

## STRUCTURE OF THE ELECTRONIC BANDS OF THE OD MOLECULE. PART IV (SPIN DOUBLING)

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**ABSTRACT.** The theoretical formula derived by Hill and Van Vleck for the energy difference (ignoring the magnetic effect of molecular rotation) between the components of a doublet  $\pi$ -state, representing any intermediate stage of coupling, has been verified by application to the observed data of the spin-doublet widths of the OD molecule. Contrary to the observations of Johnston, the agreement between the experimental and calculated values is shown to be fairly satisfactory, considering the approximation made in the theoretical derivation. Incidentally, type value of the spin-coupling constant for the upper electronic state,  ${}^2\Sigma^+$  of the OD molecule, is believed to have been determined as equal to 0.2, which cannot otherwise be estimated unless the satellite branches are also identified.

The spin-doublet widths for the OH and OD molecules are compared and, as observed by Johnston and by Shaw and Gibbs, the latter are found to be larger, although the OD molecule is heavier. The variation of the difference between these widths with  $K$  indicates a maximum at  $K=6$ . This is shown to be in complete agreement with the theoretical value derived from Hill and Van Vleck's formula.

### INTRODUCTION

Using the method of the old quantum theory, Kemble<sup>1</sup> first derived energy formulae for diatomic molecules which are applicable over portions of the transition range between Hund's Case (a) and Case (b). Hill and Van Vleck<sup>2</sup> later treated the problem by the new quantum mechanics and obtained for doublet electronic states, representing any stage of coupling, the following closed formula for the rotational energy,

$$W = B_r \left[ (J + \frac{1}{2})^2 - \Lambda^2 \pm \frac{1}{2} \{ 4(J + \frac{1}{2})^2 + \lambda(\lambda - 4)\Lambda^2 \}^{\frac{1}{2}} \right] \quad \dots (1)$$

where  $\lambda = A/B_r$  and  $\Lambda = 1$  for the  $\pi$ -state; the upper and lower signs refer to the two component states  ${}^2\pi_{\frac{1}{2}}$  and  ${}^2\pi_{1\frac{1}{2}}$  respectively. The above equation gives the combined effects of the rotational and spin energy in a given state. The energy difference between the two doublet components due to spin effects alone

could not be separated out ; but Hill and Van Vleck obtained from (1), by simplification, the doublet energy difference approximately as

$$\delta = B_v [ \{ 4(J + \frac{1}{2})^2 + \lambda(\lambda - 4)\Lambda^2 \}^{\frac{1}{2}} - (2J + 1) ] \quad (2)$$

The equation was tested by them, by reference to the spin doublets of the (1, 0) band of OH at  $\lambda 2811$ . Except for a small discrepancy, the observed and calculated values were found to agree well and better than was shown earlier by Kemble. The discrepancy was ascribed to the neglect of the contribution towards the doublet interval arising from the magnetic field developed by molecular rotation.

In a recent paper Dawson and Johnston<sup>2</sup> applied the formula to the various OH bands and concluded that it failed to reproduce accurately the spin-doubling spacing obtained from experimental data. The failure of the equation when applied to the spin doublets of the OD molecule was also briefly reported by Johnston<sup>2</sup> but the detailed data have not so far been published.

The recent work of the author<sup>3</sup> on the structure of the OD bands has enabled a detailed study of the validity of Van Vleck's equation, which forms the subject of this paper.

#### RESULTS AND DISCUSSION

To obtain the experimental values of the electronic spin width the usual method is adopted. We have<sup>4</sup>

$$Q_1(K) = F_1'(K) - F_1''(K)$$

and 
$$Q_2(K) = F_2'(K) - F_2''(K).$$

Hence

$$\begin{aligned} F_2''(K) - F_1''(K) &= [Q_1(K) - Q_2(K)] - [F_1'(K) - F_2'(K)] \\ &\quad - [Q_1(K) - Q_2(K)] - \gamma \cdot K \end{aligned}$$

where  $\gamma$  is a small constant representing the spin doubling in the upper state  ${}^2\Sigma^+$ . Similarly,

$$\begin{aligned} F_2''(K) - F_1''(K) &= [R_1(K) - R_2(K)] - \gamma(K + 1) \\ &= [P_1(K) - P_2(K)] - \gamma(K - 1). \end{aligned}$$

In Van Vleck's theoretical equation the difference between the terms  $F_1''(K)$  and  $F_2''(K)$  was ignored so that when the mean of these terms is taken, the experimental value should agree with the theoretical value if the equation is correct. We therefore write

$$\begin{aligned} \delta &= \frac{1}{2} [ \{ F_2''(K) - F_1''(K) \} + \{ F_2''(K) - F_1''(K) \} ] \\ &= \frac{1}{2} [ \{ Q_1(K) - Q_2(K) \} + \frac{1}{2} \{ (P_1(K) - P_2(K)) + (R_1(K) - R_2(K)) \} ] - \gamma K \quad \dots \quad (3) \end{aligned}$$

TABLE I  
Spin-doublet widths in the OD molecule for  $v''=1$

K	R doublets			Q doublets			P doublets			Mean	
	(1,1)	(2,1)	(3,1)	(1,1)	(2,1)	(3,1)	(1,1)	(2,1)	(3,1)	R and P	Q
1	(125.5)		130.9	131.2	132.7	132.0	126.9	128.4	132.8	128.9	132.0
2	115.8	116.4	117.5	116.2	116.6	118.8	115.7	116.2	116.9	116.4	117.2
3	102.8	103.0	105.6	103.7	103.9	104.1	101.0	105.3	104.0	104.1	103.9
4	92.9	94.4	94.5	92.7	91.8	93.5	93.1	93.9	93.9	93.8	92.7
5	84.9	85.4	85.5	83.3	84.1	84.4	84.2	84.1	84.8	84.8	83.9
6	78.0	76.6	77.3	76.7	77.3	76.7	77.1	77.4	77.0	77.2	76.9
7	69.6	71.2	70.8	70.6	70.0	69.5	70.4	70.3	70.9	70.5	70.2
8	64.9	65.3	65.0	64.3	64.2	62.6	65.3	65.8	65.4	65.4	63.7
9	61.4	61.2	60.8	60.5	60.3	59.5	62.3	61.1	60.6	61.2	60.1
10	56.6	57.9	56.9	55.3	55.6	55.6	50.5	56.8	56.8	56.9	55.5
11	52.6	(47.2)	54.1	51.9	51.6	52.2	52.7	53.3	53.6	53.3	51.9
12	51.9	—	49.1	49.0	48.9	46.4	52.0	50.0	50.2	50.6	48.1
13	48.3	—	48.3	46.0	46.4	44.0	47.7	47.7	47.8	48.0	45.5
14	(41.0)	—	43.6	42.0	43.4	—	44.0	45.5	45.2	44.6	43.0
15	(45.5)	—	—	40.5	40.9	—	44.3	43.1	—	44.3	40.7
16	40.2	—	—	39.7	38.9	—	42.3	40.9	—	41.1	39.3
17	40.4	—	—	37.8	37.6	—	39.7	39.3	—	39.8	37.7
18	37.5	—	—	35.1	36.4	—	38.2	38.4	—	38.0	35.8
19	35.9	—	—	34.3	35.1	—	36.1	36.9	—	36.3	34.7
20	33.1	—	—	33.6	32.9	—	34.1	35.7	—	34.3	33.3
21	33.6	—	—	31.9	32.0	—	34.9	34.8	—	34.4	32.0
22	32.6	—	—	30.6	31.0	—	33.8	33.7	—	33.4	30.8
23	(34.3)	—	—	29.6	30.9	—	32.7	32.6	—	32.7	30.3
24	30.0	—	—	32.0	29.8	—	(26.8)	31.2	—	(30.6)	30.9
25	(35.2)	—	—	28.2	27.6	—	31.9	31.3	—	31.6	27.9
26	31.6	—	—	27.3	—	—	31.0	30.2	—	30.9	27.3
27	28.4	—	—	26.0	—	—	30.4	—	—	29.4	26.0
28	28.3	—	—	25.8	—	—	30.4	—	—	29.3	25.8
29	30.1	—	—	24.8	—	—	30.0	—	—	30.1	24.8
30	31.4	—	—	25.2	—	—	29.1	—	—	30.2	25.2
31	30.2	—	—	27.8	—	—	28.4	—	—	29.3	27.8

TABLE II

*Spin-Hamilton parameters*

K	$v''=0$					$v''=1$				
	OD		OII		Diff. ( $\delta_d - \delta_h$ )	OD		OII		Diff. ( $\delta_d - \delta_h$ )
	Obs.	Calc.	Obs.	Calc.	Obs.	Obs.	Calc.	Obs.	Calc.	Obs.
1	131.1	130.7	126.22	—	4.9	130.5	131.4	126.5	—	4.0
2	116.1	—	103.45	—	12.6	116.8	—	104.7	—	12.1
3	103.8	102.9	86.72	—	17.1	104.0	104.1	87.0	—	17.0
4	92.7	—	74.21	—	18.5	93.3	—	74.9	—	18.4
5	83.7	82.8	63.83	63.60	19.9	81.4	81.2	65.3	65.14	19.1
6	76.4	—	56.39	—	20.0	77.1	—	57.5	—	19.6
7	69.7	68.1	50.40	—	19.3	70.4	69.6	51.7	—	18.7
8	64.0	—	44.82	—	19.2	64.6	—	47.0	—	17.6
9	59.3	57.4	41.52	—	17.8	60.7	58.8	43.4	—	17.3
10	55.4	—	38.22	36.75	17.2	56.2	—	39.9	37.85	16.5
11	51.8	49.3	35.40	—	19.4	52.6	50.6	36.2	—	16.4
12	48.7	—	32.81	—	15.9	49.1	—	34.1	—	15.3
13	45.9	43.0	30.88	—	15.0	46.8	44.2	31.7	—	15.1
14	43.5	—	29.25	—	14.2	43.8	—	30.0	—	13.8
15	41.7	38.1	27.79	25.50	13.9	42.5	39.2	28.7	26.31	13.8
16	39.7	—	26.39	—	13.3	40.2	—	27.7	—	12.5
17	37.9	34.2	25.36	—	12.5	38.8	35.2	25.6	—	13.2
18	36.7	—	24.11	—	12.6	36.9	—	24.8	—	12.1
19	35.7	30.9	23.50	—	12.2	35.5	31.9	23.9	—	11.6
20	33.2	—	22.38	19.46	10.8	33.8	—	23.1	20.08	10.7
21	33.0	28.2	22.17	—	10.8	33.2	29.2	22.0	—	11.2
22	31.9	—	20.97	—	10.9	32.1	—	20.8	—	11.3
23	31.2	26.0	20.44	—	10.8	31.5	26.8	19.8	—	11.7
24	30.5	—	19.90	—	10.6	30.8	—	20.3	—	10.5
25	30.4	24.1	19.55	15.71	10.9	29.8	24.8	19.2	16.23	10.6
26	—	—	18.72	—	—	29.1	—	19.1	—	10.0
27	—	—	18.34	—	—	27.7	23.1	17.7	—	10.0
28	—	—	17.61	—	—	27.6	—	—	—	—
29	—	—	17.47	—	—	27.5	21.5	—	—	—
30	—	—	17.16	13.17	—	27.7	—	—	—	—

TABLE II (contd.)

K	$v''=2$				Diff. ( $\delta_d - \delta_k$ )	$v''=3$	
	OD		OH			OD	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.
1	131.5	131.2	126.2	—	5.3	132.0	132.4
2	117.2	—	106.2	—	11.0	118.0	—
3	105.0	104.2	89.1	—	15.9	105.0	105.0
4	94.5	—	76.2	—	18.3	95.5	—
5	86.2	84.5	66.6	66.58	19.6	86.4	86.3
6	78.7	—	58.8	—	19.9	79.0	—
7	72.0	70.0	52.4	—	19.6	72.4	71.7
8	66.1	—	47.3	—	18.8	69.5	—
9	61.4	59.1	44.6	—	16.8	62.3	60.7
10	56.7	—	39.8	38.91	16.0	60.6	—
11	53.8	50.8	37.6	—	16.2	53.8	52.5
12	50.5	—	34.6	—	15.9	48.8	—
13	47.3	44.6	32.0	—	15.3	—	—
14	46.4	—	31.7	—	14.7	—	—
15	44.5	39.5	29.8	27.09	14.7	—	—
16	39.9	—	28.5	—	11.4	—	—
17	39.2	35.5	—	—	—	—	—
18	38.8	—	—	—	—	—	—
19	36.6	32.2	—	—	—	—	—
20	34.2	—	—	—	—	—	—
21	31.5	29.4	—	—	—	—	—

In Table I the doublet intervals derived according to the above equation are shown in detail for the bands having the final state  $v''=1$ . For the remaining bands the observed average values only are given in Table II.<sup>7</sup> It should be noted that the correction term  $\gamma K$  is ignored, as the value of  $\gamma$  has not been determined for the OD bands. The tables also give the calculated values of  $\delta$  in

each case, in determining which from equation (2) the following mean values of the constants have been adopted (they are in  $\text{cms.}^{-1}$ ):

$$\begin{aligned} B_0'' &= 9.80, & B_3'' &= 9.08 \\ B_1'' &= 9.57, & A &= -139.4. \\ B_2'' &= 9.40 \end{aligned}$$

The agreement between the observed and the calculated values is close for small rotational quantum numbers, but for large values of  $K$  there are markedly increasing divergencies. The difference (obs. - calc.), however, varies linearly with  $K$ . The representative curves drawn for  $v''=0$  in fig. 1 bring out these features clearly; the linear relation from curve (3) may be expressed as

$$\delta(\text{obs.}) - \delta(\text{calc.}) = 0.2 K.$$

The constant 0.2 obviously represents the small factor  $\gamma$  of equation (3). It is of the right order of magnitude that should be expected for the OD molecule, for which the spin-coupling constant  $A$  is  $-130.4$ , nearly the same as that for OH. If this correction, depending on  $\gamma K$  is made in each of the observed values, according to equation (3), the agreement becomes very close even for large rotational quantum numbers. The outstanding differences after this correction are to be ascribed to the approximation made in deriving equation (2) and perhaps partly to observational errors.

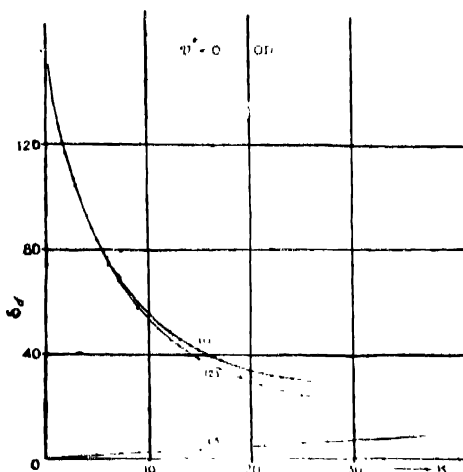


FIG. 1

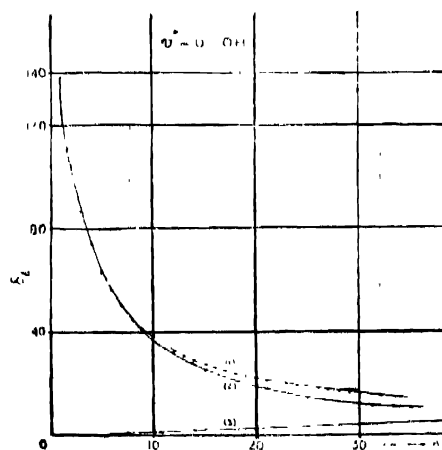


FIG. 2

*Explanation of figures* :—In these, curve (1) represents the observed, curve (2) the calculated values and curve (3) the differences plotted against  $K$ .

The author therefore considers, contrary to what Johnston had observed, that Van Vleck's theoretical equation represents the electronic spin doubling in the doublet  $\pi$ -state of the OD molecule fairly accurately. In the light of the above view, the data for the OH molecule given by Johnston and Dawson are re-examined. The curves in Fig. (2) are drawn for  $v''=0$  for OH, similar to those in Fig. (1) for OD. The linear curve (3) in this figure gives the value of  $\gamma_{OH}=0.2$  which agrees very well with that determined otherwise by Almy<sup>8</sup> as equal to 0.216. Dawson and Johnston appear to have omitted the correction factor  $\gamma K$ , in estimating the observed values of the spin-doublet spacing. If this correction is applied, the agreement becomes very satisfactory even for the larger values of  $K$  as well.

Incidentally, it is desirable to point out that the above discussion provides perhaps a new method for obtaining the spin doubling constant  $\gamma$  of the upper state  $^2\Sigma^+$  of the OD molecule, which cannot otherwise be determined from observational data alone, unless the satellite branches are also identified.

COMPARISON OF THE SPIN-DOUBLET INTERVALS  
IN OH AND OD

It was reported by Johnston<sup>4</sup> and also by Shaw and Gibbs,<sup>9</sup> from as yet unpublished data, that the spin-doublet spacing is larger for the OD than for the OH molecule, though the former is the heavier of the two. Johnston also observed that the difference in the spin-doublet widths for the two isotopic molecules is zero at the origin and increases rapidly with  $K$  up to a maximum and then approaches zero asymptotically. The present detailed data confirm the above observations as is evident from Table II. It is possible from these data further to verify the validity of Van Vleck's theoretical equation, as is shown below.

Equation (2) for the spin-doublet interval may be written as

$$\delta_h = B_h \{ (y^2 + M)^{\frac{1}{2}} - y \}$$

$$\delta_d = B_d \{ (y^2 + N)^{\frac{1}{2}} - y \}$$

where  $\delta_h$  and  $\delta_d$  are the spin doublet widths for the OH and the OD molecules,  $B_h$  and  $B_d$  are the respective constants and

$$y = 2K + 1$$

$$M = (A/B_h^2) [(A/B_h) - 4]$$

$$N = (A/B_d^2) [(A/B_d) - 4].$$

If the value of  $(\delta_d - \delta_h)$  is plotted against  $K$ , the value of  $K$  for which the curve shows a maximum is given by the condition,

$$\frac{d(\delta_d - \delta_h)}{dy} = B_h \left[ \frac{y}{\sqrt{y^2 + M}} - 1 \right] - B_d \left[ \frac{y}{\sqrt{y^2 + N}} - 1 \right] = 0.$$

Taking the first three terms in the expansion of

$$\left[ 1 + \frac{M \text{ or } N}{y^2} \right]^{-\frac{1}{2}}$$

the value of  $y$  when the above condition is satisfied is given by

$$y^2 = \frac{\sqrt[3]{(N^2 B_d - M^2 B_h)}}{N B_d - M B_h}.$$

Substituting the values of the constants given above for the OD molecule and the corresponding constants for the OH molecule,<sup>10</sup> we obtain that the maximum occurs at

$$K = 5.7 \text{ for } v'' = 0, K = 6.0 \text{ for } v'' = 1, K = 6.2 \text{ for } v'' = 2.$$

Fig. 3 shows a curve for  $v'' = 1$  between  $\delta_d - \delta_h$  and  $K$  similar to that shown by Johnston<sup>4</sup> for  $v'' = 0$ . It indicates a maximum at  $K = 6$ , in beautiful agreement with the theoretical value.

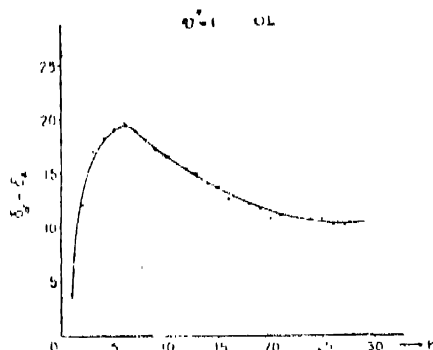


FIG. 3

The author is indebted to Dr. K. R. Rao for his interest in the work and to the Andhra University for the award of a Fellowship.

#### REFERENCES

- 1 Kemble, *Phy. Rev.*, **50**, 387 (1927).
- 2 Hill and Van Vleck, *Phy. Rev.*, **32**, 250 (1928).
- 3 Dawson and Johnston, *Phy. Rev.*, **43**, 980 (1933).
- 4 Johnston, *Phy. Rev.*, **46**, 80 (1934).
- 5 Sastry and Rao, (Part I), *Ind. Jour. Phy.*, **15**, 27 (1941) ; Sastry, (Part II), *Ind. Jour. Phy.* In press) ; Sastry, (Part III), *Ind. Jour. Phy.* (In press).
- 6 Jevons, *Report on Band Spectra*, 171.
- 7 The data quoted in these tables are taken from the author's papers referred to above for all the bands except for (0, 0), (2, 0) and (3, 1) which are from Ishaq, *Proc. Nat. Inst. Sci. Ind.*, **3**, 389 (1939) and *Proc. Roy. Soc.*, **A 159**, 110 (1937).
- 8 Almy, *Phy. Rev.*, **36**, 1495 (1930).
- 9 Shaw and Gibbs, *Phy. Rev.*, **46**, 124 (1934).
- 10 Johnston, Dawson and Walker, *Phy. Rev.*, **43**, 478 (1933).