

STRUCTURE OF THE ELECTRONIC BANDS OF THE OD MOLECULE—PART VI (ISOTOPIC SHIFT)

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ABSTRACT. From the constants of the OH molecule, the vibrational and rotational isotope shift in the OH and OD band heads have been calculated. In estimating the rotational shift, a direct method of using Hill and Van Vleck's theoretical expression for the rotational energy for doublet electronic states representing any stage of coupling, has been adopted. When the total calculated shifts are compared with the observed shifts obtained directly from experiment, large discrepancies are found. No electronic shift could be postulated and, if it exists, it is estimated to be less than a unit of wave number.

INTRODUCTION

It was pointed out in Part I of this series of papers that OH and OD form an interesting pair of isotopic molecules, the band structure of which yields valuable information on the isotopic effect in band spectra. Apart from the conventional treatment of the isotopic effect in molecular spectra, Johnston and Dawson¹ considered from unpublished data the isotope effect on the spacings of the spin components and the Λ -coupling electronic isotopic effect associated with the 2π components of the OH and OD molecules. These considerations have been dealt with by the author in the earlier parts.

In a short note, Johnston and Dawson² reported at first the presence of a large electronic isotope shift, amounting approximately to about 10 cm^{-1} in the lines at the head of the (1,0) band. Later, they considered the isotopic displacements of three of the heads, (2,0), (1,0) and (0,1).³ In deriving the total displacements, they have calculated the vibrational, rotational and spin coupling effect separately and indicated that there is agreement between the calculated and observed displacements if, instead of postulating a large electronic shift, the spin coupling effect is taken into account. It must be pointed out, however, that according to their own calculations, the agreement is close only in the case of the (2,0) band and perhaps also of the (1,0) band, but in the (0,1) band there is a difference as large as about 10 cm^{-1} .

In H^1H^1 and H^1H^2 band systems, a large electronic shift, as high as 136 units was observed by Jeppesen⁴, Dicke⁵, and Dicke and Lewis⁶, from a study of the H_2 , HD, D_2 band systems observed that these electronic shifts could be accounted for by taking correction terms arising from the interaction between the electronic motion and the rotation and vibration in the case of diatomic molecules. These correction terms, discussed by Van Vleck⁷, become very important in the case of such light isotopic molecules as H_2 , HD, etc.

In view of the theoretical importance of the determination of the isotope shifts in bands where H and D are involved, a detailed study of the isotope effect in OH and OD bands has been attempted by the author. In this paper the shifts of the heads of the various bands are considered, as was done by Johnston and Dawson, but following a more direct method in the evaluation of the shift. In a later paper, the method will be applied for studying the displacements of the various lines in the individual bands. A very direct and appropriate method⁶ of investigating the isotope effect would be to determine with a high degree of precision the constants of both the molecules of OH and OD and to determine therefrom the values of the first, second and third powers of the mass factor and to compare these with the corresponding values from mass spectra data. For this purpose, experiments must be carried out with mixtures of ordinary and heavy water, obtaining thus the band systems of both the molecules without any relative mechanical shifts. Such a method is found practicable if the study is made on the (2,0) and (3,1) bands of these molecules; the results will be published in the next part of these papers.

CALCULATION OF THE ISOTOPE SHIFT

Vibrational shift.—The vibrational isotope displacement of the (v' , v'') band can be directly determined from the equation (Jevons' Report, p. 213):

$$v_v^i - v_v = (\rho - 1) \{w'_e (v' + \frac{1}{2}) - w''_e (v'' + \frac{1}{2})\} - (\rho^2 - 1) \{x'_e w'_e (v' + \frac{1}{2})^2 - x''_e w''_e (v'' + \frac{1}{2})^2\} + (\rho^3 - 1) \{-\} \text{etc.} \dots \quad (1)$$

The values of the constants used in this and the succeeding equations are listed in Table II at the end. For the (1,0) band the shift is obtained as -697.64 units.

Rotational shift.—The rotational isotopic displacement of a band line is given by the expression (Jevons' Report, p. 216):

$$v_r^i - v_r = (\rho^2 - 1) \{B'_e N'^2 - B''_e N''^2\} - (\rho^3 - 1) \{\alpha' U' N'^2 - \alpha'' U'' N''^2\} + (\rho^4 - 1) \{D'_e N'^4 - D''_e N''^4\} + \text{etc.} \dots \quad (2)$$

neglecting higher terms.

In estimating the proper values of N' and N'' in equation (2), use is made of general expression for the rotational energy derived by Hill and Van Vleck (Jevons' Report, p. 124) for doublet electronic states representing any intermediate stage of coupling between Hund's Case (a) and Case (b).

$$F(J) = B_v \left[(J + \frac{1}{2})^2 - \Lambda^2 \pm \sqrt{\left\{ (J + \frac{1}{2})^2 - \frac{\Lambda^2 A}{B_v} \left(1 - \frac{A}{4B_v} \right) \right\}} \right] \quad (3)$$

neglecting the small term involving γ and the term in D_e .

The following illustration shows the calculation for the (1,0) band:

(a) The band lines are expressed by the formula

$$v = v_0 + (B' + B'')M + (B' - B'' + D' - D'')M^2 + 2(D' + D'')M^3. \dots \quad (4)$$

By differentiation,

$$(dv/dM) = (B' + B'') + 2M(B' - B'' + D' - D'') + 6M^2(D' + D''). \quad \dots (5)$$

Equating this to zero we get the value of M corresponding to the head. In general this value is not integral. Hence in choosing the proper value, that particular nearest integer is adopted for which the value of ν is maximum. This procedure is considered to be justifiable as the band is degraded to the red. Perhaps the experimental value of M might be preferred to that derived from equation⁴ in the above manner but it is to be noticed that even the experimental value is not unique, the head of the band often being assigned two or more values of J, for want of adequate resolution.

Substituting the values of the rotational constants shown in Table II at the end, we obtain $M = 6.58$. The proper integer chosen is $M = 7$; the head of the band (1,0) then corresponds to $J' = 7$, and $J'' = 6$.

(2) Hence for the initial state, from equation (3) $N'^2 = 48.75$ and for the final state $N''^2 = 34.25$.

(3) Substituting these values of N' and N'' in equation (2) we obtain,

$$\nu_f - \nu_r = 6\nu_r = -59.67.$$

The results obtained in the case of all the bands in the above manner have been collected in Table I. In the fifth column of this table are given the shifts directly obtained from the measurements on the plates in which the OH and OD bands are obtained in juxtaposition on either side of the standard Fe arc spectrum.

TABLE I*
Isotopic shifts

Band (ν', ν'')	Vibrational	Rotational	Total calculated shift	Observed shift	Obs.-Calc.
(0, 0)	+ 76.7	- 90.1	- 13.4	- 12.4	+ 1.0
(1, 0)	- 697.6	- 59.7	- 757.3	- 749.3	+ 8.0
(2, 0)	- 1380.2	- 46.8	- 1427.0	+ 1414.8	+ 12.2
(3, 0)	- 1971.2	- 39.7	- 2010.9	- 1994.5	+ 16.4
(0, 1)	+ 1014.8	- 140.4	+ 874.4	+ 860.6	- 13.8
(1, 1)	+ 240.6	- 75.3	+ 165.3	+ 166.7	+ 1.4
(2, 1)	- 442.0	- 52.8	- 494.8	- 486.7	+ 8.1
(3, 1)	- 1033.1	- 40.7	- 1073.8	- 1061.8	+ 12.0
(2, 2)	+ 418.7	- 63.5	+ 355.2	+ 358.6	+ 3.4
(3, 2)	- 172.3	- 45.8	- 218.1	- 200.1	+ 18.0

* The values quoted in the above table are a revision of those published in *Current Science* (Vol. X, No. 8, 1941 pp. 362-63). In the note

(1) in estimating the vibrational shifts the third term in y', w' , has been omitted,

(2) in estimating the rotational shifts from the general expression the value of M , is directly substituted for N , hence the difference.

The last column in the table shows rather large discrepancies between the observed and the calculated values, the differences showing an increase with increasing values of v' . It is possible that they may be due partly to the uncertainty in the choice of M , but on calculation with different integral values of M a change of only 2 to 3 units in the final values of the rotational shift is obtained.

A definite electronic isotope shift cannot be postulated; and, if at all there is one, it must be less than a unit as the observed *minus* calculated values for the (0,0) and (1,1) bands are only of this order. It would seem therefore that the differences are to be ascribed either to the inadequacy of or the approximations made in the theoretical expression used for the rotational energy; for instance, in neglecting the terms $D_v J^2(J+1)^2$, and the small term involving γ ; it must be emphasised also that the errors in the evaluation of the various constants for the OH molecule adopted in obtaining the shifts cannot be negligible.

TABLE II

Values of the Constants¹

$H^1 = 1.00778$;	$\rho^{-1} = -0.271931$;	$\rho^3 - 1 = -0.614062$.	
$H^2 = 2.01363$;	$\rho^2 - 1 = -0.469915$;	$\rho^4 - 1 = -0.719011$.	
$O = 16.000$			
$\omega'_e = 3184.1$;	$x'_e \omega'_e = 97.7$		
$\omega''_e = 3734.9$;	$x''_e \omega''_e = 82.6$		
$B'_e = 17.375$	$B''_e = 19.009$	$D'_e = -2.07 \cdot 10^{-3}$	$D''_e = -1.97 \cdot 10^{-3}$
$B'_0 = 16.954$	$B''_0 = 18.663$	$a' = 0.838$	$a'' = 0.686$
$B'_1 = 16.101$	$B''_1 = 17.952$	$\beta' = 4.3 \cdot 10^{-5}$	$\beta'' = 5.0 \cdot 10^{-5}$
$B'_2 = 15.233$	$B''_2 = 17.216$	$\gamma'_e = -0.0075$	$\gamma''_e = -0.0125$
$B'_3 = 14.350$	$A = 141.0$		

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† Extrapolated value.