STRUCTURE OF THE ELECTRONIC BANDS OF THE OD MOLECULE. PART V. Λ-DOUBLING

By M. G. SASTRY

ABSTRACT. The Λ-doubling in the $^2\Pi$ states of the OD molecule has been examined in the light of Mulliken's deductions from Van Vleck's theoretical equations. The doublet difference $\delta\nu_{2dc}(K) - \delta\nu_{1dc}(K)$ is found to vary nearly linearly with K. Comparison of the Doubling in OH and OD molecules has confirmed the conclusion of Johnston that it is smaller for OD than for OH. The ratio is determined to be about 0.31 slightly higher than that obtained by Johnston.

INTRODUCTION

The theory of Λ-type doubling has been developed especially by Van Vleck[1] for $^1\Pi$, $^2\Pi$ and other states of diatomic molecules. Mulliken,[2] in a comprehensive paper, restated Van Vleck's equations in a convenient form for application to experimental data. The following expressions have been deduced for the doubling (in Mulliken's notation) :

$$\delta\nu_{2dc} = \lceil(\tfrac{1}{2}p_0 + q_0)(1 + 2X^{-1} - Y.X^{-1}) + 2q_0X^{-1}(J - \tfrac{1}{2})(J + 1\tfrac{1}{2})\rceil(J + \tfrac{1}{2}) \quad \dots (1)$$

$$\delta\nu_{1dc} = |(\tfrac{1}{2}p_0 + q_0)(-1 + 2X^{-1} - Y.X^{-1}) + 2q_0X^{-1}(J - \tfrac{1}{2})(J + 1\tfrac{1}{2})|(J + \tfrac{1}{2}). \quad \dots (2)$$

Hence

$$\delta\nu_{2dc}(J) - \delta\nu_{1dc}(J) = (p_0 + 2q_0)(J + \tfrac{1}{2}) \quad \dots (3)$$

$$\delta\nu_{2dc}(J) + \delta\nu_{1dc}(J) = \lfloor(p_0 + 2q_0)(2 - Y)(J + \tfrac{1}{2})$$
$$+ 4q_0(J - \tfrac{1}{2})(J + \tfrac{1}{2})(J + 1\tfrac{1}{2})\rfloor X^{-1}. \quad \dots (4)$$

Mulliken applied equations (3) and (4) to a number of molecules among which are the OH and others which correspond to intermediate coupling case between (a) and (b). It was emphasised that, for large values of J, the effect of "rotational stretching" of the molecules must be considered in evaluating the constants.

Dawson and Johnston[3] and later Johnston,[4] while investigating the structure of the OH bands, have examined the question of Λ-doubling. For $v'' = 0$, 1 and 2, they have shown that the difference $\delta_1(K) - \delta_2(K)$ which in Mulliken's notation is the same as $\delta\nu_{2dc}(J) - \delta\nu_{1dc}(J)$ varies directly with K and not with $(K + \tfrac{1}{2})^2$. They have concluded that Van Vleck's theoretical equation has thereby failed, to fit for OH, by quite a large factor. Mulliken's deduction [refer equation (3)] shows that the variation is in keeping with Van Vleck's theory.

In the light of data obtained by the writer of the Λ-doubling in the $^2\Pi$ states of the OD molecule an attempt is made to examine this question.

RESULTS

All the values* of the Λ-doubling for the two components of the $^2\Pi$ states corresponding to $v''=0$, 1, 2 and 3 have been collected in Tables I and II. For each state, the mean values are obtained utilising the data of different bands having the same final state. (The convention of 'signs' defined by Mulliken, *loc. cit.*, p. 103, has been adopted.)

TABLE I

Λ-doubling (δ_1 for $^2\Pi_{1\frac{1}{2}}$ levels)

K	$v''=0$				$v''=1$				$v''=2$			$v''=3$
	0,0	1,0	2,0	Mean	1,1	2,1	3,1	Mean	2,2	3,2	Mean	3,3
1	.o	−.1	.7	.2	−1.2	.5	.5	−.4		.2	.2	
2	−.16	−.3	.5	0	−.6	.2	−.3	−.4	−.9	−.3	.6	
3	−.33	−.1	−.3	−.2	−.5	.9	.2	−.2	−.5	−10	−.8	−.3
4	+.49	−.2	−6	−.4	−.3	−.5	.1	.1	−.4	−.1	−.7	.2
5	−.65	−.3	−.6	−.5	−.4	−.1	.1	.1	−1.5	−.1	−.8	−1.1
6	−.59	−.5	−.7	−.6	.2	3	.5	.2	−.6	−.1	−.4	0
7	−.70	−7	−.7	−.7	0	−.2	−7	−.3	.3	−.2	.1	1.8
8	−1.08	−.6	−.8	−.8	−.7	−.8	−.9	−.8	−.6	−1.1	−.9	−.2
9	−1.40	−.8	−1.2	−1.1	−1.2	−1.3	−1.2	−1.2	−1.9	−1.3	−1.6	−1.4
10	−1.53	−.9	−1.3	−1.2	−1.8	−1.6	−1.3	−1.6	−3.7	−1.5	−2.6	−1.0
11	−1.90	−1.1	−1.9	−1.6	−2.3	−1.7	−1.7	−1.9	−2.6	−1.8	−2.2	−1.2
12	−2.01	−1.9	−2.0	−2.0	−2.9	−1.5	−2.1	−2.2	−3.8	−1.5	−2.7	
13	−2.43	−2.4	−2.1	−2.3	−2.7	−1.8	−2.3	−2.3	−2.5	−2.1	−2.3	
14	−2.82	−3.3	−2.8	−3.0	−3.2	−2.6	−2.6	−2.8	−2.5		−2.5	
15	−3.35	−3.2	−3.0	−3.2	−3.5	−3.0		−3.3	−3.2		−3.2	
16		−3.8	−3.7	−3.8	−3.0	−3.6		−3.3	−4.3		−4.3	
17		−4.3	−3.8	−4.1	−4.4	−3.9		−4.2	−3.5		−3.5	
18		−4.0	−3.9	−4.0	−3.8	−4.7		−4.3	−3.5		−3.5	
19		−4.9	−1.2	−4.9	−4.8			−4.8	−3.6		−3.6	
20		−4.8		−4.8	−4.8			−4.8	−5.4		−5.4	
21		−5.7		−5.7	−5.8			−5.8	−5.8		−5.8	
22		−5.8		−5.8	−6.2			−6.2	−7.1		−7.1	
23		−6.1		−6.1	−4.6			−4.6	−8.3		−8.3	
24		−6.6		−6.6	−6.2			−6.2				
25		−7.7		−7.7	−8.6			−8.6				
26		−9.7		−9.7	−8.1			−8.1				
27					−7.3			−7.3				
28					−8.8			−8.8				
29					−10.0			−10.0				
30					−11.9			−11.9				
31					−12.6			−12.6				
32					−11.2			−11.2				
33					−8.7			−8.7				
34					−9.3			−9.3				

Taken from Parts I, II, and III of this series of papers.

TABLE II
Λ-doubling (δ_2 for $^2\Pi_{\frac{3}{2}}$ levels)

K	$v''=0$				$v''=1$				$v''=2$			$v''=3$
	0,0	1,0	2,0	Mean	1,1	2,1	3,1	Mean	2,2	3,2	Mean	3,3
1	.39	−7	.1	−.1			⁻1 5	⁻ 5				
2	.26	5	−.1	.2	− ·6	4	·5	− .2		− ·7	− 7	
3	·15	·3	−·3	.1	·3	−·3	.8	·3	2.9	0	1·5	−1.0
4	.28	−·1	·3	.2	8	·7	·7	·7	2.8	·7	1.8	−·6
5	·27	·2	·3	·3	1 4	·5	.6	.8	1.9	·3	1.1	−·8
6	.39	−.2	5	2	− 1	−·3	·5	0	− .2	.2	0	− ·2
7	28	.2	.4	3	0	4	1·3	6	−1.6	7	1.2	.2
8	.08	·5	·3	·3	·6	2	9	.6	.6	·5	.6	1·1
9	·06	−·1	1	0	− .1	− 2	.1	− 1	− .2	1.0	− .1	·4
10	−.11	−.2	·3	0	− 7	4	.1	− .1	−1.4	.1	− ·7	2
11	− 26	−.2	−.2	− 2	− ·4	·3	1.1	·3	−2 6	—	−2 6	.9
12	−·29	−·4	−·2	−·3	− .6	—	1 3	1·3	−3 0	—	−3.0	—
13	−·73	−·1	−·5	−.4	.8	—	1.8	1 8	−1 7	—	1.7	—
14	−·90	−·7	—	−.8	−2 1	—	—	—	2 7	—	2.7	—
15	·	—	—	—	·3	—	—	—	.7	—	.7	—
16	—	—	—	—	− 1.8	—	−	—	−2.1	—	−2.1	—
17	—	—	—	—	− 1 6	—	—	—	−2.6	—	− 2.6	− −
18	—	—	—	—	−1·7	−	—	—	− 1.7	—	−1.7	—
19	—	—	—	—	−3.8	—	—	—	−3.2	—	−3 2	—
20	—	—	—	—	−3.5	—	—	—	− ·3	—	− ·3	—
21	—	—	—	—	−3 4	—	—	—	—	—	—	—
22	—	—	—	—	−3 6	—	—	—	—	—	—	—
23	—	—	—	—	−4.9	—	—	—	—	—	—	—
24	—	—	—	—	−5 3	—	—	—	—	—	—	—
25	—	—	—	—	−3·4	—	—	—	—	—	—	—
26	—	—	—	—	−5.0	—	—	—	—	—	—	—
27	—	—	—	—	−5.6	—	—	—	—	—	—	—
28	—	—	—	—	−6 1	—	—	—	—	—	—	—
29	—	—	—	—	−6 3	—	—	—	—	—	—	—
30	—	—	—	—	−7·3	—	—	—	—	—	—	—
31	—	—	—	—	−8.3	—	—	—	—	—	—	—

Table III gives the values of $\delta_2 - \delta_1$, *i.e.*, of the difference $\delta v_{2dc}(K) - \delta v_{1dc}(K)$ for the OD bands corresponding to $v''=0$. The data for the other states, $v''=1$, 2, etc. (particularly the components due to $^2\Pi_{\frac{1}{2}}$ state of each level) are too meagre and too uncertain (as they are derived from the R_1 and R_2 branches) to be considered as a basis for this discussion and hence have not been shown in this Table.

Curve (a) shows the variation of the above difference with K. A general, almost linear, relation is obvious, consistent with Mulliken's equation (3). With higher K values, there appears to be a slight departure from linearity, indicating presumably the effect of " rotational stretching " referred to by Mulliken.

CURVE (a)

$v'' = 0 (oD)$

⟶ K

CURVE (a)
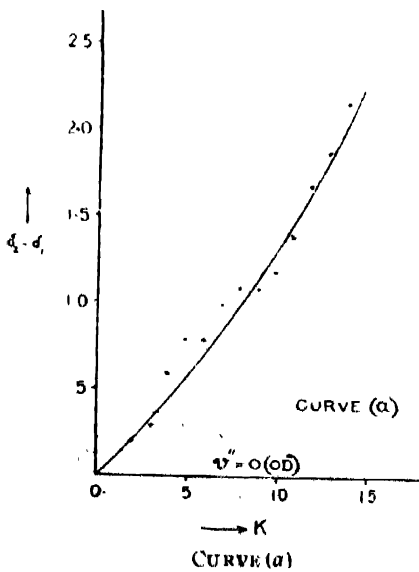
COMPARISON OF OH AND OD

Distinct from the conventional method of studying the isotope effect in band spectra, Johnston[4] referred to the isotope effect in Λ-doubling in the $^2\Pi$ states

TABLE III

Λ-doublet differences $(\delta_2 - \delta_1)$ for $v'' = 0$, in OD bands

K	δ_1	δ_2	$(\delta_2 - \delta_1)$
1	.2	-.1	-.3
2	0	.2	.2
3	-.2	.1	.3
4	.4	.2	.6
5	-.5	.3	.8
6	-6	2	8
7	-7	.3	1.0
8	-.8	.3	1.1
9	-1.1	0	1.1
10	-1.2	0	1.2
11	-1.6	-.2	1.4
12	-2.0	-.3	1.7
13	-2.3	-.4	1.9
14	-3.0	-.8	2.2
15	-3.2	—	—
16	-3.8	—	—
17	-4.1	—	—
18	-4.0	—	—
19	-4.9	—	—
20	-4.8	—	—
21	-5.7	—	—
22	-5.8	—	—
23	-6.1	—	—
24	-6.6	—	—
25	-7.7	—	—
26	-9.7	—	—

TABLE IV

Λ-doubling in $^2\Pi_{1\frac{1}{2}}$ states of OD and OH molecules

K	v''=0			v''=1			v''=2			v''=3
	OH	OD	Ratio	OH	OD	Ratio	OH	OD	Ratio	OD
1	− .33	.2	--	− .3	− .4	—	− .1	.2	—	—
2	− .40	0	—	− .4	− .4	---	—	− .6	—	—
3	− .59	− .2	.33	− .6	− .2	---	− .9	− .8	--	.3
4	− .99	− .4	.40	− .9	− .1	—	− .8	− .7	—	.2
5	− 1.40	− .5	.36	− 1.5	1	—	− 1.5	− .8	.53	− 1.1
6	− 2.07	− .6	.28	− 1.8	.2	.11	− 1.2	− .4	.33	0
7	− 2.61	− .7	.27	− 2.5	− .3	.12	− 2.1	− .1	--	1.8
8	− 3.34	− .8	.24	− 3.4	− .8	.23	− 2.9	− .9	.31	− .2
9	− 4.29	− 1.1	.26	− 4.2	− 1.2	.29	− 5.2	− 1.6	.30	− 1.4
10	− 5.13	− 1.2	.24	− 4.7	− 1.6	.34	− 6.2	− 2.6	.42	− 1.0
11	− 6.18	− 1.6	.26	− 6.3	− 1.9	.30	—	− 2.2	--	− 1.2
12	− 7.03	− 2.0	.28	− 6.8	− 2.2	.32	—	− 2.7	—	—
13	− 7.74	− 2.3	.30	− 6.9	− 2.3	.33	—	− 2.3	--	--
14	− 8.94	− 3.0	.33	− 8.2	− 2.8	.34	—	− 2.5	--	—
15	− 10.03	− 3.2	.32	− 9.3	− 3.3	35	—	− 3.2	—	—
16	− 11.25	− 3.8	34	− 10.5	− 3.3	.31	—	− 4.3	--	—
17	− 12.27	− 4.1	33		− 4.2	...	—	− 3.5	-	—
18	− 13.36	− 4.0	30	---	− 4.3	---	.	− 3.5	..	.
19	− 14.99	− 4.9	.33	---	− 4.8	—	. -	− 5.6		
20	− 16.30	− 4.8	30	—	− 4.8	..		− 5.4	—	-
21	− 15.54	− 5.7	—	—	− 5.8	---	—	− 5.8	—	..
22	− 17.68	− 5.8	.33	—	− 6.2	--	—	− 7.1	—	—
23	− 19.5	− 6.1	.31	—	− 4.6	---	---	− 8.3	...	.
24	− 20.8	− 6.6	.31	—	− 6.2	—	--	—	—	.
25	− 21.6	− 7.7	.36	—	− 8.6	—	—	—	—	--
26	− 25.1	− 9.7	—	—	—	—	—	—	—	--
			Mean .31			Mean .28			Mean .34	

of the OII and the OD molecules. Curves have been drawn by him (from as yet unpublished data) showing the variation of the doubling with K for the states $^2\Pi_{1\frac{1}{2}}$ and $^2\Pi_{\frac{1}{2}}$ for $v''=0$ in the case of the two molecules. The doubling in the OD molecule is found to be much smaller than for the OH molecule for the same value of K. The ratio of the spacings is stated to be 0.284.

Table IV presents the values of δ_{OD} and δ_{OH} for the $^2\Pi_{1\frac{1}{2}}$ state for $v''=0$, 1, 2 and 3. The data on the OD bands are due to the writer and those on the OH bands are quoted from Dawson and Johnston's paper,[3] with the signs changed. The results are presented in curves (b) and (c) for the two isotopic
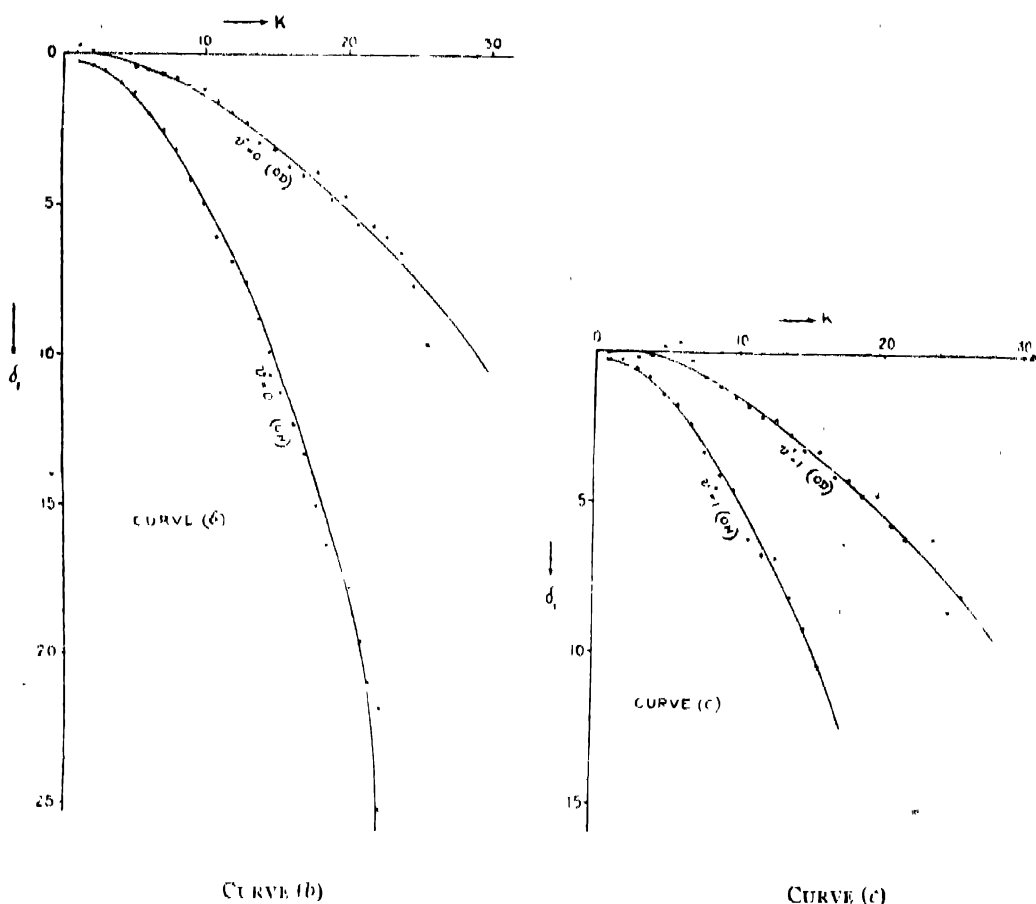
CURVE (b)

CURVE (c)

molecules for $v''=0$ and 1. (These curves slope downwards and not upwards as indicated by Johnston if Mulliken's convention of signs referred to above is adopted.) The curves clearly indicate that, in magnitude, the Λ-doubling in the OD molecule is less than that in OH for the same value of K in all the vibrational states. The ratio between δ_{OD} and δ_{OH} is on an average about 0.31.

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ANDHRA UNIVERSITY,
     WALTAIR

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[4] Johnston, *Phy Rev*, **45**, 80 (1934).