃ obtained from our data: 0.5 cm-atm in a column above the cloud deck. If scattering effects are important in the atmosphere, then we may still interpret this upper-limit (and others in this work) as being half the total abundance in a mean free path through the atmosphere at the frequency of interest.

The Saturn model given by Weidenschilling and Lewis (1973) shows an ammonia cloud having a base at a density of about 2 bars, and a temperature of 155 K. By even the most pessimistic assumptions, there should be several meter-atmospheres of NH₃ above the base of the NH₃ cloud. For example, if we assume a mean density for the cloud of 5 x 10⁻⁴ gm/l and a uniform density over a height of 10 km (both very conservative values compared to the Weidenschilling and Lewis model), we derive an equivalent gas abundance of 6.6 m-atm NH₃. Most of that will exist as cloud particles, and may not be spectroscopically evident, especially if the mean particle size is small. However, there will be variations in the local cloud density, which provide the opportunity to see deeper
than is typical. The vapor pressure of NH$_3$ gas in equilibrium with the solid is a very steep function of temperature in the range 150-100 K. Between 100 K and 120 K, for example, the vapor pressure varies by a factor of 140 (see Cruikshank and Murphy 1973). Consequently, where clear spaces occur in the cloud deck and lower-lying warmer regions are visible, much greater quantities of the gas are liable to be available for absorption. If global variations in cloud density are significant, then it is possible that we would not see even 0.5 cm-atm of the gas in whole-planet spectra, but visible spectroscopy (in the 6450-A band) would yield detection of about 100 cm-atm, in a particular region of the disk, and at another time. In this regard, it is important to obtain new spectra in the search for NH$_3$ in regions that appear to be "clearer."

One convenient test is the apparent methane abundance; parts of the planet disk where methane absorption is strong are probably more free from the obscuration of high clouds, and are thus better regions in which to detect ammonia. However, that is true only in a reflecting-layer model. It is possible that the presence of a high cloud could cause a larger apparent methane abundance, if the cloud produces considerable scattering within it.

There is a very strong absorption in NH$_3$ frost at 3.0 $\mu$m (Kieffer and Smythe 1973). The absence of any
such broad absorption in our Saturn spectra indicates that frost absorptions should be unimportant throughout the 1-3 μm region. If the cloud particles are much smaller than a wavelength, however, as appears to be the case for Jupiter (Tomasko et al 1974), then we would not expect to see the absorption band at all, if we may draw an analogy with the behavior of frost spectra (Kieffer 1970). It may be difficult to infer the nature of the assumed ammonia cloud on Saturn from infrared spectroscopy alone.
III. A Search for C\textsubscript{2}H\textsubscript{2} on Saturn

Acetylene is a simple hydrocarbon which can form readily from photolytic products of CH\textsubscript{4} in the upper atmosphere of the outer planets (Strobel 1973). Its presence has already been established on Jupiter by Ridgway (1974); the \( \nu_5 \) fundamental band at 775 cm\textsuperscript{-1} appears in emission. Its strength indicates an abundance of roughly 0.2 cm-atm. Spectra of similar quality for Saturn are just recently available (see below); no clear evidence of the 775-cm\textsuperscript{-1} band appears in the low-resolution spectrum of Gillett and Forrest (1974). The many similarities between Saturn and Jupiter suggest that C\textsubscript{2}H\textsubscript{2} may be a detectable gas in the Saturn atmosphere.

Our search for C\textsubscript{2}H\textsubscript{2} is made possible by the existence of a reasonably strong band at 6560 cm\textsuperscript{-1}, where the Saturn spectrum is not too heavily dominated by CH\textsubscript{4} absorption (figure 9). The absence of NH\textsubscript{3} is beneficial; the Jupiter spectrum is controlled by NH\textsubscript{3} here, where Cruikshank and Binder (1968) made a search for acetylene at lower resolution (about 10 cm\textsuperscript{-1}).

The Saturn 0.5-cm\textsuperscript{-1} spectrum near 6560 cm\textsuperscript{-1} (figure 9) shows very few features that are not adequately accounted for by CH\textsubscript{4}, and certainly too few lines coincident with the regular P and R branches of the acetylene band. Our comparison laboratory spectrum, obtained with the same interferometer and spectral resolution, shows
the strongest lines to be about 80% deep, for an abundance of 8.6 cm-atm. We estimate that one-third of this amount would be readily detectable if it were in the Saturn atmosphere path. With a conservative air-mass factor of two, the column abundance upper limit is 1.5 cm-atm.

This value is clearly not as small as we would like, considering the 0.2 cm-atm detected by Ridgway on Jupiter. Other investigators are known to have higher-resolution Saturn spectra than our own (de Bergh et al. 1973); these could be used to give a more-exacting test to the acetylene abundance.

Tokunaga et al. (1975) have reported the detection on Saturn of \( \text{C}_2\text{H}_6 \) (ethane) in the 825-cm\(^{-1}\) band used by Ridgway for his discovery of that molecule on Jupiter. Both \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_2 \) appear in emission on Jupiter. That fact implies that the lines are formed high in the atmosphere, where a temperature inversion may occur. In such a case, the lines we seek at 6560 cm\(^{-1}\) may be narrow enough that the equivalent widths will be small, even with broadening by planetary rotation. The vertical distribution of \( \text{C}_2\text{H}_2 \) is expected to be limited by chemical reactions that destroy it at lower levels, whereas \( \text{C}_2\text{H}_6 \) can survive, so that much larger column densities are possible for ethane (Strobel 1969).

Acetylene has a very strong fundamental absorption at 3287 cm\(^{-1}\) (Herzberg 1945), which does not appear in our
Saturn spectra of that region (figure 11). With laboratory spectra of this band, a very stringent test for the molecule could be performed; we are at present forced to accept the weaker test, without being able to constrain Strobel's models. We have assumed these to be at least qualitatively appropriate for Saturn.
IV. A Search for H₂S on Saturn

Hydrogen sulfide is the fully reduced form of sulfur, and, in the hydrogen-rich atmospheres of Jupiter and Saturn, a logical compound to bind the presumed-existing sulfur, much as N is bound in NH₃, C in CH₄, and P in PH₃ (O is assumed to exist in H₂O). However, as Lewis (1969) and Lewis and Prinn (1970) have shown, H₂S combines chemically with NH₃ to form solid NH₄SH. Weidenschilling and Lewis (1973) incorporated this reaction in their cloud models, which show for Saturn an ammonium hydrosulfide deck well below the ammonia cloud that presumably limits the penetration of 1-3 μm radiation. Thus, it would be surprising to detect H₂S in any appreciable amounts near the ammonia cloud.

The nearly ideal location of the weak H₂S band studied by Cruikshank and Binder (1968) and by Pilcher (1973) in their Jupiter search makes the effort attractive for the case of Saturn. The Q-branch at 6290 cm⁻¹ falls in a region where there is virtually no CH₄ absorption, and we presumably see the continuum reflectivity of a cloud deck (but see section VI B 1). Our Saturn spectrum of resolution 0.5 cm⁻¹ shows detailed agreement with the lunar spectrum near the expected frequency of the center of the H₂S band, 6289.3 cm⁻¹ (figure 9). We estimate conservatively that an absorption of depth 8% would be readily detectable here. The 2-cm⁻¹ spectrum published
by Allen, Cross, and Wilson (1950) shows 29% depth for the Q-branch at an abundance of 106 cm-atm. If we make the rough approximation that the unresolved line central depth depends linearly on abundance, then an 8% feature would correspond to an abundance of about 30 cm-atm. Again employing the airmass factor of 2, we arrive at a column-abundance upper limit of 15 cm-atm. Since this value is not very restrictive, considering the expected H₂S distribution and the NH₃ upper limit, we have not attempted to include temperature effects on the strength of the Q-branch.

Hydrogen sulfide may yet be detected on Jupiter and Saturn without the use of atmosphere entry probes. Unfortunately, one of the strongest bands, at 1290 cm⁻¹, is coincident with a strong band of CH₄. However, there may be a good opportunity to detect H₂S if one can make observations from above the bulk of telluric water vapor. Then, the region near the strong 3789-cm⁻¹ band will become accessible—a region fairly free of absorption in CH₄, NH₃, and H₂. Observations should be made into portions of the Jovian disk where 5-μm emission is strong; such areas are most likely free from material obscuring the lower-lying levels.
V. A Search for methane on Pluto and Triton

Pluto and Triton share a number of characteristics which lead one to study them together. They both lie in the outer reaches of the planetary solar system, and are dense, moon-like bodies different from the four major planets. Both objects are about 14th visual magnitude. Their colors are similar: they have flat, low, slightly reddish reflectivities, typical of many satellites of Jupiter, Saturn, and Uranus. They have not dissimilar radii. Triton is probably less than 4000 km in diameter, while an upper limit of 6800 km has been placed on the diameter of Pluto.

We are concerned here with the possibility of atmospheres on Pluto and Triton. Under conditions of radiative equilibrium, blackbodies at the appropriate distances from the sun would have temperatures near 50 K for Triton and 40 K for Pluto. All common gases would probably condense on the surfaces or escape under the low gravity. McGovern (1973) concluded that Pluto and Triton were unlikely to have more than tenuous CH₄ atmospheres, given their radii, densities, and probable exospheric temperatures. (See Hart [1974] for a discussion of a Ne atmosphere for Pluto.) Yet, the problem is not that simple. Internal heat sources could bring about a situation in which thin atmospheres might exist, even if only above the warmer parts of the body, or during warm parts
of the orbit. We must also consider that a molecule escaping from Triton must escape from Neptune as well, or it may be recaptured by Triton again later. The example of Titan, which is known to have a dense methane atmosphere, prevents us from categorically denying the existence of such an atmosphere for Pluto and Triton. If these two objects condensed from the original solar nebula near their present distances from the sun, their temperatures at that time would probably have been low enough to ensure that much primeval methane was retained (see Lewis 1973). In fact, methane may well be a large fraction of all satellites beyond the orbit of Saturn. The escape velocities for Pluto, Triton, and Titan are nearly the same, although quite uncertain for Pluto and Triton. Therefore, if the temperatures were somehow large enough (no measurements exist), it is likely that a methane atmosphere would survive on either Pluto or Triton.

The only published spectroscopy of Pluto is that by Kuiper (1952). His 340 A/mm plates showed no evidence of the 6190-A band of CH₄. Similar data and results were obtained for Triton. More recently, Spinrad (1969) performed spectrophotometry of Triton with a 90-A bandpass to search for the 6190 band. His comparison of the intensity at 6200 A with that at 6100 A led to an upper limit of 8 m-atm CH₄ above the Triton surface.

Ideally, we would use one of the much stronger
near-infrared bands of CH\textsubscript{4} rather than the weak 6190 band. The 7250-A band is an obvious choice. But spectroscopy at reasonable dispersions, say 50 A/mm, makes exorbitant demands on telescope time for 14th magnitude objects unless a sensitive image intensifier tube is used. At the time of our investigation, there was an RCA 2-stage image tube with S20 cathode available for use with the Mauna Kea 224-cm telescope Cassegrain spectrograph. At 50 A/mm, exposures of Pluto and Triton could be obtained in the 6190 A region in roughly one hour. The sensitivity of this tube falls rapidly to the red, so that stronger bands of CH\textsubscript{4} were not accessible.

In April and May, 1973, we obtained three spectra of Pluto and four of Triton, covering the range 5850-7000 A. Prints of the best spectra are presented as figure 12, and microphotometer tracings in figure 13. The most prominent features are the telluric O\textsubscript{2} band at 6870 A and solar H\textalpha\textsubscript{C} at 6563 A. The band of methane we seek consists of many narrow lines which would not be resolved in these data, but would appear as a shallow depression with a width at half-depth of about 20 A. The very strong absorption in this band for Neptune can be seen in the spectrum next to that of Triton in figure 12. No apparent methane absorption occurs in our plates of Triton or Pluto. We therefore consider if a valuable upper limit to the abundances of the gas can be obtained. In the
Fig. 12. Spectra of Pluto, Triton, and Neptune, 5850 - 7100 A. Original dispersion 52.2 A/mm. Neon comparison spectrum.
Fig. 13. Microphotometer tracings of Pluto and Triton spectra. Position of expected CH₄ band is indicated. N: noise spike. Dark spots caused by electric discharges in the image tube produce emission-type features in the Pluto spectrum, 6070-6840 Å (see fig. 12).
case of Pluto, of course, no such upper limit has been published.

The absorption of Hα is the only reliable feature in our spectra that has an equivalent width near that of the expected broad methane band. Indeed, very few other solar lines can be found at all. We have measured the equivalent widths of Hα in the best Pluto and Triton plates in microphotometer tracings of the spectra, shown in figure 13. Hα is not saturated in the core for high resolution solar spectra, and is certainly not black in the center at 50 A/mm. Thus, we do not expect serious departures from linearity in the transformation from intensity to density, and we regard the traces as sufficiently accurate representations of the intensity spectra. The Hα line areas were measured with a polar planimeter, along with those of simulated 6190 band profiles drawn on the traces of that part of the spectrum. The 6190 band was assumed to have a width of 20 A, and its depth was made twice that of the largest noise feature in the traced region. Such a profile would be readily apparent if it occurred in any of our spectra.

For convenience and ease of comparison with the work of Spinrad, we have chosen the Jupiter 6190-A band as our abundance calibration. This was necessary because of the lack of laboratory spectra of the band at our resolution. In our attempts to obtain laboratory spectra with
the same spectrograph, no absorption was detected even at an abundance of 13 m-atm. The Jupiter 6190-A band was found by Boyce (1968) to have an equivalent width of 16.9 A at the center of the disk. We shall assume, as did Spinrad, that the Jovian abundance of 150 m-atm CH₄ applies to the 6190-A band. We employ Boyce's measurement to facilitate comparison with Spinrad's calculation.

We measured the Hα line in the solar atlas of Migeotte et al (1956) to have an equivalent width of 2.37 A. The best Triton plate was found to have a 6190-A upper limit of 1.07 A; for Pluto we obtained 1.19 A. We now employ the formula:

\[ \eta \frac{W_\text{CH}_4}{W_\lambda} \leq \frac{W_\lambda}{W_\lambda} \cdot \eta \frac{W_\text{CH}_4}{W_\lambda} \text{ (Jupiter)} \]

in which \( \eta \) is the mean airmass for Pluto or Triton, \( \eta \) the same for Jupiter, \( W_\text{CH}_4 \) are the abundances of methane for either object, and the \( W_\lambda \) are the equivalent widths. We shall take \( \eta = 3 \) for Triton and Pluto, since those are disk-integrated measurements, and \( \eta = 2 \) for the Jovian center-of-disk spectrum. For Triton, then,

\[ W_\text{CH}_4 \leq \frac{2}{3} \left( \frac{1.07}{16.9} \right) \cdot 150 \text{ m-atm} = 6.3 \text{ m-atm} \]

and for Pluto

\[ W_\text{CH}_4 \leq \frac{2}{3} \left( \frac{1.19}{16.9} \right) \cdot 150 \text{ m-atm} = 7.0 \text{ m-atm} \]

The upper limit for Triton is as low as that of
Spinrad; in view of our non-detection of 13 m-atm in the laboratory, however, these numbers should not be taken too firmly. If the equivalent width of Hα in our low-resolution spectra is greater than 2.37 Å, our upper limits would have to be increased by the same factor. The limit for Pluto is new, but not really low enough to bring any surprises. The temperature of the surface would need to be roughly twice what we expect it is before much methane could be freed from the solid state. A vastly improved upper limit for both objects will result when photoelectric measurements are performed to seek the 7250 or 8800-Å methane bands.

In Table 3 are presented the results of the search performed in this work for H₂O on Jupiter, NH₃, C₂H₂, and H₂S on Saturn, and CH₄ on Triton and Pluto. Also shown are the recent results of other investigators seeking the same information.
Table 3
Upper Limits on Column Abundances

<table>
<thead>
<tr>
<th>Reference</th>
<th>Jupiter</th>
<th>Saturn</th>
<th>Triton</th>
<th>Pluto</th>
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<td></td>
<td>H₂O</td>
<td>NH₃</td>
<td>C₂H₂</td>
<td>H₂S</td>
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<td>Fink, Belton (1969)</td>
<td>40 pm ppt.</td>
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<td></td>
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<tr>
<td>Traub, Carleton (1973)</td>
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<td></td>
</tr>
<tr>
<td>This work</td>
<td>10 &quot;</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>7 m-atm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
<td>Cruikshank (1969)</td>
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<tr>
<td>infrared</td>
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<tr>
<td></td>
<td>1.5 cm-atm</td>
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<tr>
<td></td>
<td>15 cm-atm</td>
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</tr>
<tr>
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VI. Hydrogen on Saturn and Jupiter

A. Introduction

Molecular hydrogen is the most abundant constituent of the Jupiter and Saturn atmospheres. It has been retained since the formation of the solar system because of the high original mass of the two protoplanets and their considerable distances from the sun. Lighter planets (Uranus and Neptune) may have lost hydrogen relative to heavier elements during planet accretion and the early luminous phase of solar contraction. The detailed explanation for the outer planet abundance is, however, by no means complete (Cameron 1973). In spite of the large abundances of hydrogen in the atmospheres, the study of the planets' H₂ absorption spectra has been difficult, because the molecule has no permanent dipole moment. Consequently, its normal vibration-rotation spectrum is inactive. However, the molecule has a weak quadrupole absorption spectrum; the 2-0, 3-0, and 4-0 bands of the quadrupole spectrum have been detected since 1960, when Kiess, Corliss, and Kiess reported the discovery of the 8000 to 8500-A lines of the 3-0 band on Jupiter. Cloud-top temperatures have been inferred from the relative strengths of lines in the 3-0 band, and column abundances for H₂ from the equivalent widths of lines in the 3-0 and 4-0 bands (see for example Fink and Belton 1969). The Q(1) line of the 2-0 band has recently been detected at 8075 cm⁻¹ in spectra of Jupiter and Saturn (de Bergh et al 1974). The small equiva-
lent widths of the quadrupole lines, their collision-narrowed profiles, and their apparent spatial and temporal variation have made interpretation difficult. In time, a large number of spectra with good spatial and temporal coverage should significantly constrain models of the vertical cloud structure for both planets. Considerable theoretical effort has been devoted already to the modelling of the Jovian atmosphere to accommodate H₂ line observations (Hunt 1973a and 1973b).

During collisions, the H₂ molecule may briefly acquire a dipole moment, during which time the molecule can absorb at its frequencies of rotation and vibration. Collisions are frequent at high pressure, and hence the "pressure-induced" bands of H₂ may play an important role in the infrared radiation balance of the major planets. The principal source of opacity in the thermal infrared, in fact, is probably the pure-rotational pressure-induced band of H₂ (Trafton and Munch 1969).

There exist also vibrational bands of the pressure-induced spectrum (Welsh 1969). The 3-0 band was noted in the 8000-A spectra of Uranus and Neptune by Herzberg (1952), thereby establishing the existence of H₂ on the major planets. That band is apparently too weak to be manifested in the spectra of Jupiter or Saturn, which have much lower abundances in the optically accessible layers. Recently, the 2-0 pressure-induced band has been invoked to explain absorption
in the 8000-9000 cm\(^{-1}\) region on Jupiter and Saturn (de Bergh et al 1974). Upper limits of 34 km-amagat for Jupiter and 63 km-amagat for Saturn were placed on the amount of H\(_2\) that could contribute to the depression of the continuum in that frequency range. The center of the 2-0 band is unfortunately coincident with a strong band of CH\(_4\); the extent of absorption in the wings of this band cannot be readily accounted for without high-abundance laboratory spectra and comprehension of the effects of scattering, determined from methane absorption in other parts of the spectrum. The H\(_2\) contribution is therefore uncertain.

In 1966 Danielson presented an analysis of low resolution (\(\lambda/\Delta\lambda \sim 40\)) Jupiter spectra from the balloon-borne Stratoscope II experiment. The 1-0 pressure-induced H\(_2\) fundamental band was invoked to explain a broad absorption centered near 2.25 \(\mu\)m. Although the analysis was qualitatively correct, the details presented several problems that will be discussed in section B1.

Cruikshank, Fink, and Larson noticed the probable appearance of the S(1) line of the H\(_2\) fundamental band at 4800 cm\(^{-1}\) in their spectra of Saturn obtained jointly with Kuiper (Fink and Larson 1971). The absorption was also evident in the Saturn spectrum of Johnson (1970), but was not identified. Both of those spectra showed contamination by radiation from the rings of Saturn. Johnson's Jovian
spectra show the same line, with a signal-to-noise ratio probably sufficient to permit considerable improvement over the results of Danielson's earlier work.

The pressure-induced bands of H₂ offer great potential for the study of major planet atmospheres. Since the absorption results from the collision of two molecules, the monochromatic and integrated absorption coefficients depend on the square of the density. A collision is necessary to induce a temporary dipole moment in the H₂ molecule; absorption of radiation may occur while the dipole exists. The collision rate for a single molecule is proportional to the density; for the ensemble of molecules, the collision rate increases with the square of the density. If scattering effects are unimportant, the transmission in a path of length \( l \) and density \( \rho \) is given by

\[
\frac{I_\nu}{I_\nu} = \exp\left[-\nu \propto(\nu, T) \rho^2 l\right]
\]

where \( \propto \) has units amagat\(^{-2} \). The amagat is a unit of relative density; any gas at STP has a density of 1 agt. The strong density dependence implies in principle that very accurate determinations of base-level (reflecting-layer) density can be made for planets whose atmospheres are satisfactorily represented by a reflecting-layer model. An atmospheric temperature profile must be assumed. The temperature-dependence of the absorption coefficient \( \propto \) is sufficiently weak, however, that present uncertainties in
atmospheric temperatures will not produce much uncertainty in derived densities.

The 1-0 vibration-rotation band consists of three major components at planetary-atmosphere temperatures: the $Q$ transitions ($\Delta J = 0$) occurring near 4200 cm$^{-1}$, the 4500-cm$^{-1}$ $S(0)$ line ($\Delta J = +2$) arising from $J = 0$ molecules (parahydrogen), and the $S(1)$ line at 4750 cm$^{-1}$, which is due to $J = 1$ (ortho) molecules. The relative strengths of the three components depend on the temperature and ortho/para ratio. Details of the band shape also are affected by the presence of foreign molecules (see for example Chisholm and Welsh 1954).

The great widths of the component lines in pressure-induced bands arise from the uncertainty principle: $\Delta E \Delta t \sim \hbar$. Since the collisions are of short duration, the molecular vibration energy is relatively uncertain, so that absorption may occur over a wide range of photon-energies. With decreasing temperature, the collision duration increases, and the energy is better defined; the absorption profiles consequently become more narrow.

Because of the large line widths, we may make use of the abundant information contained in the line shape using low-resolution spectra. This fortunate circumstance is to be contrasted with the study of the $H_2$ quadrupole and $3 \nu_3$-band methane lines. Only recently has it been possible to analyze line shapes of these narrow features. We require
that the instrumental resolution element be less than the characteristic width of lines in a band. For the $S(1)$ line at 4750 cm$^{-1}$, whose high-frequency wing lies in a region relatively free from contamination by other absorption features, the width measured from the line center to the high-frequency wing at half depth varies between 50 and 120 cm$^{-1}$ for temperatures in the range 40-200 K (Hunt and Welsh, 1964). Spectra with resolutions near 10 cm$^{-1}$ and high signal-to-noise ratio are readily obtainable now for Saturn and Jupiter (and have, in fact, existed for several years). Consequently, even center-to-limb studies of the $H_2$ pressure-induced line shapes are presently possible. Such work is urgently needed, and should be undertaken by those with appropriate equipment.

We discuss here the 1-0 $S(1)$ line in the Saturn whole-disk 0.5 cm$^{-1}$ spectrum, parts of which have been analyzed in previous sections, and also in Jupiter spectra of the same resolution. We will perform analysis of the line shapes in terms of a reflecting-layer model and a simple scattering model.

B. Analysis

1. Preliminary reduction

The data used in this work are presented in figure 14, which shows the Jupiter and Saturn spectra between 4000 and 6000 cm$^{-1}$. The telluric absorption can be seen in
Fig. 14. Spectra of Jupiter (top) and Saturn, 4000 - 6000 cm\(^{-1}\). Resolution = 0.5 cm\(^{-1}\). Selected absorption features due to planetary CH\(_4\), Jovian NH\(_3\), and telluric CO\(_2\) are indicated.
the lunar spectrum presented earlier in figure 8 (section IIB). Evidently, the planetary intensity is near zero at 4750 cm\(^{-1}\), and the signal-to-noise ratio is adequate to show the shape of the broad absorption centered at 4750.

The high-resolution data were chosen here because they reveal certain important fine structure due to CH\(_4\), not because the resolution was necessary for the line profile study. Comparisons with lower-resolution spectra, typically at 8 cm\(^{-1}\), show excellent agreement in details of the shape of the feature at 4750 cm\(^{-1}\).

For study of the H\(_2\) line on Saturn, the first step in the reduction procedure is to eliminate any possible intensity contribution from the ring, which is bright at certain frequencies where the disk is dark. During observations, the placement of the two sky subtraction beams was chosen to achieve cancellation of the part of the ring obscuring the disk. One beam was placed concentric with the disk, and the other placed to intercept an area of the rings equal to the ring area falling across the disk. However, such an approach is not perfectly effective because of telescope guiding errors. Consequently, the measured spectra do contain some contamination from radiation of the rings. We have therefore eliminated the residual ring contribution in the data by the following procedure. A zero level is drawn between the 4100-4200 cm\(^{-1}\) region, where the rings are dark because of H\(_2\)O frost absorption,
and the level near 5300 cm\(^{-1}\), where telluric H\(_2\)O absorbs strongly. The 4100-4200 cm\(^{-1}\) region is strongly absorbed by disk H\(_2\) and CH\(_4\). We would prefer to draw the high-frequency zero level where the signal trace is relatively flat, because the cores of very strong, narrow lines can overshoot the true zero level in these unapodized spectra. The effect is apparent in the H\(_2\)O band region near 5300 cm\(^{-1}\) (figure 14). For Saturn, however, the flat region near 5800 cm\(^{-1}\), strongly absorbed by disk methane, is contaminated by radiation from the ring, which is brightest there. Thus, we may not estimate the zero level at 5800 cm\(^{-1}\). There are, however, narrow regions in the 5300-cm\(^{-1}\) H\(_2\)O band where the level "settles" between abrupt absorption edges. The Jupiter spectrum shows several such regions, where the level agrees with the zero determined at 4100 and 5800 cm\(^{-1}\) (no ring contamination problem exists for Jupiter). We have estimated the Saturn zero level in these regions of the H\(_2\)O band. The results of this procedure appear to be good; for both planets the derived zero levels are almost perfectly flat between 4000 and 5800 cm\(^{-1}\).

In future work, apodized spectra should be employed, to minimize the zero-level overshoot in the H\(_2\)O band.

At 4550 cm\(^{-1}\), where the rings are bright, there is a strong Q-branch absorption in CH\(_4\) that should make the disk totally absorbing at that frequency. We have assumed that any signal level existing at 4550 cm\(^{-1}\) is due to the
rings. Knowing the ring spectrum measured with the same instrument (Cruikshank and Pilcher 1974), it was possible to subtract at all frequencies of interest the appropriate fraction of the 4550 cm\(^{-1}\) signal from the original Saturn spectrum. The magnitude of the correction at 4750 cm\(^{-1}\), in the core of the S(1) \(H_2\) line, is small enough that it can be confidently stated that the disk is not totally absorbing at that frequency. The same result appears to be true for Jupiter.

In order to remove the slope of the solar continuum and the instrumental response function, the planetary spectra were divided by lunar spectra. The process was performed by hand at a set of discrete frequencies, in spite of the capability to do it in the Digilab data system, for the following reasons. First, it is more reliable to estimate the planetary and lunar continua in the CO\(_2\) bands at 4850 and 4970 cm\(^{-1}\) by visual inspection than to perform a machine ratio through the strong absorptions themselves (see figure 14). Second, the planetary data represent an average of runs taken at varying airmasses and telluric H\(_2\)O abundances. The moon was not always available for convenient reference measurements during the assigned observing time, so that we were not able to monitor atmospheric effects as frequently as we wished.

Ideally, lunar spectra should be obtained temporally near each planetary observation, and the resulting ratio spectra
finally averaged together. A ratio of our grand-average planetary spectrum to any particular lunar spectrum would produce inaccurate intensities in the wing of the 5200 cm\(^{-1}\)\(\text{H}_2\text{O}\) band.

Derived spectral ratios were then multiplied by the lunar spectral reflectivity determined from Apollo 11 soil samples (McCord and Johnson 1970) and scaled to 1.00 at 4900 cm\(^{-1}\)--a frequency where the signal is high and telluric contamination is low. The lunar reflectivity varies by only 7% in the range 4600-5100 cm\(^{-1}\). The high-frequency calculation cut-off at 5100 cm\(^{-1}\) was chosen because of the inability to judge the behavior of the planetary signal in the telluric \(\text{H}_2\text{O}\) band.

The spectral activity of \(\text{CH}_4\) and \(\text{NH}_3\) must be considered before we can discuss the \(\text{H}_2\) line shape, since the first two compounds dominate the remainder of the 3000-10000 cm\(^{-1}\) spectra of Jupiter and Saturn. Both \(\text{NH}_3\) and \(\text{CH}_4\) have strong absorption bands near the center of the \(\text{H}_2\) fundamental band at 4500 cm\(^{-1}\) (2.2 \(\mu\)m). Cruikshank and Binder (1968) presented laboratory spectra of large quantities of \(\text{CH}_4\) in the region 4500-5250 cm\(^{-1}\) (1.9-2.22 \(\mu\)m). Their figure 14 is reproduced here together with our reduced intensity profile of Saturn as figure 15. The continuum level for the Saturn data is taken to be at the top of the diagram. We note that, for the largest abundance, 120 m-atm, there is 50% absorption at 4720 cm\(^{-1}\), due to the R-branch of
Fig. 14  Spectra of CH₄ 1.90-2.22 μ, medium resolution. All spectra were made with 40 m absorption tube and have 3 m laboratory air path in spectrometer superimposed (about 18 microns precipitable H₂O). (a) blank run, tube evacuated, (b) 1.68 m-atm CH₄ at 0.042 atm pressure, (c) 3.37 m-atm at 0.084 atm, (d) 13.1 m-atm at 0.34 atm, (e) 26.3 m-atm at 0.66 atm, (f) 52.6 m-atm at 1.32 atm, (g) 120 m-atm at 3 atm.

Fig. 15. Spectra of methane (Cruikshank and Binder 1968) and the relative intensity of Saturn. The continuum level for Saturn is the top edge of the figure.
the band centered at 4550 cm\(^{-1}\). This absorption edge will shift to higher frequencies with increasing abundance. Although very weak methane lines in the Saturn spectrum are matched in intensity by laboratory spectra with abundances on the order of 100 m-atm (see section IID), the regions of strong absorption, such as the edge of the \(2 \nu_3\) band at 6000 cm\(^{-1}\), are fit well by spectra having a few tens of meter-atmospheres. The implication is that the total path of CH\(_4\) traversed by photons in the atmosphere depends on the monochromatic absorption coefficient for CH\(_4\). Such behavior is characteristic of a scattering atmosphere in which gas absorption is greater than continuum absorption. Regions where the absorption coefficients are small, such as 6300 cm\(^{-1}\), will show stronger gas absorption relative to regions of large absorption coefficient than is the case for a laboratory gas-cell spectrum. However, it is not evident in the Saturn or Jupiter spectra that major changes take place in the overall behavior of bands: where absorption coefficients are small, absorption is low, and absorption is great when the coefficients are large. From the degree of absorption shown in Cruikshank and Binder's curve \((e)\) at 2.09 \(\mu m\), assuming that the intensity at 2.04 \(\mu m\) represents the true continuum, we estimate that roughly 2500 m-atm would be required to create the 97% absorption in the Saturn spectrum at 2.09 \(\mu m\) (4790 cm\(^{-1}\)). Such a large abundance is quite at variance with our expec-
tations, and does not agree with the behavior of CH₄ bands elsewhere in the spectrum.

The laboratory CH₄ spectra of figure 15 were recorded at room temperature. The location of the peak absorption near 4610 cm⁻¹ in those data is in accord with the expected behavior of the R branch of the ν₂ + ν₃ band that is centered at 4550 cm⁻¹. At lower temperatures, the frequency of peak R-branch absorption will shift to lower values, owing to the shift in the maximum of the Boltzmann factor governing the population of the various J-manifolds. Indeed, the intensity in the lines above 4600 cm⁻¹ will fall greatly with the temperature. At 150 K, the peak absorption is expected to occur near the J = 4 manifold, at about 4595 cm⁻¹.

A few of these J-manifolds are just visible in both the Saturn and Jupiter spectra, between 4570 and 4650 cm⁻¹. Their appearance matches that in the laboratory spectra with an abundance of about 30 m-atm, and supports the contention that the absorption at higher frequencies is not CH₄. The planetary spectra show a minimum at 4750 cm⁻¹, which would not appear in a methane spectrum without very great absorption at 4600 cm⁻¹. A final argument against methane as the primary cause of absorption in the range 4700-5000 cm⁻¹ is the notable lack of structure expected for CH₄ bands. These show the effects of a near-random superposition of many lines of widely varying in-
tensities.

The broad feature that concerns us can not be the result of NH$_3$ absorption. On Saturn, the signs of ammonia are weak if present at all (section IIE). On Jupiter, we note the regular structure of the 5050-cm$^{-1}$ $\nu_3 + \nu_4$ band very clearly (figure 14). The bands lying in the 4250-4600 cm$^{-1}$ region are somewhat stronger than the one at 5050 cm$^{-1}$, and can be expected to add to the absorption of CH$_4$ up to perhaps 4600 cm$^{-1}$. There is certainly no possibility that the slope at 4800-5000 cm$^{-1}$ is caused by NH$_3$. Laboratory spectra indicate that the opposite slope would result as the wings of the 5050 cm$^{-1}$ band fill in at high abundances.

The minimum at 4750 cm$^{-1}$ is in excellent agreement with the center of the S(1) line of the 1-0 H$_2$ band. The frequency of maximum absorption coefficient in this line, which is actually three lines nearly superimposed, does not vary with changing temperature and density by more than 25 cm$^{-1}$ (see for example figure 4 in Chisholm and Welsh 1954). A minimum in the absorption coefficient occurs near 4625 cm$^{-1}$, which fact, together with the CH$_4$ absorption, explains the small rise in the planetary intensities at 4650 cm$^{-1}$. The H$_2$ absorption coefficient decreases monotonically at frequencies above the line core, and is non-zero at wavenumbers well above 5000 cm$^{-1}$ even for temperatures below 100 K. This character matches the
behavior of the planetary feature, which extends into the complex absorption of the H$_2$O band. The trend of the planetary intensity can be judged by comparing signal levels on either side of the 4970-cm$^{-1}$ CO$_2$ band and noting the lunar spectrum in the same region (figure 8).

The line center is apparently not completely absorbing, for Jupiter or Saturn. Since the spectral resolution element is much narrower than the line width, we can accurately determine the central intensity; this is approximately 0.5 per cent of the estimated continuum for Saturn, and 1 per cent for Jupiter. The uncertainty in these values arises primarily from determining the zero level. A worst-case assessment of errors would give both planets zero intensity in the line core, but that is unlikely to be true. The existence of planetary radiation at frequencies near 4650 cm$^{-1}$ provides powerful additional data for establishing the important core intensity and fitting the overall line shape with models.

We do not know the planetary line profile near 5100 cm$^{-1}$ because of telluric CO$_2$ and H$_2$O absorption. The H$_2$ line shape is further obscured by CH$_4$ absorption and, for Jupiter, NH$_3$. We can estimate the 5100-cm$^{-1}$ value of $I_y/I_{\text{continuum}}$, however, by making certain assumptions. The intensities of Saturn and Jupiter are large near 6300 cm$^{-1}$, where CH$_4$ absorption is minimal. The Jovian spectrum is depressed somewhat by NH$_3$ here, but Saturn
shows only telluric features for a region nearly 100 cm$^{-1}$ wide. If we assume that the planet continua at 5100 cm$^{-1}$ are at the same levels as at 6300 cm$^{-1}$, we may proceed. The 5100 cm$^{-1}$ continuum level will be in error to the extent that we are unable to account for broad, featureless absorption at the higher frequency. For example, there may be depression of the continuum due to absorption by NH$_3$ cloud particles, or by the wing of the H$_2$ band itself. Such effects would not be readily discernible in our spectra, since there is no other part of the spectra where the continuum level is as accessible. Signal levels are low in the higher-frequency windows, and the effects of changing interferometer alignment are more severe there also.

The similarity of the continuum levels at 6300 cm$^{-1}$ and in the 3300-cm$^{-1}$ region implies that NH$_3$ frost is not responsible for absorption at either frequency. We shall find also that it is unlikely H$_2$ contributes more than a few per cent absorption at 6300 cm$^{-1}$, because the line core at 4750 cm$^{-1}$ is not totally absorbing.

We calculate the 5100-cm$^{-1}$ continuum level by the formula:

$$I(5100) = I(6300) \frac{I_{moon}(5100)}{I_{moon}(6300)} \cdot \frac{R_{moon}(6300)}{R_{moon}(5100)}$$

[15]

where $R$ is reflectivity.
To account for the effects of CH₄ and NH₃ at 5100 cm⁻¹, we have used the methane spectra of Cruikshank and Binder (figure 15) and our own ammonia spectra (see section IIC). We estimate that there is no more than 10% reduction in the continuum intensity from CH₄ for Jupiter and Saturn. Absorption by NH₃ in the spaces between the evident manifolds of the 5050-cm⁻¹ band is no more than 11% for 25 cm-atm abundance; this value produces a good match to the overall appearance of the Jupiter NH₃ spectrum in this region. These estimates produce errors in the relative contribution of H₂ to the total 5100 cm⁻¹ opacity, but not in the calculation of the planetary values of Iᵥ/Iᶜ (5100). We shall derive upper and lower limits to this latter value, and retain them throughout the process of fitting planetary data to models.

The lower limit to the 5100 cm⁻¹ value of Iᵥ/Iᶜ is determined by drawing the lowest curve that can be smoothly extended from the 4900 cm⁻¹ region through the signal level at 5025 cm⁻¹ and yet fall above the peaks of intensity that occur in the H₂O band. In the lunar spectrum, we notice that there is a narrow window at 5300 cm⁻¹. In a spectrum of 0.5 cm⁻¹ resolution, the peak intensity is typically about 0.85 of the estimated continuum level at that frequency. This value will fluctuate with the telluric H₂O abundance, of course, but if we use the window in the planetary spectrum to get a lower limit on the planetary
continuum, we may use the upper limit on the window transmission: 100%. We also note from the lunar spectrum that in typical conditions the absorption by H$_2$O at 5025 cm$^{-1}$ is only roughly 5%, implying that the true planetary signal level is 105% of the measured level at that point. The lowest smooth curve drawn through the points derived at 5025 cm$^{-1}$ and at 5300 cm$^{-1}$ has a value of $I_\nu/I_c$ at 5100 cm$^{-1}$ equal to 0.45 for Saturn and 0.26 for Jupiter.

In order to obtain an upper limit to the 5100-cm$^{-1}$ value of $I_\nu/I_c$, we assume that the observed signal level at 5025 cm$^{-1}$ for Saturn is the result of depression by H$_2$, CH$_4$, and telluric H$_2$O. We allow for 5% depression by CH$_4$ and 5% by H$_2$O, and then double the contributions arbitrarily to give a pure-H$_2$ Saturn continuum level that is 123% of the apparent 5025 cm$^{-1}$ signal level. A smooth curve drawn from the 4900 cm$^{-1}$ region through the high point at 5025 cm$^{-1}$ gives us a working upper limit for the 5100 cm$^{-1}$ intensity. The derived value is $I_\nu/I_c = 0.63$ for Saturn. On Jupiter, we introduce a 6% effect from continuous NH$_3$ absorption at 5025 cm$^{-1}$ in addition to CH$_4$ and H$_2$O. Doubling the expected contribution, we derive a pure-H$_2$ continuum that is 139% of the measured level at 5025 cm$^{-1}$. Extending the line from 4900 cm$^{-1}$ through this point, we obtain an upper limit of 0.36 for the value of $I_\nu/I_c$ at 5100 cm$^{-1}$ for Jupiter.

Using the upper limits obtained, we may roughly
estimate the percentage of the planetary absorption due to \( \text{H}_2 \). For Saturn, invoking 10% \( \text{CH}_4 \) absorption, we conclude that there is between 30 and 49% absorption by \( \text{H}_2 \) at 5100 cm\(^{-1}\). For Jupiter, with 10% \( \text{CH}_4 \) absorption and 11% \( \text{NH}_3 \) absorption, the \( \text{H}_2 \) contribution is between 55% and 67%. Our conclusions depend, of course, on the assumption of a flat planetary continuum between 5100 and 6300 cm\(^{-1}\). However, we are probably fair in stating that the \( \text{H}_2 \) absorption on Jupiter is deeper and more extensive than that on Saturn. Whether this is due to greater abundance, higher temperature, or a combination of these effects, we are not yet certain. The reduced planetary values of the relative intensity \( I_y/I_c \) are given in Table 4.

At this point, we should comment on the earlier observations of this band in the literature. Danielson (1966) correctly eliminated the effect of methane absorption in his Stratoscope spectra; his data show the same trend in the 4500-5200 cm\(^{-1}\) region as do our spectra. However, his instrumental resolution element was of the same order as the \( \text{H}_2 \) line width, making line profile fitting inaccurate. Danielson assumed that the abundance-density product characterizing the Jovian atmosphere was 30 km-amagat\(^2\). He then matched a 248 K absorption profile to the observed spectrum. The assumption of an abundance parameter and consequent fitting to extract a temperature is a highly suspect procedure, in view of the much weaker temperature
<table>
<thead>
<tr>
<th>Frequency</th>
<th>Jupiter</th>
<th>Saturn</th>
</tr>
</thead>
<tbody>
<tr>
<td>4600 cm⁻¹</td>
<td>0.009</td>
<td>0.0</td>
</tr>
<tr>
<td>4625</td>
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<td></td>
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<tr>
<td>4700</td>
<td>0.0225</td>
<td></td>
</tr>
<tr>
<td>4725</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>4750</td>
<td>0.005</td>
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</tr>
<tr>
<td>4775</td>
<td>0.017</td>
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</tr>
<tr>
<td>4875</td>
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<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>4925</td>
<td>0.19/.193</td>
<td></td>
</tr>
<tr>
<td>4950</td>
<td>0.233/.243</td>
<td></td>
</tr>
<tr>
<td>4975</td>
<td>0.278/.306</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>0.319/.366</td>
<td></td>
</tr>
<tr>
<td>5025</td>
<td>0.355/.438</td>
<td></td>
</tr>
<tr>
<td>5050</td>
<td>0.391/.513</td>
<td></td>
</tr>
<tr>
<td>5075</td>
<td>0.424/.579</td>
<td></td>
</tr>
<tr>
<td>5100</td>
<td>≈.45/.63</td>
<td></td>
</tr>
</tbody>
</table>

Lower limit/Upper limit
dependence of the absorption coefficient relative to the
dependence on density. If a reasonable temperature had
been used as a starting point, it may have been possible
to derive a reflecting layer density and column abundance
from the Stratoscope data. Danielson's work has been
criticized previously by Cruikshank and Binder (1968),
who pointed out the inadequacy of such low-resolution
data in determining the shape of the Jupiter spectrum
near 1.5 \( \mu \)m (6670 cm\(^{-1}\)) and the resultant error in
assessing the importance of ammonia absorption.

We already mentioned the Jupiter and Saturn ob­
servations of Johnson (1970) and Fink and Larson (1971).
It is curious that no attempt was made to study the \( \mathrm{H}_2 \)
effects in these spectra, after the work of Danielson.
The necessary theoretical and laboratory work on the \( \mathrm{H}_2 \)
band was essentially complete in the late 1960's (Welsh
1969). We have taken absorption coefficients for pure,
normal (ortho/para ratio = 3:1) \( \mathrm{H}_2 \) from figures in several
papers from the molecular spectroscopy literature (Chisholm
and Welsh 1954, Hunt and Welsh 1964, Watanabe and Welsh

2. Reflecting-Layer Model (RLM)

Having the reduced planetary spectra at hand, to­
gether with absorption coefficients for \( \mathrm{H}_2 \), we can begin
to model the atmospheres and attempt to fit the observa-
tions. The logical initial choice, both in terms of parametric simplicity and relevance to previous studies, is the reflecting-layer model, in which a certain abundance of absorbing gas containing no scatterers overlies an abrupt diffusely scattering (Lambert) surface. Encrenaz and Owen (1973) have summarised the H$_2$ quadrupole observations of Saturn, all of which were interpreted with the RLM. De Bergh et al (1973) used this model to reduce observations of the Saturn methane $3\nu_3$ band. Trafton and Macy (1974) found a scattering model inadequate for reduction of the $3\nu_3$ band of Saturn, and the RLM preferable.

The Jupiter observations have led to rather different conclusions. The quadrupole lines exhibit variability in time and with position on the disk that are inconsistent with a RLM. The methane $3\nu_3$ band has been studied with both scattering and reflecting layer models. Bergstralh (1973) concluded that the RLM has but limited usefulness for the methane band analysis, and that complex scattering models are most promising.

In our model, the H$_2$ gas is characterized by a single density and temperature at the reflecting level, and some distribution of density and temperature with altitude. The reflecting surface has a certain reflectivity which determines the continuum albedo of the planet. Since the behavior of the line absorption is always speci-
fied by the ratio of intensity in the line to intensity in the continuum, the absolute value of the continuum intensity, determined by the reflectivity, is not of concern here.

The functional dependence of the $\text{H}_2$ absorption is given by equation [14]. It is fortunate that the density dependence, which is strong, is also well-defined, while the temperature dependence, complex in nature, is weak. Therefore, we need not be too precise in our specification of the model-atmosphere temperature. Because of the weak temperature dependence, we shall assume an isothermal atmosphere, with a temperature that is compatible with previous estimates of the cloud-level values. Errors introduced by this assumption will be discussed later.

Laboratory absorption coefficients are not available at all desired temperatures. There is, in particular, a gap between 95 K and 195 K. Absorption coefficients for the various temperatures are given in Table 5 and plotted in figure 16. The variation with temperature is not well-behaved; there are unknown measurement and drafting errors that may appear in the data, which were read from published graphs. The 95 K curve (Chisholm and Welsh 1954) has an exceptionally weak wing and core, compared to the 77 K data, distilled from two sources. Rather than attempt to interpolate between the published curves, we have instead generated coefficients for 130 and 150 K, using the ap-
Table 5

Absorption Coefficients for Normal H₂

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>20K (calc.)</th>
<th>77K</th>
<th>95K</th>
<th>130K</th>
<th>150K (calc.)</th>
<th>195K</th>
<th>248K</th>
<th>300K</th>
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<tr>
<td>4600</td>
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<td>0.20</td>
<td>0.314</td>
<td>0.345</td>
<td>0.359</td>
<td>0.368</td>
<td>0.443</td>
<td>0.435</td>
</tr>
<tr>
<td>4625</td>
<td>0.17</td>
<td>0.185</td>
<td>0.27</td>
<td>0.325</td>
<td>0.346</td>
<td>0.389</td>
<td>0.44</td>
<td>0.43</td>
</tr>
<tr>
<td>4650</td>
<td>0.135</td>
<td>0.215</td>
<td>0.262</td>
<td>0.348</td>
<td>0.372</td>
<td>0.43</td>
<td>0.477</td>
<td>0.45</td>
</tr>
<tr>
<td>4675</td>
<td>0.14</td>
<td>0.30</td>
<td>0.29</td>
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<td>0.44</td>
<td>0.519</td>
<td>0.49</td>
<td>0.485</td>
</tr>
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<td>4700</td>
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<td>0.478</td>
<td>0.352</td>
<td>0.544</td>
<td>0.545</td>
<td>0.582</td>
<td>0.518</td>
<td>0.53</td>
</tr>
<tr>
<td>4725</td>
<td>1.00</td>
<td>0.61</td>
<td>0.415</td>
<td>0.634</td>
<td>0.618</td>
<td>0.608</td>
<td>0.525</td>
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<td>0.513</td>
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<tr>
<td>4800</td>
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<td>0.15</td>
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<td>0.112</td>
<td>0.176</td>
<td>0.188</td>
<td>0.21</td>
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<td>0.085</td>
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<td>0.158</td>
<td>0.219</td>
<td>0.235</td>
</tr>
<tr>
<td>4975</td>
<td>0.065</td>
<td>0.056</td>
<td>0.043</td>
<td>0.109</td>
<td>0.118</td>
<td>0.138</td>
<td>0.198</td>
<td>0.21</td>
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<tr>
<td>5000</td>
<td>0.055</td>
<td>0.047</td>
<td>0.031</td>
<td>0.095</td>
<td>0.103</td>
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<td>0.18</td>
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</tr>
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<td>0.023</td>
<td>0.084</td>
<td>0.091</td>
<td>0.104</td>
<td>0.162</td>
<td>0.17</td>
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<td>0.089</td>
<td>0.144</td>
<td>0.152</td>
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<td>0.053</td>
<td>0.03</td>
<td>0.011</td>
<td>0.067</td>
<td>0.073</td>
<td>0.077</td>
<td>0.127</td>
<td>0.14</td>
</tr>
<tr>
<td>5100</td>
<td>0.06</td>
<td>0.026</td>
<td>0.006</td>
<td>0.061</td>
<td>0.067</td>
<td>0.066</td>
<td>0.112</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Units: amagat⁻² x 10⁻⁹
Fig. 16. Absorption coefficients for normal H₂ at various indicated temperatures (from Table 5).
The coefficients in the range 4600-5100 cm\(^{-1}\) are taken to be the summation of contributions from five lines: the \(S_1(1), S_0(1), Q_1(1)\), and the double transitions \(S_0(1) + Q_1(J), S_0(0) + Q_1(J)\). Here \(S\) implies \(\Delta J = +2\), \(Q:\Delta J = 0\), where \(J\) is the rotational quantum number. The subscript is the change in vibrational quantum number, and the term in parentheses is the original value of \(J\) for the molecule undergoing the transition. In double transitions each molecule of the colliding pair undergoes a transition simultaneously, with the absorption of a single photon. Each double-transition line is the sum of contributions for \(J = 0\) and \(J = 1\). All the lines of interest except \(Q_1(1)\) arise from quadrupolar interactions that may occur over a wide range of inter-molecular distances. The line shapes for such interactions are identical. The \(Q_1(1)\) line results from electron overlap forces that decrease exponentially with molecular separation; the line is wider than the quadrupolar lines, since the effective duration of the overlap-force interaction is shorter, but the high-frequency wing shape is the same far from the line center, where the \(S(1)\) lines occur (Chisholm and Welsh 1954).

In the region of interest, the line shapes of each of the components may be expressed by:

\[
\alpha_\nu = \frac{\alpha_0}{(\nu - \nu_0)^2/\delta^2 + 1} \quad \nu \geq \nu_0
\]
where $\alpha_o$ is the absorption coefficient at the line center $v_o$, and $\delta$ is a line-width parameter, equal to the distance between $v_o$ and the frequency where $\alpha_v = 1/2 \alpha_o$ in the high-frequency wing. This width is the same for all of the lines under consideration except $Q_1(1)$. The width varies directly as the square root of temperature, although for the $Q$ line the low-temperature dependence changes slope (Watanabe and Welsh 1967). We have summed the contributions to the total absorption coefficient, using values of $\alpha_o$ given by Hunt and Welsh (1964), and also their line-widths and ratios for the relative strengths of the double transitions. Their data was obtained at 77 and 195 K; we have interpolated the fairly well-behaved line parameters to acquire values appropriate to 130 and 150 K. The lower temperature is compatible with measurements of Saturn in the methane $3\nu_3$ band, and the higher temperature is an often-quoted value appropriate to the top of the Jovian ammonia cloud deck. The adequacy of the calculation was tested by comparing absorption coefficients derived at 77 K and 195 K with the measurements
of Hunt and Welsh; there are discrepancies in the region below the frequency of the line center. However, most of the fitting process between models and planetary spectra occurs where the best signal-to-noise ratio obtains: 4800-5000 cm$^{-1}$. Here the agreement with published spectra was good, and generated confidence in the worth of the intermediate-temperature calculations. Figure 16 shows the results for 150 K together with data obtained from the literature.

The calculations we have performed could be done more accurately with the information available to workers in that field, who have left details of interest here out of their publications. The refinement of absorption coefficient calculations is one of several aspects of the planetary H$_2$ investigations that can be profitably pursued in the near future.

The strong density dependence of the relative intensity shown in equation [14] makes the isothermal atmosphere a more reasonable assumption, since the lower atmosphere layers are weighted more heavily than in other modes of line formation. The Saturn models of Weidenschilling and Lewis (1973) and Palluconi (1972) both indicate a temperature drop of about 45 K in one scale height above the NH$_3$ cloud region. Qualitatively, we see that the relaxation of the isothermal assumption will lead to the inclusion of lower-temperature absorption coefficients
in the summation of the contributions from differing density layers. The resulting line profile will resemble that of an isothermal atmosphere slightly cooler than the one we are using here.

The variation of density with altitude is an important feature of any RLM. In conformity with the isothermal assumption, we investigate the use of an exponential decline:

\[ \rho(h) = \rho_0 \exp(-h/H) \quad [16] \]

where \( \rho_0 \) is the density at the base level, \( h \) is altitude above the base, and \( H \) is the scale height, equal to

\[ H = kT/\mu g \]

Here \( k \) is Boltzmann's constant, \( T \) temperature, \( \mu \) the molecular weight, and \( g \) the gravitational acceleration.

Let us consider the relative intensity in the vicinity of an \( H_2 \) pressure-induced line produced by two successive vertical traversals of the model atmosphere in question. If we characterize the atmosphere as a collection of parallel layers, each having thickness \( l \) and density \( \rho_i \), then the resulting intensity is

\[ \frac{I_v}{I_c} = \prod_i \exp(-2\nu \alpha \rho_i \frac{l}{2}) \]

\[ = \exp(-2\nu \alpha \sum_i \rho_i^2 l) \quad [17] \]

using equation [14]. Going now to the case of infinitely
many layers, we get
\[ \sum_{i} \rho_{i}^{2} l \rightarrow \int_{0}^{\infty} \rho_{0}^{2}(l) \, dl \]
\[ = \int_{0}^{\infty} \rho_{0}^{2} \exp(-2h/H) \, dh \]
\[ = \frac{1}{2} H \rho_{0}^{2} \quad \text{so that} \]
\[ \frac{I_{\nu}}{I_{C}} = \exp \left( -\nu \propto_{\nu} H \rho_{0}^{2} \right) \quad \text{[18]} \]

Thus, the relative intensity in a double vertical path through an isothermal atmosphere of pure H$_2$, in which the density obeys an exponential decay with altitude, is identical to that in a cell with uniform density $\rho_{0}$ and length $H$. If the emerging radiation has traversed an airmass exceeding that for normal traversal by a factor $\eta$, then $H$ is to be multiplied by $\eta$ in equation [18]. From [18] and a knowledge of the observing geometry, we may create model line profiles carrying the parametric quantity $H \rho_{0}^{2}$. Having found a fit to the planetary data, we may assume an $H$ and extract $\rho_{0}$, or vice-versa. The H$_2$ abundance for the exponential model is also obtained and equals $\rho_{0} H$.

A more realistic assumption than the isothermal model is the adiabatic decline:
\[ T = T_o - \Gamma h \] where

\[ \Gamma = \frac{3 \nu}{k} \left( \frac{\gamma - 1}{\gamma} \right) \]

and

\[ \gamma = \frac{C_P}{C_V} = \frac{\text{specific heat at constant pressure}}{\text{specific heat at constant volume}}. \]

Here \( T_o \) is the temperature at the base level. This model is only valid over a certain altitude range, since \( T \) goes to zero. We shall retain the isothermal description for calculation of absorption coefficients, but allow the density-versus-altitude relation to be modified by the adiabatic assumption. The density is now given by

\[ \rho(h) = \rho_0 \left( 1 - \frac{\Gamma h}{T_o} \right)^{-\frac{1}{\gamma - 1}} , \quad h < \frac{T_o}{\Gamma} \quad [19] \]

(see Moroz 1967, p. 69). If we incorporate this expression into [17], the resulting relative intensity for the vertical double traversal is:

\[ \frac{I_v}{I_C} = \exp \left( -\gamma \alpha_v \rho_0^2 \frac{T_o}{3\Gamma} \right). \]

This has the same dependence as [18], but with \( H \) now replaced by \( T_o/3\Gamma \). Clearly, the density dependence of the line profile has not been changed by using the adiabatic law. Either model, exponential or adiabatic, involves the assumption of a temperature and the parameters \( g \) and \( \nu \).

\( \gamma \) is not a strong function of composition and may be taken equal to 1.4, the value appropriate to \( H_2 \). If the same \( T \),
\( \rho \) are assumed in both models, the values of \( H \) and \( T_o/3T \) differ by only 17\%, which difference has about a 7\% effect on the then-derived value of \( \rho_o \). In the following work, we shall consider the exponential model unless stated otherwise.

Our observations of Jupiter were made with the interferometer's 18 arc-sec diameter aperture centered on the planet disk. The largest included value of the single-traversal airmass was 1.11. Consequently, we use simple vertical-path calculations for comparison with the Jovian data.

The entire disk of Saturn was observed (excepting the fraction obscured by the ring); therefore, we must compute line profiles which take into account the contributions to the relative intensity from all parts of the disk. Since Saturn was near opposition, we have assumed that the direction cosines \( \mu \) and \( \rho_o \) for impinging and emerging rays are the same. Then equation [18] is used with \( H \) replaced by \( H/\rho \).

The disk-averaged intensity is given by

\[
\left( \frac{I_v}{I_c} \right)_{\text{disk}} = \frac{\int_0^1 \left( \frac{I_v}{I_c} \right) 2\pi n \, dn}{\int_0^1 2\pi n \, dn}
\]
where \( C = \gamma \alpha \rho_o^2 \). The radial integration variable has been defined so that \( \rho = \sqrt{1 - n^2} \).

A computer program was written to calculate the relative intensity given by equations [18] and [20]. The input to the program consisted of sets of absorption coefficients for various temperatures. Plots of the relative intensity were generated, separately for Saturn and Jupiter, with varying values of the quantity \( \rho_o^2 \). We will discuss the fitting of the planetary data to the RLM in the next section, following a discussion of scattering models.

3. Homogeneous Scattering Model (HSM)

Although the RLM has been found useful for many studies of line absorption in the Jovian and Saturnian atmospheres, there is clearly some scattering occurring in both, because cloud layers are not abrupt and unbroken boundaries. Extensive studies of the center-to-limb variation of the equivalent width of the 6190-A \( \text{CH}_4 \) band (Teifel 1969) are not compatible with the RLM, and imply for Saturn and Jupiter the existence of a tenuous haze with a volume scattering coefficient near \( 10^{-7} \text{ cm}^{-1} \).
red wavelengths, absorption line formation apparently requires consideration of scattering effects. Near 2 \( \mu m \) it may not be the same situation at all; however the center-to-limb variations of the CH\(_4\) \( 3\nu_3 \) band were found also to behave in accordance with scattering models (Bergstralh 1973) and if the scattering at 0.619 \( \mu m \) is pure Rayleigh scattering, the effects should be 9.8 times weaker at 1.1 \( \mu m \). In the interest of completeness in this study of the H\(_2\) \( S(1) \) line, we therefore consider how the line profile would appear if formed in a scattering atmosphere.

Chamberlain (1970), following the work of Chandrasekhar (1950), van de Hulst (1952) and others, has provided a convenient introduction to the behavior of absorption lines in hazy planetary atmospheres. We shall employ his assumptions: the atmosphere is semi-infinite, isotropic scattering occurs with no redistribution of the frequency of the photons, and the single-scattering albedos are independent of depth. In such a case, the relative intensity in the line is

\[
\frac{I_\nu}{I_c} = \frac{\omega_\nu}{\omega_c} \frac{H(\omega_\nu, \rho) H(\omega_\nu, \rho_o)}{H(\omega_c, \rho) H(\omega_c, \rho_o)} \tag{21}
\]

where the single-scattering albedo is \( \omega_c \) in the continuum and \( \omega_\nu \) at frequency \( \nu \) in the line, \( \rho \) and \( \rho_o \) are the direction cosines for rays entering and leaving the atmosphere, and \( H(\omega, \rho) \) are the Chandrasekhar (1950) H-
functions for isotropic scattering. Since Jupiter and Saturn were both near opposition during our observations, we shall assume \( \rho = \rho_0 \). Also, we shall employ the convenient van de Hulst (1952) approximation to the H-functions:

\[
H(\tau, \rho) = \frac{H(1, \rho)}{1 + \rho \sqrt{3(1 - \tau)}}
\]

which is accurate to within 6% over the entire range of \( \rho \) and \( \tau \). Errors will tend to cancel here, since we are dividing the H-functions. We now have

\[
\frac{I_\nu}{I_c} = \frac{\tau_\nu}{\tau_c} \left( \frac{1 + \rho \sqrt{3(1 - \tau_c)}}{1 + \rho \sqrt{3(1 - \tau_\nu)}} \right)^2 \tag{22}
\]

and we note that the function \( H(1, \rho) \) has conveniently dropped out. Expression [22] will be used in the preparation of model line profiles for different values of \( \rho \), and will also be integrated over the disk to provide models for the Saturn data comparison.

For a given temperature and density, we have a set of values of \( \alpha_\nu \) (the absorption coefficients in amagat\(^{-2}\) units are converted to cm\(^{-1}\) units by multiplying by \( \nu \rho^2 \)). We select a value for the volume scattering coefficient \( \sigma \), also in cm\(^{-1}\) units, and the continuum single-scattering albedo \( \omega_c \). From Chamberlain (1970), we have:
\[ \sigma_v = \frac{\sigma}{\alpha_v + \kappa + \sigma} \]

where \( \kappa \) is the continuous absorption coefficient. Then

\[ \sigma_v^{-1} = \frac{\alpha_v}{\sigma} + \frac{\kappa + \sigma}{\sigma} = \frac{\alpha_v}{\sigma} + \frac{1}{\sigma_c}. \quad [23] \]

A computer program calculates \( \sigma_v \) from [23] and then \( I_v/I_c \) from [22]. For Jupiter, \( \nu = 1 \) is used, and a family of plots is generated in which one or more of the variables \( \rho, T, \sigma, \) and \( \sigma_c \) is changed.

For Saturn, we need to sum the contributions to the quantity \( I_v/I_c \) from all parts of the disk. We compute the area-weighted integral of [22]:

\[ (I_v/I_c)_{\text{disk}} = 2 \frac{\sigma_v}{\sigma_c} \int_0^1 \left( \frac{1 + \rho \sqrt{1 - \eta^2}}{1 + Q \sqrt{1 - \eta^2}} \right)^2 \eta \, d\eta \]

where \( \rho = \sqrt{3(1 - \sigma_c)}; \quad Q = \sqrt{3(1 - \sigma_v)}. \)

The final result is:

\[ (I_v/I_c)_{\text{disk}} = 2 \frac{\sigma_v}{\sigma_c} \left[ \frac{1}{Q^2} \left( \ln (1 + Q) - \frac{Q}{1 + Q} \right) + \frac{2\rho}{Q^3} \left( -2 \ln (1 + Q) + Q + \frac{Q}{1 + Q} \right) + \frac{\rho^2}{Q^4} \left( 3 \ln (1 + Q) + \frac{Q^2}{2} - 2Q - \frac{Q}{1 + Q} \right) \right] \quad [24] \]
This expression was calculated for various values of $\rho$, $T$, $\sigma$, and $\omega_c$.

We now present a sample of the computer-generated line profiles to demonstrate the behavior of the RLM and HSM. In each figure, we introduce the reduced planetary data as a dotted line; only disk-integrated profiles will appear with the Saturn data, and only center-of-disk profiles with the Jupiter spectrum.

In figure 17 is shown the temperature dependence of the RLM profiles for Saturn. Curves are plotted for 77 K, 150 K (coefficients calculated), and 248 K, for the parametric value $13.2 \text{ km-agt}^2 = \rho^2 \omega H$. This value gives the best fit to the Saturn data at 150 K. The general strengthening of the line wings with temperature is evident.

Figure 18 presents the 150 K disk RLM profile for densities $\rho_o = 0.4$, 0.5, 0.6, and 0.7 amagat, assuming a constant $H = 50 \text{ km}$ (appropriate for Saturn). Here we see the extremely rapid change of relative intensity with density that is valuable in attempting to determine $\rho_o$. For the Saturn spectrum as drawn and the 150 K absorption coefficients, it is clear that the acceptable range of densities is small indeed.

The Jupiter spectrum is presented in figure 19 together with RLM center-of-disk profiles for 150 K, 195 K, and 248 K. With the derived relative intensity
Fig. 17. Reflecting-layer model $H_2$ S(1) line profiles for $\nu_2^2H = 13.2$ km-sec$^{-2}$ and indicated temperatures. The planetary profile is shown as the dashed line.
Fig. 18. Reflecting-layer model line profiles for 150K, H = 50km, and indicated densities in amagats.
Fig. 19. Reflecting-layer model line profiles for $j_{o^2}^H = 18.2$ km-agt$^2$ and indicated temperatures.
at 5100 cm\(^{-1}\) as low as it is for the data, clearly the lower-temperature profiles do not fit well. This problem will be discussed in the next section.

In figure 20 is shown the behavior of HSM profiles as certain parameters are changed. The upper portion shows the disk-integrated profile for 77 K, for a density of 1 amagat, volume scattering coefficient \(\sigma = 10^{-7} \text{ cm}^{-1}\), and varying \(\omega_c\) as follows: 1, 0.95, 0.80, 0.50. In the lower part of the figure the value of \(\omega_c\) is fixed at 1.0, while the scattering coefficient assumes the values \(\sigma = 5 \times 10^{-6}, 5 \times 10^{-7}, \text{ and } 5 \times 10^{-8}\). For all frequencies, the relative intensity increases with \(\sigma\) and decreases with \(\omega_c\). The effect of changing the density \(\rho\) amounts to multiplying all values of \(\alpha_\nu\) by a constant; this is equivalent to dividing \(\sigma\) by the same constant (see equation [23]). Changes in \(\sigma\) or \(\rho\) affect the line profile much as changes in density affect the RLM profiles. We note that it is not possible to "hold" the core value of \(I_\nu/I_c\) and adjust parameters so that the wing has an arbitrary slope. Thus the temperature of the model, which governs line width, is still important in determining the ability of the HSM to fit planetary data.

The center-to-limb variation of the \(S(1)\) line is presented for both the RLM and HSM in figure 21, although we have acquired no information about the actual variation for Saturn or Jupiter. It may be seen, as expected, that
Fig. 20. Behavior of homogeneous-scattering model line profiles for 77K, $\rho = 1$ agt. Upper: $\sigma = 5 \times 10^{-7}$ cm$^{-1}$, various single-scattering albedos indicated. Lower: $\sigma_z = 1$, various scattering coefficients.
Center-to-limb variation in the RLM and HSM at 150K. Upper: reflecting-layer model, direction cosine $p$ indicated. Lower: homogeneous scattering model, $\sigma = 5 \times 10^{-7} \text{cm}^{-1}, \alpha = 1, \rho = 1 \text{ agt.}$
in the RLM the line becomes stronger near the limb, since the radiation passes through more hydrogen in being reflected at the boundary level. The HSM produces a weaker line near the limb, since photons entering the atmosphere at large angles from the normal will penetrate less deeply before being scattered; such photons will have a greater chance of leaving the atmosphere after the first scattering. Less gas will lie in the total scattered path of such photons, and consequently absorption will be weaker. The HSM employed here involves an isotropic particle scattering function. More realistic forward scattering phase functions produce an even stronger decrease in line strength toward the limb. Because of the opposing behavior of the RLM and HSM, the center-to-limb variation is very deterministic. Because of the great natural width of the line, the effects should be easily discernible. The importance of observing the actual behavior of the lines in planetary spectra cannot be over-emphasized.

The next two figures plot the results of comparisons between the HSM line profiles and the Jupiter and Saturn spectra. In figure 22, curves for 77 and 130 K and density 1 amagat are shown. These temperatures bracket the expected range of Saturn temperatures above the cloud level. Scattering coefficients were chosen to give a reasonably good overall fit to the planetary profile,
Fig. 22. Homogeneous scattering model line profiles (disk-integrated) for $\theta = 1 \text{ agt}$, $\kappa = 1$.

77K: $\sigma = 2 \times 10^{-7}\text{ cm}^{-1}$. 130K: $\sigma = 2 \times 10^{-8}\text{ cm}^{-1}$. 
although the choice is obviously somewhat arbitrary here. Continuum scattering albedos of 1.0 were used to allow the maximum benefit to be taken from the plotted curves of figure 20 (all lower- curves fall above the one for \( \sigma_c = 1.0 \)).

Figure 23 shows the Jupiter profile and the HSM curves for 77 K and 130 K again. The scattering coefficients are the same as in the previous figure, but now the albedos are less than 1.0 because there is a real chance of fitting the Jupiter curve at 77 K, and the 130 K curve is much more appropriate in shape than it was for Saturn.

C. Discussion

1. Saturn

The RLM appears to give the best fit to the Saturn \( \text{H}_2 \) line profile. In figures 17 and 18, we see that the not-unreasonable temperature of 150 K gives a good match to the data for the parameter \( p_o \text{H}^2 = 13.2 \text{ km-agt}^2 \). The curve for 195 K provides an even better fit, but for nearly the same value, 12.1 km-agt\(^2\). There are several possible origins for the fact that higher-temperature curves give a better fit than the profiles for the expected values (95 - 130 K). First, the region of line formation may be deeper in the atmosphere than the level of the uppermost cloud top. The Saturn model of Weiden­schilling and Lewis indicates that a cloud of \( \text{NH}_4\text{SH} \) lies
Fig. 23. Homogeneous scattering model line profiles (center of disk) for $J = 1.77K$: $\sigma = 2 \times 10^{-7} \text{ cm}^{-1}$, $\alpha_0 = 0.94$. $130K$: $\sigma = 5 \times 10^{-8} \text{ cm}^{-1}$, $\alpha_0 = 0.5$. 
near temperatures of 200 K. If the upper cloud (presumably NH₃) is optically thin at 5000 cm⁻¹, the S(1) line may well be formed in layers at temperatures above 150 K. The strong density dependence of the absorption will ensure that the deeper, hotter layers predominate in the line formation. However, the cloud model also indicates densities near 8 amagats at the NH₄SH level; such densities would produce, in the RLM, heavy absorption in the line core and much less intensity in the wings than we find. As we shall see, the observations imply densities less than 1 amagat for virtually any assumed temperature. It is the lack of total absorption in the core that prevents us from fitting the observations with high-density models, if the RLM is accepted.

Another means of explaining the high-temperature curves' matching the data is an error in the continuum level assumed at 5100 cm⁻¹. If the continuum were lower, the values of \( I_\nu/I_C \) would be higher, the line would have a more narrow shape, and would be fit by lower-temperature models. Such a lowering of the continuum could arise if there were a broad absorption near 5000 cm⁻¹ that does not also occur at 6300 cm⁻¹, where the continuum is derived. Candidates for such an absorption are NH₃ frost and NH₄SH in suspended solid form. The former has a band at 5000 cm⁻¹ that is the analog of the gas absorption seen on Jupiter near 5050 cm⁻¹. However, the frost also has a
much stronger absorption at 3300 cm\(^{-1}\), as we mentioned in section II F, absent in the Saturn spectrum. \(\text{NH}_4\text{SH}\) is characterized by an absorption much like the \(\text{H}_2\) absorption itself, becoming weaker from 4500 to 5000 cm\(^{-1}\) (Kieffer and Smythe 1973). Again, however, there is a strong absorption near 3300 cm\(^{-1}\) which would be evident. Possibly, other compounds or elements (sulfur?) are spectroscopically active. Certainly the visible coloring agent of the Saturn clouds has not been identified. It is not unreasonable to suppose that the continuum intensity changes by perhaps 10% between 6300 and 5100 cm\(^{-1}\); this is the preferred means of explaining our inability to fit the Saturn data with temperatures in the 95 - 130 K range. We have chosen, however, to retain the neutral assumption that the continua are of the same intensity; the magnitude of errors induced in the density and abundance is still small. Adoption of the deep-cloud explanation given in the previous paragraph necessitates some distrust in the RLM, since at small values of the upper cloud must become important.

If the parameter \(\rho_0^2\text{H} \equiv X\) is adopted from the fitting of the 150 K curves to the planetary spectrum, we may derive \(\rho_0\) and the \(\text{H}_2\) abundance \(W \equiv \rho_0\text{H}\) as follows:

\[
\rho_0 = \sqrt{\frac{X}{\text{H}}} \quad ; \quad W = \sqrt{X \text{H}}
\]

[25]
The scale height $H = kT/\rho g$ is first calculated. We adopt $g = 1000 \text{ cm sec}^{-2}$, $\rho = 2.25 \text{ amu}$ (following Weidenschilling and Lewis for a solar-composition atmosphere), and $T = 130 \text{ K}$. Then $H = 48 \text{ km}$, and with $X = 13.2 \text{ km-agt}^2$, we have

$$f_0 = 0.52 \text{ amagat}, \quad W = 25.2 \text{ km-agt}.$$  

It may be readily seen that errors in both $X$ and $H$ are reduced by the square-root dependence of $f_0$ and $W$. A complete assessment of errors will follow a discussion of the HSM line profiles for the Saturn $S(1)$ line.

It is clear in figure 22 that neither the 77 K nor 130 K HSM profiles can be adjusted to fit the basically narrow Saturn line. If a 5100-\text{cm}^{-1} continuum correction is introduced in the opposite sense from that necessary for the RLM, the line will appear broader, and a better fit will ensue. However, the core will also become less intense, and it is difficult to get a strongly absorbing core in the HSM without very low-intensity wings as well. Moreover, depression of the 6300-\text{cm}^{-1} region without concomitant absorption at 5000 cm$^{-1}$ seems unlikely, considering the behavior of the materials mentioned above.

If there is no continuum variation, the HSM may be accepted only if absorption occurs in regions below 77 K. In Palluconi's model (1972), there are no such regions at reasonable pressures; the atmospheric minimum
is 77 K. The coexistence of low temperatures and high enough pressure to create appreciable absorption is unlikely.

The cores of HSM profiles tend, as was mentioned, not to become strongly absorbing. In this regard, it is worthwhile considering that the Saturn whole-disk observations may result from the superposition of a deeply absorbing profile, at values of $p$ near 1.0, with a more intense line profile originating in a higher scattering haze layer seen near the limb. The RLM profiles might then indeed give a fit for small densities and abundances, since most of the intensity would arise from scattering layers high in the atmosphere. The HSM profiles would be too flat, because the center-of-disk contribution would tend to elevate the line wings. Such a hybrid model may have great worth (Danielson and Tomasko 1969), but would be prematurely applied here, since we know nothing of the center-to-limb variations, and the RLM is nearly satisfactory up to this point.

The errors in the values of $\rho_0$ and $W$, determined from the 150 K RLM profile fit to the Saturn data, may be best judged by letting all the errors fall in such a way as to maximize or minimize the derived quantities. These errors are noted in Table 6, and represent uncertainties in three processes: obtaining absorption coefficients, building model atmospheres, and reducing planetary spectra.
### Table 6
Sources of Error

<table>
<thead>
<tr>
<th>Size or Nature of Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Absorption coefficients</td>
</tr>
<tr>
<td>1. Errors in laboratory measurements</td>
</tr>
<tr>
<td>2. Drafting errors in published curves</td>
</tr>
<tr>
<td>3. Errors in reading published curves</td>
</tr>
<tr>
<td>4. Errors in calculating $\alpha_v$ for intermediate temperatures</td>
</tr>
<tr>
<td>B. Models (RLM)</td>
</tr>
<tr>
<td>1. Effect of including enhancement by 20% He</td>
</tr>
<tr>
<td>2. Effect of reducing ortho/para ratio from 3.0 to 2.47 (equilibrium at 145K)</td>
</tr>
<tr>
<td>3. Effect of dropping isothermal assumption</td>
</tr>
<tr>
<td>4. Effect of using adiabatic $T(h)$</td>
</tr>
<tr>
<td>5. Errors in scale height (primarily due to $T$)</td>
</tr>
<tr>
<td>C. Data reduction</td>
</tr>
<tr>
<td>1. Errors in drawing line profile through noise</td>
</tr>
<tr>
<td>Sources of Error</td>
</tr>
<tr>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>C. Data reduction (continued)</td>
</tr>
<tr>
<td>2. Errors in drawing zero level</td>
</tr>
<tr>
<td>3. Error in estimating Saturn ring</td>
</tr>
<tr>
<td>contribution</td>
</tr>
<tr>
<td>4. Estimation of 5100 cm(^{-1}) continuum level</td>
</tr>
<tr>
<td>a. Variation of apparent lunar continua</td>
</tr>
<tr>
<td>b. Error in drawing lunar continuum</td>
</tr>
<tr>
<td>c. Errors in assessing lunar reflectivity</td>
</tr>
<tr>
<td>ratio due to ignorance of portion viewed</td>
</tr>
<tr>
<td>d. Variation of apparent planet continua (Due to</td>
</tr>
<tr>
<td>mis-registration of co-added interferograms)</td>
</tr>
<tr>
<td>e. Error in drawing planet 6300 cm(^{-1})</td>
</tr>
<tr>
<td>continuum</td>
</tr>
<tr>
<td>f. Variation of interferometer alignment</td>
</tr>
<tr>
<td>(not independent of a., d.)</td>
</tr>
<tr>
<td>5. Error in assessing amplitude of planet intensity</td>
</tr>
<tr>
<td>at 5100 cm(^{-1})</td>
</tr>
</tbody>
</table>
We cannot, of course, assess errors arising from the invalidity of the RLM or the assumption of a flat continuum between 5100 and 6300 cm\(^{-1}\). To derive an upper limit on the value of \( \rho_0 \), we let the absorption coefficients be as small as possible within measurement and calculating errors, and contrive to make \( I_\nu/I_0 \) as small as possible. New line profile families are plotted with the altered coefficients, and a best fit is obtained to the strongly-absorbing worst-case planet data. We get a value of \( X = 22.5 \text{ km-agt}^2 \), yielding, with \( H = 37 \text{ km} \) (for \( T = 100 \text{ K} \)), \( \rho_0 \) (max) = 0.78 agt. The corresponding value of \( W \) is obtained by using the maximum value \( H = 55 \text{ km} \): \( W \) (max) = 35.2 km-agt. To derive a lower limit on \( \rho_0 \) and \( W \), the absorption coefficients are modified by including the maximum errors so as to increase the \( \alpha_\nu \). Curves for different \( X \) are then generated, and a fit is made to the planetary profile having the highest possible values of \( I_\nu/I_0 \). The result is a matching for \( X = 8.1 \text{ km-agt}^2 \), yielding, with \( H = 55 \text{ km} \) (150 K), \( \rho_0 \) (min) = 0.38 agt and \( W \) (min) = 17.2 km-agt, using \( H = 37 \text{ km} \). Inclusion of the effects of the adiabatic model decreases \( \rho_0 \) and \( W \) by 8% to give 0.35 agt and 15.9 km-agt. The derived Saturn abundance and density are now finally stated, with maximum assessable uncertainties:

Base-level density: \( \rho_0 = 0.52 \pm 0.26 \) amagat \(- 0.17 \)
H₂ abundance above reflecting layer: \( W = 25.2 \pm 10 \text{ km-amagat} \)

This value of density contrasts sharply with that in the nominal Saturn model of Weidenschilling and Lewis; their NH₃ cloud deck occurs between 4 and 5 amagats. It is unlikely that a departure from the solar N : H ratio could produce a great change in the level of the top of the NH₃ cloud, unless (for example) S:N > 1, in which case the N would be trapped as NH₄SH. More likely, a change is required in the choice of initial pressure for their cloud model. Weidenschilling and Lewis assumed \( P = 60 \text{ bars at 400 K} \). If this pressure is reduced by a factor of 8, to 7.5 bars, then the NH₃ cloud top is at roughly 0.25 bar, or density about 0.5 amagat. There do not appear to be serious problems with this alteration; the vertical extent of the clouds is reduced (as they mention) because condensation will occur at lower temperatures. The maximum cloud density will be reduced, along with the cloud optical depth. The apparent cloud top will, however, remain at the same temperature level as long as it is optically thick.

Encrenaz and Owen (1973) estimated the RLM base-level pressure using the width of a CH₄ line at 6819 Å. They derived a pressure \( P_0 = 1.26 \text{ atm} \) assuming a temperature of 80 K. This corresponds to a density of
4.3 amagat. If the temperature is taken to be 150 K, the density is reduced only to 3.1 amagat. Their pressure is an upper limit; the methane line may not be a singlet, and there may be some guiding-induced Doppler smearing of the line. However, there is apparently disagreement with our derived density. The latest estimate of the base pressure from 3 $\nu_3$ band measurements (de Bergh et al. 1974) is also high: 2.8 ± 0.6 atm. However, that group's work on the $H_2$ 2-0 band near 8700 cm$^{-1}$ resulted in a maximum partial pressure for $H_2$ of 0.6 ± 0.3 atm for Saturn, which gives a density 1.1 amagat for 150 K. That is only a factor of 2 greater than our result. They mention that scattering effects are probably responsible for the discrepancies between $H_2$ and CH$_4$ results, even though the 2-0 band is at virtually the same wavelength as the 3 $\nu_3$ band.

Until scattering effects can be shown to be important at 5000 cm$^{-1}$, which may occur after center-to-limb studies are done, we are inclined to accept the RLM for the 1-0 $H_2$ band analysis. The low density and abundance are to be expected if scattering effects are less strong at the lower frequencies. Possibly all higher-frequency results should hereafter be considered only in a scattering context, and the 1-0 band results considered as a closer approximation to the true above-cloud values. Certainly the $S(1)$ line is much better suited to the determination of density than are lines formed by collisional broadening.
The $H_2$ abundance we have derived, 25 km-amagat, is also in conflict with previously determined values, as we might expect, since $W = \rho_0 H$. In particular, the quadrupole lines in the visible region give, with the RLM, $76 \pm 20$ km-amagat (Encrenaz and Owen 1973). The upper limit obtained from the 2-0 band was $63 \pm 23$ km-amagat (de Bergh et al., 1974). The same arguments regarding scattering apply as in density determinations. It is entirely possible to get such discrepancies if photons at one wavelength encounter much more gas in their traversal of the atmosphere than photons of a longer wavelength. Where the volume scattering coefficient is low (large mean free path), a large part of the total path of a photon may be in the cloud, and absorptions will indicate high abundance. If $\sigma$ is high, and it may be, near 5000 cm$^{-1}$, a larger percentage of the total absorption will result from the above-cloud gas, and the FLM will give results closer to the truth.

If we assume a solar C/H ratio of 1:2880 (Hunt 1974) then the $CH_4/H_2$ ratio should be 1:1438. Using our derived $H_2$ abundance, we are led to expect 17.5 m-amagat of $CH_4$ above the reflecting layer. This is of the right magnitude to produce certain features of the Saturn methane spectrum, such as the low intensity between manifolds of the $2 \nu_3$ band near 6000 cm$^{-1}$. The appearance of the spectrum here does not seem to be strongly dependent
on the spectral resolution; the Saturn spectrum of Connes et al (1969), having resolution 1.7 cm⁻¹, does not show in this region appreciably less detail than our own data. Consequently there is some basis for invoking rather small abundances of CH₄; the well-studied weak-band absorption by the 3ν₃ and 6190-A bands requires abundances some 3-4 times larger. Since parts of the Saturn spectrum are fit by methane spectra with several tens of m-atm of the gas, we cannot say that the planetary C/H ratio is non-solar.

2. Jupiter

The Jovian S(1) line spectrum is more problematic than that of Saturn. Both the RLM and HSM give good matches to the data, but for widely differing temperatures, neither of which is what we expected. The implication is that the assumptions made are incomplete or wrong to some degree.

In figure 19 are presented the RLM curves to fit the Jupiter data. The best match occurs for a temperature near 248 K. Profiles for 195 K and 300 K (not shown) are not as closely matching. Lower-temperature profiles are notably too narrow.

As for Saturn, we may consider that the upper cloud is optically thin at 5000 cm⁻¹, so that lower, hotter regions are seen, or that the continuum chosen in this region is too high, making Iᵥ/Iᵥ too small. The first
choice is attractive for Jupiter because of the well-known high emission of the planet near 2100 cm$^{-1}$ (Westphal et al 1974). Conceivably the same lower regions, having temperatures above 200 K, that cause the 2100-cm$^{-1}$ emission are the regions of formation of the S(1) line. In this case, if we accept the 248 K profiles as physically realistic, the best-fitting curve has a value of $X = 18.2 \text{ km-agt}^2$. Taking $g = 2400 \text{ cm sec}^{-2}$, $\mu = 2.25 \text{ amu}$, and $T = 200 \text{ K}$, we get a value for the scale height of $H = 30.6 \text{ km}$. This then implies:

$$\varrho_0 = \sqrt{\frac{X}{H}} = 0.77 \text{ agt}; W = \sqrt{XH} = 23.6 \text{ km-agt}.$$ 

In the Jupiter model of Weidenschilling and Lewis, the lower (NH$_4$SH) cloud exists between 3 and 3.5 amagat density. That value can be reduced to agree with our derived value if their base pressure, 25 bars at 400 K, is reduced to about 5 bars. Then, however, the pressure at the base of the NH$_3$ cloud goes to about 0.2 bar. Such a low pressure conflicts with the recently-derived pressure level for $3 \nu_3$ CH$_4$ band formation, $2.0 \pm 0.5 \text{ atm}$ (de Bergh et al 1974) and the effective pressures for H$_2$ quadrupole line formation, $1 - 4 \text{ atm}$ (Hunt and Bergstralh 1974). It is unquestionably of limited value to apply the RLM to the CH$_4$ and quadrupole lines; the center-to-limb variation of the former was found by Bergstralh (1973) to be inconsistent with that model, and the wide variations in quad-
rupole line equivalent widths are certainly indicative of complex atmospheric vertical structure. Bergstralh found an inhomogeneous scattering model of the form used by Danielson and Tomasko (1969) to fit the $3\nu_3$ observations. It is of interest that the pressure in that model is not an important parameter. If the RLM pressures quoted above are taken, however, to be indicative of some mean level of formation in the Danielson-Tomasko model, still there is disagreement with a base density of less than 1 amagat at the lower cloud.

The alternative explanation for the $S(l)$ line shape is the acceptance of an erroneous continuum level. We earlier proposed broadband absorption by NH$_3$ or NH$_4$SH particles. In the case of Jupiter, the 3300-cm$^{-1}$ region is strongly absorbed by NH$_3$ gas. Consequently, we cannot rule out the possibility that either of the solid constituents is absorbing near 5000 cm$^{-1}$. The weak solid-NH$_3$ absorption in the 6600-cm$^{-1}$ region is obscured by effects of the gas. A change in the 5000-cm$^{-1}$ continuum of approximately 50% would be necessary to make the Jupiter profile match curves for 150 K. Without evidence for the existence of a continuum absorber we cannot change the continuum to facilitate analysis. It should be noted, however, that if the continuum were changed, derived densities and abundances would still be low, as they are for Saturn.
The application of the HSM to the Jovian profile produces interesting results. Similarly with Saturn, the planetary profile is much too narrow to be fit by temperatures in the range 100 - 200 K (see figure 23). For 77 K, it is possible to achieve a good matching, for density 1 agt, $\sigma = 2 \times 10^{-7}$ cm$^{-1}$, and $\sigma_\infty = 0.94$. This result is surprising, and perhaps meaningless, because the Jovian atmosphere is not expected to have such low temperatures in regions of sufficiently high density to produce the H$_2$ line. In center-of-disk spectra such as concern us here, penetration of the tenuous hazes that may exist at high altitudes (Greene and Smith 1974) should be most complete. Adjustment of the continuum level can be performed with the HSM, too, of course. However, in view of the larger number of parameters in the HSM, the present lack of center-to-limb variation data, and the low confidence we would have in any single desired parameter, the HSM will not be further discussed here.

Once center-to-limb studies are performed for Jupiter, the need for scattering models will be known. If they are found to be useful, probably a simple two-layer model should be employed, because the HSM has already been found largely inadequate. The model of Danielson and Tomasko (1969) is particularly attractive because of its resemblance to the theoretical cloud-layer models of Weidenschilling and Lewis (1973). Another pos-
sibility is that a haze overlying a cloud will give useful predictions. Such an approach has been taken by Macy (1974). It may arise, of course, that the upper cloud deck is sharply defined, and that the H$_2$ line is formed above it as in the RLM. More likely, however, the spatial inhomogeneities across the Jovian disk result in different levels of line formation at different places, and in general the upper cloud may be of intermediate importance rather than either optically thick or so thin that line formation occurs below it.

D. Conclusions

The high-frequency wing of the pressure-induced fundamental band of H$_2$ has been found to be valuable for the study of the upper regions of Jupiter and Saturn where the atmospheric pressure is on the order of one bar. The shape of the $S(1)$ line of this band is similar in both planets, suggesting that the H$_2$ abundances above the clouds are of the same magnitude, and that the densities near the clouds are also similar. The detailed line shapes, however, imply that line formation is a more complex process on Jupiter. In order to explain the data for Jupiter with a reflecting-layer model, it is necessary either to assume that the line is formed beneath the upper ammonia cloud deck, or that a strong continuum absorption occurs near 5000 cm$^{-1}$ that does not occur in the 6300-cm$^{-1}$ region. The Saturn spectrum is consistent with the reflecting-
layer model. For both planets the amount of $H_2$ required to produce the observed absorption is much less than the quantity invoked to explain the 3-0 and 4-0 quadrupole lines of $H_2$. Presumably scattering effects are responsible for the discrepancies.

The most needed new information in the S(1) line analysis is the variation of the line shape with position on the planet disk. It will then be possible to assess the importance of scattering effects, and thereby determine to what parts of the atmospheres derived parameters refer.

Study of the $H_2$ line will also benefit from a reappraisal of the accuracy of published absorption coefficients and theoretical line parameters. New laboratory investigations at temperatures in the range 77 - 200 K would be most welcome. The impetus for such efforts must come from the astronomical community, although the experimental work is probably most readily undertaken with existing equipment in various physical laboratories.

Attention is also needed to the expansion of models of the planetary atmospheres. When the absorption coefficients' temperature-dependence is successfully described (as we have done to first-order here to derive coefficients for 150 K), the total effect of the variation of temperature with altitude may be included in models. Of great importance is the derivation of an expression for the relative intensity in the Danielson-Tomasko model, and predictions
of the center-to-limb variation in this model for various cloud and abundance parameters.

It is anticipated that observations of Jupiter and Saturn from aircraft or satellites will show the $H_2$ band in more detail. The region $5000 - 5300 \text{ cm}^{-1}$ is of interest, and especially $3800 - 4100 \text{ cm}^{-1}$, if methane is not too strong there. The low-frequency wing of the 1-0 band is particularly temperature-sensitive.

In time the pressure-induced fundamental band may come to play as important a role in the Earth-based study of Jupiter and Saturn as the quadrupole lines have to date. Hopefully infrared spectroscopy with interferometric techniques will become a more widespread observing technique as advances are made in detection sensitivity. Even now the study of the band is overdue; pertinent data has been available for years to several groups doing planetary investigations.

I invite and expect discussion of this work in the astronomical community, and hope that it will inspire more attention to this particular line of planetary atmosphere research.
VII. Summary

This work is a study of Jupiter, Saturn, Triton, and Pluto by spectroscopic techniques. Spectra of Jupiter and Saturn in the 1-3 \( \mu m \) (10000 - 3300 cm\(^{-1}\)) region were obtained with a Michelson interferometer. We describe the operation of the instrument and the theory of the optical sky subtraction system used in conjunction with it. The principle of sky subtraction is applied to the design of a far-infrared photometer. We obtained spectra of Jupiter in the 8200-A region with a dispersion of 1.7 A/mm to search for Jovian H\(_2\)O. Spectra of Triton and Pluto in the range 5850 - 7000 A were obtained at 50 A/mm in an attempt to detect the existence of methane atmospheres on those bodies.

The searches for H\(_2\)O on Jupiter and CH\(_4\) on Triton and Pluto were not successful, although the data were of high quality. It was possible, however, to derive from the infrared spectroscopy new upper limits to the abundances of NH\(_3\), C\(_2\)H\(_2\), and H\(_2\)S on Saturn (results are given in Table 3).

We present the principal achievements of this work in section VI. Jupiter and Saturn are found to show clear evidence of absorption by the S(1) line of the 1-0 pressure-induced band of H\(_2\). We generate models of the line shape in both reflecting-layer and scattering atmospheres, and compare the predictions of these to the
planetary data. Both planets appear to have less hydrogen above the region of line formation than is needed to explain observations of the H$_2$ quadrupole lines. The S(1) pressure-induced line requires further study, particularly of the center-to-limb variations in line shape. This and future work promises valuable insights into the atmospheric structure of Jupiter and Saturn.
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