OH EMISSION BANDS IN THE SPECTRUM OF THE NIGHT SKY. II

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ABSTRACT

A detailed analysis has been made of the vibrational constants for the ground state of OH, combining the observations of the night-sky rotation-vibration bands with laboratory data for the ultraviolet electronic OH bands. Systematic deviations were observed from the band positions predicted by ω_e and $\omega_e x_e$ from the ultraviolet bands. The deviations show, however, that the assignment of terms in $\omega_e y_e$, $\omega_e z_e$, . . . , would not have any physical significance. The relative intensities have been determined for the night-sky bands from 9000 to 5500 A. The resultant values show systematic changes of band intensity within each Δv sequence. A brief investigation of the band intensities under conditions of radiative equilibrium for cases of resonance and thermal excitation shows that the OH bands are probably produced by a chemical resonance mechanism and, further, that collisional de-excitation effects may be present. The temperature in the OH stratum was found to be $260° \pm 5°$ K from the distribution of energy in the resolved P branches and from the ratio of intensity between the P, Q, and R branches.

(7, 2) 6870 A OH BAND

A spectrum obtained subsequent to the publication of the author's tables of wave lengths[1] has recorded the (7, 2) transition near 6870 A with sufficient intensity for measurement. Inasmuch as the P branch of this band is obscured by the O_2 telluric absorption band at 6900 A, the wave lengths for the P branches are uncertain. The relatively sharp R and Q branches, however, could be measured with good accuracy. The wave lengths and intensities for the (7, 2) OH band are shown in Table 1.

TABLE 1

SUPPLEMENTARY WAVE-LENGTH VALUES FOR THE (7, 2) OH BAND

$\lambda_{(air)}$ (A)	$\nu_{(vac)}$ (Cm^{-1})	I	Branch	$\lambda_{(air)}$ (A)	$\nu_{(vac)}$ (Cm^{-1})	I	Branch
6838.2	14619.7	6	R	6921	14(445)	1	P_2
6867.6	557.1	5	Q	6951	(382)	2	P_3
6893	(503)	1	P_1	6982	(318)	1	P_4

VIBRATIONAL CONSTANTS FOR OH

The vibrational constants for the $^2\Pi$ ground state of OH have been redetermined with more significance than was possible in the previous report[1] by the simultaneous use of high-dispersion data for the $v = 0$, 1, and 2 levels as obtained from the ultraviolet electronic OH bands. A further refinement was made by locating the origins of the infrared OH bands, using the rotational lines of the P branch wherever possible. For bands in which the doublet structure of the P branch was resolved, the mean position of the lines of equal J number was used. For the (7, 3) and (8, 3) bands, the strong component, $^2\Pi_{3/2}$, of the J-splitting was used. To avoid ambiguity, the origin of the P branch was taken as defined by the equation

$$\nu_0 = P_J(\nu) + (B_{v'} + B_{v''}) J - (B_{v'} - B_{v''}) J^2 . \tag{1}$$

It should be noted that this definition does not include a small constant term, $\Lambda(B_{v'} - B_{v''})$, which occurs in other definitions. Table 2 shows the wave-number positions of the

[1] A. B. Meinel, *Ap. J.*, 111, 555, 1950.

origins for the *OH* bands. The (4, 0) band origin was estimated from the P line, and the Q branch, using the interval (origin $- Q$), was determined from the (6, 2) and (5, 1) bands. This procedure was necessary because most of the P branch of the (4, 0) band is obscured by the strong A-band absorption at 7600 A. The origin of the weak (7, 2) band was similarly estimated from the observed Q and R branches.

TABLE 2

EXTRAPOLATED *OH*-BAND ORIGINS

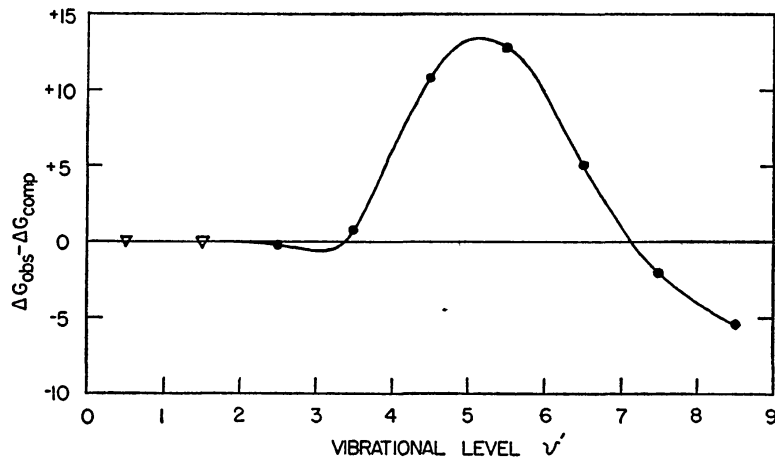| J	(7, 3) (Cm^{-1})	(6, 2) (Cm^{-1})	(5, 1) (Cm^{-1})	(9, 4) (Cm^{-1})	(4, 0) (Cm^{-1})	(8, 3) (Cm^{-1})	(7, 2) (Cm^{-1})
$\frac{3}{2}$	11325.9	11983.9	12633.6	12901.4	....	13733.6	....
$\frac{5}{2}$	26.2	83.6	33.4	898.2	13284.9 ($O-Q$)	33.7	(Q−R) 14564.9 ($O-Q$)
$\frac{7}{2}$	26.2	83.9	33.2	....	13285.8	35.4	64.4
$\frac{9}{2}$	....	83.8	34.4	....	....	35.2	....
Av....	11326.4	11983.8	12633.6	12899.8	13285.4	13734.5	14564.6
Comp.....	11297.2	11957.7	12622.2	12879.4	13284.7	13707.5	14535.6
O−C.....	29.2	24.1	11.4	20.4	0.7	27.0	29.0

FIG. 1.—This graph shows the difference between $\Delta G_{v+1/2}$ observed for the higher levels and the $\Delta G_{v+1/2}$ terms predicted by the constants of *OH* determined from the electronic bands.

Systematic differences are observed when the measured band positions are compared to the band positions predicted by the values of ω_e and $\omega_e x_e$ that are well defined for the lowest vibrational levels by the electronic bands. The differences must arise from neglecting higher-order terms, such as $\omega_e y_e$, $\omega_e z_e$, etc. Figure 1 shows the difference in wave numbers between $\Delta G_{v+1/2}$ observed for the higher vibrational levels and the $\Delta G_{v+1/2}$ terms predicted by the known constants for the lower levels. From the shape of this curve, it is obvious that many higher-order terms would be required to adequately represent the vibrational levels up to $v = 9$. The nature of the potential function for the $^2\Pi$ state above $v = 4$ is therefore such that specifying an $\omega_e y_e$, . . . , would not have any physical significance. It is therefore felt that the constants for the $^2\Pi$ state of *OH* given

by Herzberg[2] cannot be modified to fit the observations of the rotation-vibration OH bands. These constants are as follows:

$$\omega_e = 3735.21 , \qquad \omega_e x_e = 82.81 .$$

It should be noted that the relative wave numbers determined by the author have a probable error of $< \pm 0.5$ cm^{-1}, while the absolute wave numbers may have a probable error as large as ± 2 cm^{-1}. An absolute error, however, does not affect the shape of the curve except near the ends, since it is determined from the wave numbers of overlapping transitions.

RELATIVE OH-BAND INTENSITIES

The spectra obtained by the author were microphotometered and reduced to correct relative intensities as described in the previous paper.[1] These intensities have provided a basis for comparing the relative OH-band intensities. The intensity for the weak (7, 2) band was determined from a recent spectrogram covering the 7000 A region in more de- tail. The Q branch of the OH bands was selected for intercomparison, since the Q branch is quite narrow, resembling more nearly a monochromatic line. The intensities of the Q branches are tabulated relative to the intensity of the 6300 A [O I] line. Since the 6300 A emission is very variable, with respect to both diurnal and auroral effects, the inten- sity was defined by the plates obtained on two quiet nights. The diurnal effect was averaged by exposures extending from approximately 1.5 hours after sunset to 1.5 hours before sunrise. As a consequence, most of the twilight enhancement was avoided. The effective intensity of the 6300 A [O I] line is therefore not much greater than it would be during the middle of the night.

The author is greatly indebted to Dr. J. Dufay for permission to refer to unpublished spectra of the visible region of the night-sky spectrum for the study of the OH intensities. Publications by Dufay concerning the extension of the OH-band system into the visible region are forthcoming.[3] The spectra were obtained with a two-prism Cojan spectro- graph, having an aperture of 246 mm and a focal length of 160 mm. The resulting dis- persion varied from 300 A/mm at 6000 A to 700 A/mm at 8000 A. With this spectro- graph Dufay has been able to resolve the rotational structure of the P branches of the (8, 2), (9, 3), and (6, 1) OH bands, confirming the identification of these transitions by the author.[4]

The OH-band intensities relative to the 6300 A [O I] line have been estimated for the bands in the region 5000–6500 A from a microphotometer tracing of one of Dufay's spectra. Although the wave-length sensitivity calibration of the emulsion (Eastman 103a-E) was not given, it has been possible to estimate the band intensities by referring to the standard characteristics of this emulsion. The resulting values can therefore be used only to give rough values for the relative intensities. They are, however, of sufficient accuracy to enable an extension of the OH intensity scale.

The values of the Q-branch intensities of OH relative to the 6300 A [O I] line for all observed OH bands are given in Table 3. The intensities determined from bands observed by the author are given to three significant figures, except for the weak (7, 2) band at 6870 A. The intensities estimated from Dufay's spectra are given to two figures, al- though the second place is uncertain. The last column in Table 3 gives the relative num- bers of transitions per second for each band, according to the equation

$$\frac{I_{em}}{\nu^4} = (\text{Const.}) \, N_{v'} f_{v', \, v''} . \tag{2}$$

[2] G. Herzberg, *Molecular Spectra*, Vol. 1 (New York: D. Van Nostrand Co., 1950).

[3] J. Cabannes, J. Dufay, M. Dufay, *C.R.*, **230**, 1233, 1950.

[4] A. B. Meinel, *Ap. J.*, **111**, 433, 1950.

The intensities of the bands in each Δv sequence show a strong increase with larger v'' values. A discontinuity, however, exists between $v'' = 9$ and $v'' = 10$. The transitions originating from $v'' = 9$ give rise to the strongest bands in the $\Delta v = 5$ and $\Delta v = 6$ sequences. This situation also appears to apply to the $\Delta v = 4$ sequence, since the $(9, 5)$ band is in the 1μ region, where strong night-sky radiations have been detected.[1] On the other hand, no bands have been observed that originate from the level $v'' = 10$. This fact establishes an upper limit at

$$I(10, v'') < \tfrac{1}{20} I(9, v'').$$

(3)

TABLE 3

OH RELATIVE INTENSITY AND TRANSITION RATIOS

Transition (v', v'')	Intensity Ratio	Wave Number (Cm^{-1})	$[Nf(OH)Q]/$ $[Nf(O\,I)]$
$(7, 3)$	25.00	11323	96.4
$(6, 2)$	9.25	11977	28.5
$(5, 1)$	5.25	12625	13.1
$(4, 0)$	1.00	13278	2.0
$(9, 4)$	2.88	12890	6.61
$(8, 3)$	1.50	13724	2.68
$(7, 2)$	0.63	14560	0.91
$(6, 1)$	0.30	15380	0.34
$(5, 0)$	<0.10	16200	<0.10
$(9, 3)$	0.50	15970	0.50
$(8, 2)$	0.30	16980	0.23

OH-BAND INTENSITIES IN RADIATIVE EQUILIBRIUM

RESONANCE EXCITATION

For the case in which the primary excitation mechanism populates a single excited level, the equilibrium equations for all lower vibrational levels may be readily obtained. In the following discussion we shall assume that the primary mechanism gives rise to a population in level $v = 9$. The population N_9 will then be distributed among the lower levels, according to the transition probabilities $9 \rightarrow 8$, $9 \rightarrow 7$, $\ldots$, . In turn, the population that has appeared in level 8 will be redistributed among the still lower levels. The array of equations representing the resulting secular equilibrium conditions are as follows:

$$1 = N_9 f_{98} + N_9 f_{97} + N_9 f_{96} + N_9 f_{95} + \ldots + N_9 f_{90}$$

$$N_9 f_{98} = N_8 f_{87} + N_8 f_{86} + N_8 f_{85} + \ldots + N_8 f_{80}$$

$$N_9 f_{97} + N_8 f_{87} = N_7 f_{76} + N_7 f_{75} + \ldots + N_7 f_{70}$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

(4)

$$N_9 f_{91} + N_8 f_{81} + N_7 f_{71} + N_6 f_{61} + \ldots = N_1 f_{10}$$

$$N_9 f_{90} + N_8 f_{80} + N_7 f_{70} + N_6 f_{60} + \ldots + N_1 f_{10} = 1.$$

In order to evaluate the equilibrium expressions for each vibrational level, we must investigate the transition probabilities. In the case of rotation-vibration bands, the

transition probabilities have a strong dependence on $\Delta v = v' - v''$. If the vibration of the molecule were strictly harmonic, the only permitted transitions would be transitions with $\Delta v = 1$. On the other hand, for anharmonic vibration, transitions with $\Delta v = 2, 3, \ldots$, become possible; however, the transition probability decreases rapidly with increasing Δv. The observed vibrational levels show that the OH molecule has a very anharmonic potential function for the ground $^2\Pi$ state. Preliminary computations show, however, that the transition probability decreases by an order of more than 10 with a change from $\Delta v = n$ to $\Delta v = n + 1$. If we assume that the transition probabilities are related by an equation of the form

$$f_{v', \, v''-1} = \eta \, (v') \, f_{v', \, v''} \qquad\qquad (\eta < \tfrac{1}{10}) , \quad (5)$$

we can write

$$N_8 f_{87} = N_9 f_{98} \left\{ \frac{N_9 f_{98}}{N_9 f_{98} + \ldots + N_9 f_{91}} \right\} ,$$

$$N_8 f_{86} = N_9 f_{98} \left\{ \frac{N_9 f_{97}}{N_9 f_{98} + \ldots + N_9 f_{91}} \right\} . \qquad (6)$$

$$\vdots \qquad\qquad \vdots$$

Then the equilibrium of level 7 is given by

$$N_9 f_{97} + N_8 f_{87} = N_9 f_{97} + N_9 f_{98} \left[\frac{N_9 f_{98}}{1 - N_9 f_{90}} \right] . \qquad (7)$$

If we now use the above assumption for η, the total number of transitions per second into level 7 is given by

$$N_9 f_{97} + N_8 f_{87} = N_9 f_{98} \, [\eta + N_9 f_{98}] . \qquad (8)$$

Again using the definition of η and $N_9 f_{98} = 1 - \eta + \eta^2 - \ldots$, we can write

$$N_9 f_{97} + N_8 f_{87} = N_9 f_{98} \, [1 + \eta^2 - \ldots] , \qquad (9)$$

from which we see that the total number of transitions per second into level 7 is equal to the total number of transitions into level 8, with an error of the order of η^2. This procedure can be extended to show that the total number of transitions per second into all levels subsidiary to 9 are very nearly equal to the number between 9 and 8. As a consequence of the above equilibrium conditions, we also can show that

$$\frac{N_v f_{\Delta v = n}}{N_{v-1} f_{\Delta v = n}} = \left[\frac{\eta \, (v)}{\eta \, (v - 1)} \right]^{n-1} . \qquad (10)$$

Since the observed band intensity is related to Nf by equation (2), we can evaluate the ratios of Nf for the observed bands. These ratios are shown in Table 4. The mean ratio, weighted according to the reliability of the band intensities, is approximately 2.8. The fact that this ratio is the same for the $\Delta v = 4, 5$, and 6 sequences indicates that η must be small. There are two possible explanations for the observed ratio of 2.8 for the bands. First, the ratio could be explained by an exponential increase in the transition probabilities, with v'' of the form

$$f_{\Delta v = n} = (2.8)^{v''} \eta^{n-1} f_{\Delta v = 1} . \qquad (11)$$

A second explanation is that collisional de-excitation may be affecting the populations in each level.

The effective radiative transition probability when collisional de-excitation is present is

$$f_{v', v''}^{(1)} = \frac{1}{1 + \dfrac{c}{\sum_i f_{v, i}}} f_{v', v''};$$ (12)

hence the collisional term must be comparable to the sum of the transition probabilities in order to be of importance. If we look at the expression for the transition probability of a vibrational transition,

$$P_{nm} = \frac{1}{a} \int_{-\infty}^{\infty} R_n R_m (p - p_0 u) \, du,$$ (13)

TABLE 4
Observed *OH*-Band *Nf* Ratios

$\Delta v = 4$		$\Delta v = 5$		$\Delta v = 6$	
Transition	*Nf* Ratio	Transition	*Nf* Ratio	Transition	*Nf* Ratio
....	....	$\dfrac{(9, 4)}{(8, 3)}$	2.47	....	....
$\dfrac{(7, 3)}{(6, 2)}$	3.4	$\dfrac{(8, 3)}{(7, 2)}$	2.68	$\dfrac{(9, 3)}{(8, 2)}$	2.2
$\dfrac{(6, 2)}{(5, 1)}$	2.18	$\dfrac{(7, 2)}{(6, 1)}$	2.9	....	....
$\dfrac{(5, 1)}{(4, 0)}$	5.25	$\dfrac{(6, 1)}{(5, 0)}$	>3.4	....	....

we see that the transition probability is directly proportional to the coefficient of the change of the dipole moment with u, since $\int R_n R_m p \, du = 0$ from the orthogonality properties of the wave functions. Therefore, since the *OH* bands are entirely permitted, Σf cannot be small unless the $p_0 u$ term is small. The possibility of an experimental determination of the dipole moment of *OH* is being considered by Herzberg. On the other hand, if *OH* can combine readily with another constituent of the upper atmosphere, the reaction may produce a large collisional cross-section. Since $f_{\Delta v=1}$ is likely to be of the same order of magnitude for the higher vibrational levels, the collisional effect would be the same for each level, thereby producing the observed ratios. The question as to the origin of the observed ratio cannot be resolved, however, until accurate relative transition probabilities can be computed. This problem becomes very difficult for large values of v' and v''.

It is interesting to note that the *OH* bands arising from transitions to $v'' = 0$ are considerably weaker than anticipated from the ratio of 2.8. This effect may be due to reabsorption of the emissions by *OH* molecules in the lowest vibrational level.

THERMAL EXCITATION

If the mechanism producing the initial populations is due to "thermal excitation," not considering for the moment the observed break at $v = 9$, the ratio of the band

strengths will be different from the preceding case. The term "thermal excitation" does not imply thermodynamic equilibrium but indicates that the excitations are due to collisions with particles having a Maxwellian velocity distribution $f(E)$, characterized by a definite temperature. Since the relative concentration of OH must be small compared to the other constituents of the upper atmosphere, we can neglect the effect of the discrete energy states of OH on the velocity distribution of the particles. The rapid escape of energy in the form of radiation, however, will prevent the establishment of thermodynamic equilibrium populations in the excited states. Even when collisions are of sufficient frequency to produce noticeable collisional de-excitations, the nonconformance to thermodynamic equilibrium populations will hold because of the downward radiative cascade characteristic of rotation-vibration bands.

If we neglect collisional de-excitations on level v, then the total of all radiative transitions into v, plus the collisional excitations from the ground state into v, must equal the number of radiative transitions out of level v. The secular equations are then of the form

$$\sum_{i \geqslant v+1} N_j f_{j, \, v} + \int_{E_v}^{\infty} f(E) \, dE = \sum_{i \leqslant v} N_v f_{v, \, j}. \tag{14}$$

With the assumption that η is smaller than 0.1 we can extend the development of the preceding section to show that

$$N_v f_n = [\eta (v)]^{n-1} \sum_{j \geqslant v+1} \int_{E_j}^{\infty} f(E) \, dE, \tag{15}$$

where $\Delta v = n$. Then

$$\frac{N_v f_n}{N_{v-1} f_n} = \left[\frac{\eta (v)}{\eta (v-1)} \right]^{n-1} \sum_{j \geqslant v+1} \frac{\int_{E_j}^{\infty} f(E) \, dE}{\int_{E_{j-1}}^{\infty} f(E) \, dE} \tag{16}$$

or

$$\frac{N_v f_n}{N_{v-1} f_n} = \left[\frac{\eta (v)}{\eta (v-1)} \right]^{n-1} \left[1 + \frac{\int_{E_{v-1}}^{E_v} f(E) \, dE}{\sum_{j \geqslant v+1} \int_{E_j}^{\infty} f(E) \, dE} \right]^{-1} \leqslant \left[\frac{\eta (v)}{\eta (v-1)} \right]^{n-1}. \tag{17}$$

As a consequence, the total number of transitions and the intensity should increase for each successively lower vibrational level at the same rate, as new primary excitations are added. Such an excitation mechanism as thermal excitation would therefore favor the lower vibrational levels. The observed intensities, however, show a strong decrement in the opposite sense. This fact would mean that the effect of collisional de-excitation or the variation of the transition probability with v' would have to be increased over that required under the assumption that the primary excitation is predominantly to a single level. Moreover, thermal excitation would require a discontinuity in the transition probabilities between $v = 9$ and $v = 10$. It is therefore very likely that the observed OH bands are due to an energy resonance selectively populating the level $v = 9$.

TEMPERATURE OF THE OH STRATUM

The fact that the structure of the OH bands can be observed in detail offers an excellent opportunity to determine the temperature of the OH stratum. Three methods appear to be feasible. The first and most direct method is to use the rotational-line intensities of the $^2\Pi_{3/2}$ component of the resolved P branches. A second method is to utilize the

relative total intensities of the P, Q, and R branches. The third method is provided by the observation that the $^2\Pi_{1/2}$ component, which lies 138 cm^{-1} above the ground component $^2\Pi_{3/2}$, is considerably weaker. We shall examine each of these methods in detail.

P-BRANCH ROTATIONAL TEMPERATURE

The intensity of a rotational line is given by the expression

$$I_{\text{em}} = (\text{Const.})\, i\, (J')\, e^{-F(J')/kT} , \tag{18}$$

where $i(J')$ is the intensity factor and $F(J')$ is the rotational energy of the upper rotational level J'. For a $^2\Pi$ state in which there is no coupling between rotational and electronic motion (Hund's case a), the intensity factors $i(J)$ are given by

$$P(J') = \frac{(J'+1+\Omega)(J'+1-\Omega)}{J'+1} ,$$

$$Q(J') = \frac{(2J'+1)\,\Omega^2}{J'(J'+1)} , \qquad (\Omega = \tfrac{1}{2},\ \tfrac{3}{2}) \tag{19}$$

$$R(J') = \frac{(J'+\Omega)(J'-\Omega)}{J'} .$$

Since the coupling parameter A/B_v equals 7.3 for OH, the assumption of Hund's case a coupling is good only for very low J values. With the low temperature encountered in the upper atmosphere, however, the intensity drops off so rapidly that the lines of low J are the only lines of appreciable intensity.

The evaluation of $F(J') = B_v J'(J'+1)$ depends upon both the mode of excitation and the density. If the excitation is from the ground level by electronic excitation and if the density is very low, then no redistribution of energy will occur among the rotational levels. In this case $F(J')$ should be evaluated with the rotational constant for the ground state. This effect has been noted in laboratory studies of H_2 emission bands at very low pressures.[2] On the other hand, if the OH molecule is formed in the excited state or if there is a collisional redistribution among the rotational levels, then the rotational constant for the upper state $B_{v'}$ should be used. Since a is large for the $^2\Pi$ state of OH, the value of $B_{v'}$, where

$$B_v = B_e - a\,(v+\tfrac{1}{2}) \qquad\qquad (B_e = 18.86) ,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (a = 0.69) , \tag{20}$$

will change considerably with v. The effect will be to change the computed temperature by the factor

$$\frac{B_{v'}}{B_e - \tfrac{1}{2}a} . \tag{21}$$

In all the following computations the value of the rotational constant for the *upper state* is assumed, since a preliminary determination by Roach and Elvey[5] places the OH stratum at about 80 km, where the atmospheric density is still high. This assumption is shown to be correct when we consider the temperature indicated by the relative total intensities of the P, Q, and R branches for different transitions.

The curves obtained for the rotational-line intensities of the P branch of the (6, 2) transition for temperatures of 100°, 200°, and 300° K are shown in Figure 2. The observed line intensities are given in Table 5. When two entries are shown under a single date, the
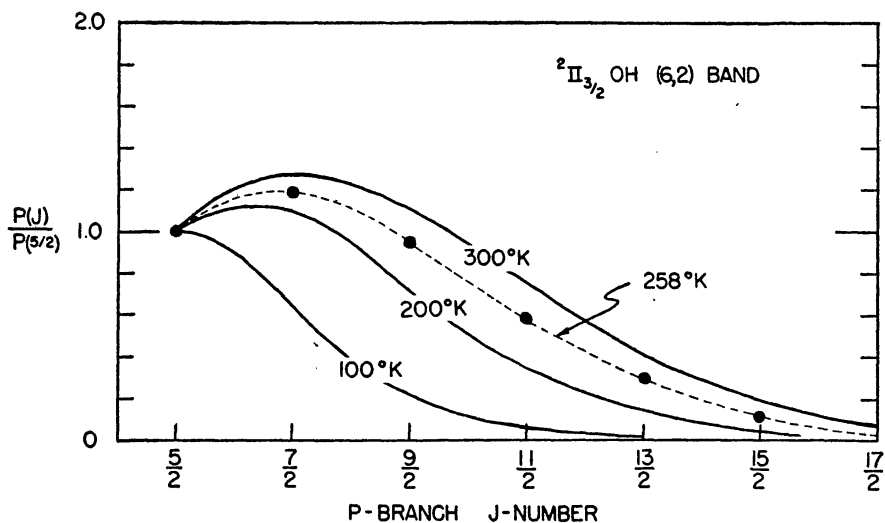
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[5] Private communication.

FIG. 2.—Rotational-line intensities for the resolved $^2\Pi$ P branch of the (6, 2) 8347 A band of OH as a function of the temperature.

TABLE 5

OBSERVED P-BRANCH ROTATIONAL-LINE INTENSITIES
(6, 2) 8347 A OH BAND

$P(J)$	Dec. 29	Dec. 29	Jan. 4	Jan. 6	Jan. 7	Jan. 7
$\frac{5}{2}$......	1.00	1.00	1.00	1.00	1.00	1.00
$\frac{7}{2}$......	1.29	1.26	1.07	1.18	1.15	1.18
$\frac{9}{2}$......	0.98	1.00	0.91	1.01	0.98	0.92
$1\frac{1}{2}$......	0.62	0.64	0.62	0.60	0.58	0.59
$1\frac{3}{2}$......	0.35	0.34	....	0.27	....	0.28
$1\frac{5}{2}$......				0.16		

(6, 2) 8347 A OH BAND (*Continued*)

$P(J)$	Jan. 10	Jan. 19	Jan. 26	Jan. 27	Av.	258° K
$\frac{5}{2}$......	1.00	1.00	1.00	1.00	1.00	1.00
$\frac{7}{2}$......	1.32	1.09	1.14	1.24	1.19	1.19
$\frac{9}{2}$......	0.89	0.81	0.95	0.97	0.94	0.95
$1\frac{1}{2}$......	0.49	0.54	0.61	0.62	0.59	0.59
$1\frac{3}{2}$......	0.16	0.32	0.30	0.35	0.30	0.30
$1\frac{5}{2}$......	0.11	0.19	0.12	....	0.14	0.12

(5, 1) 7918 A OH BAND

$P(J)$	Jan. 6	Jan. 10	Jan. 19	Jan. 26	Av.	265° K
$\frac{5}{2}$......	1.00	1.00	1.00	1.00	1.00	1.00
$\frac{7}{2}$......	1.13	1.20	1.28	1.14	1.19	1.19
$\frac{9}{2}$......	1.01	1.00	0.86	0.96	0.96	0.93
$1\frac{1}{2}$......	0.74	0.35	0.71	0.63	0.60	0.57
$1\frac{3}{2}$......	0.44	0.15	....	....	0.30	0.28

measurements are for different regions of the sky but are recorded on the same plate. The spectra obtained on January 19, 26, and 27, 1950, also showed auroral emissions at 8446 and 7774 A; however, no effect is apparent with respect to either the intensities or the rotational temperature of the *OH* bands. The average values observed for the (6, 2) band, plotted in Figure 2, correspond to a temperature of 258° ± 3° K, while for the (5, 1) band the temperature is 265° ± 5° K. The best mean value can be taken as 260° K.

RELATIVE BRANCH INTENSITY TEMPERATURE

We may obtain a second estimate of the rotational temperature by comparing the total intensities of the *P*, *Q*, and *R* branches. This method, however, is more sensitive than the *P*-branch method to changes in the molecular coupling. The theoretical values of the ratio P/Q and R/Q are plotted in Figure 3 for pure case *a* coupling and as a func-
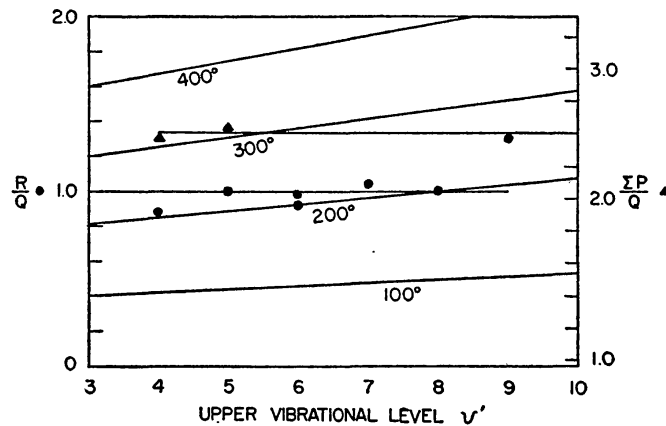

FIG. 3.— Branch intensity ratios for the *OH* bands as a function of the temperature

tion of the upper vibrational level of the transition. The circles represent observed ratios of R/Q, which can be readily determined, since both branches have the same general appearance. The triangles represent observed ratios of P/Q. The points for R/Q appear to fall systematically lower than those for P/Q. This effect can be attributed to the fact that the coupling is not strictly case *a*. The mean value of the temperature agrees well, however, with the value of 260° K determined from the rotational-line intensities within the *P* branch.

The assumption that the rotational constant should be taken as the B_v value for the upper state instead of $B_0 = B_e - \frac{1}{2}a$ is shown to be correct in Figure 3. Instead of being constant, the points for the ratio R/Q for transitions having different upper vibrational levels have the same slope as the theoretical curve.

DOUBLET RATIO TEMPERATURE

The fact that the $^2\Pi_{1/2}$ state, which lies 138 cm^{-1} higher than the ground state $^2\Pi_{3/2}$, is considerably weaker would indicate a vibrational temperature. The observed ratio of the $^2\Pi$ components of the (6, 2) and (5, 1) transitions is

$$\frac{^2\Pi_{1/2}}{^2\Pi_{3/2}} = 0.317 = e^{Ahc/kT} = e^{A/0.695\,T}, \tag{22}$$

where $A = 138$ cm^{-1} for the doublet splitting. This ratio corresponds to a temperature of 172° ± 10° K.

The assumption that this value is a valid temperature presupposes that the excita-

tion mechanism does not redistribute the excitation energy between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. This supposition would be strictly correct if the excitation were radiative; however, the exciting emission would be at 3820 A. No strong emissions are present in this well-observed region. The possibility that the doublet ratio does indicate a temperature is not definitely excluded. The more likely explanation, however, is that the primary excitation energy is sufficient to populate the lower $^2\Pi_{3/2}$ component of the ninth vibrational level but is insufficient to populate strongly the higher $^2\Pi_{1/2}$ component. If, on the other hand, the energy spectrum of the excitation were due to a temperature and if the mean excitation energy exactly coincided with the $^2\Pi_{3/2}$ component of the level $v = 9$, then the ratio would indicate a correct temperature. Conversely, if this mechanism holds, we can reverse the reasoning to locate the mean energy of the primary excitation. If we assume a Boltzmann distribution of energies corresponding to a temperature of 260° K, the maximum of the excitation energy would be at 3.242 e.v.

OH STRATUM TEMPERATURE

In view of the preceding discussion, the doublet ratio cannot be seriously considered in establishing a temperature without exact knowledge of the excitation mechanism. The temperature of the OH stratum will therefore be taken as given by the relative branch intensities and the P-branch rotational-line intensities as

$$T (OH) = 260° \pm 5°K .$$

This value is rather high, considering that the author has obtained a temperature considerably less than 200° K for the O_2 band at 8640 A, which also arises from a stratum below 100 km.[6]

It is interesting to speculate on temperature determinations in the upper atmosphere in view of the discovery of hydride emission bands. Since the OH bands are extremely intense and since the transition probability is very small for the observed transitions, the number of OH molecules may be sufficient to contribute significantly to the composition of the upper atmosphere. Regardless of the origin of the OH, the dissociation equilibrium will favor atomic hydrogen in the extreme upper atmosphere. This hydrogen, however, would be very difficult to detect spectrographically, since the excited states are very high. As a consequence, no efficient excitation mechanism would be available from the low-energy sources present in the upper atmosphere. The presence of hydrogen, even in relatively small proportions, will very effectively lower the mean molecular weight of the upper atmosphere. It is well known that temperature determinations based on physical phenomena that require a knowledge of the molecular weight invariably give temperatures higher than are observed by spectroscopic methods. A solution to this long-standing discrepancy is therefore suggested by the presence of very intense hydride emission bands. In order to obtain quantitative data, however, information is needed with respect to the excitation mechanism and the absolute transition probabilities of the OH bands.

[6] J. Kaplan, *Phys. Rev.*, **78**, 82, 1950.