Physics. — *"On the Structure of the Ultra-Violet Bands of Water Vapour."* By G. H. DIEKE. (Communicated by Prof. P. EHRENFEST).

The so-called ultra-violet emission bands of water vapour have been the subject of an extensive study[1]). They were formerly ascribed to the H_2O molecule, or else to oxygen[2]). WATSON's[3]) researches, however, rendered it probable that the bands are due to the OH-molecule which is formed in the discharge tube or the flame. Also the structure of the bands pleads in favour of a di-atomic molecule.

After some investigators had arranged part of the lines in series, HEURLINGER[4]) succeeded in aranging almost all the lines of the band $\lambda\,3064$ in twelve branches, which he called $P_1^k, Q_1^k, R_1^k, P_2^k, Q_2^k, R_2^k\,(k=1, 2)$. This band is the representative of a class of bands, which HEURLINGER calls "bands with doublet-series". A characteristic of this class is that the lines for small numbers in the series cannot be represented by DESLANDRES's formula.

The theoretical interpretation of the "H_2O"-bands, however, presented difficulties[5]). In contrast with many other bands there are here in one band no combination relations which allow us to isolate the terms. Recently the band $\lambda\,2811$ was measured by WATSON[3]), who succeeded in showing that its structure is perfectly analogous to the structure of the band $\lambda\,3064$, and that the two bands must belong to the same final state. WATSON found again that the lines themselves do not satisfy the simple theory of band spectra, but that this is more or less the case with the doublet middles.

When use is made of WATSON's measurements, and these are combined with those of GREBE and HOLTZ[6]) of the band $\lambda\,3064$, it appears possible to get a full insight into the formal structure of these bands without it being necessary to make any supposition concerning the structure of the molecule emitting the bands. The values of all the rotational terms besides a constant — can be calculated, and from the course of the rotational energy as a function of the quantum number m conclusions can then be drawn concerning the structure of the molecule. In this communication, however, only the formal structure of the bands will be derived and we will not enter into the structure of terms themselves and the conclusions that may be drawn from them.

[1]) Earlier literature in KAYSER, Handbuch der Spectroscopie, Bd. V.

[2]) W. STEUBING, Ann. d. Phys. **33**, p. 553, 1910; **39**, p. 1408, 1912. A. REISS, ZS. f. phys. Chemie **88**, p. 513, 1914.

[3]) W. W. WATSON, Astroph. Journal **60**, p. 145, 1924.

[4]) T. HEURLINGER, Untersuchungen über die Struktur der Bandenspektra, Lund, 1918.

[5]) Compare A. SOMMERFELD, Atombau und Spektrallinien, 3rd impr., p. 527.

[6]) L. GREBE und O. HOLTZ, Ann. d. Phys. **39**, p. 1243, 1912.

TABLE I.

m	$Q_1{}^1(m) - P_1{}^1(m+1)$		$R_1{}^1(m) - Q_1{}^1(m+1)$		$Q_2{}^1(m) - P_2{}^1(m+1)$		$R_2{}^1(m) - Q_2{}^1(m+1)$	
	λ 3064	λ 2811	λ 3064	λ 2811	λ 3064	λ 2811	λ 3064	λ 2811
2	61.36	61.02**	60.94*	61.01	83.61*	83.52*	83.74	83.88
3	101.48*	101.41	101.11*	101.05	117.77	117.90	118.50	118.40
4	140.68*	140.49	140.29	140.14*	152.91	152.60	153.97	153.76
5	178.81	178.87	178.78	178.66*	187.73	187.66	189.62	189.68
6	216.19	216.46*	216.58	216.89	222.70	222.74	225.64	225.18**
7	253.13*	253.11	253.91	254.26*	257.37*	257.76*	261.57*	262.02*
8	288.96*	289.18	290.84	290.43**	292.15**	292.23	297.47*	297.66
9	324.53	324.89*	327.30*	327.23	326.42	326.58	333.28*	333.52*
10	359.38*	359.51	363.22	363.07*	360.20	360.37*	368.87*	368.81
11	393.75	393.76	398.67	398.92	393.87	394.01*	404.10*	404.16
12	427.35	426.72	433.87*	433.78	426.88	427.22	439.30*	439.38*
13	460.41	460.27*	468.24	468.87*	459.38	459.20*	473.24	473.45
14	492.78	493.05	502.14	502.32	491.40	491.65	507.17	506.81*
15	524.46	525.21	535.76*	535.90	522.61	522.90	540.48*	540.78
16	555.43*	555.44	568.27	568.69	553.18	553.33	573.25	573.35
17	585.92	585.85	600.34	600.65*	583.30	583.16	605.43	606.00*
18	615.54	615.40*	631.80	632.48*	612.68	612.31	636.80	637.26
19	644.24	644.15*	662.76	663.38*	640.99	640.77	667.02	668.16
20	672.08	671.73*	692.70*	—	668.70	668.25	697.73	—
21	699.20*	699.62*	722.17	—	695.28	695.92*	727.13	—

m	$Q_1{}^2(m) - P_1{}^2(m+1)$		$R_1{}^2(m) - Q_1{}^2(m+1)$		$Q_2{}^2(m) - P_2{}^2(m+1)$		$R_2{}^2(m) - Q_2{}^2(m+1)$	
	λ 3064	λ 2811	λ 3064	λ 2811	λ 3064	λ 2811	λ 3064	λ 2811
2	—	58.96	—	—	80.50*	80.58	—	—
3	97.04*	98.17*	—	—	111.09*	114.07*	—	—
4	135.37*	135.08	—	134.51	147.14	146.48**	—	140.20**?
5	171.94	172.05	171.92	172.06	180.96	180.74	—	180.68*?
6	208.09	207.68	208.33*	207.77**	214.34	213.80**	216.78	217.08
7	243.29*	243.74*	243.75	243.68*	247.72	247.53	251.49	252.97**
8	277.82	277.96*	279.48	280.05**	280.72	280.84	285.62	286.34**
9	311.96	311.15*	314.24	—	314.54*	313.74	320.14	—
10	345.48	344.94*	384.73	—	346.66	346.93*	354.73	—
11	378.57	378.21	382.77	—	378.69	—	389.52	—

I. The differences:

$$Q_i^1 (m) - P_i^1 (m + 1) \qquad \text{and} \qquad R_i^1 (m) - Q_i^1 (m + 1)$$

have within the limits of the errors of observation the same value in $\lambda\,3064$ and $\lambda\,2811$. (Cf. table I [1]), i. e. $Q_i^1 (m)$, $P_i^1 (m+1)$ and $R_i^1 (m+1)$ must have the same initial state, which we call $F_i^1(m)$ [2]. ($F_i^1 (m) =$ energy divided by h). We may, therefore, write:

$$\left. \begin{aligned} P_i^1 (m) &= F_i^1 (m-1) - f_i^P (m) \\ Q_i^1 (m) &= F_i^1 (m) \quad\;\; - f_i^Q (m) \\ R_i^1 (m) &= F_i^1 (m+1) - f_i^R (m) \end{aligned} \right\} \quad \cdots \cdots \quad (1)$$

From the fact that

$$Q_i (m) - P_i (m + 1) \neq R_i (m) - Q_i (m + 1)$$

follows that the equation

$$f_i^P (m) = f_i^Q (m) = f_i^R (m)$$

which is satisfied in a normal band, *cannot* be valid here.

Analogous relations hold for the branches P_i^2, Q_i^2, R_i^2 [3]).

II. The six branches P_i^1, Q_i^1, R_i^1 $(i = 4, 2)$ form one band (which we shall call I), and the six branches P_i^2, Q_i^2, R_i^2 another one (II), belonging to another oscillation jump. If, therefore, we ascribe the band $\lambda\,3064$ I to the oscillation transition $n_1 \to n_2$, we obtain the following scheme for the oscillation jumps of the other bands [4]).

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[1]) In the tables * denotes that one, ** that more than one of the lines, from which the differences have been calculated, coincide with other lines.

[2]) When judging about the agreement, it should be borne in mind that no importance should be attached to the second decimal. Nor is it impossible that the presence of satellites has affected the accuracy of the measurements.

[3]) The lines of the branch $\lambda\,3064$ II R_2, which could not be classified by HEURLINGER, are given by FORTRAT (Journal de phys. **5**, p. 20, 1924) according to his new measurements. They do not, however, fit into any of the combination relations following from the structure given here. FORTRAT himself already pointed out that the relation $R_1 - R_2 = P_1 - P_2 - \delta$ expected by HEURLINGER, is not fulfilled.

If FORTRAT's lines are, however, arranged in the reversed order, then they satisfy all the combination relations within the limits of the errors of observation. For the calculation of the values in the tables I and II this arrangement has been chosen.

It appears from the values with a ? in the tables that the lines $\lambda = 2876,336$ and $\lambda = 2875.500$ in the band $\lambda\,2811$ cannot be considered as $R_2^2 (4)$ and $R_2^2 (5)$.

[4]) On the assumption that $n_1 = n_2 = 0$ which is the most probable one the oscillation constants can be calculated from the provisional position of the zero lines. If the oscillation energy according to KRATZER is written $h n \nu^0 (1 - nx)$, one gets

$$\nu_1{}^0 = 3085.4; \qquad \nu_1{}^0 x_1 = 97.4; \qquad \nu_2{}^0 (1 - x_2) = 3569.8.$$

$$
\begin{array}{ccc}
 & \text{I.} & \text{II.} \\
\lambda\,3064 & n_1 \to n_2 & n_1 + 1 \to n_2 + 1 \\
\lambda\,2811 & n_1 + 1 \to n_2 & n_1 + 2 \to n_2 + 1
\end{array} \qquad \cdots \quad (2)
$$

That the pieces called I and II of what is called usually a band are in reality two different bands with different oscillation jumps is rendered probable by the fact that the quotient of the term differences in I and II is independent of m, which is an indication that only the constant B, which contains the moment of inertia, is different in the term formulae. A direct confirmation of this is obtained with the aid of the combination relations. According to the above scheme $\lambda\,3064\,\text{II}$ and $\lambda\,2811\,\text{I}$ must have the same initial state. Apart from small irregular deviations which must be attributed to errors of observation the differences $R_i^2(m) - P_i^2(m)$ in $\lambda\,3064$ and $R_i^1(m) - P_i^1(m)$ in $\lambda\,2811$ now appear actually to have the same values (table II 5th—7th columns). This confirms, therefore, the scheme of the oscillation transitions, and proves at the same time that:

$$
f_i^P(m) = f_i^R(m) = f_i(m).
$$

III. When the upper indices are omitted and f_i' is written instead of f_i^Q, the six branches of a band are represented by:

$$
\begin{aligned}
P_1(m) &= F_1(m-1) - f_1(m) & \qquad P_2(m) &= F_2(m-1) - f_2(m) \\
Q_1(m) &= F_1(m) \quad\;\, - f_1'(m) & \qquad Q_2(m) &= F_2(m) \quad\;\, - f_2'(m) \quad . \quad (3) \\
R_1(m) &= F_1(m+1) - f_1(m) & \qquad Q_2(m) &= F_2(m+1) - f_2(m)
\end{aligned}
$$

Now the term-differences, and with them the relative values of the terms can all be calculated. One gets

$$
\triangle F_i(m-1) = F_i(m+1) - F_i(m-1) = R_i(m) - P_i(m)
$$

$$
\triangle f_i(m) = f_i(m+2) - f_i(m) = R_i \quad (m) \quad - P_i(m+2) \qquad\qquad (i = 1, 2)
$$

$$
\triangle f_i'(m) = f_i'(m+2) - f_i'(m) = R_i(m+1) - Q_i(m+2) + Q_i(m) - P_i(m+1)
$$

These values are given in the tables II and III.

HEURLINGER already observed that $R_1(m) - P_1(m)$ and $R_2(m) - P_2(m)$ differ by a small, about constant amount. This means that the difference between $F_1(m)$ and $F_2(m)$ will increase slowly and almost linearly with m. It is further seen from the tables that the difference between $f_i(m)$ and $f_i'(m)$ increases with m^2, and this may be interpreted as a small difference in the moments of inertia of the molecules in the conditions $f_i(m)$ and $f_i'(m)$.

On the other hand the values of f_1 and f_2 show comparatively great differences for small m; they approach each other more and more with increasing m, which indicates that f_1 and f_2 belong to a different direction of rotation.

The interpretation of the other properties of the terms would necessitate a further discussion of the structure of the molecule, and will therefore be omitted in this communication.

The analogy with the $(C+H)$-band $\lambda\,3900$, to which HEURLINGER already drew the attention, is corroborated by the combination relations. The same scheme (3) which applies to the bands considered here, was

TABLE II.

m	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda\,3064$ I	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda\,3064$ I	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda\,3064$ II	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda\,3064$ II	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda\,2811$ I	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda\,2811$ I	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda\,2811$ II	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda\,2811$ II
2	101.44	101.39	—	—	96.66*	96.74	—	—
3	168.94	169.48	—	—	160.75*	160.88	—	—
4	236.35	236.99	—	—	224.60*	225.02	213.51*	205.82**?
5	303.69	304.08	288.87	—	288.47	288.90	273.73	271.92**?
6	370.16	370.70	352.20	352.18	352.02	351.95*	333.71*	333.75
7	436.10	436.78	414.44	414.84	414.90*	415.50*	392.44	394.48**
8	501.80*	501.90**	476.85	476.96	476.59*	477.37	451.51*	451.80*
9	566.27*	566.81**	537.90	537.79	538.04	538.60	—	—
10	630.26	630.69*	598.47	599.11	598.45*	599.12	—	—
11	693.15	693.48*	658.05	659.75	658.51	658.89	—	—
12	755.30*	755.94*	717.13	717.42	717.05	717.90**	—	—
13	815.97	816.40	774.69	—	774.49*	775.27	—	—
14	875.65	876.15	832.66	—	830.72*	830.60**	—	—
15	934.09	934.50*	—	—	886.42*	886.92	—	—
16	991.03	991.53	—	—	940.70*	940.41	—	—
17	1046.81	1047.25	—	—	992.13	992.85*	—	—
18	1100.84	1101.27	—	—	1043.13	1043.26	—	—
19	1153.46	1153.25	—	—	1092.22	1092.39	—	—
20	1204.26	1204.61	—	—	—	—	—	—
21	1253.42	1253.71	—	—	—	—	—	—
22	1300.49	1300.87	—	—	—	—	—	—
23	1346.43	—	—	—	—	—	—	—
24	1389.58*	—	—	—	—	—	—	—
25	1431.01	—	—	—	—	—	—	—

TABLE III.

m	$\Delta f_1 (m)$ $R_1 (m) - P_1 (m+2)$		$\Delta f_2 (m)$ $R_2 (m) - P_2 (m+2)$		$\Delta f_1' (m)$ $Q_1 (m) - P_1 (m+1) +$ $R_1 (m+1) - Q_1 (m+2)$		$\Delta f_2' (m)$ $Q_2 (m) - P_2 (m+1) +$ $R_2 (m+1) - Q_2 (m+2)$	
	λ 3064 I	λ 2811 I	λ 3064 I	λ 2811 I	λ 3064 I	λ 2811 I	λ 3064 I	λ 2811 I
2	162.42	162.42	201.51	201.78	162.47*	162.07**	201.11	201.92*
3	241.79	241.54	271.47	271.00	241.77*	241.55*	271.74	271.66
4	319.10	319.01*	341.70	341.48	319.46*	319.15*	342.53	342.28
5	394.97	395.12	412.32	412.42	395.39	395.76	413.27	412.84**
6	469.71*	470.00	483.01	482.94*	470.10	470.72**	484.27*	484.76*
7	542.87*	543.44*	553.72	554.25*	543.97*	543.54**	554.84**	555.42*
8	615.37	615.32*	623.89**	624.24	616.26**	616.41	625.43**	625.75*
9	686.68	686.74	693.48**	693.89	687.75	687.96**	695.29*	695.39
10	756.97	756.83*	762.74*	762.82*	758.05*	758.43	764.30*	764.53*
11	826.02	825.71	830.98*	831.38	827.62*	827.54	833.17*	833.39**
12	894.28*	894.05*	898.68*	898.58**	895.59	895.59*	900.12	900.67
13	961.02	961.92**	964.64	965.10	962.55	962.59*	966.55	966.01**
14	1026.60	1027.53*	1029.78	1029.71*	1028.54*	1028.95*	1031.88*	1032.13
15	1091.19	1091.34	1093.66*	1094.11	1092.73	1093.90*	1095.86	1096.25
16	1154.19	1154.54	1156.55	1156.51	1155.77*	1156.09*	1158.61	1158.33*
17	1215.88	1216.05	1218.11	1218.31*	1217.72	1218.33*	1220.10	1220.42
18	1276.04	1276.63	1277.79	1278.03	1278.30	1278.78**	1279.70	1280.47
19	1334.84	1335.11	1335.72	1336.41	1336.94*	—	1338.72	—
20	1391.90	—	1393.31	—	1394.25	—	1395.83	—
21	1447.57	—	1448.68	—	1449.44*	—	1450.83	—
22	1501.25*	—	1502.35	—	1503.67	—	—	—
23	1553.77	—	—	—	1555.69*	—	—	—
24	1603.77	—	—	—	1606.09	—	—	—

found for the $(C+H)$-band by KRATZER [1]). The analogy, however, does not hold for the structure of the terms themselves, which cannot be represented here by KRAMERS and PAULI's formula or by its extension given by KRATZER.

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[1]) A. KRATZER, ZS. f. Phys. **23**, p. 298, 1924.

In the $(C+H)$-band $\lambda\,3900$ KRATZER assumed terms F'_i in Q_i, which might differ somewhat from F_i. The presence of such terms in the "watervapour bands" is not excluded. No certainty can, however, be obtained on this head from the available observations.

Satellites.

HEURLINGER found that some lines are accompanied by satellites, and FORTRAT [1]) proved by new measurements that the presence of satellites is no exception, but the rule in most of the branches. The presence of these satellites may be due to other combinations between the same terms as are also responsible for the main lines. The available measurements, however, do not enable us to come to a positive decision, and it is very well possible that there are still other terms differing little from those found already. Especially in the Q-branches the matter is very complicated on account of the presence of satellites. If it is tried to use for the derivation only the terms found, Q_2 with its three satellites is e.g. represented by (from red to violet):

$$F_1\,(m) - f'_2\,(m); \quad \underline{F_2\,(m) - f'_2\,(m)}; \quad F_1\,(m) - f_2\,(m); \quad F_2\,(m) - f_2\,(m).$$

For not too small m the last satellite must, however, be further distant from the main line than was observed by FORTRAT, and if the accuracy of the measurements has not been vitiated by the concurrence of several faint lines, this would suggest the presence of another term which may be identical with F'_i (cf. p. 177). For so far as the accuracy of the measurements admits of a judgment, the satellites of P_1 and R_2 are quantitatively represented by:

$$\sigma\,P_1 = F_2\,(m-1) - f_1\,(m); \qquad \sigma\,R_2 = F_1\,(m+1) - f_2\,(m).$$

More extensive measurements of the satellites, also in the band $\lambda\,2811$ will without doubt be able to give information about those particulars of the fine structure of the $O+H$-bands, about which so far no certain decision was possible.

Perhaps the circumstance that the "H_2O"-bands were observed by WOOD and his collaborators [2]) in fluorescence, may offer a possibility of arriving at a definite decision by which molecule these bands are emitted. The said investigators found that in nitrogen contaminated by watervapour the "H_2O"-bands appear in fluorescence, but not in dry nitrogen, not when it is contaminated by oxygen either. If WATSON's view, that the bands must be ascribed to the OH-molecule, is correct,

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[1]) R. FORTRAT, Journal de phys. **5**, p. 20, 1924.

[2]) R. W. WOOD, Phil. Mag. 20, p. 707, 1910.

    R. W. WOOD and G. A. HEMSALECH, Phil. Mag. 27, p. 899, 1914.

    C. F. MEYER and R. W. WOOD, Phil. Mag. 30, p. 449, 1915.

the appearance of the bands in fluorescence would have to be explained in this way that excited N_2 molecules, through impacts of the second kind, dissociate an H_2O-molecule into an excited (or ionized) OH-molecule and an H-atom. If so this is not a case of true fluorescence, and in pure sufficiently diluted water-vapour, where impacts of the second kind cannot take place, the fluorescence would, accordingly, have to disappear, whereas it would have to continue to exist if it was due to the H_2O-molecules.

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