

# THE ATMOSPHERES OF THE PLANETS\*

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(With Plates III and IV)

## ABSTRACT

This paper gives a review of the present status of spectroscopic investigations of planetary atmospheres including that of the earth. In the case of the earth's atmosphere the recent discovery of OH in the spectrum of the night sky by Meinel is discussed and its importance for the phenomena in the upper atmosphere is pointed out. The spectroscopic detection of CO<sub>2</sub> in the atmospheres of Venus and Mars is described in some detail and laboratory investigations aiming at more accurate determinations of CO<sub>2</sub> content, pressure and temperature in these atmospheres are discussed. The observations of CH<sub>4</sub> absorption bands in the major planets and the satellite Titan are summarized and the possibility of detecting molecular hydrogen by means of the quadrupole rotation-vibration spectrum is outlined. It is probable that one of the unidentified features in the spectrum of Uranus and Neptune is due to the 3-0 band of the pressure-induced rotation-vibration spectrum of H<sub>2</sub>.

*A. Introduction.*—The last twenty years have seen considerable advances in our knowledge of the constitution of planetary atmospheres. Much of the new information is due to spectroscopic investigations. The following report is mainly concerned with this spectroscopic aspect of the subject. Even with this limitation a comprehensive account is not possible within the available space and I shall select for more detailed discussion mainly those topics in which I have been especially interested.

*B. The atmosphere of the earth.*—The composition of the atmosphere of the earth is well known from direct chemical analyses. The main constituents are nitrogen, oxygen, carbon dioxide, argon, helium and the other inert gases, and water vapour (see Table III.)

A good deal of the new information about our atmosphere has been derived from a study of its *absorption spectrum*, i.e., from a study of the spectrum of the sun observed through the atmosphere. It was soon found that the spectrum of any celestial object breaks off rather abruptly at about 3000Å. while the spectrum of a distant light source on the surface of the earth does not break off in this way.

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As is well known, the break-off observed in the case of celestial spectra is due to the ozone layer which exists at an average height of 25 km. By comparison with laboratory experiments it has been found that the ozone layer is equivalent to 3 mm. atm., i.e., to a layer of 3 millimetre thickness of ozone at atmospheric pressure. In this way the presence of ozone in the upper atmosphere was first established.

While in the laboratory the ozone absorption becomes negligible at about 2200Å. no light transmission is observed below 2200Å. in the atmosphere. The reason for this additional absorption is probably the continuum joining on to a weak ultra-violet band system of O<sub>2</sub> which was found nineteen years ago.<sup>1</sup>

Quite recently in the United States solar spectra have been taken from V2 rockets at great heights, above the ozone layer. The spectrum extends under these conditions to about 2200Å. where it seems to be fairly sharply limited. The O<sub>2</sub> absorption just mentioned will have little effect at the heights reached by V2 rockets, but there is a discrete absorption due to the NO molecule which under the low dispersion used may give rise to an apparent cut-off at 2200Å. if a sufficient amount of NO is present in the upper atmosphere.

In the visible, red and near infra-red part of the spectrum there occur strong absorption bands of oxygen which represent two forbidden electronic transitions of this molecule. In addition water bands representing overtone and combination bands of the rotation-vibration spectrum are very prominent.

Farther in the infra-red the intensity of the water bands increases and in addition strong bands of carbon dioxide and ozone occur. By a more detailed examination of the infra-red spectrum two important constituents of the atmosphere, N<sub>2</sub>O and CH<sub>4</sub>, have only recently been discovered, the first by Adel<sup>2</sup> and Shaw, Sutherland, and Wormell,<sup>3</sup> and the second by Migeotte.<sup>4</sup> These gases

<sup>1</sup>G. Herzberg, *Naturwiss.*, vol. 20, p. 577, 1932.

<sup>2</sup>A. Adel, *Astrophys. J.*, vol. 90, p. 627, 1939; vol. 93, p. 509, vol. 94, p. 451, 1941.

<sup>3</sup>J. H. Shaw, G. B. B. M. Sutherland and T. W. Wormell, *Phys. Rev.*, vol. 74, p. 978, 1948.

<sup>4</sup>M. V. Migeotte, *Phys. Rev.*, vol. 73, p. 519, 1948; *Astrophys. J.*, vol. 107, p. 400, 1948.

occur with an amount of approximately 0.8 and 1.7 cm. atm. respectively. Finally, quite recently Migeotte<sup>5</sup> has detected small traces of carbon monoxide, even at places like the Jungfrauoch where no contamination of the atmosphere is present. Goldberg and his collaborators<sup>6</sup> have also reported the presence of minute amounts of ammonia, but this is still doubtful.

It is important to note that the gases nitrogen, argon and helium, of which the first is the most abundant constituent of our atmosphere, do not give rise to any absorption whatever in the accessible region of the spectrum of the earth's atmosphere.

More detailed information about the upper atmosphere has been obtained by a study of the *emission spectra* of the aurora and of the night sky. The auroral spectra indicate the presence of atomic oxygen, nitrogen, sodium and hydrogen and of neutral and ionized molecular nitrogen. The strong occurrence of the forbidden lines of atomic oxygen and nitrogen is in conformity with the extremely low pressures prevalent in the upper atmosphere. In the spectrum of the light of the night sky, just as in the spectrum of the aurora, the green line of atomic oxygen is the most prominent feature in the visible region. But unlike the spectrum of the aurora the spectrum of the night sky in the visible and in the ultra-violet region contains only forbidden transitions of molecular nitrogen and oxygen, the Vegard-Kaplan bands of N<sub>2</sub> and the near ultra-violet forbidden bands of O<sub>2</sub> referred to earlier.

Quite recently Meinel<sup>7</sup> has obtained beautiful high dispersion spectra of the near infra-red part of the night sky and has observed in this spectral region both the atmospheric oxygen bands in emission and a series of diatomic hydride bands which were quickly identified as being due to the OH molecule. Figure 1 (pl. III) gives a reproduction of one of Meinel's spectra. When Dr. Meinel asked me what kind of transition the new OH bands found by him could represent it occurred to me that no new electronic transition of OH involving the ground state can be expected in the near infra-red and that therefore Meinel's bands must be rotation-vibration

<sup>5</sup>M. V. Migeotte, *Phys. Rev.*, vol. 75, p. 1108, 1949.

<sup>6</sup>O. C. Mohler, L. Goldberg and R. R. McMath, *Phys. Rev.*, vol. 74, p. 352, 1948.

<sup>7</sup>A. B. Meinel, *Astrophys. J.*, vol. 111, pp. 207, 555, 1950.

bands of the OH molecule, i.e., transitions between the various vibrational levels of the electronic ground state. Upon calculating the positions of the bands 4-0, 5-1, 6-2, 7-3, and 8-3, 9-4, from the known vibrational constants of the OH molecule I found an

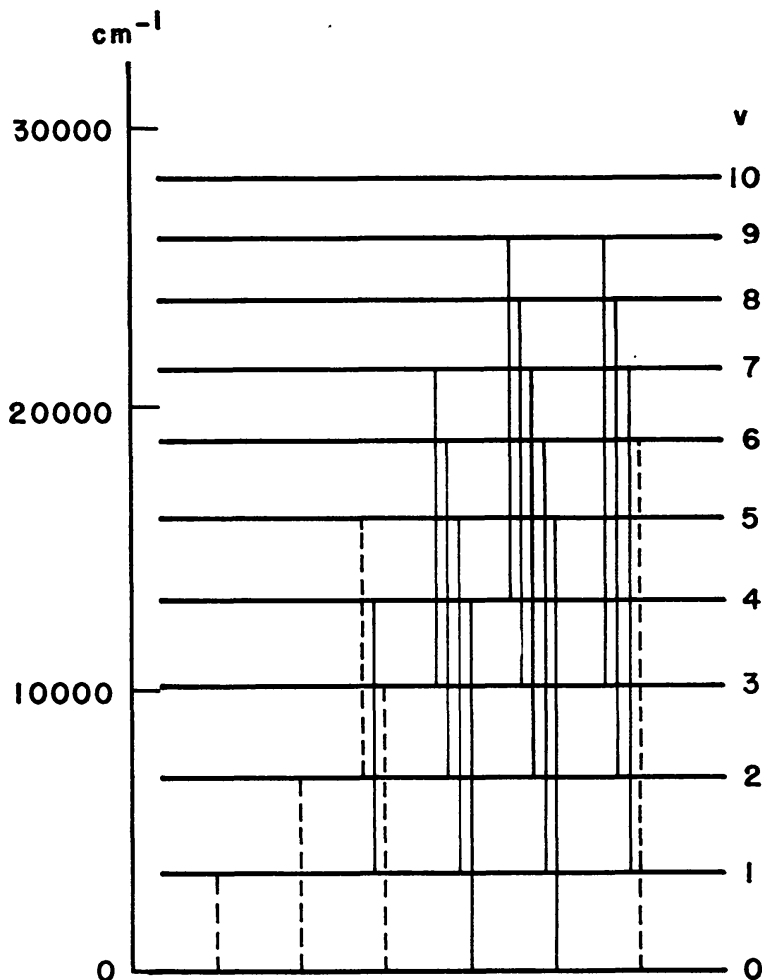


FIG. 2.—Vibrational energy levels of the OH molecule in its ground state. The transitions giving rise to the observed Meinel bands are indicated by solid vertical lines; those giving rise to bands as yet unobserved are indicated by broken lines.

exact and convincing agreement with Meinel's observed bands. Figure 2 shows the observed transitions in an energy level diagram. Later, Meinel<sup>8</sup> and Cabannes and Dufay<sup>9</sup> found additional weaker bands which fit in the 5-0, 6-1, . . . and 6-0, 7-1, . . . sequences.

<sup>8</sup>A. B. Meinel, *Astrophys. J.*, vol. 111, p. 433; vol. 112, p. 120, 1950.

<sup>9</sup>J. Cabannes, J. Dufay and M. Dufay, *C.R.*, vol. 230, p. 1233, 1950.

There can, therefore, be no question that Meinel's bands are rotation-vibration bands of the OH molecule.

The intensity of the main group of Meinel's bands, i.e., 4-0, 5-1, etc. is of the same order as that of the green auroral line. It is well known that the intensity in a progression of rotation-vibration bands decreases very rapidly with increasing change of vibrational quantum number,  $\Delta v$ . On the basis of the interpretation of Meinel's bands it must, therefore, be expected that much stronger bands appear farther in the infra-red and correspond to the sequences 3-0, 4-1, etc., 2-0, 3-1, etc., and 1-0, 2-1, etc. (see figure 2). The intensity in each successive sequence should increase by a factor of the order of 20.

Now it is very significant that a very strong near infra-red radiation of the night sky at 10400A. has been discovered by Stebbins, Whitford and Swings<sup>10</sup> five years ago by means of infra-red sensitive photoelectric cells. There can be no question that this radiation at 10400A. is due to the 3-0 sequence of OH. The sequences 2-0, and 1-0, which will be stronger by a factor of at least 10 and 100, respectively, have still to be discovered. At any rate, the OH molecule gives rise to the strongest feature of the night sky spectrum thus far known and on the other hand is a constituent that had not been considered for the upper atmosphere until early in 1950.

In addition to the spectrum of the aurora and the ordinary night sky luminescence the spectrum of *twilight* has been studied by various investigators and the occurrence of the yellow sodium line and of the blue bands of ionized molecular nitrogen,  $N_2^+$ , has been observed. They are considered to be produced as fluorescence by the sunlight striking the upper layers of the atmosphere.

Much work has been done in the past two decades on the interpretation of the phenomena observed in the upper atmosphere. In the top layers of the atmosphere upon absorption of far ultra-violet radiation from the sun all atoms and molecules are subject to ionization and in this way the well known ionospheric layers are produced which are so important for radio-wave propagation. Somewhat lower in the atmosphere when the very far ultra-violet

<sup>10</sup>J. Stebbins, A. E. Whitford and P. Swings, *Astrophys. J.*, vol. 101, p. 39, 1945.

has been absorbed there is still ultra-violet light of sufficiently short wave-length to cause photo-dissociation of molecular nitrogen and molecular oxygen. The former occurs for wave-lengths below 1270A., the latter for wave-lengths below 1750A. I might mention here that quite recently at Ottawa Dr. Douglas has confirmed the mechanism which was suggested three years ago<sup>11</sup> as leading to the dissociation of the nitrogen molecule, i.e., he showed that there really is a very sharp predissociation limit at 1270A. and that, therefore, dissociation of N<sub>2</sub> must necessarily occur even though not at a very fast rate. The occurrence of both N<sub>2</sub> and N<sub>2</sub><sup>+</sup> bands in auroral spectra shows that the dissociation of N<sub>2</sub> in the upper atmosphere is by no means complete.

Photo-dissociation of molecular oxygen occurs down to much lower heights in the atmosphere. At the lower levels the continuum joining on to the near ultra-violet O<sub>2</sub> bands mentioned previously (i.e. below 2425A.) leads to photo-dissociation at a slow rate. In these layers collisions of O atoms and O<sub>2</sub> molecules will occur frequently and it is in this way that the O<sub>3</sub> molecules of the ozone layer are formed.

The occurrence of OH as an important constituent of the upper atmosphere and the emission of its rotation-vibration spectrum may be explained by two mechanisms which may, also in other respects, be of importance in the upper atmosphere. The first one, which is likely to take place only at comparatively great heights, is the two-body recombination of O and H atoms, present in the upper atmosphere, according to the reaction

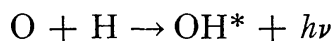
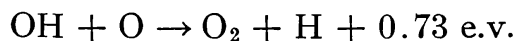


Figure 3 shows the potential energy curves of the states of OH arising from normal atoms as well as that of the upper state of the ultra-violet OH bands. It is possible that the  $^2\Sigma^-$  state has a shallow minimum and that when the atoms collide in this state, in a very small fraction of the collisions, a quantum jump will occur to that part of the potential energy curve of the ground state that corresponds to the vibrational levels involved in the emission of the Meinel bands. Once the OH molecule has been formed and has settled in one of the lowest vibrational levels it will, upon

<sup>11</sup>G. Herzberg and L. Herzberg, *Nature*, vol. 161, p. 283, 1948.

collision with another oxygen atom, form  $O_2$  and H according to the reaction



This reaction, unlike the first one, is a fast reaction and will occur substantially at every favourable collision. In this way the hydrogen atoms with which we started out are formed back again; they may be considered as a catalyst which causes the recombination of oxygen atoms to form  $O_2$  molecules, a process that otherwise is very unlikely to happen.

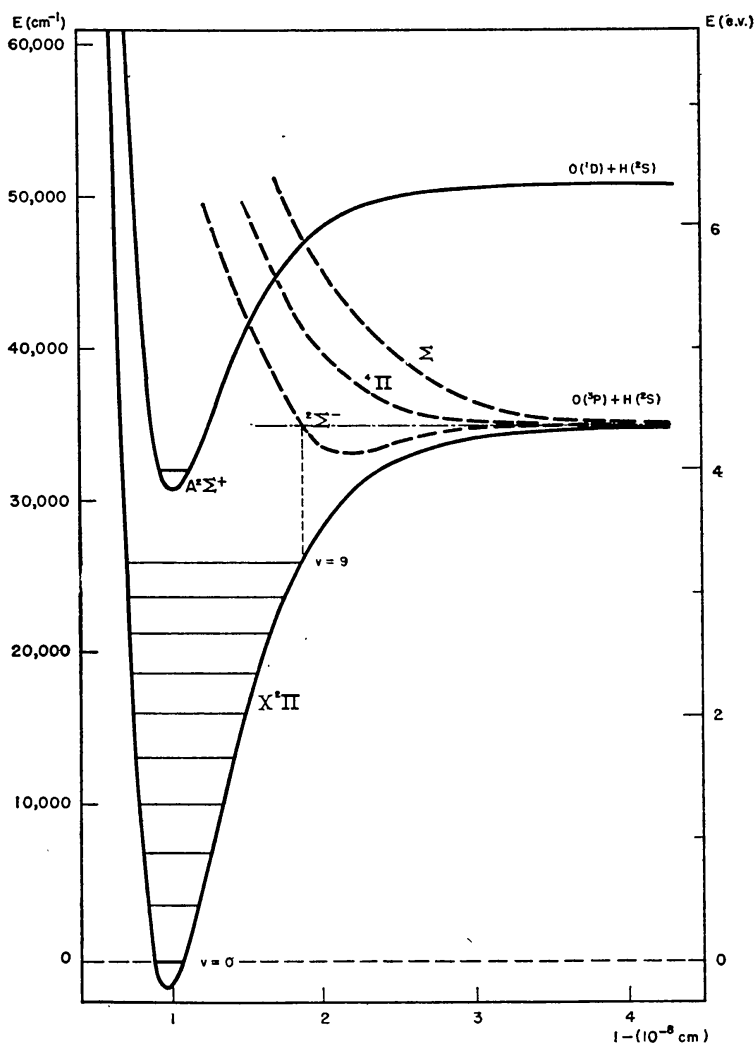
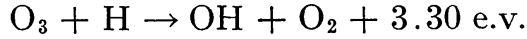
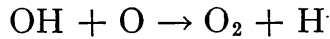


FIG. 3.—Potential curves of the OH molecule. The full-line curves correspond to the two observed electronic states, the broken-line curves correspond to three additional states arising from normal atoms but not yet observed.

An alternative mechanism for the emission of the Meinel bands which is likely to be operative at lower altitudes is one in which a hydrogen atom reacts not with an O atom but with an O<sub>3</sub> molecule according to the reaction

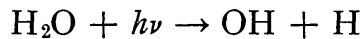


This reaction gives just sufficient energy to excite the highest of the vibrational levels observed by Meinel. It will again be followed by the reaction



which again results in the re-formation of free hydrogen atoms. They serve now as catalysts both for the decomposition of O<sub>3</sub> and for the formation of O<sub>2</sub>. I might mention that this second mechanism was independently suggested by Bates and Nicolet and by myself at a recent meeting in Pasadena. Since then Bates and Nicolet<sup>12</sup> have shown that the second mechanism accounts in a semi-quantitative way for the height of the OH emission found by Roach, Petit, and Williams<sup>13</sup> to be 70 km.; this mechanism also accounts for the number of photons emitted.

The formation of the H atoms necessary for the excitation of the Meinel bands may occur in several ways; but one of the most likely, also discussed by Bates and Nicolet, is the photo-dissociation of H<sub>2</sub>O vapour by light below 1830Å. according to



One other interesting point is the question of the *temperature* in the upper atmosphere. Some years ago Vegard and Tønsberg<sup>14</sup> found from a study of auroral spectra under medium dispersion that the temperature in the region where the aurorae occur is approximately 220° K. The method by which this temperature determination was made is illustrated in figure 4 (pl. III), which shows the structure of a band of N<sub>2</sub><sup>+</sup> obtained in the laboratory at

<sup>12</sup>D. R. Bates and M. Nicolet, *Publ. Astron. Soc. Pac.*, vol. 62, p. 106, 1950; *C.R.*, vol. 230, p. 1943, 1950.

<sup>13</sup>F. E. Roach, H. Petit, and D. R. Williams, *J. Geophys. Res.*, vol. 55, p. 183, 1950.

<sup>14</sup>L. Vegard and E. Tønsberg, *Geophys. Publ.*, vol. 13, no. 1, 1940; vol. 16, no. 2, 1944



three different temperatures. It is seen how the intensity distribution in the two branches of the band changes: with increasing temperature the maximum of intensity in each branch goes to higher quantum numbers. It is clear that conversely by observing the intensity distribution it is possible to draw conclusions about the temperature at which the bands are produced even if the bands are not resolved, and that is precisely what Vegard and Tønsberg did.

Now it is very significant that Meinel's spectra supply, with much greater certainty, temperatures of the same order as found by Vegard. Figure 1 shows clearly that the intensity maximum in the P branch of each of the OH bands occurs at a very low  $K$  value.<sup>15</sup> It must, of course, be understood that the temperatures so obtained are rotational temperatures. They will be equal to the true temperature only if there is thermal equilibrium. Undoubtedly this is not the case; but it does seem unlikely that the translational temperatures could be much higher than the rotational temperatures determined in this way.

In this connection a difficulty arises since the intensity of the twilight emission leads one to conclude that there must be many more atoms at a level of 700 kilometres than would correspond to a temperature of 220° K. Similarly the temperatures obtained from ionospheric data are very much higher. It seems probable that the temperature 220° K. applies only to the lower parts of the upper atmosphere, i.e., the region between 70 and 150 km. It would be most desirable to determine the temperature from the spectra of high aurorae or of the twilight flash by the same method as used by Vegard and Meinel.

*C. The atmospheres of the terrestrial planets.*—It has been known for a long time that the planets Venus and Mars have atmospheres. Visual observations of Venus indicate a very high albedo such as obtained for clouds and in the case of Mars the variation of the polar caps with the seasons definitely indicates the presence of an atmosphere even though it may be rather tenuous.

In discussing the spectra of these planets it must be remembered that certain gases like nitrogen and argon do not absorb in the

<sup>15</sup>For a more detailed discussion see A. B. Meinel, *Astrophys. J.*, vol. 112, p. 120, 1950.

accessible region and in addition that terrestrial absorptions may hide planetary absorptions. No characteristic features were found in the spectra of Venus and Mars until 1932 when Adams and Dunham<sup>16</sup> observed for the first time the near infra-red spectrum of Venus. They found three characteristic absorption bands between 7000 and 9000Å. Figure 5 (pl. IV) shows a reproduction of a spectrum of Venus taken by Adams and Dunham exhibiting two of the absorption bands. Notice the very simple structure of these bands which is characteristic of either a diatomic or a linear polyatomic molecule. From the spacing of the lines in these bands it was soon concluded that they must be due to the CO<sub>2</sub> molecule, representing overtone and combination bands of its rotation-vibration spectrum. This interpretation was confirmed by laboratory investigations which will be discussed presently. On the basis of this interpretation it is to be expected that much stronger CO<sub>2</sub> bands occur farther in the infra-red. Indeed, when Kuiper studied for the first time the spectrum of Venus between 2.5 and 0.8 $\mu$  he found a large number of strong absorption bands. Figure 6 shows one of the Venus spectra obtained by Kuiper. Some of the absorption bands in this spectrogram are due to water vapour or

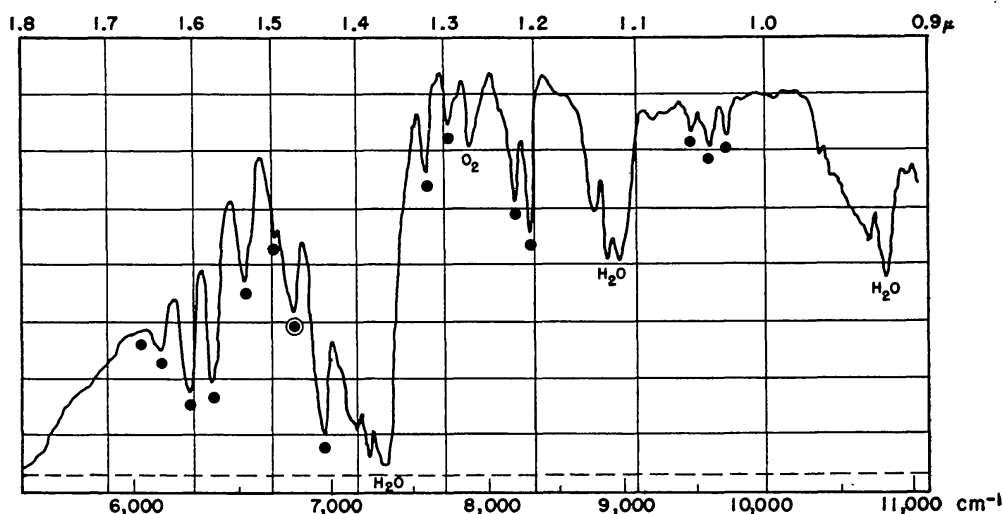


FIG. 6.—Infra-red spectrum of Venus (after Kuiper<sup>18</sup>). The absorption minima marked by heavy dots are due to CO<sub>2</sub> bands; the minimum marked by a circled dot is probably due to C<sup>13</sup>O<sub>2</sub>. The broken line at the bottom corresponds to zero intensity.

<sup>16</sup>W. S. Adams and Th. Dunham, *Publ. Astron. Soc. Pac.*, vol. 44, p. 243, 1932.

O<sub>2</sub> in the earth's atmosphere; but all of the others (marked by heavy dots) are due to CO<sub>2</sub>, (see figure 9). The weak band at 1.47 $\mu$  adjacent to the strong band at 1.43 $\mu$  is very probably due to the isotope C<sup>13</sup>O<sub>2</sub>.

It seems probable that in addition to the large amounts of CO<sub>2</sub> there are also small amounts of CO present in the atmosphere of Venus but a special search made for some of the overtone bands of CO has not resulted in any positive evidence. It must, however, be kept in mind that the sensitivity of detection is not very great, not as great by far as that with which Migeotte detected CO in the atmosphere of the earth.

Molecular oxygen and water vapour are more difficult to detect in any planetary atmosphere because of the presence of these gases in our own atmosphere. However, when the planet is in quadrature and is moving toward or away from us the Doppler shift is sufficiently large that under high dispersion the terrestrial and planetary lines could be separated. In this way it has been established by Dunham<sup>17</sup> that in the atmosphere of Venus there can be not more than 2 per cent. of the amount of oxygen and water vapour present in the earth's atmosphere.

Kuiper has recently applied his infra-red spectrometer to the planet Mars; two representative spectra are reproduced in figure 7, together with a spectrum of the moon for comparison. At about 1.6 $\mu$  there is a slight depression of the spectral curve of Mars, compared to the moon, and this was clearly present in all spectra of Mars. It occurs precisely at the place of two strong CO<sub>2</sub> bands, at 1.60 and 1.57 $\mu$ . There is also evidence for other CO<sub>2</sub> bands at 2.0 $\mu$ . In this way the presence of carbon dioxide in the atmosphere of Mars was established. The amount of carbon dioxide in Mars derived from the spectra is very much smaller than in Venus and only of the same order of magnitude as in the atmosphere of the earth.

Attempts were made to detect quite a series of other gases in the atmosphere of Mars. Dunham<sup>17</sup> showed that oxygen and water vapour cannot be present to an extent greater than 0.15 per cent. of that on the earth. SO<sub>2</sub>, which has a fairly strong ultra-

<sup>17</sup>Th. Dunham, Jr., in Kuiper's "The Atmospheres of the Earth and Planets," p. 286, 1949.

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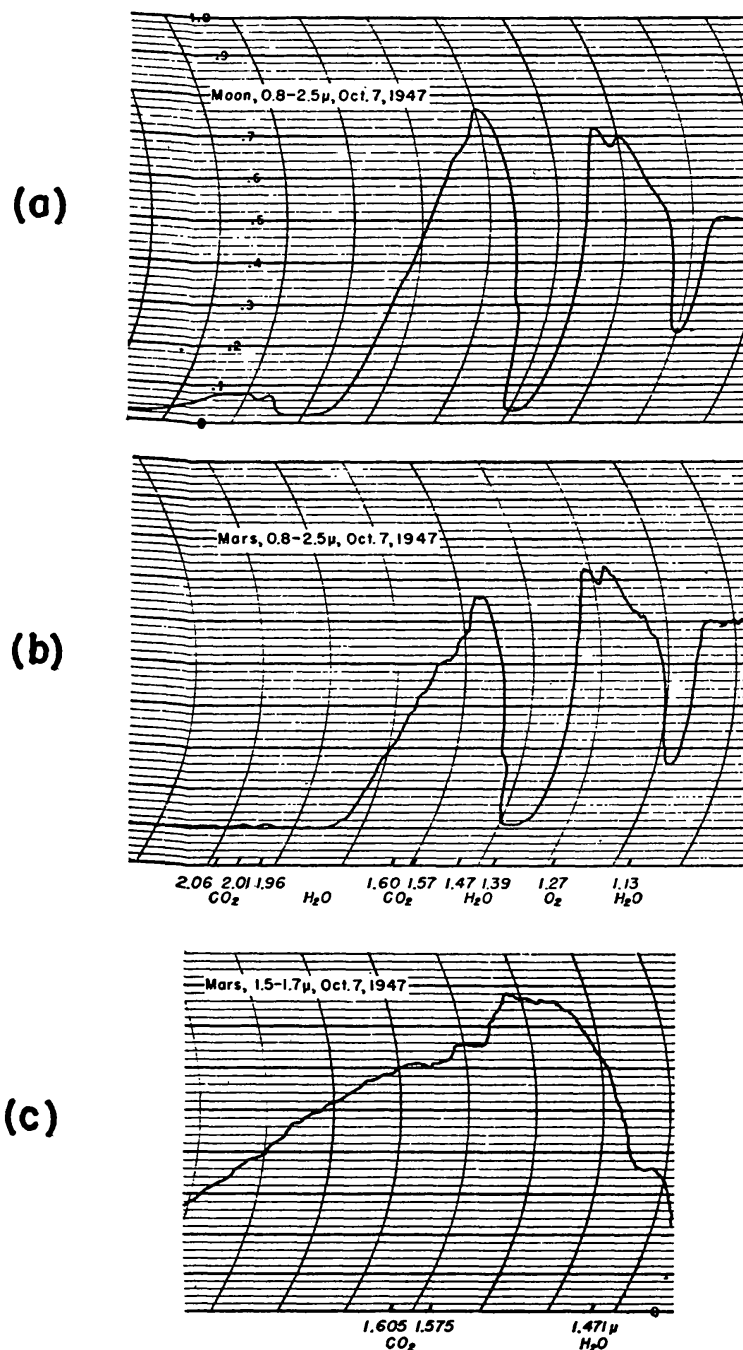


FIG. 7.—Infra-red spectra of Mars (after Kuiper<sup>18</sup>). (a) Spectrum of the moon for comparison; (b) spectrum of Mars, same dispersion as (a); (c) spectrum of Mars in region of CO<sub>2</sub> bands with twice the dispersion. Note that the vertical arcs in (a) and (b) do not appear at corresponding positions in the spectrum.

violet absorption, was shown by Kuiper<sup>18</sup> to be absent with a detection limit of 0.03 mm. atm. Similar remarks apply to ozone. No evidence was obtained for N<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> in the infra-red spectra. Again it must be remembered that nitrogen, hydrogen and argon would escape observation even if they were present in large quantities.

At first sight the detection of carbon dioxide in the atmosphere of Mars may lead one to believe that the idea put forward many times in the past that the polar caps of Mars are due to solid carbon dioxide is correct. However, in the laboratory, the spectrum of light reflected from solid carbon dioxide shows only faint indications of CO<sub>2</sub> absorption bands in the region investigated (below 2.0 $\mu$ ) whereas the spectrum reflected from ordinary snow shows a very strong absorption starting at 1.5 $\mu$  and leading to an abrupt termination of the reflection spectrum at this wave-length. The infra-red spectrum of the polar caps of Mars obtained by Kuiper<sup>18</sup> does terminate at 1.5 $\mu$  and therefore suggests very strongly that they consist of H<sub>2</sub>O snow rather than solid CO<sub>2</sub>. This result is also in better agreement with reasonable temperatures obtained by bolometric means. In view of the variation of the polar caps with the Martian seasons it follows indirectly that water vapour must be present although the amount, as mentioned before, must be very small.

Up to now no evidence for an atmosphere on Mercury or on the moon has been found. In the case of the moon the occultation of stars indicates that the density of the atmosphere must be less than 10<sup>-5</sup> of that of the atmosphere of the earth. The lack of polarization of the light from the shadows near the terminator indicates that the density must be less than 10<sup>-6</sup> atmospheres.<sup>19</sup> Considering that the heavier gases are more likely to be held back by the moon than the lighter ones Kuiper<sup>18</sup> has recently tested for SO<sub>2</sub>; but this test came out to be entirely negative and if SO<sub>2</sub> is present it must be there to an extent of less than 0.003 mm. atm. On the other hand, it seems rather probable that there must be at least a very tenuous atmosphere on the moon on account of the

<sup>18</sup>G. P. Kuiper, "The Atmospheres of the Earth and Planets," p. 304, 1949.

<sup>19</sup>V. G. Fessenkoff, *Astron. J. Soviet Un.*, vol. 20, pt. 2, p. 1, 1943; O. Struve, *Astrophys. J.*, vol. 100, p. 104, 1944.

## PLATE III

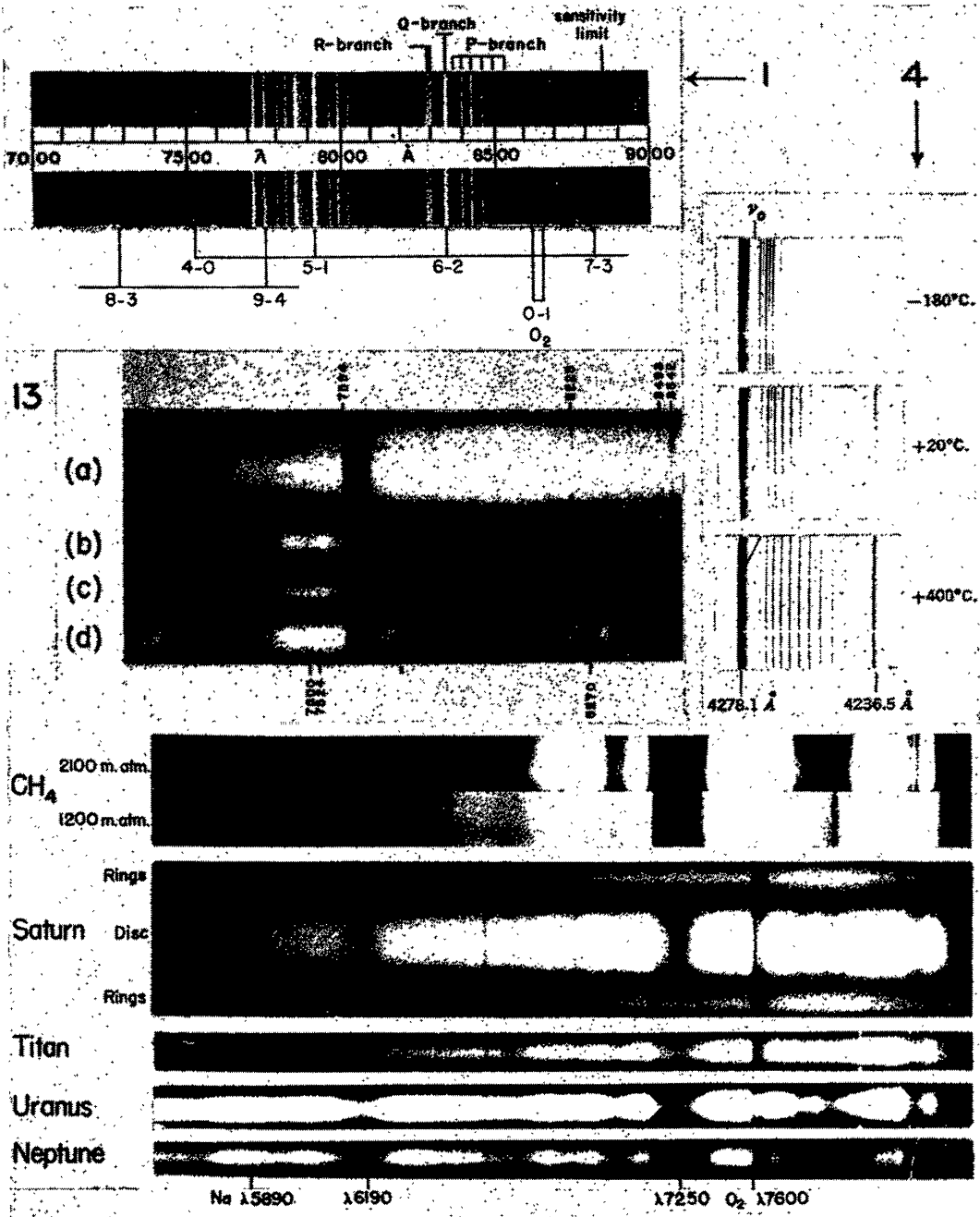


FIG. 1.—Near infra-red spectrum of the night sky (after Meinel<sup>7</sup>). Two identical spectra. In the top one the fine structure of one of the bands is indicated by leading lines; in the bottom one the *Q* branches of each of the Meinel bands are marked and the vibrational numbering given. Note the 0-1 band of the atmospheric oxygen system (the 0-0 band is absent on account of absorption in the lower atmosphere).

FIG. 4.—Fine structure of the  $N_2^+$  band 4278.1 Å. at  $-180^\circ\text{C}$ .,  $20^\circ\text{C}$ ., and  $400^\circ\text{C}$ ., illustrating temperature determination from band spectra. The band consists of two branches, *P* and *R*, on opposite sides of the band origin  $\nu_0$ . The *P* branch forms the head of the band and is not completely resolved. The *R* branch consists of a series of lines whose separation increases to shorter wave-lengths.

FIG. 13.—Spectra of Uranus showing unidentified features (after Kuiper<sup>30</sup>). (a) Spectrum of Venus for comparison; (b), (c), (d) spectra of Uranus of different density.

FIG. 11.—Spectra of Saturn, Titan, Uranus and Neptune, and laboratory absorption spectra of methane in the region 5500 to 8800 Å. (after Kuiper<sup>24</sup>).

## PLATE IV

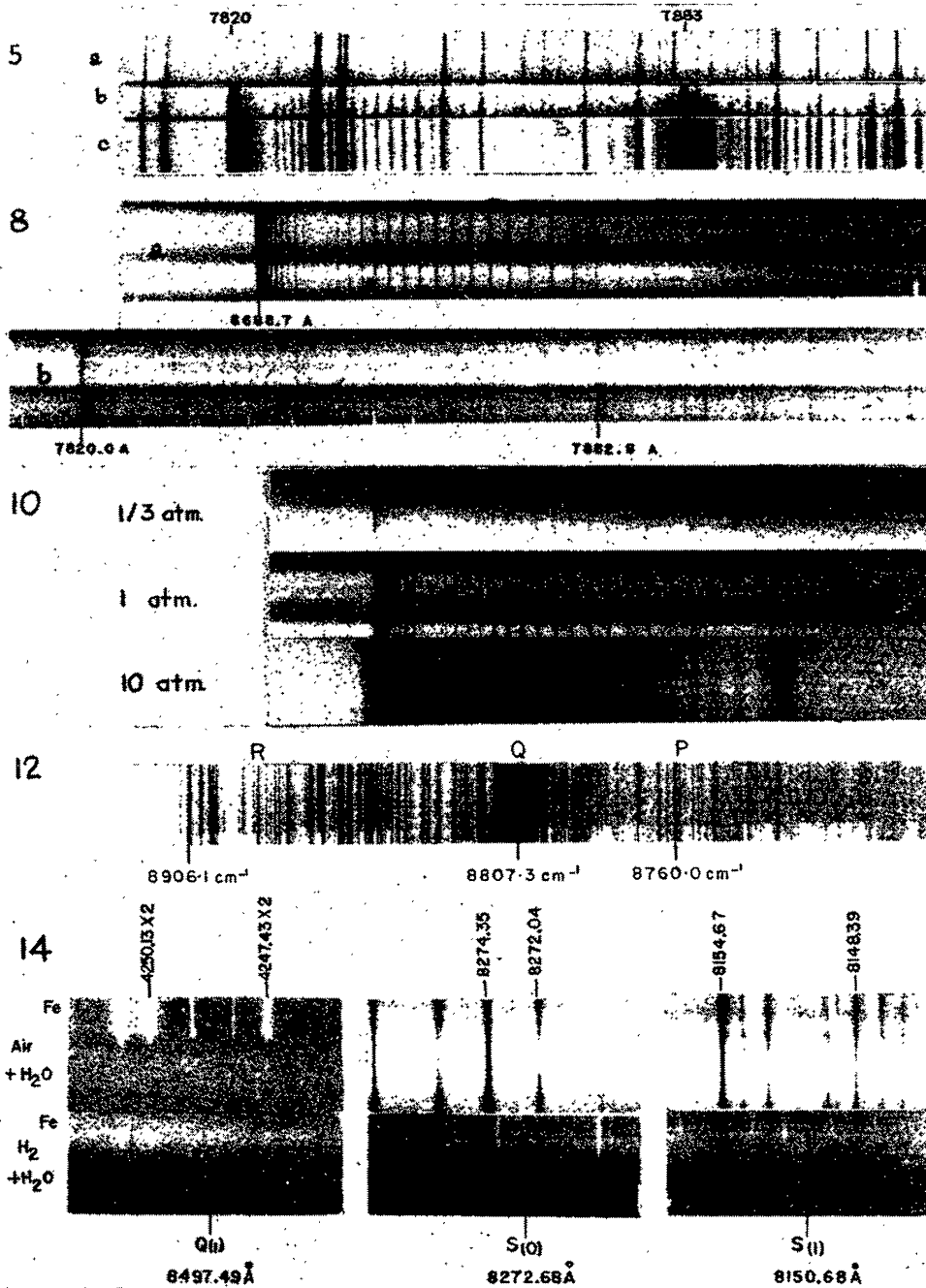


FIG. 5.—Part of the photographic infra-red spectrum of Venus showing two CO<sub>2</sub> bands (after Adams and Dunham<sup>16</sup>). The top strip gives the solar spectrum for comparison; the bottom strip was obtained from the original spectrum, reproduced in the middle strip, by moving the plate in the copying process.

FIG. 8.—Parts of the photographic infra-red absorption spectrum of CO<sub>2</sub> obtained in the laboratory with a path of 2200 m. at a pressure of 1 atm. (after Herzberg<sup>21</sup>). The band 7883 Å. is overlapped by an H<sub>2</sub>O band; this accounts for the irregularly spaced lines.

FIG. 10.—Pressure broadening in the CO<sub>2</sub> band at 8689 Å. The three spectra were all taken with the same path length of 2200 m.

FIG. 12.—Fine structure of the CH<sub>4</sub> absorption band at 1.135 μ. The letters R, Q, P indicate the regions of the corresponding branches.

FIG. 14.—Three lines of the 3-0 quadrupole rotation-vibration band of the H<sub>2</sub> molecule (after Herzberg<sup>22</sup>). Top: spectrum of moist air for comparison; bottom: spectrum of moist hydrogen with an absorbing path of 5000 m. at a pressure of 9 atm.

gases released when meteorites strike its surface. The density of this atmosphere may be expected to be of the same order as that in the head of a comet, which is usually considered to be due to the emanations from the meteorites forming the nucleus. Just as in a comet, solar radiation will produce fluorescence of this atmosphere and this fluorescence should be observable. However, even if the fluorescence were as strong as it is for a bright comet it is unlikely that it would have been observed so far because of the bright light from the moon. Some time ago I suggested the use of a coronagraph for detecting the fluorescence of the lunar atmosphere,<sup>20</sup> but such observations have not yet been carried out.

Both for the purpose of estimating more accurately the amounts of CO<sub>2</sub> in the atmospheres of Venus and Mars and in order to obtain information about the physical conditions in these atmospheres it is necessary to study the absorption of CO<sub>2</sub> in the laboratory with long absorbing paths. Immediately after the discovery of the CO<sub>2</sub> bands in the atmosphere of Venus Dunham<sup>17</sup> studied in the laboratory the absorption spectrum of CO<sub>2</sub> at high pressure (up to 10 atm.) with an absorbing path of 43 metres. In this way he obtained a diffuse band at 7820A., i.e. at the place of one of the Venus bands. On account of the broadening of the lines at high pressure it is clearly not possible to obtain an accurate estimate of the amount of CO<sub>2</sub>. It was for this reason that I set up at Yerkes Observatory a large absorption tube in which it was possible to obtain absorbing paths up to 5000 metres. It was hoped that in this way it would be possible to observe the Venus bands under a pressure comparable to that in the Venus atmosphere.

The optical arrangement used has been described previously.<sup>21</sup> With this method I have photographed the spectrum of CO<sub>2</sub> at different pressures and path lengths under high resolution. Figure 8 (pl. IV) shows parts of the laboratory spectrum of CO<sub>2</sub> near 8000A. obtained with an absorbing path of 2200 m. at a pressure of 1 atm. The three CO<sub>2</sub> bands in this spectrum are those first observed in the spectrum of Venus by Adams and Dunham. The two bands in the spectrum of Venus reproduced in figure 5 are of about the

<sup>20</sup>G. Herzberg, *Pop. Astron.*, vol. 54, p. 414, 1946.

<sup>21</sup>G. Herzberg in Kuiper's "The Atmospheres of the Earth and Planets," p. 346, 1949.



same intensity as those in the laboratory spectrum, figure 8b. The fine structure is developed in about the same way. At longer wave-lengths additional photographic infra-red bands have been found both in the laboratory<sup>21</sup> and in the spectrum of Venus.<sup>22</sup> Still farther in the infra-red the spectrum of CO<sub>2</sub> has been investigated with the aid of Dr. Kuiper's infra-red spectrometer and a large number of absorption bands have been found. Figure 9 shows two recordings, one with 88 m. path and the other with 1400 m. path. Comparing these with Kuiper's infra-red spectrum of Venus, figure 6, it is seen that all absorption bands in Venus are accounted for.

The original object of the research, namely to obtain a more precise figure for the amount of carbon dioxide in the atmosphere of Venus, has not yet been accomplished. Different amounts are obtained depending on the particular bands used for comparison. The weaker the bands the greater is the amount of carbon dioxide estimated. For example, the strong bands near  $1.6\mu$  in the Venus spectrum of figure 6, are roughly matched by the corresponding laboratory bands in figure 9a obtained with a path of 88 m. atm. while the weak bands at  $1.05\mu$  appear stronger in Venus than in the laboratory spectrum obtained with 1400 m. atm. (figure 9b). The reason for this inconsistency appears to be the re-emission of light in the stronger absorption bands, the effect of scattering in the atmosphere which is different for different bands,<sup>23</sup> and the effect of pressure broadening which also affects the apparent intensities of the bands. Quite recently Kuiper<sup>24</sup> has found very considerable and rather rapid changes in the intensities of the CO<sub>2</sub> bands in Venus corresponding to changes of the absorbing path lengths by almost a factor of 10 and apparently due to rapid changes in the height of the cloud layer in the Venus atmosphere.

The laboratory CO<sub>2</sub> bands reproduced in figure 8 show clearly the usual regular distribution of intensity particularly in the P branch. A very similar intensity distribution is shown by the Venus bands in figure 5 and indicates that the temperature in

<sup>22</sup>G. Herzberg, unpublished, see *Astron. J.*, vol. 52, p. 147, 1947.

<sup>23</sup>Compare H. C. van de Hulst in Kuiper's "The Atmospheres of the Earth and Planets," p. 49, 1949.

<sup>24</sup>G. P. Kuiper, *Reports on Progress in Physics*, vol. 13, p. 247, 1950.

those parts of the Venus atmosphere in which the absorption takes place is of the order of  $300^\circ \pm 50^\circ$  K.<sup>25</sup> If a more accurate photometric comparison were carried out it would be possible to de-

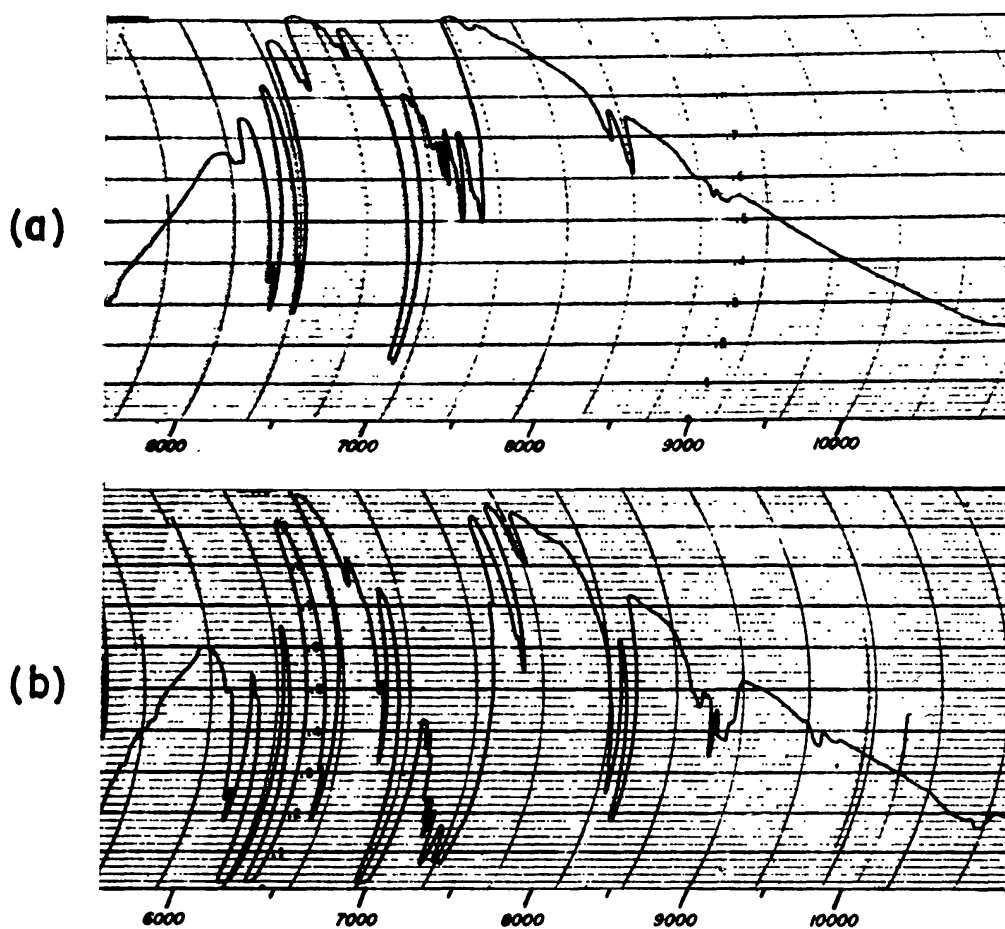


FIG. 9.—Infra-red absorption spectrum of  $\text{CO}_2$  obtained in the laboratory with a path of (a) 88 m., (b) 1408 m. at a pressure of 1 atm. (after Kuiper and Herzberg<sup>18</sup>). These spectra were obtained with the same spectrometer as figure 6 but with a different recorder giving curved rather than straight ordinates, and a narrower slit width giving higher resolution. Most of the  $\text{CO}_2$  bands show two minima corresponding to *P* and *R* branches.

termine this temperature with much greater precision; but this has not yet been done.

As mentioned before, the  $\text{CO}_2$  bands become more and more diffuse with increasing pressure. As an illustration figure 10 (pl. IV) shows the 8690A. band of  $\text{CO}_2$  obtained at three different pressures,

<sup>25</sup>A. Adel, *Astrophys. J.*, vol. 86; p. 337, 1937.

$\frac{1}{3}$  atm., 1 atm., and 10 atm. Even in going from  $\frac{1}{3}$  to 1 atm. there is a distinct broadening of the lines and in going to 10 atm. the lines become quite broad. The three spectra shown were all taken at the same path length. It would have been better to have used a constant product of pressure and path length, but these spectra were actually taken for a different purpose. Nevertheless, if one compares them with the spectrum of Venus, figure 5, it is quite clear that the pressure in the Venus atmosphere can hardly exceed 1 atm. by more than a factor of 2. No specific experiments with mixtures of carbon dioxide and other gases have as yet been carried out; but, judging from the experience with other gas mixtures not involving  $\text{CO}_2$ , there can be no question that a broadening similar to that observed in pure  $\text{CO}_2$  would also occur when  $\text{CO}_2$  is mixed with other gases. Therefore, we must conclude that the total pressure in the Venus atmosphere in the layers in which absorption takes place cannot be greater than 2 atm. The amount of  $\text{CO}_2$  found in the atmosphere of Venus on the basis of the known gravity on the surface yields a pressure of the order of  $\frac{1}{2}$  atm., so that it follows that  $\text{CO}_2$  is certainly one of the major constituents of the atmosphere.

The actual surface of Venus is obscured from us by a very heavy cloud layer as indicated by the high albedo of this planet. It appears certain that these clouds do not consist of water droplets since the amount of water vapour in the Venus atmosphere is smaller than 2 per cent. of what is present on the earth. At one time Wildt<sup>26</sup> suggested that these clouds are due to a solid polymer of formaldehyde ( $\text{H}_2\text{CO}$ ). But if this were correct there should be absorption bands of monomeric  $\text{H}_2\text{CO}$  in the ultra-violet. Such absorption bands are not observed.<sup>27</sup> According to Kuiper<sup>18</sup> the clouds are in all probability due to dust which is present in large quantities because of the lack of water.

Just as in the case of the atmosphere of the earth the emission spectrum of the atmosphere of Venus, if it could be observed, would throw additional light on the phenomena taking place in this atmosphere. One should, therefore, try to observe the spectrum of the dark side of Venus and see whether there is an analogue to both the night sky luminescence and to the aurorae in the earth's

<sup>26</sup>R. Wildt, *Astrophys. J.*, vol. 86, p. 321, 1937.

<sup>27</sup>R. Wildt, *Astrophys. J.*, vol. 92, p. 247, 1940; vol. 96, p. 312, 1942.

atmosphere. However, for any such investigation it would be necessary to use a coronagraph in which the occulting disk has the shape of the image of the bright part of Venus.

*D. The atmospheres of the major planets.*—It has been known for a long time that the spectra of the major planets exhibit a large number of characteristic absorption bands in the near infra-red, the red and even, in the case of Uranus and Neptune, in the green part of the spectrum. Most of these absorption bands were first identified by Wildt<sup>28</sup> as being due to methane and ammonia. Figure 11 (pl. III) shows spectra of Saturn, Uranus and Neptune and, for comparison, laboratory spectra of methane of similar dispersion obtained by Kuiper and Phillips with the large absorption tube at Yerkes Observatory. It is seen that the strong absorption bands of methane correspond exactly with the strong absorption bands in the planetary atmospheres (except of course the oxygen absorption due to the earth's atmosphere and various solar Fraunhofer lines). Even in the case of the weaker bands there is an exact correspondence. But it appears that the weaker bands are relatively stronger in the planetary spectra than in the laboratory spectra. This is obviously due to the different depth of penetration of sunlight for weak and strong absorption bands. In addition the effect of re-emission and scattering mentioned previously in the case of Venus must be considered. Using the weak bands for comparison it appears that there are about 500 m. atm. of methane in the atmospheres of Jupiter and Saturn and about 10 m. atm. of ammonia in Jupiter. The amounts of methane in Uranus and Neptune are much larger and may be of the order of 4000 m. atm. However, these are only very rough estimates.

Kuiper<sup>29</sup> made the important observation that the spectrum of one of Saturn's satellites, Titan, shows the main methane bands. This spectrum is included in figure 11. The methane bands are clearly visible. Titan is the only satellite in the solar system for which an atmosphere has been established in this way. On the other hand, the outermost planet, Pluto, whose spectrum

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<sup>28</sup>R. Wildt, *Naturwiss.*, vol. 20, p. 851, 1932.

<sup>29</sup>G. P. Kuiper, *Astrophys. J.*, vol. 100, p. 378, 1944.

was also investigated by Kuiper,<sup>29</sup> does not show any evidence of absorption bands, that is, no evidence of an atmosphere.

Figure 12 (pl. IV) shows a photographic infra-red absorption band of methane obtained in the laboratory under high resolution. In spite of the symmetry of the molecule the absorption band shows a very complicated fine structure. Therefore it will not be as easy as in the case of the CO<sub>2</sub> bands of Venus to determine the temperatures of the atmospheres of the major planets from the planetary spectra even if these were obtained with sufficient dispersion, which is not yet the case. No fine structure analysis of the methane absorption bands here under consideration has yet been made from laboratory data. Therefore the only way to decide which individual fine structure lines correspond to high rotational levels and which correspond to low rotational levels is to study the absorption spectrum of methane in the laboratory at very low temperature. Such an investigation is in preparation at Ottawa. Once this has been carried out and high dispersion spectra of the outer planets have been obtained, fairly reliable temperatures of the atmospheres of these planets should be obtainable.

Kuiper<sup>30</sup> recently has obtained the spectra of Uranus and Neptune under somewhat higher dispersion and has established a number of features which are not present in the spectra of Jupiter and Saturn and which apparently cannot be identified with any absorption bands of methane or ammonia observed in the laboratory. In figure 13 (pl. III) Kuiper's spectra of Uranus are reproduced. The additional features are one diffuse band at 8270A. and a series of five almost equidistant diffuse lines near 7500A.

In view of the large amount of methane and ammonia in the atmospheres of the major planets it appears probable and may be expected on the basis of any reasonable theory of the origin of the planetary atmospheres that large amounts of hydrogen are present in these atmospheres. But hydrogen, like nitrogen and other elementary molecules, does not exhibit an ordinary infra-red spectrum since it has no dipole moment; and all electronic transitions of H<sub>2</sub> that can occur in absorption lie in the far ultra-violet which is inaccessible in astronomical spectra. However, as I

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<sup>30</sup>G. P. Kuiper, *Astrophys. J.*, vol. 109, p. 540, 1949.

pointed out twelve years ago,<sup>31</sup> if the amounts of hydrogen present are sufficiently large there is a possibility that they may be detected by means of the *quadrupole rotation-vibration spectrum* of the hydrogen molecule. This spectrum arises because the hydrogen molecule has a quadrupole moment which changes during the vibration of the molecule. The intensity of absorption in this spectrum is so small that path lengths of the order of 20 km. atm. are required to give a noticeable absorption. It was only two years ago that two bands, 2-0 and 3-0, of this spectrum were observed in the laboratory by means of the large absorption tube at Yerkes Observatory.<sup>32</sup> Figure 14 (pl. IV) shows three of the lines of the 3-0 band. Table I gives the wave-lengths of the observed

TABLE I  
QUADRUPOLE ROTATION-VIBRATION LINES OF H<sub>2</sub>

Designation	$\lambda_{air}$ (A.)	Designation	$\lambda_{air}$ (A.)
2-0	$\left\{ \begin{array}{l} Q(1) \\ S(0) \\ S(1) \\ S(2) \end{array} \right.$	3-0	$\left\{ \begin{array}{l} Q(1) \\ S(0) \\ S(1) \\ S(2) \end{array} \right.$
	$\left. \begin{array}{l} 12379.90_4 \\ 11892.49_9 \\ 11618.97_8 \\ 11379.22_4 \end{array} \right\}$		$\left. \begin{array}{l} 8497.491 \\ 8272.686 \\ 8150.680 \\ 8046.438 \end{array} \right\}$

lines of both bands. As shown by the spectrogram of figure 14, which was taken in the second order of a 21-foot grating, the H<sub>2</sub> quadrupole lines are exceedingly sharp and therefore difficult to detect except under very high resolution. Such high resolution has not yet been applied to the spectra of the major planets; and under lower resolution no indication of the presence of these lines has been found. From the present evidence one can only say that the amount of hydrogen present is probably less than 200 km. atm.

It is a very striking fact that the unidentified feature at 8270A. observed by Kuiper in the spectra of Uranus and Neptune agrees within the accuracy of the measurements with the line designated

<sup>31</sup>G. Herzberg, *Astrophys. J.*, vol. 87, p. 428, 1938.

<sup>32</sup>G. Herzberg, *Nature*, vol. 163, p. 170, 1949; *Can. J. Research*, vol. A28, p. 144, 1950.

$S(0)$  of the 3-0  $H_2$  band in Table I. At very low temperatures the line  $S(0)$  would be the only one of the quadrupole lines that could occur because then only the rotational level  $J = 0$  would be present. On the other hand, the distinctly diffuse nature of the observed feature in Uranus and Neptune (it is about  $80 \text{ cm.}^{-1}$  wide) excludes the possibility that it is the quadrupole line. However, Welsh, Crawford and Locke<sup>33</sup> have observed a *pressure induced spectrum* of molecular hydrogen which occurs at precisely the wavelengths of the quadrupole spectrum. They have observed only the 1-0 vibrational transition of hydrogen. The absorption curve observed by them is shown in figure 15. The maxima corresponding to the individual rotational lines have a half-width of about  $250 \text{ cm.}^{-1}$ . More recently Crawford, Welsh, and MacDonald<sup>34</sup>

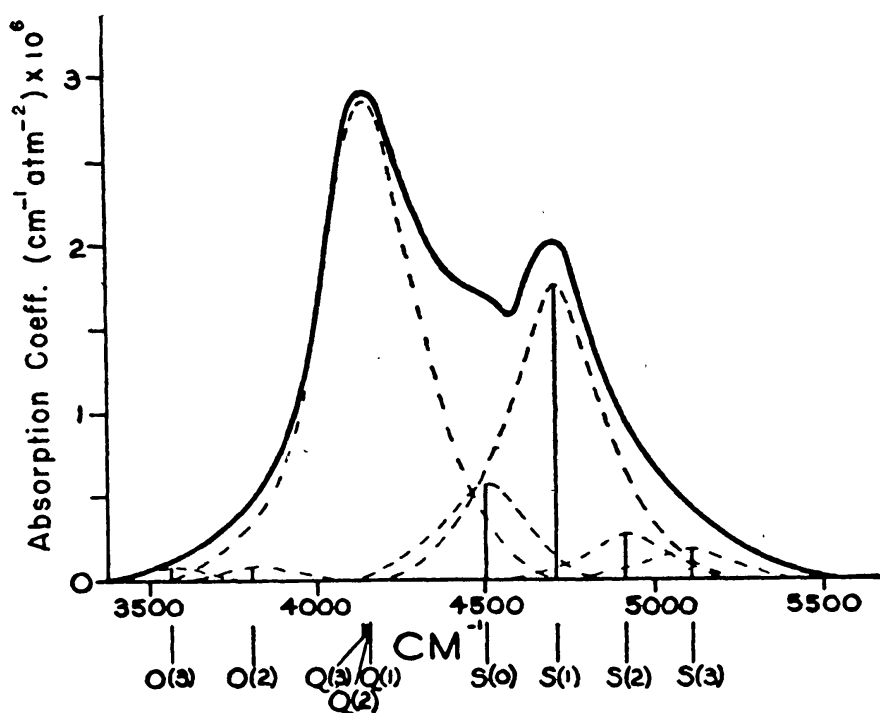


FIG. 15.—The 1-0 band of the pressure induced infra-red absorption spectrum of molecular hydrogen (after Welsh, Crawford and Locke<sup>33</sup>). The broken-line curves indicate the resolution of the absorption curve into component lines.

<sup>33</sup>H. L. Welsh, M. F. Crawford, and J. L. Locke, *Physic. Rev.*, vol. 76, p. 580, 1949.

<sup>34</sup>M. F. Crawford, H. L. Welsh, and J. C. F. MacDonald, *Physic. Rev.*, vol. 80, p. 469, 1950.

have established that the line width decreases considerably at lower temperatures. It therefore appears most probable that the unidentified feature at 8270A. in the spectrum of Uranus and Neptune is due to the  $S(0)$  line of the 3-0 band of the pressure induced rotation-vibration spectrum of hydrogen. The only other line of this band to be expected at very low temperatures is  $Q(0)$  at 8485A.; but it is hidden by a strong  $\text{CH}_4$  band.

Experiments are in preparation at Ottawa to observe these lines at liquid air temperature in hydrogen of high pressure with a long absorbing path. Crawford and Welsh have observed their spectrum at pressures as low as 10 atm. Although the intensity decreases with the square of the pressure it appears very probable that at a pressure of 2 atm. and a path length of 100 km. atm. the 3-0 band of the pressure induced spectrum will be observable. If this interpretation of the 8270A. feature turns out to be correct it would enable one not only to obtain an estimate of the pressure and the amount of molecular hydrogen in the atmospheres of the major planets but also to determine the temperature from the width of this absorption feature.

The fact that the 8270A. feature has not been observed in Jupiter and Saturn does not necessarily mean that there is less molecular hydrogen in these atmospheres but may be due to the much greater width of this feature at the higher temperatures prevalent on these planets.

If the abundance ratio of deuterium and hydrogen in the atmospheres of the major planets is of the same order as on the earth or greater and if the amounts of molecular hydrogen are as great as previously suggested it may be possible to detect deuterium by means of the ordinary infra-red spectrum of the HD molecule.<sup>31</sup> Recently this spectrum has been observed in the laboratory.<sup>35</sup> Table II gives the observed lines. Two of the unidentified features observed in the spectrum of Uranus and Neptune, at 7471 and 7524A., do actually coincide with the HD lines  $P(1)$  and  $P(2)$  of the 4-0 band while the corresponding  $R$  lines are overlapped by a strong  $\text{CH}_4$  band. However, since the remaining features found by Kuiper, at 7500 and 7546A., do not fit in, this agreement is probably fortuitous.

<sup>35</sup>G. Herzberg, *Nature*, vol. 166, p. 563, 1950.



According to the radiation laws the temperature  $T$  of an object at a distance  $r$  from the sun is  $T = k/\sqrt{r}$  where  $k$  is a constant. Determining  $k$  from the known mean temperature of the surface of the earth one obtains a temperature of  $-200^\circ$  and  $-220^\circ$  C. for the surface temperatures of Uranus and Neptune respectively. At these low temperatures the vapour pressure of methane would be far too low to yield the large amounts of methane indicated by the spectra of these planets. Either the methane is liquid or solid and the absorption bands that we observe belong to the liquid or

TABLE II  
ROTATION-VIBRATION LINES OF HD

Designation	$\lambda_{air}$ (A.)	Designation	$\lambda_{air}$ (A.)		
3-0	$P(3)$	9929.391	4-0	$P(2)$	7525.770
	$P(2)$	9821.967		$P(1)$	7467.490
	$P(1)$	9726.456		$R(0)$	7377.428
	$R(0)$	9570.843		$R(1)$	7345.652
	$R(1)$	9510.792		$R(2)$	7322.760
	$R(2)$	9462.576		$R(3)$	7308.764
	$R(3)$	9426.249			

solid, or the temperature must be appreciably higher than would follow from an application of the radiation laws. A decision will be possible as soon as high dispersion spectra of Uranus become available.

Figure 11 shows the spectrum of the rings of Saturn in addition to that of the disk. As was to be expected the spectrum of the rings does not show any evidence of the methane bands. Similarly one would have expected that in the infra-red the spectrum of the rings would be neutral. However, Kuiper observed with his infra-red spectrometer a sharp drop of intensity at  $1.5\mu$  just as for the polar caps of Mars. This observation indicates rather definitely that the particles making up Saturn's rings must either be covered with ice or consist of ice or, to put it more conservatively, they must be covered by a substance producing a cut-off at  $1.5\mu$  similar to that of ice.

*E. Conclusion.*—As a summary of the investigations of the chemical constitution of planetary atmospheres we list in Table III the abundances or limits to the abundances of the various gases according to Kuiper. In addition, as we have seen, a good deal of information about the physical conditions in the atmospheres of the planets has been obtained. Further progress in this field depends on the possibility of obtaining planetary spectra of higher dispersion and

TABLE III

COMPOSITIONS OF PLANETARY ATMOSPHERES AFTER KUIPER (Amounts in cm. atm.)

	N <sub>2</sub>	O <sub>2</sub>	CO	H <sub>2</sub> O	CO <sub>2</sub>	N <sub>2</sub> O	SO <sub>2</sub>	O <sub>3</sub>	NH <sub>3</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
Earth*	625000	168000		(1000)	220	0.8		0.3		1.7		
Mercury					<30							
Venus		<500	<100	<10	100000	<100			<4	<20	<3	<1
Mars		<250		< 5	440	<200	<0.003	<0.05	<2	<10	<2	<1
Jupiter									700	15000		
Saturn							<0.01	<0.1	200	35000		
Uranus							<0.01	<0.1		150000		
Neptune										250000		
Moon							<0.0003	<0.005				
Titan									<300	20000		

\*The abundances of the inert gases are A 7440, Ne 14, He 4.2, Kr 0.8 and Xe 0.06.

on the results of laboratory work of the type indicated in the preceding discussion. In particular, spectra of higher dispersion would make it possible to ascertain the presence and determine the abundance of rare isotopes. These abundances would be of interest in connection with various theories of the origin of the planetary atmospheres. It may be recalled that in certain stars the carbon isotope C<sup>13</sup> has an unusually high abundance and it would be interesting to ascertain whether or not such deviations from the terrestrial abundance occur also within the planetary system.

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