A New Band in the Spectrum of the OH Molecule

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Although the ultraviolet "water vapor" bands were among the earliest molecular spectra to undergo extensive investigation, heretofore only six bands have been reported. These involve transitions between the (0, 1, 2) vibrational levels of an excited $^2\Sigma$ state and the (0, 1) vibrational levels of the normal $^2\Pi$ state. With improved conditions for exciting the spectrum we have obtained 91 lines, heretofore unreported, in the neighborhood of the (0′, 1″) band at λ3428. 44 of these lines prove to be extensions of λ3428; 54 lines (including 11 in common with λ3428) form a new band with a head at λ3484; and 4 lines remain unidentified. Analysis of the new band identifies it as the (1′, 2″) band of the water vapor system. Rotational constants for the normal $^2\Pi$ electronic state of OH are: $B_e''=19.025$, $\alpha''=0.724$, $D_e''=-1.97\times10^{-3}$, $\beta''=5.0\times10^{-5}$, and $r_e''=0.964\times10^{-8}$ cm. Vibrational constants are: $\omega_e''=3734.9$ and $x_e''\omega_e''=82.6$. Rotational and vibrational constants for the excited $^2\Sigma$ state are also evaluated and are tabulated.

INTRODUCTION

THE well-known "water vapor" bands which are produced in the combustion of substances rich in hydrogen, and in an electrical discharge through water vapor, are among the earliest molecular spectra recorded in the literature,[2] and have been the subject of numerous subsequent investigations.[3] At one time assigned to H_2O, then to O_2,[4] the bands were eventually identified with the neutral OH molecule.[5] The bands, of which those heretofore reported are listed in Table I, belong to a ($^2\Sigma\rightarrow{}^2\Pi$) transition and occur in the ultraviolet region of the spectrum. The $^2\Pi$ term has been identified with the normal state of the molecule. Each band possesses six principal branches (double P, double Q, and double R branches). Intense exposures of the strong λ3064 band shows additional satellite branches, a portion of which also make their appearance on long exposures of the weaker bands.[6]

TABLE I. *Wave-lengths (international Angstroms) of the band heads of the OH system, with the vibrational assignments.*

	$v''=0$	1
$v'=0$	3064	3428
1	2811	3122
2	2608	2875

The difficulty of obtaining satisfactory photographs of the weaker bands, or of the weaker lines of the strong bands, is greatly enhanced by the presence of a very considerable continuous background, presumably due to hydrogen, which increases toward the red end of the spectrum. Probably for this reason, as well as the fact that the bands removed from the (0, 0) member at λ3064 are progressively more difficult to excite, only the bands at λ3064 and at λ2811 have been subject to any very thorough analysis, and even for these bands the analyses are incomplete with respect to the classification of numerous weak lines which appear throughout the bands.

[1] Dawson, Du Pont Fellow in Chemistry.

[2] Liveing and Dewar, Proc. Roy. Soc. **A30**, 498, 580 (1880); ibid. **A33**, 274 (1882); Phil. Trans. **129**, 271 (1880), cf. also Deslandres, Ann. Chim. Phys. **14**, 257 (1888); Comptes Rendus **100**, 854 (1888).

[3] Among the more notable of these are: Grebe and Holtz, Ann. d. Physik **39**, 1243 (1913); Heurlinger, *Dissertation*, Lund (1918); Fortrat, J. Phys. Radium **5**, 20 (1924); Watson, Astrophys. J. **60**, 145 (1924); Dieke, Proc. Acad. Sci. Amsterdam **28**, 174 (1925); Jack, Proc. Roy. Soc. **A115**, 373 (1927) and, ibid. **A118**, 647 (1928); Tanaka, Proc. Roy. Soc. **A108**, 594 (1925); Kemble, Phys. Rev. **30**, 387 (1927); Hill and Van Vleck, Phys. Rev. **32**, 250 (1928); Mulliken, Phys. Rev. **32**, 388 (1928); Almy, Phys. Rev. **35**, 1495 (1930); and Almy and Rahrer, Phys. Rev. **38**, 1816 (1931).

[4] Steubing, Ann. d. Physik **33**, 553 (1910) and, ibid. **39**, 1408 (1912); Reiss, Zeits. f. physik. Chemie **88**, 513 (1914). See also Fortrat, reference 3.

[5] Cf. Watson, and Mulliken, reference 3.

[6] For a more complete résumé of the band structure and its interpretation, cf. Mulliken, reference 3, who has admirably summarized our present knowledge of the spectrum.

Several months ago, in the effort to detect isotopes of hydrogen[7] we made some intense exposures of λ3064 and the adjacent regions toward the red. Although unsuccessful in our immediate objective we succeeded in greatly reducing the continuous background and obtained plates which showed, throughout the spectrum, many score lines not hitherto recorded in the literature. We have recently measured the plates in the neighborhood of the (0′, 1″) band at λ3428. In addition to extending the principal branches of λ3428 to the extent of some 44 lines we have found 54 new lines (including 11 in common with λ3428) which form a new band with a band head at λ3484. The present paper presents the details of these measurements and of the assignments, which identify the band at λ3484 as a new band in the OH system.

Experimental Procedure

The arrangements for exciting the spectrum were similar, in the main, to whose employed by Watson and by Jack. The water vapor flowed through a heavy walled Pyrex capillary through which the discharge passed. The capillary was viewed end-on through a quartz window.

The continuous background which appeared in long exposures gave us some concern. By introducing a slow stream of oxygen through a capillary which extended beneath the surface of the distilled water we were successful in greatly reducing this troublesome factor, without appreciable change in the intensity of the OH bands.

The bands were photographed with a Hilger E 185 prism spectrograph, which gives a dispersion of about 4.4A per mm in the region of λ3500, and were taken on Eastman "Speedway" plates. Although one exposure was allowed to run for 40 hours we found that, because of the intensification of the background, no new features appeared after about the eighth or tenth hour. The use of Eastman's "Opaque" as a plate backing reduced halation, which was a factor in the long exposures.

Measurements of the Bands λλ3428 and 3484

Tables II, III and IV contain *all* lines which appeared on our plates between λ3429 and λ3570. Although we obtained several plates which show the new lines recorded in these tables, the measurements are all taken from a single plate, chosen because of its superior focus in the neighborhood of λ3500. This plate was a five hour exposure with a slit width of 0.001 mm. The measurements were made with a Gaertner comparator and each value recorded in the tables is an average of at least four independent readings. The values of the measurements for individual lines were ordinarily reproducible to within 0.05A (= 0.4 cm^{-1}) but, in extreme cases, our measurements showed deviations, among themselves of twice this amount. Our plates were calibrated in terms of standard iron lines which were photographed both before and after the OH exposures.[8] Except where overlapping occurs, we believe that the measurements of individual lines are probably good to within about 0.05A.

Intensities are based on an empirical scale (0–10) as they appear to the eye. The letter *d* following the intensity rating indicates that the line in question has the appearance of an unresolved doublet; *h* indicates that the line appeared hazy; *t* indicates a line that is assigned in two places while *q* marks a line used in more than two assignments. In Table II lines printed in bold faced type have previously been reported by Jack although the assignments of wave-lengths are our own. Lines marked with an asterisk (*) are substitutes for assignments made by Jack. These substitutions are justified either by interpola-

[7] Since then, discovered by Urey, Brickwedde and Murphy, Phys. Rev. **39**, 164 (1932); ibid. **40**, 1 (1932).

[8] Because of a slight shift in the relative positions of the iron standards, which was found subsequently to have been due to a movement in the plate holder during the adjustments between exposures, the measurements on the original plate were employed only to give line *differences* among the lines of the OH bands. The absolute wavelengths were determined with the aid of a later plate, in which the shifts due to plate holder adjustments were avoided. On this plate we compared the positions of fifteen of the sharpest lines of λ3428 with adjacent iron lines. The measurements on the original plate were then related to these fifteen lines as secondary standards. Our measurements of the 75 lines in λ3428 which had previously been measured by Jack averaged 0.05A higher (about 0.4 cm^{-1} lower) than his but the difference appears to be real, and not related to any source of error in our calibration, since our measurements of 200 lines in λ3064, on the same plate, agreed to within an average 0.01A of Grebe and Holtz' values for the same lines.

TABLE II. λ3428 *band.*

K	λ air	Intensity	ν vac.	λ air	Intensity	ν vac.	K	λ air	Intensity	ν vac.	λ air	Intensity	ν vac.
		R_1			R_2				Q_1			Q_2	
1	3450.44	7 *t*	28973.5	3465.66	1	28846.3	11	3477.30	4	28749.7	3481.86	4	28712.0
2	3447.95	7	28994.5	3460.52	2 *t*	28889.6	12	3480.15	4	28726.2	3484.45	5 *q*	28690.7
3	3445.34	9 *dq*	29016.5	3456.00	3	28926.9	13	3483.21	3	28700.9	3487.28	2	28667.4
4	3442.89	9	29037.1	3451.98	6	28960.6	14	3486.59	2	28673.1	3490.49	5 *t*	28641.1
5	3440.43	5	29057.9	3448.41	7	28990.7	15	3490.12	5 *q*	28644.1	3493.94	7 *dq*	28612.8
6	3438.14	5	29077.2	3445.34	9 *dq*	29016.5	16	3493.94	7 *dq*	28612.8	3497.60	8 *dq*	28582.1
7	3436.07	10 *q*	29094.7	3442.41	9 *q*	29041.2	17	3498.15	5	28578.4	3501.62	3	28550.1
8	3433.86	9 *dq*	29113.5	3439.93	3	29062.1	18	3502.72	3	28541.1	3506.04	5	28514.1
9	3432.38	10 *dt*	29126.0	3437.83	3	29079.8	19	3507.53	5 *t*	28502.0	3510.70	8 *t*	28476.2
10	3431.08	5	29137.0	3436.05	10 *q*	29094.7	20	3512.66	3	28460.4	3515.79	7 *t*	28435.0
11	3429.76	4	29148.3	3434.49	3	29108.1	21	3518.13	3	28416.1	3521.14	4 *t*	28391.8
12	3428.88	5	29155.7	3433.37	2	29117.6	22	3524.03	4 *q*	28368.6	3526.97	1	28344.8
13	3428.38	8 *t*	29160.0	3432.38	10 *dt*	29126.0	23	3530.26	2 *t*	28318.4	3533.18	1	28295.0
14	3428.02	9 *t*	29163.0	3431.91	10 *dq*	29130.0	24	3536.95	1	28264.9	3539.76	1	28242.4
15	3428.02	9 *t*	29163.0	3431.91	10 *dq*	29130.0*	25	3544.04	2 *t*	28208.3	3546.91	0	28185.5
16	3428.38	8 *t*	29160.0	3431.91	10 *dq*	29130.0	26	3551.55	0	28148.7	3554.42	1 *t*	28126.0
17	3429.18	5	29153.2	3432.93	2	29121.3	27	3559.89	0 *hq*	28082.8	3562.34	0	28063.5
18	3430.31	5	29143.6	3433.86	9 *dq*	29113.5	28	3567.78	0 *t*	28020.7			
19	3431.91	10 *dq*	29130.0	3435.43	5	29100.2							
20	3433.86	9 *dq*	29113.5	3437.30	5	29084.3			P_1			P_2	
21	3436.07	10 *q*	29094.7	3439.60	3	29064.9	1	3462.56	7	28872.2			
22	3439.02	3	29069.8	3442.41	9 *q*	29041.2	2	3468.15	10 *t*	28825.6	3480.89	6	28720.0
23	3442.41	9 *q*	29041.2	3445.34	9 *dq*	29016.5	3	3473.77	6 *t*	28778.9	3484.45	5 *q*	28690.7
24	3446.09	2	29010.2	3449.42	2	28982.2	4	3479.27	5	28733.4	3488.44	8 *dq*	28657.9
25	3450.44	7 *t*	28973.5	3453.73	1	28945.9	5	3484.88	5 *t*	28687.2	3493.01	8 *t*	28620.4
26	3455.24	1	28933.3	3458.53	10 *t*	28905.8	6	3490.49	5 *t*	28641.1	3497.60	8 *dq*	28582.1
27	3460.52	2 *t*	28889.6	3464.00	0	28860.2	7	3496.37	7 *t*	28592.9	3502.97	3	28539.1*
							8	3502.32	1	28544.4	3508.40	5 *t*	28494.9
		Q_1			Q_2		9	3508.40	5 *t*	28494.9	3514.02	6 *t*	28449.3
1	3458.53	10 *t*	28905.8	3473.77	6 *t*	28778.9*	10	3514.65	1	28444.2	3519.90	4	28401.8
2	3460.06	10	28893.0	3472.61	8 *t*	28788.5	11	3521.14	4 *t*	28391.8	3526.11	0	28351.7*
3	3461.54	10	28880.6	3472.15	10 *q*	28792.3	12	3527.54	1 *t*	28340.3	3532.51	1	28300.4
4	3463.06	9	28868.0	3472.15	10 *q*	28792.3	13	3534.51	1	28284.4	3538.99	0	28248.6
5	3464.59	10	28855.2	3472.61	8 *t*	28788.5	14	3541.74	1 *t*	28226.7*	3545.86	2 *d*	28193.9*
6	3466.31	8	28840.9	3473.33	5	28782.5	15	3548.93	0 *dt*	28169.5	3552.97	0	28137.5
7	3468.15	10 *t*	28825.6	3474.42	3	28773.5	16	3556.22	0	28111.8	3560.52	0 *t*	28077.8
8	3470.14	7	28809.0	3475.89	5	28761.3	17	3564.04	0 *t*	28050.1	3567.78	0 *t*	28020.7
9	3472.15	10 *q*	28792.3	3477.62	4	28747.0*							
10	3474.73	3	28770.9	3479.55	3	28731.1*						PQ_{12}	
							1				3477.89	1	28744.8*

tions between the lines of the respective branches or by the combination relations.

Table IV contains the only lines, in the region included within the tables, which remain unassigned. It is possible that these lines belong to an unidentified (2′, 3″) band. Indeed, they correspond quite well with the positions of lines calculated for this band. A number of lines beyond λ3570 also correspond to calculated (2′, 3″) lines or to extensions of either λ3428 or λ3484. However, the lines are extremely weak and the number observed are insufficient to let us be certain as to their identification.

APPLICATION OF THE COMBINATION PRINCIPLE TO λ3484, AND THE ASSIGNMENT OF VIBRATIONAL QUANTUM NUMBERS

It is apparent from Fig. 1, which is a Fortrat diagram of the line assignments recorded in Tables II and III, that λ3484 possesses the same general structure as does λ3428, which is typical of other members of this system. Identification of the new band[9] is made complete by application of the combination principle. The relationships between the respective lines of the bands and the corresponding term values of the molecule are

[9] Shaw (Phys. Rev. **37**, 1548 (1931)) reported the discovery of a group of lines which had the appearance of a band head at about λ3525 and suggested that these might belong to OH. No details were published. It is probable that Shaw observed the Q_2 head at λ3523. The fact that Shaw states that he observed no new features in λ3428 precludes the possibility of his observing the true band head at λ3484. Because of their greater intensity the *Q* branches would make their appearance first.

TABLE III. λ*3484 band.*

K	λ air	Intensity	ν vac.	λ air	Intensity	ν vac.
		R_1			R_2	
1	3501.12	0	28554.1	3516.71	0	28427.6
2	3498.73	2	28573.6	3512.33	3 *t*	28463.0
3	3496.37	7 *t*	28592.9	3507.53	5 *t*	28502.0
4	3493.94	7 *dq*	28612.8	3503.70	1	28533.1
5	3492.10	1	28627.9	3500.44	1	28559.7
6	3490.12	5 *q*	28644.1	3495.60	8 *dq*	28582.1
7	3488.44	8 *dq*	28657.9	3495.09	2	28603.4
8	3487.03	0	28669.5	3493.01	8 *t*	28620.4
9	3485.58	1	28681.4	3491.32	0	28634.3
10	3484.45	5 *q*	28690.7	3490.12	5 *q*	28644.1
11	3483.80	2 *q*	28696.1	3489.06	1 *t*	28652.8
12	3483.80	2 *q*	28696.1	3488.44	8 *dq*	28657.9
13	3483.80	2 *q*	28696.1	3488.44	8 *dq*	28657.9
14	3484.08	0	28693.8	3488.44	8 *dq*	28657.9
15	3484.88	5 *t*	28687.2	3489.06	1 *t*	28652.8
16	3486.03	0	28677.7	3490.12	5 *q*	28644.1
17				3491.59	0	28632.1
		Q_1			Q_2	
1	3509.09	2	28489.3	3527.77	2 *t*	28362.6
2	3510.70	8 *t*	28476.2	3524.03	4 *q*	28368.6
3	3512.33	3 *t*	28463.0	3523.42	4 *t*	28373.5
4	3514.02	6 *t*	28449.3	3523.42	4 *t*	28373.5
5	3515.79	7 *t*	28435.0	3524.03	4 *q*	28368.6
6	3517.73	3	28419.3	3525.07	2	28360.1
7	3519.90	4	28401.8	3526.56	1	28348.1

K	λ air	Intensity	ν vac.	λ air	Intensity	ν vac.
		Q_1			Q_2	
8	3522.14	3	28383.8	3528.11	1	28335.7
9	3524.77	2 *t*	28362.6	3530.26	2 *t*	38318.4
10	3527.54	1 *t*	28340.3	3532.70	1	28298.9
11	3530.55	1	28316.1	3535.37	2 *q*	28277.5
12	3533.87	1	28289.5	3538.45	1	28252.9
13	3537.53	1	28260.2	3541.74	1 *t*	28226.7
14	3541.38	2 *t*	28229.5	3545.61	2 *dt*	28195.9
15	3545.61	2 *dt*	28195.9	3549.62	0	28164.0
16	3550.30	0	28158.6	3554.06	1	28128.8
17	3555.19	0	28119.9	3558.90	0	28090.6
18	3560.52	0 *t*	28077.8	3564.04	0 *t*	28050.1
19	3566.23	0	28032.9	3569.68	0	28005.8
		P_1			P_2	
1	3513.02	0	28457.4			
2	3518.56	1	28412.6	3531.81	1	28306.0
3	3524.03	4 *q*	28368.6	3535.37	2 *q*	28277.5
4	3529.89	0	28321.4	3539.49	1	28244.6
5	3536.38	2 *q*	28277.5	3544.04	2 *t*	28208.3
6	3541.38	2 *t*	28229.5	3548.93	0 *dt*	28169.5
7	3547.44	0	28181.3	3554.42	1 *t*	28126.0
8	3553.68	0	28131.8	3559.89	0 *hq*	28082.8
9	3559.89	0 *hq*	28082.8	3566.23	0 *t*	28032.9
10	3566.62	0	28029.8			
					$P_{Q_{12}}$	
1				3528.84	1	28329.8

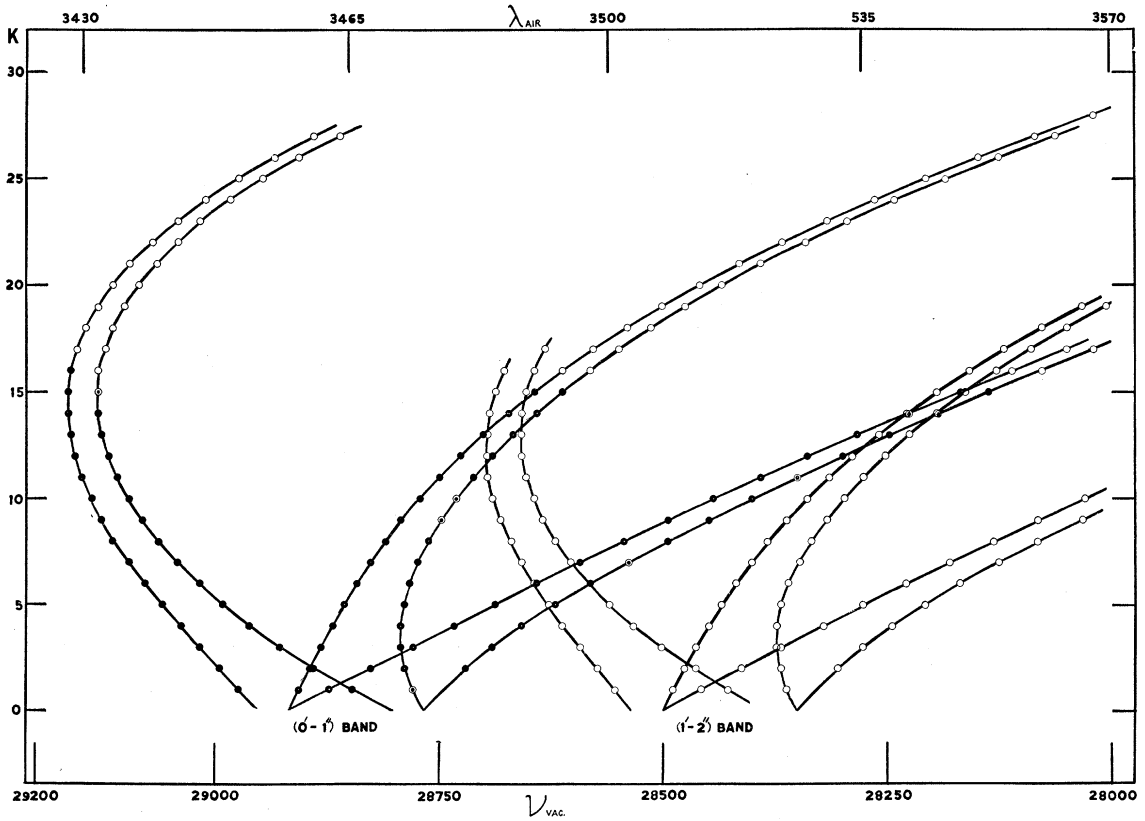

FIG. 1. Fortrat diagrams for λλ3428 and 3484. Black dots, lines identified by Jack; circle-dots, reassignments; circles, new lines.

given by the following set of equations:[10]

$$P_1(K)=F_1'(K-1)-F_{1B}''(K), \quad (1a)$$
$$P_2(K)=F_2'(K-1)-F_{2B}''(K), \quad (1b)$$
$$R_1(K)=F_1'(K+1)-F_{1B}''(K), \quad (1c)$$
$$R_2(K)=F_2'(K+1)-F_{2B}''(K), \quad (1d)$$
$$Q_1(K)=F_1'(K)-F_{1A}''(K), \quad (1e)$$
$$Q_2(K)=F_2'(K)-F_{2B}''(K). \quad (1f)$$

From the first four of these equations,

$$R_1(K)-P_1(K)=F_1'(K+1)-F_1'(K-1)=\Delta_2F_1'(K), \quad (2a)$$
$$R_2(K)-P_2(K)=F_2'(K+1)-F_2'(K-1)=\Delta_2F_2'(K), \quad (2b)$$

and from the last four,

$$R_1(K)-Q_1(K)=F_1'(K+1)-F_1'(K)+F_{1A}''(K)-F_{1B}''(K)=\Delta_1F_1'(K+\tfrac{1}{2})+\delta_1(K), \quad (3a)$$
$$R_2(K)-Q_2(K)=F_2'(K+1)-F_2'(K)+F_{2A}''(K)-F_{2B}''(K)=\Delta_1F_2'(K+\tfrac{1}{2})+\delta_2(K), \quad (3b)$$

where the δ_1 and δ_2 terms represent the intervals between the A and B components which arise from Λ type doubling and are set equal to $F_A''(K)-F_B''(K)$.

Table V gives values of Δ_2F_{12}' computed for λ3484 as well as for the six bands identified previously. Each of these figures is the *average* of the Δ_2F' values calculated by Eqs. (2a) and (2b), but differs only slightly from either Δ_2F_1' or Δ_2F_2' since the difference in these quantities is of the order of magnitude of only 0.2 cm^{-1}. From this table it is apparent that the *upper* vibrational level of λ3484 is identical with that of λ2811 and of λ3122 and so is the $(v'=1)$ level. This assignment, together with the individual line assignments in the Q and R branches, is confirmed by the $(R-Q)$ combinations. These were computed for λ3484, for λ2811 and for λ3122, by the use of Eqs. (3a) and (3b) and are shown in Table VI where values of Δ_1F_1' and of Δ_1F_2' are tabulated separately.

TABLE IV. *Unassigned lines in the region between λ3429 and λ3570.*

λ air	Intensity	ν vac.
3561.17	0	28072.7
3564.78	0	28044.3
3565.24	0	28040.7
3568.73	0	28013.2

[10] For the typical energy level diagram and for the meanings of symbols cf. Mulliken, reference 3.

TABLE V.[11] $R_{12}(K)-P_{12}(K)$ *for the OH bands.*

K	λ2608	λ2811	λ2875	λ3064	λ3122	λ3428	λ3484
1	90.7	96.7		101.4		101.4	97.2
2	152.3	160.8		169.2		169.3	159.0
3	212.6	224.8	209.6	236.7		236.9	224.4
4	271.3	288.7	272.8	303.8	(288.9)	303.2	288.9
5	333.6	352.0	333.7	370.4	352.2	370.5	350.9
6	392.6	415.2	393.5	436.4	414.6	435.2	413.6
7	(451.8)	477.0	451.7	501.8	476.9	502.0	477.0
8	509.8	538.3		566.5	537.8	568.2	537.7
9	567.4	598.8		630.5	598.8	630.8	600.0
10	623.1	658.7		693.3	658.9	692.9	(660.9)

TABLE VI.

	$R_1(K)-Q_1(K)$			$R_2(K)-Q_2(K)$		
K	λ3484	λ2811	λ3122	λ3484	λ2811	λ3122
1	64.8	64.6	——	65.0	64.7	——
2	97.4	96.6	——	94.4	96.0	——
3	129.6	128.7	——	128.5	128.2	——
4	163.5	161.1	——	159.6	160.0	——
5	192.9	192.8	188.7	191.1	191.9	——
6	224.8	225.2	223.1	222.0	223.5	——
7	256.1	256.4	255.1	255.3	254.3	——
8	285.7	287.5	286.8	284.7	285.1	——
9	318.8	318.5	319.2	315.9	315.8	——
10	350.4	348.8	351.1	345.2	346.3	——
11	380.0	379.2	383.2	375.3	375.9	——
12	406.6	408.2	——	405.0	405.6	——
13	435.9	436.6	——	431.2	433.8	——
14	464.3	465.5	——	462.0	461.9	——
15	491.3	492.8	——	488.8	489.4	——
16	519.1	520.0	——	515.3	515.9	——
17	——	——	——	541.5	542.0	——

[11] In this and in the succeeding tables the frequencies for the lines in λ3428 are taken from our Table II, while the data of the following authors was employed in obtaining combination relationships in the other bands; λλ3064 and 3122, Grebe and Holtz (except in Table VI, in which the data of Fortrat was employed for λ3122); λλ2811 and 2875, Watson; and λ2608, Jack.

The following combinations give term differences in the *lower* levels of the respective bands:

$$R_1(K-1)-P_1(K+1)=F_1'(K)-F_{1B}''(K-1)-F_1'(K)+F_{1B}''(K+1)=\Delta_2F_{1B}(K)$$
$$=\Delta_2F_1''-\tfrac{1}{2}[\delta_1(K+1)-\delta_1(K-1)], \quad (4a)$$

$$R_2(K-1)-P_2(K+1)=F_2'(K)-F_{2B}''(K-1)-F_2'(K)+F_{2B}''(K+1)=\Delta_2F_{2B}''(K)$$
$$=\Delta_2F_2''-\tfrac{1}{2}[\delta_2(K+1)-\delta_2(K-1)], \quad (4b)$$

$$R_1(K-1)-Q_1(K)=F_1'(K)-F_{1B}''(K-1)-F_1'(K)+F_{1A}''(K)$$
$$=\Delta_1F_1''(K-\tfrac{1}{2})+\tfrac{1}{2}[\delta_1(K)+\delta_1(K-1)], \quad (5a)$$

$$R_2(K-1)-Q_2(K)=F_2'(K)-F_{2B}''(K-1)-F_2'(K)+F_{2A}''(K)$$
$$=\Delta_1F_2''(K-\tfrac{1}{2})+\tfrac{1}{2}[\delta_2(K)+\delta_2(K-1)]. \quad (5b)$$

By taking averages of (4a) and (4b) and of (5a) and (5b), respectively, *average* $\Delta F''$'s are obtained. These take the form:

$$\Delta_2F_{12}''=R_{12}(K-1)-P_{12}(K+1)+\tfrac{1}{4}[\delta_1(K+1)-\delta_1(K-1)+\delta_2(K+1)-\delta_2(K-1)], \quad (4c)$$

$$\Delta_1F_{12}''=R_{12}(K-1)-Q_{12}(K)-\tfrac{1}{4}[\delta_1(K)+\delta_1(K-1)+\delta_2(K)+\delta_2(K-1)]. \quad (5c)$$

Hill and Van Vleck[3] give an equation for the rotational and coupling energies which, when extended to include the rotational stretching term given by Kemble[3] may be put in the form

$$F''(K)=\pm A\Lambda/2+B''[\{(K+\tfrac{1}{2})\pm\tfrac{1}{2}\}^2-\Lambda(\Lambda\pm1)\pm(B''/A\Lambda)\{[(K+\tfrac{1}{2})\pm\tfrac{1}{2}]^2-\Lambda^2\}$$
$$+(D''/B'')(K+\tfrac{1}{2})^4+\cdots], \quad (6)$$

where $B''=h/8\pi^2I$, $\Lambda=1$ for OH, D'' is the rotational stretching constant and A is the proportionality factor in the expression for the magnetic coupling energy of the doublet II states, and is equal to the separations of the double P, Q and R branches at their origins. The upper signs go with the F_1 rotational states while the lower signs go with the F_2 levels. For average rotational term values [such as are involved in Eqs. (4c) and (5c)] Eq. (6) may be expressed in the form

$$F_{12}''(K)=B''[(K+\tfrac{1}{2})^2+\tfrac{1}{4}-\Lambda^2+(B''/A\Lambda)(K+\tfrac{1}{2})+(D''/B'')(K+\tfrac{1}{2})^4+\cdots]. \quad (7)$$

From Eq. (7) the following relationships are easily obtained:

$$\Delta_2F_{12}''(K)=4B''(K+\tfrac{1}{2})+2(B''^2/A\Lambda)+8D[(K+\tfrac{1}{2})^3+(K+\tfrac{1}{2})]+\cdots, \quad (8a)$$

$$\Delta_1F_{12}(K-\tfrac{1}{2})=2B''K+B''^2/A\Lambda+D''(4K^3+K)+\cdots. \quad (8b)$$

Table VII gives values of Δ_2F_{12}'', calculated by Eq. (4c), and of B'', calculated by Eq. (8a), for λλλ3064, 3428 and 3484. Table VIII gives values of Δ_1F_{12}'' and of B'' calculated by Eqs. (5c) and (8b), respectively. In employing Eqs. (8a) and (8b) we set A equal to 140.3 cm^{-1}, 140.9 cm^{-1} and 141.5 cm^{-1} for the respective λ3064, λ3428 and λ3484 bands. These values were obtained by graphical extrapolation of the experimentally observed doublet separations for the three bands, making use of the Q, of the P and of the R branches. We evaluated the D's for use in Eqs. (6), (7) and (8a, b) from the equation

$$D_v=D_e+\beta(v+\tfrac{1}{2}), \quad (9)$$

in which we calculated D_e and β from the theoretical formulae

TABLE VII. $R_{12}(K-1)-P_{12}(K+1)$ *combinations.*

K	λ3064		λ3428		λ3484	
	Δ_2F_{12}''	B''	Δ_2F_{12}''	B''	Δ_2F_{12}''	B''
2	182.0	18.72	175.1	17.99	167.8	17.21
3	256.5	18.72	246.5	17.98	235.4	17.16
4	330.0	18.69	318.3	18.02	305.0	17.25
5	403.2	18.67	387.8	17.95	374.0	17.30
6	476.0	18.67	458.7	17.98	440.6	17.27
7	547.8	18.64	527.7	17.95	506.3	17.22
8	619.0	18.64	596.5	17.95	573.4	17.25

$$D_e = -4B_e^3/\omega_e^2 \quad (10)$$

$$\beta = \alpha^2/6\omega_e + (20\alpha B_e^2 + 32x_e B_e^3)/\omega_e^2. \quad (11)$$

The latter equation is due to Kemble.[12] These equations had, of course, to be solved by a series of approximations since accurate values of B_e and of β are dependent on the solutions of Eqs. (8a, b).

Comparison of the B'''s in Tables VII and VIII show clearly that the lower vibrational level of λ3484 is the $(v''=2)$ level, heretofore unobserved.

TABLE VIII. $R_{12}(K-1)-Q_{12}(K)$ *combinations.*

K	λ3064		λ3428		λ3484	
	Δ_1F_{12}''	B''	Δ_1F_{12}''	B''	Δ_1F_{12}''	B''
2	72.1	18.65	69.1	17.85	68.4	17.63
3	109.7	18.72	105.5	17.98	100.0	17.03
4	146.9	18.73	141.4	18.01	135.9	17.30
5	183.6	18.71	176.4	17.96	170.6	17.35
6	220.0	18.68	211.5	17.95	203.0	17.22
7	256.2	18.67	245.8	17.90	236.7	17.24
8	292.2	18.67	280.8	17.93	268.4	17.14
9	327.7	18.66	315.2	17.94	301.9	17.19
10	362.9	18.66	348.7	17.93	335.0	17.23
11	397.5	18.65	381.1	17.89	366.7	17.22
12	431.9	18.66	414.9	17.93	398.6	17.23
13	465.2	18.65	447.0	17.92	428.0	17.17
14	498.3	18.65	479.5	17.95	457.9	17.15
15	530.8	18.65	510.8	17.95	488.5	17.19
16	562.3	18.65	540.6	17.94	517.8	17.19
17	593.3	18.65	571.2	17.97	546.1	17.19

ROTATIONAL AND VIBRATIONAL CONSTANTS FOR THE OH BANDS

Average values of B'' were computed, for each of the bands, from Tables VII and VIII and are given in Table IX. In obtaining averages of the B's we discarded those which were computed from ΔF_{12}'s of less than 200 cm^{-1} and weighted the remainder in proportion to the corresponding magnitudes of the ΔF_{12}'s. We did this since the errors in individual B's must lie almost entirely in the errors of measurement of the four lines used in each combination.

Our values of the B'''s and of I_e'' differ from those published by Jack[3] due, in part, to the fact that Jack neglected the last term in Eq. (4c) (which effects B to the extent of about 0.02 cm^{-1} in the region in which Jack employed the data) but due, principally, to our use of the improved formula of Hill and Van Vleck and to our use of Eqs. (10) and (11) to evaluate De'' and β''.

[12] E. C. Kemble, J. Opt. Soc. Am. **12**, 1 (1926).

TABLE IX. *Rotational constants.*[13]

Lower state $^2\Pi$	Upper state $^2\Sigma$
$Be''=19.025$	$Be'=17.384$
$B_0''=18.663$	$B_0'=16.954$
$B_1''=17.952$	$B_1'=16.101$
$B_2''=17.216$	$B_2'=15.233$
$\alpha''=0.724$	$\alpha'=0.860$
$D_e''=-1.97\times10^{-3}$ (calc.)	$D_e'=-2.07\times10^{-3}$ (calc.)
$\beta''=5.0\times10^{-5}$ (calc.)	$\beta'=4.3\times10^{-5}$ (calc.)
$I_e''=1.454\times10^{40}$ g cm^2	$I_e'=1.591\times10^{40}$ g cm^2
$r_e''=0.964\times10^{-8}$ cm	$r_e'=1.009\times10^{-8}$ cm

For convenience, we also include in Table IX the rotational constants for the $^2\Sigma$ level. The B_v's for this level are taken from Jack. The other constants were evaluated, by us, from the same relationships employed in getting the constants for the $^2\Pi$ level.

In calculating the null lines of the various bands of the OH system we have employed the equations

$$\nu_{01} = P_1(1) + F_1''^*(1) - F_1'(0) \quad (12a)$$

$$\nu_{02} = Q_{12}(1) + F_2''^*(1) - F_2'(0) \quad (12b)$$

since these combinations involve the smallest corrections for null point energy. The (F')'s were calculated by the equation due to Kemble,[3]

$$F'(K) = B'(K+\tfrac{1}{2})^2 + D'(K+\tfrac{1}{2})^4 \quad (13)$$

and the (F''^*)'s by the use of the formula

[13] Kemble[3] also gave equations for the rotational energy. For high rotational quantum numbers he gives an equation which may be put in the form

$$F''(K) = B''\left[(K+\tfrac{1}{2})^2 - \Lambda^2 + \frac{D''}{B''}(K+\tfrac{1}{2})^4 \mp \frac{P(P+2\alpha)s^3}{(K+\tfrac{1}{2})}\right]$$

where the last term, which corrects for the magnetic coupling energy of the doublet II states and which may be evaluated from A and from other easily evaluated constants, goes out in the expression for $F_{12}''(K)$. Kemble's equation leads to respective B_0, B_1 and B_2 values of 18.50, 17.78 and 17.02 cm^{-1}, which were reported by us in a preliminary abstract [Phys. Rev. **43**, 374 (1933)]. While, with these values of B'' and Jack's values of D'', Kemble's equation empirically reproduces the data above about $(K=8)$ it lacks the theoretical soundness of Hill and Van Vleck's equation, subsequently derived. Hence, derived constants, such as (I'')'s, (r'')'s, D_e'''s, etc., are inexact by Kemble's equation but are correct by the equation of Hill and Van Vleck.

$$F''^{*}(K)=F''(K)-F''(K-\tfrac{1}{2}) \qquad (14)$$

in which the (F'')'s were evaluated by Eq. (6). The expedient represented by Eq. (14) is necessary since Eq. (6) does not solve for rotational energy alone but for a combination of rotational energy with magnetic coupling energy, the latter itself being a function of K.

Tables X and XI show the schemes of null lines, obtained by Eqs. (12a) and (12b) for the F_1 and F_2 states, respectively. Vibrational energy increments are shown in italics. An asterisk indicates that the ${}^{P}Q_{12}$ (1) line employed in (12b) has been assigned in more than one place.

From the italicized term differences in Tables X and XI we have evaluated the vibrational constants which are given in Table XII. Those term differences which involve null lines marked with one or more asterisks were given a weighting of one-third relative to the other values included in the tables. The vibrational constants for the upper electronic level agree substantially with those given by Birge[14] except for an evident printers error in Birge's tabulation.

TABLE X. *Null lines of the* $^2\Pi_{\frac{3}{2}}$ *branches of the OH bands.*

	$v''=0$		1		2
$v'=0$	32,464.96	*3569.56*	28,895.4		
	2,988.77		*2,988.8*		
1	35,453.73	*3569.50*	31,884.23	*3404.4*	28,479.8
	2,793.27		*2,793.18*		
2	38,247.00	*3569.59*	34,677.41		

TABLE XI. *Null lines of the* $^2\Pi_{\frac{1}{2}}$ *branches of the OH bands.*

	$v''=0$		1		2
$v'=0$	32,325.84	*3570.1*	28,755.7		
	2,988.70		*2,989.5*		
1	35,314.54*	*3569.35*	31,745.19**	*3404.9*	28,340.3
	2,793.80		*2,792.98*		
2	38,108.34**	*3570.17*	34,538.17		

TABLE XII. *Vibrational constants.*

$\omega_e''=3734.9$	$\omega_e'=3184.1$
$x_e''\omega_e''=82.6$	$x_e'\omega_e'=97.7$

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[14] Birge, page 232 of National Research Council Report on Molecular Spectra in Gases.