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The Constitution of the Atmospheres of the Giant Planets

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An analysis is made of the absorption spectra of the major planets: Jupiter, Saturn, Uranus, Neptune. Approximately forty of the rotation-vibration bands are identified as due to absorption by the methane molecule, and are correlated in terms of the fundamental frequencies of vibration. It appears that methane is the major constituent of the atmospheres of these distant bodies, the quantity in the absorbing strata increasing markedly from Saturn to Neptune. The absence of any appreciable amount of other hydrocarbon material is demonstrated.

THE major planets: Jupiter, Saturn, Uranus and Neptune bear great resemblance to one another. They are strikingly different from the terrestrial planets: Mercury, Venus, Earth, and Mars. Fig. 1 shows to scale the relative diameters of these eight bodies, and to another scale shows their relative distances from the Sun. It is at once apparent that whereas the earth-like planets are very small and proximate to the sun, the major ones are colossal, and journey in the remote regions of the solar system. In contradistinction to the short years and long days of the minor planets, the giant planets rotate in from ten to fifteen hours and require exceedingly long times to traverse their orbits. Whereas, of the small planets Venus,[1] Earth, and Mars possess appreciable atmospheres, each of the large ones is surrounded by a vast one, as is evidenced by the high albedos and rich solar spectra of the major planets. Some photographs of these spectra,[2] taken at the Lowell Observatory, are shown in Fig. 2. A partial list[2] of the approximate positions of the bands is given in Table I which suffices to show how the absorptions are distributed through the spectra of the several planets.

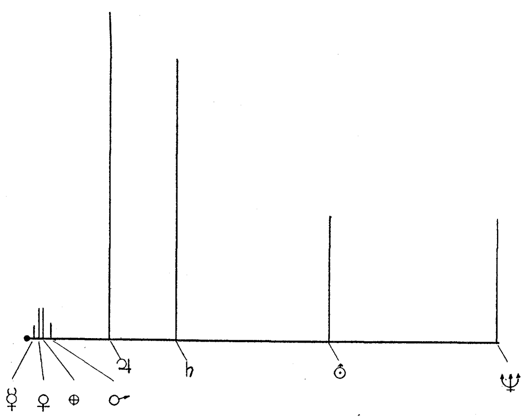

FIG. 1. The solar system.

During the course of the investigation which led to the analysis of these spectra, many gases were examined. This paper will, however, be confined to the methane molecule CH_4 which has

TABLE I. *Partial enumeration of the bands in the spectra of the major planets.*

		Planets					Planets		
Band (μμ)	J	S	U	N	Band (μμ)	J	S	U	N
441				*	647	*			
459				*	656			*	*
486			*	*	661			*	*
509			*	*	668	*	*	*	*
521				*	681			*	*
534				*	702	*	*	*	*
537			*	*	719	*	*		
543	*	*	*	*	726	*	*	*	*
576	*	*	*	*	782		*		
597			*	*	.	.	.	.	.
609			*	*	.	.	.	.	.
614		*	*	*	.	.	.	.	.
619	*	*	*	*	.	.	.	.	.

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[1] Mercury. The small mass of this planet and the intense heating it receives from the sun have long since dissipated its atmosphere.

Venus. This planet has a very extensive atmosphere which appears to consist almost wholly of carbon dioxide. See Phys. Rev. **46**, 240L (1934).

Earth. The Earth possesses an atmospheric equivalent of five mile-atmospheres. The most abundant constituents are, of course, nitrogen and oxygen.

Mars. Mars has practically no oxygen and only a very small quantity of water vapour as compared with the earth. Astrophys. J. **79**, 308 (1934). The Martian atmosphere is rarer than the Earth's. Clouds have been noted in it at a height of fifteen miles, still the pressure at the surface is probably only a small fraction of that of the Earth.

[2] Lowell Observatory Bulletin No. 42; Monthly Notices of the Royal Astronomical Society **93**, No. 9 (1933).

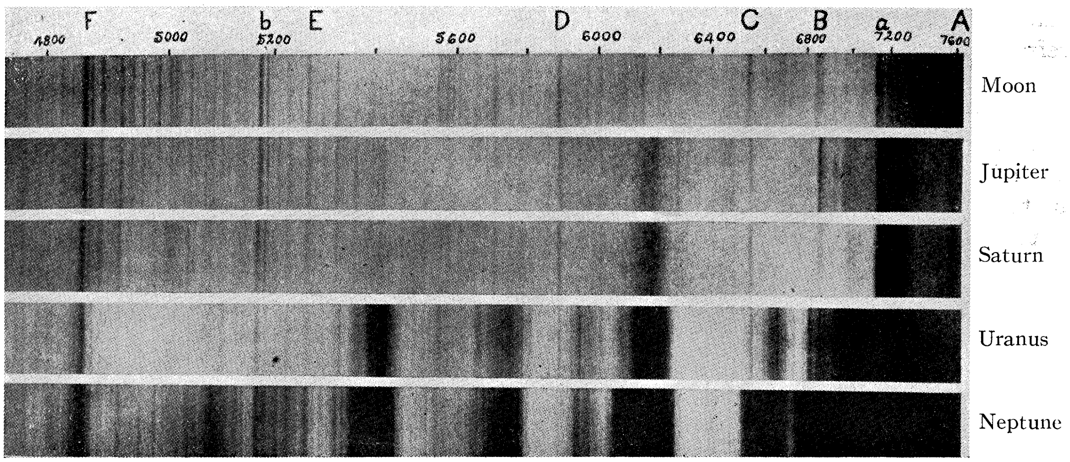

FIG. 2. The solar spectra of the major planets.

proved to be the major constituent of the giant planet atmospheres.[3]

DESCRIPTION OF APPARATUS

For the duplication of the spectra of the vast gaseous envelopes of the major planets recourse must be had to correspondingly long path-lengths in the laboratory. To meet the demands of this occasion a special absorption cell was constructed to withstand high pressures and provide a long normal path-length. A photograph of the apparatus is shown in Fig. 3.

Constructed from several sections of high pressure steam tubing, the absorption cell has a diameter of 5 cm and a length of 22.5 meters. Each of the windows, plateglass of two centimeter thickness, is separated from the cell end and the restraining cap by soft lead gaskets. The gas is passed into the evacuated cell directly from the high pressure cylinders by copper connecting coils. Pressures of about forty atmospheres have been maintained for weeks without appreciable loss. The radiation from a small incandescent source is condensed and guided down the tube by a large aperture spherical lens. At the remote extremity of the cell is situated a plane mirror with micrometer screw adjustment. The beam of radiation thus travels back down the tube creating a normal path-length of 45 meters and an aperture of approximately 1/1000. The parallel light leaves the gas chamber through a total reflecting prism, becomes incident upon a cylindrical lens, and is thrown as a sharp line upon the slit of the spectrograph. The latter is of the Littrow type. Its glass prism is especially

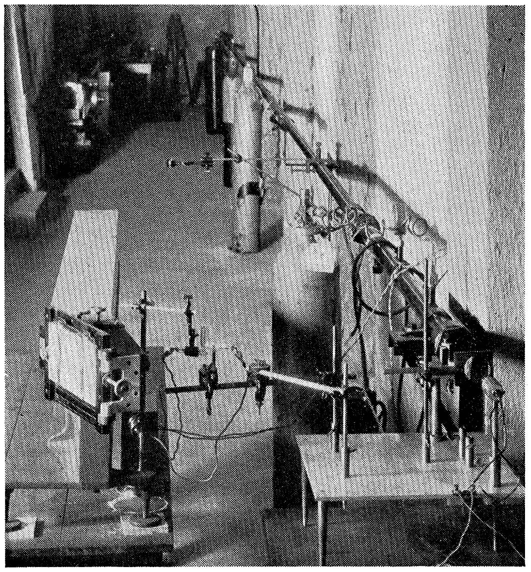

FIG. 3. The apparatus with which the planetary spectra were duplicated.

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[3] Jupiter and Saturn contain small amounts of ammonia (NH_3) as was demonstrated by R. Wildt of Gottingen who compared the spectrum of this gas with the Lowell Observatory spectra of Jupiter and Saturn. He was also able to identify the bands at 5430A, 6190A and 7260A of the planets as due to methane, by means of a formula developed by Dennison and Ingram for the sequence $n\nu_3$ (see reference 4).

suitable because of its high dispersion in the less refrangible end of the spectrum. For a survey of the red and infrared regions, the Eastman plates 1–B, 1–N, 1–P, 1–Q were found especially convenient. The exposure times varied from a few seconds and few minutes for the 1–B and 1–N plates, respectively, to from one-half to several hours for the hypersensitized 1–P and 1–Q. The spectrum of neon served for comparison purposes.

THE INFRARED SPECTRUM OF THE CH_4 MOLECULE

Though the pentatomic molecule, methane, possesses nine degrees of internal freedom, it possesses but four distinct fundamental frequencies of vibration.[4] This is a consequence of the spherical symmetry of the molecule. The fundamental vibrations are diagrammed in Fig. 4.

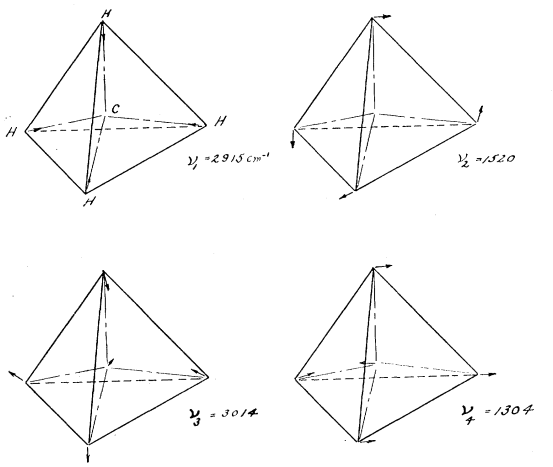

FIG. 4. The fundamental vibrations of the methane molecule.

The single vibration ν_1 consists of a symmetrical motion of the four hydrogen atoms toward the carbon atom which may be supposed to remain at rest. The H atoms retain their symmetrical positions at the corners of a regular tetrahedron all through the motion.

In the vibration ν_2 the carbon atom is again stationary, while the hydrogen atoms move in small ellipses on the surface of a sphere about the carbon as a center, but always keeping equidistant from the carbon atom. Since their motion is isotropic in two dimensions, this is a double vibration.

ν_3 is essentially a $C-H$ vibration. The whole motion is isotropic in space. ν_3 is thus a triple vibration. The vibration ν_4 is a motion of the carbon atom relative to the frame of the four hydrogens. Again the motion is isotropic in space, and therefore has the weight three. ν_3 and ν_4 have the same symmetry character, but because of the nature of the forces involved ν_3 is greater than ν_4.

Of the four fundamentals, it is clear that only ν_3 and ν_4 will be active in infrared absorption, since the highly symmetrical oscillations ν_1 and ν_2 will involve no change in the electric moment of the molecule. The selection rules governing the appearance of the infrared spectrum consequently forbid the absorption of the frequencies $n\nu_1+m\nu_2$, where n and m may take all integral values including zero. The absence of this set of absorptions consitutes a great simplification in the appearance of the methane spectrum. If it were not for this fact, the planetary spectrum would be a much more difficult one to unravel.

The tetrahedral symmetry which is responsible for the simple distribution of the absorption centers throughout the spectrum, is at the same time the cause of the very complex fine-structure pattern inherent in each of the high harmonics and combination bands found in the planetary spectrum. An idea of the complexity of the fine structure may be gained from the following examination of the harmonics of ν_3. An analysis by Dennison and Ingram[5] based upon the three degrees of freedom of this mode taken in conjunction with the tetrahedral symmetry of the molecular force field has shown that the vibrational energy levels $n\nu_3$ are multiple, with a multiplet separation which is small in comparison with the fundamental frequency; in fact, of the same order of magnitude as the rotational structure. Thus, when n is the order of the harmonic, approximately $\frac{1}{4}(n+1)(n+2)$ bands superpose to form a single composite band $n\nu_3$. For example, such a band as the $7\nu_3$ one in the planets is actually a superposition of some eighteen bands. It is not surprising, therefore, that such a band should prove difficult of resolution.

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[4] Astrophys. J. **62**, 84 (1925).

[5] Dennison and Ingram, Phys. Rev. **36**, 1451 (1930).

IDENTIFICATION

λ(μμ)	V_1	V_2	V_3	V_4
441	0	0	9	0
460	0	0	8	1
486	0	0	8	0
502	0	0	0	16
504	0	1	7	0
509	0	0	7	1
521	1	0	6	0
523	0	0	1	13
534	0	0	0	15
543	0	0	7	0
557	0	0	1	12
568	0	1	6	0
571	0	0	0	14
576	0	0	6	1
595	1	0	5	0
597	0	0	1	11
614	0	0	0	13
619	0	0	6	0
643	0	0	1	10
656	0	1	5	0
662	0	0	0	12
668	0	0	5	1
702	1	0	4	0
720	0	0	0	11
725	0	0	5	0
782	0	1	4	0
788	0	0	0	10
798	0	0	4	1
861	1	0	3	0
874	0	0	0	9
886	0	0	4	0
980	0	0	0	8
987	0	1	3	0
1009	0	0	3	1
4543 cm^{-1}	0	1	1	0
4315	0	0	1	1
4217	1	0	0	1
4122	0	1	0	2
3014	0	0	1	0
2824	0	1	0	1
2600	0	0	0	2
1304	0	0	0	1

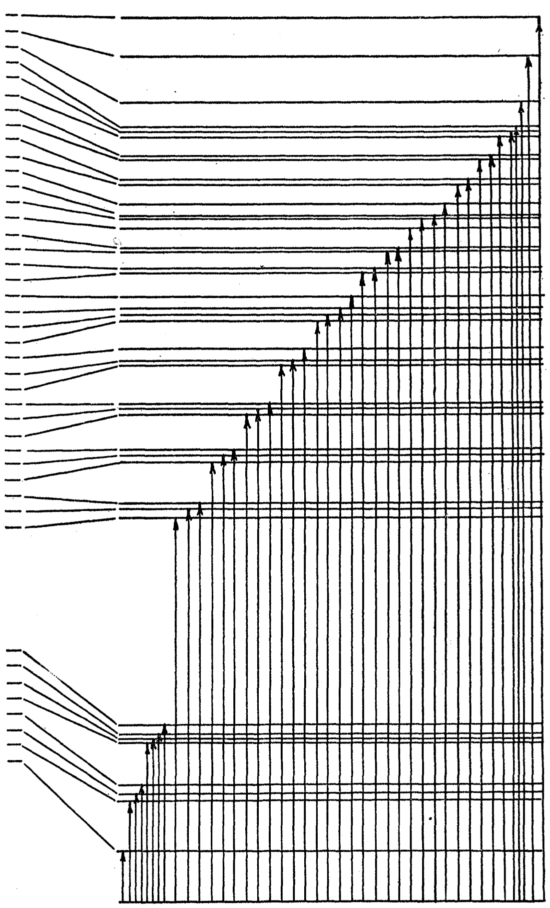

FIG. 5. The identification of the planetary bands and their correlation with the remote infrared spectrum of the methane molecule.

THE PLANETARY PROBLEM

By using gas pressures as high as 45 atmospheres, some twenty rotation-vibration bands have been photographed from 4500A to 10,000A. The laboratory spectra thus achieved are completely duplicated in the planetary ones. Not all of the methane bands showing in the spectra of the outer planets have as yet been detected in the laboratory, however, inasmuch as the absorption columns in Uranus and Neptune are much greater than the laboratory path-lengths described above. In conformity with expectation, the planetary bands which have been duplicated in the laboratory are the longer wave members of their respective groups. The present lack of complete duplication is, of course, no obstacle to the identification of the planetary bands. For, from those observed in the laboratory, the convergence constants of the several groups of bands may be determined; and with the aid of these coefficients the remaining planetary methane absorptions can be calculated. The absence of the frequencies $n\nu_1+m\nu_2$ means that there is a minimum of overlapping in the consequential spectral regions. The correlation is therefore rendered rather certain.

The identified planetary methane bands are indicated in Fig. 5 in their relation to the more remote infrared methane bands usually accessible to the observer in the terrestrial laboratory.[6] V_1, V_2, V_3 and V_4 are the vibrational quantum numbers; that is, the vibrational energy in zeroth approximation is given by:

$$E=\nu_1(V_1+\tfrac{1}{2})+\nu_2(V_2+1)+\nu_3(V_3+\tfrac{3}{2})+\nu_4(V_4+\tfrac{3}{2}).$$

The most remarkable sequences are $n\nu_3$ and $m\nu_4$, which for sheer extent have no equals in terrestrial band spectra of gases.

The Possibility of Other Hydrocarbons in The Planetary Atmospheres

In view of the existence of immense quantities of methane in the giant planet atmospheres, it is a matter of considerable import to ascertain whether or not other hydrocarbons are present, because of the bearing which this question has upon the problem of the formation of these atmospheres.

The field of hydrocarbons is rapidly narrowed down by the demand that these compounds must have very low boiling points if they are to be *atmospheric* constituents of the cold, outer planets.[7] Practically, the only hydrocarbons which need be considered are:

Compound	*Boiling point* (*760 mm*)
Ethane (C_2H_6)	−95°C
Ethylene (C_2H_4)	−103°C
Acetylene (C_2H_2)	−85°C

(Methane boils at −165°C and 760 mm.)

In an effort to find the solution to this problem, the rotation-vibration spectra of ethane and ethylene were examined from the violet to the photographic infrared, employing a path length of gas the equivalent of more than a mile at atmospheric pressure (actually, a 45 meter path and a gas pressure of 40 atmospheres). Such a quantity of gas is roughly comparable with that in the absorption layers of Jupiter and Saturn, but of a lower order of magnitude than that in Uranus and Neptune.

Many bands were observed. However, for our present purpose it will suffice to examine only the most intense of these with reference to their possible existence in the spectra of the major planets. In the spectral region 6000A–9000A the strongest absorption bands (arranged in order of diminishing intensity) have their centers in the neighborhood of:

C_2H_6	902μμ	742μμ	632μμ
C_2H_4	872μμ	710μμ	604μμ

Careful examination shows that these absorption centers do not exist in the planetary spectra. It is amusing to note that they flank the strongest ones in the corresponding region of the latter. These, due, of course, to methane, lie at:

886μμ 725μμ 619μμ.

It is very unlikely that the acetylene molecule is preferred to those of ethane and ethylene. We have not examined the spectrum of this gas, but the work of other observers on its band spectrum points to its absence from the major planet atmospheres. Although there are several agreements between acetylene and planetary spectra, they are at the same time coincidences with methane absorption; furthermore, there is no agreement between the relative intensities in the respective spectra; and other acetylene bands, quite as intense as these fail to appear in the planets. Finally, the simple, resolvable structure of the high frequency acetylene bands is decidedly unlike the complex, superimposed structure of the high frequency planetary (methane) bands.

We are thus led to the conclusion that the other hydrocarbons, if they are present at all in the atmospheres of the giant planets, must exist only in traces relative to the amount of methane present. Presumably, these hydrocarbons as well as many others exist below the atmospheres of the giant planets. The unanchored motion of Jupiter's Great Red Spot suggests that it is an island of solid hydrocarbon or ammonia floating in a vast hydrocarbon ocean as extensive as the planet's surface itself.

The authors wish to thank the Faculty Research Council of the University of Michigan for a grant-in-aid, and the American Academy of Arts and Sciences for a grant from its Permanent Science Fund.

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[6] To this compilation of identified planetary bands should be added the following:

843μμ	$7\nu_4+\nu_3$
942μμ	$6\nu_4+\nu_3$,

thus bringing the total number of identified bands to thirty-six.

[7] The temperatures in the outer layers of the major planet atmospheres are below −150°C, as inferred from radiometric measures.

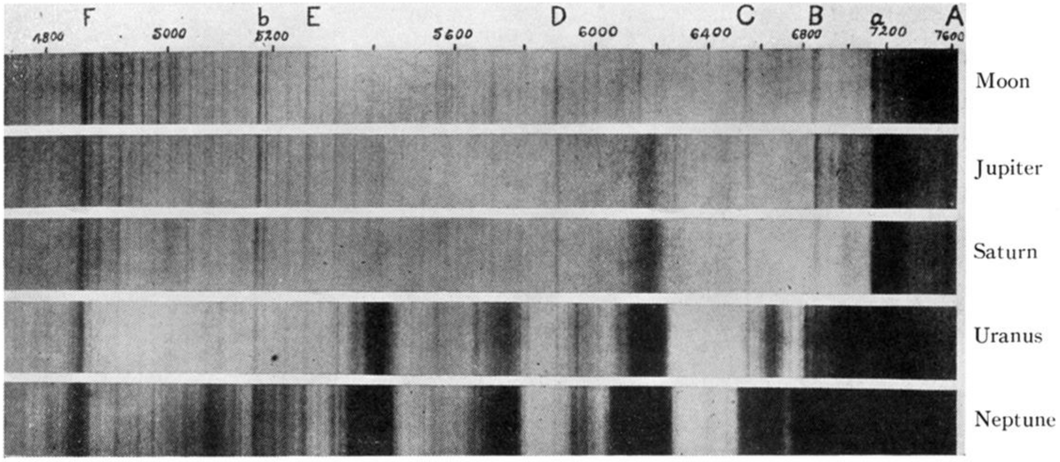

FIG. 2. The solar spectra of the major planets.

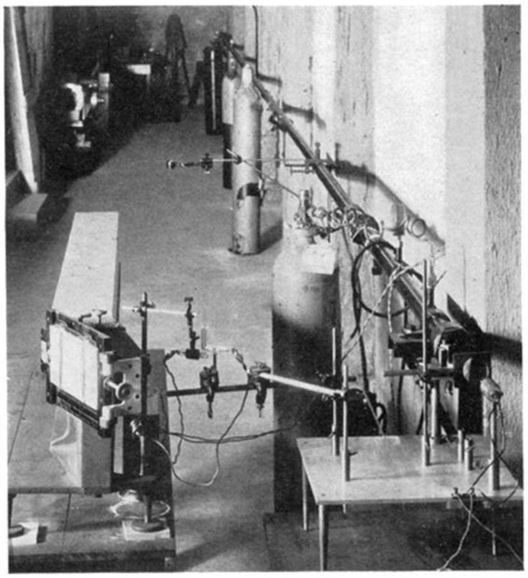

FIG. 3. The apparatus with which the planetary spectra were duplicated.