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Vibrational Frequencies of the Isotopic Water Molecules; Equilibria with the Isotopic Hydrogens

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The fundamental frequencies, anharmonicities, and vibrational modes for the molecules HDO. HTO. DTO. and T₂O are calculated on the basis of Dennison's and Darling's recent analysis of the vibrational spectrum of the H_2O molecule. The equilibrium constants for nine equilibria involving these molecules are given. Experimental values for the reactions HD+H₂O $=H_2+HDO$ and $HT+H_2O=H_2+HTO$ are compared with those calculated. It is concluded that the vibrational potential function is essentially unaltered by isotopic substitution.

HE recent work of Dennison and Darling^{1a, 1b} on the vibrational levels of the water molecule has considerably improved our knowledge of the detailed nature of the potential function in the ground state.1° As a consequence, an improvement in the calculated levels for the isotopic water molecules should result. Several authors²⁻⁶ have given results for HDO and D₂O on the older analyses of the vibration-rotation spectrum of H_2O . The agreement between the results of this research and those previously published is correlated directly with the analysis of the H₂O molecule spectrum adopted in most of the papers.

The discovery of tritium⁷ (radioactive hydrogen) has made possible further tests of the fundamental assumption of all such calculations, namely, that the potential function of a molecule shall be independent of the isotopic composition of its constituent elements. The new molecules which are subject to experimental investigation at present are HTO and DTO. The other, T_2O , has not been obtained in sufficient amounts or purity to allow examination, due to the radioactivity of tritium (half-life approximately 30 years⁸).

I. FUNDAMENTAL MODES AND FREQUENCIES

Since substitution of one of the hydrogen atoms of H_2O by D or T destroys the symmetry of the molecule, the form and interactions of the normal modes are altered rather seriously (cf. Fig. 1). In particular the secular equations for

^{*} This research was completed during tenure of a John

 ¹⁴ B. T. Darling and D. M. Dennison, Phys. Rev. 57, 128 (1940).

¹⁶ D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940). ¹⁶ Harald H. Nielsen, Phys. Rev. **62**, 422 (1942), has

recently given values for the frequencies and anharmonicities slightly different from those of Dennison and Darling. The differences are so small, however, as to have little effect on the considerations in the present paper. ² T. Förster, Zeits. f. physik. Chemie **B27**, 1 (1934).

³A. Farkas and L. Farkas, Proc. Roy. Soc. (London) A144, 467 (1934). ⁴ R. H. Crist and G. A. Dalin, J. Chem. Phys. 2, 735

^{(1934).} ⁵ B. Topley and H. Eyring, J. Chem. Phys. 2, 217

^{(1934).}

⁶T. Jones and A. Sherman, J. Chem. Phys. 5, 375 (1937).

⁷L. W. Alvarez and R. Cornog, Phys. Rev. 56, 613 (1939). ⁸ R. D. O'Neal and M. Goldhaber, Phys. Rev. 58, 574 (1940).



FIG. 1. Normal modes for isotopic water molecules.

the frequencies must be cubics. Cross and Van Vleck⁹ have discussed the problem for the general triatomic molecule, arriving at simplified general expressions leading to the secular cubic.

Dennison's and Darling's^{16, 1b} analysis gave as the expression for the first-order or simple harmonic potential energy of the water molecule

$$2V(\text{ergs}) = 8.428 \times 10^{5} (\delta r_{1})^{2} + 8.428 \times 10^{5} (\delta r_{2})^{2} + 0.7676 \times 10^{5} (R \delta \alpha)^{2} - 2(0.1051) \times 10^{5} (\delta r_{1} \delta r_{2})$$
(1)
+ 2(0.2521) \times 10^{5} (R \delta \alpha) (\delta r_{1} \delta r_{2})^{*}

where δr_1 and δr_2 are the differences in cm between the actual distances between the O atom and each of the two hydrogen atoms and the corresponding equilibrium distance, R, and $\delta \alpha$ is the difference in radians between the actual angle between the two lines joining the O atoms to the hydrogens and its equilibrium value. The equilibrium values of R and α are 0.9580A and 104° 31', respectively.

The fundamental frequencies for the six isotopic molecules based on the above potential are given in Table I. The hydrogen masses used were 1.00813, 2.01473, and 3.01705 for the H, D, and T atoms, respectively.

The normal modes are represented in Table II. where δr_1 always refers to the distance between the O atom and the heavier of the two hydrogen atoms in the molecule. The dimensionless variables, x_i , related to the normal coordinates, Q_i , by

$$x_i = 2\pi (\nu_i/h)^{\frac{1}{2}} Q_i \tag{2}$$

are used. The coefficients are adjusted to give the δr_1 , δr_2 , and $R\delta \alpha$ values in Angstroms. For classical vibrations x_i ranges from 0 to $\pm \sqrt{2}$.

An interesting characteristic of the normal modes for the asymmetric molecules is that the two stretching vibrations approximate vibrations of the hydroxyl groups with respect to the remaining hydrogen atoms, the two frequencies being separated because of the different masses. This is illustrated in Fig. 1.

The results of the application of the Teller,¹⁰ Redlich¹¹ product rule are presented in Table III. The rule rigorously requires that insofar as two molecules have identical potential energies for motions of the constituent atoms they must have identical values for the expression

$$\frac{(\pi\nu_i)^2(\pi m_i)^3}{M^3 I_A I_B I_C},$$

in which πv_i is the product of the frequencies, πm_i is the product of the masses of the constituent atoms, M is the molecular weight, and $I_A I_B I_C$ is the product of the principal moments of inertia. Column 4 of the table contains these values. The check appears to be satisfactory.

II. ANHARMONICITIES

A. Values Uncorrected for Kinetic Energy Perturbations

Dennison and Darling¹ have shown from experimental data that the anharmonicities, X_{ij} ,

TABLE I.	Fundamental	frequencies of	isotopic
	water m	olecules.	-

	H	requencies (cm ⁻¹)
Molecule	ω_3	ωι	ω_2
H ₂ O	3935.59	3825.32	1653.91
HDO	3883.8	2820.3	1449.4
D_2O	2883.79	2758.06	1210.25
DTO	2830.7	2357.1	1117.9
T ₂ O	2436.12	2296.63	1017.89
HTO	3882.6	2365.0	1374.5

in the energy expression

$$W = \omega_1(n_1 + \frac{1}{2}) + \omega_2(n_2 + \frac{1}{2}) + \omega_3(n_3 + \frac{1}{2}) + X_{11}(n_1 + \frac{1}{2})(n_1 + \frac{1}{2}) + X_{12}(n_1 + \frac{1}{2})(n_2 + \frac{1}{2}) + X_{22}(n_2 + \frac{1}{2})(n_2 + \frac{1}{2}) + X_{23}(n_2 + \frac{1}{2})(n_3 + \frac{1}{2}) + X_{13}(n_1 + \frac{1}{2})(n_3 + \frac{1}{2}) + X_{33}(n_3 + \frac{1}{2})(n_3 + \frac{1}{2})$$
(3)

¹⁰ W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L.
 Wilson, J. Chem. Soc. (London), 971 (1936).
 ¹¹ O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).

⁹ Cross and Van Vleck, J. Chem. Phys. 1, 357 (1933).
* Note: The expression (1) differs from that given in reference 1b in the sign of the fourth term on the right, apparently because of a typographical error in reference 1b.

for the H₂O and D₂O molecules are nearly in the direct ratio $(\omega_i'\omega_j'/\omega_i\omega_j)^{\frac{1}{2}}$ where the primes refer to the H₂O frequencies, a result strictly true for H₂O¹⁶ vs. D₂O³². Since both the H₂O and D₂O molecules are symmetrical, doubts arise that the method is applicable strictly to the asymmetrical molecules HDO, HTO, and DTO when compared with H₂O or D₂O. This point appears to deserve further consideration.

Expressing the potential energy in terms of the dimensionless variables x_{i} ,

$$2V = h\nu_{1}x_{1}^{2} + h\nu_{2}x_{2}^{2} + h\nu_{3}x_{3}^{2} + \alpha_{1}x_{1}^{3} + \alpha_{2}x_{2}^{3} + \alpha_{3}x_{3}^{3} + \alpha_{12}x_{1}^{2}x_{2}^{1} + \alpha_{21}x_{2}^{2}x_{1} + \alpha_{13}x_{1}^{2}x_{3} + \alpha_{31}x_{3}^{2}x_{1} + \alpha_{23}x_{2}^{2}x_{3} + \alpha_{32}x_{3}^{2}x_{2} + \alpha_{123}x_{1}x_{2}x_{3} + \beta_{1}x_{1}^{4} + \beta_{2}x_{2}^{4} + \beta_{3}x_{3}^{4} + \beta_{12}x_{1}^{2}x_{2}^{2} + \beta_{13}x_{1}^{2}x_{3}^{2} + \beta_{23}x_{2}^{2}x_{3}^{2} + \epsilon_{1}x_{1}x_{2}^{3} + \epsilon_{2}x_{2}x_{1}^{3} +$$

other odd powers of fourth order, standard perturbation theory gives expressions for the anharmonicities in terms of the potential constants. These are given in Appendix I.

Certain small adjustments in the numerical constants in these expressions were made to insure that the expression for the energy W remain a power series in $(n_i + \frac{1}{2})$. Dennison's and Darling's¹ discussion of this point is completely applicable here.

The procedure adopted has been to calculate the α_i and β_i constants for each isotopic water

TABLE II. Normal modes of isotopic water molecules.

Molecule			Modes	
H ₂ O	$\delta r_1 = \\ \delta r_2 = \\ R \delta \alpha =$	$\begin{array}{c} 0.0676x_1\\ 0.0676x_1\\ 0.000946x_1 \end{array}$	$- 0.00647 x_2 \\ - 0.00647 x_2 \\ + 0.209 x_2$	$-0.0690x_3 + 0.0690x_3 + 0x_3$
HDO	$\delta r_1 = \\ \delta r_2 = \\ R \delta \alpha = -$	$\begin{array}{c} 0.0824x_1\\ 0.00480x_1\\ -0.00295x_1\end{array}$	$-\begin{array}{c}-0.00537 x_2\\-0.00559 x_2\\+0.196 x_2\end{array}$	$+0.0063x_3$ $-0.0965x_3$ $+0.00104x_3$
D_2O	$\delta r_1 = \\ \delta r_2 = \\ R \delta \alpha =$	$\begin{array}{c} 0.0573x_1\ 0.0573x_1\ 0.0573x_1\ 0.0050x_1 \end{array}$	$-\begin{array}{c}-0.00614 x_2\\-0.00614 x_2\\+0.179 x_2\end{array}$	$-0.0591x_3$ +0.0591 x_3 + $0x_3$
DTO	$\delta r_1 = \\ \delta r_2 = \\ R \delta \alpha = -$	$\begin{array}{c} 0.0748x_1 \\ 0.0104x_1 \\ -0.00895x_1 \end{array}$	$- 0.00371 x_2 \\ - 0.00387 x_2 \\ + 0.172 x_2$	$+0.0116x_3$ $-0.0820x_3$ $+0.00486x_3$
T_2O	$\delta r_1 = \\ \delta r_2 = \\ R \delta \alpha =$	$\begin{array}{c} 0.0524x_1 \\ 0.0524x_1 \\ 0.0090x_1 \end{array}$	$\begin{array}{r} -0.00623 x_2 \\ -0.00623 x_2 \\ +0.1638 x_2 \end{array}$	$-0.0542x_3 + 0.0542x_3 + 0x_3$
нто	$\delta r_1 = \delta r_2 = R \delta \alpha = -$	$\begin{array}{c} 0.0754x_1 \\ 0.00400x_1 \\ -0.00474x_1 \end{array}$	$- \begin{array}{c} - 0.00479 x_2 \\ - 0.00509 x_2 \\ + 0.191 x_2 \end{array}$	$+0.00408x_3$ $-0.0965x_3$ $+0.00160x_3$

TABLE III	. Product	rule cheo	k on fur	ndamental	frequencies.
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Molecule	$\left(\frac{m_1m_2m_3}{M}\right)^3\frac{1}{I_AI_BI_C}$	$(\nu_1\nu_2\nu_3)^2$	$\left(\frac{m_1m_2m_3}{M}\right)^{\frac{3}{(\nu_1\nu_2\nu_3)^2}}I_AI_BI_C$
H ₂ O	$\frac{1}{\overline{7.9625}}$	6.1992	0.7783
HDO	$\frac{1}{3.2405}$	2.5204	0.7777
D ₂ O	$\frac{1}{1.1928}$	0.92659	0.7764
DTO	$\frac{1}{0.71640}$	0.55636	0.7764
T_2O	$0.\overline{41721}$	0.32433	0.7776
НТО	$\frac{1}{2.0482}$	1.5930	0.7777

molecule in terms of those for the H₂O molecule and substitute them in the above expressions. Using the expressions in Table II and equating the deformations δr_1 , δr_2 , and $R\delta\alpha$ for the two molecules leads to a linear relation between the x_i for the isotopic molecule and the x_i' for the H₂O molecule, $x_i' = \sum \gamma_{ij} x_j$.

Substitution in Eq. (4) gives expressions for the α_i and β_i for the isotopic molecule in terms of those for H₂O, α_i' and β_i' . These expressions are given in Appendix II.

Table IV gives the potential constants, those for H₂O being those from Dennison and Darling.

Table V gives the anharmonicities calculated from these constants and the equations in Appendix I.

B. Kinetic Energy Perturbations

These values for the X_{ij} 's are not quite correct because the motions of the atoms contribute zero angular momentum with respect to axes defined in terms of the equilibrium positions of the atoms only at the instant that the atoms are in these equilibrium positions. The actual motions constitute an oscillatory vibrational motion with respect to these axes. These energies are to be calculated as perturbations of the levels derived on the basis of the axes established with respect to the equilibrium positions. Weinberg and Eckart¹² have discussed this calculation, and Dennison and Darling¹ describe its application

¹² A. Weinberg and C. Eckart, J. Chem. Phys. 5, 517 (1937).

		upo		DTO	т.О	
Constant	H20	HDO	D20	DIO	1 20	
α_1	-322	-272.2	-197.4	-203.7	-149.7	-208.2
α_2	-47	- 36.9	-30.85	-22.7	-24.79	34.0
α_3	0	431.8	0	264.0	0 50	433.7
α_{12}	1	45.66	13.08	14.5	20.58	31.45
α_{21}	216	124.7	134.4	101.25	99.1	109.9
α_{13}	0	-34.39	5(0)	-07.0	0	- 19.5
α_{31}	- 909	-96.48	- 502.0	-127.0	-431.1	72.4
α_{23}	1(0	- 120.4	107.0	- 15.9	0 86.07	- 121.8
α_{32}	100	127.2	107.9	43.1	00.97	120.0
α_{123}	0	127.2	0	90.74	0	120.9
β_1	39	37.91	20.28	25.79	14.02	26.46
P 1		$-4.57 imes10^{-3}\epsilon_2$	$+0.0123\epsilon_{2}$	$-0.01002\epsilon_2$	$+1.83 \times 10^{-2} \epsilon_2$	$-0.00497\epsilon_{2}$
		$+0.00705\epsilon_{1}$	$-0.00553\epsilon_{1}$	$+0.0124\epsilon_{1}$	$-0.00824\epsilon_{1}$	$+0.00944\epsilon_{1}$
β_2	2	1.54	1.073	0.908	0.748	1.383
ß.	35	70.44	18.8	36.43	13.37	71.02
P3	00	$-2.35 \times 10^{-3} \epsilon_2$	2010	$-0.00352\epsilon_2$	20101	$-0.00332\epsilon_{2}$
		-0.0200c	$\pm 0.0375c$	-0.05356	±0.056e	-0.03626
Bis	- 116	- 72 0	-61.3		-42.55	56.8
p_{12}	-110	± 0.010026	-0.01636	0.02166	-0.024260	$\pm 0.0115 co$
		1 010100202	0.010002	0.011002	0.021202	1 0.011002
β_{13}	212	5.22	112.2	8.62	78.6	4.2
		$-0.0212\epsilon_2$		$-0.0373\epsilon_2$		$-0.0275\epsilon_{2}$
		-0.01406		-0.0271e.		-0.0177c
Ban	-108	-074	- 57 9	- 54 5	-40.8	- 92.6
P 23	, 100	$+0.0107\epsilon_{2}$	0)	$+0.0148e_{2}$		+0.0177
	· · · · · · · · · · · · · · · · · · ·	, 5.510102		1 0.011002		1 0.017702

TABLE IV.

TABLE V. Anharmonicities (uncorrected for KEP).

	H ₂ O	HDO	D ₂ O	DTO	T ₂ O	НТО
X ₁₁	-43.89	$-42.27 - 0.00686\epsilon_2$	$-22.65 + 0.0184\epsilon_2$	$-27.84 - 0.0150\epsilon_2$	-15.71 0.02745 ϵ_2	$-29.43 \\ -0.00746\epsilon_2$
X 22	-19.50	$+0.0106\epsilon_1 \\ 4.1^*$	$-0.0083\epsilon_1 - 15.92$	$+0.0186\epsilon_1$ -13.7*	$-0.0124\epsilon_1$ -8.212	$+0.0141\epsilon_{1}$ -5.91
X 33	-46.37	$-77.39 \\ -0.00353\epsilon_2$	-25.27	$-41.77 - 0.00528\epsilon_2$	-18.39	$-77.70 \\ -0.00498\epsilon_2$
X_{12}	-20.02	$-0.0290\epsilon_1 \\ -93.7^* \\ +0.01002\epsilon_2$	$+0.0375\epsilon_1 \\ -6.76 \\ -0.0163\epsilon_2$	$-0.0535\epsilon_1 \\ 13.53^* \\ +0.0216\epsilon_2$	$+0.056\epsilon_1 \\ -4.27 \\ -0.0242\epsilon_2$	$-0.0362\epsilon_1 \\ -22.45 \\ +0.0115\epsilon_2$
X 13	-155.06	$-16.00 - 0.0212\epsilon_2$	- 79.13	$-9.01 - 0.0373\epsilon_2$	- 56.79	$-11.63 \\ -0.0275\epsilon_2$
X 23	-51.1	$-0.0140\epsilon_1 \\ -40.03 \\ +0.0107\epsilon_2$	-24.32	$- \begin{array}{c} - 0.0271\epsilon_1 \\ - 20.00 \\ + 0.0148\epsilon_2 \end{array}$	-17.41	$- 0.0177 \epsilon_1 \\ - 38.35 \\ 0.0177 \epsilon_2$

* Values corrected for resonance splitting of $2\omega_2$ and ω_1 states. New value for $2\omega_2 - \omega_1$ is $[(2\omega_2 - \omega_1)^2 + \alpha_2 \pi^2]^{\frac{1}{2}}$; cf. Section on Resonance Splitting.

to the symmetrical water molecule. The Wilson and Howard¹³ Hamiltonian is used.

In general for triatomic molecules the firstorder perturbation energy due to this approximate but very simplifying choice of axes is of the form $(1/2C)\bar{P}_z^2$ where C is the moment of inertia about the axis perpendicular to the plane of the molecule and \bar{P}_{z}^{2} is the average square of the angular momentum parallel to this axis.

TABLE VI. Corrections to X_{ij} for kinetic energy perturbations (cm⁻¹).

	H ₂ O	HDO	D_2O	DTO	T ₂ O	нто
X_{12}	0	4.4	0	2.7	0	3.5
X_{13}	0	0	0	0	Ó	0
X_{23}	31.3	14.5	16.2	8.7	11.2	11.4

¹³ E. B. Wilson and J. B. Howard, J. Chem. Phys. 4, 260 (1936).

	II 2O	HDO	D ₂ O	DTO	T ₂ O	НТО
X11	-43.89	-42.27 -0.00686 ϵ_2	$-22.65 + 0.0184\epsilon_2$	$-27.84 \\ -0.0150\epsilon_2$	$-15.71 + 0.0275\epsilon_2$	-29.43 -0.00746 ϵ_2
X_{22}	- 19.50	$+0.0106\epsilon_1 \\ 4.1$	$-0.0083\epsilon_1$ -15.92	$+0.0186\epsilon_{1}$ -13.7	$-0.0124\epsilon_1$ -8.212	$+0.0141\epsilon_1$ -5.91
X 33	-46.37	$-77.39 \\ -0.00353\epsilon_2$	-25.27	$-41.77 \\ -0.00528\epsilon_2$	-18.39	$-77.70 \\ -0.00498\epsilon_2$
X_{12}	- 20.02	$-0.0290\epsilon_1 \\ -89.3 \\ +0.0100\epsilon_2$	$+0.0375\epsilon_1 \\ -6.76 \\ -0.0163\epsilon_2$	$-\begin{array}{c}-0.0535\epsilon_{1}\\13.53\\+0.0216\epsilon_{2}\end{array}$	$+0.056\epsilon_1 \\ -4.27 \\ -0.0242\epsilon_2$	$-0.0362\epsilon_1 \\ -18.95 \\ +0.0115\epsilon_2$
X_{13}	- 155.06	$-16.00 \\ -0.0212\epsilon_2$	-79.13	$-9.01 - 0.0373\epsilon_2$	-56.79	$-11.63 - 0.0275\epsilon_2$
X_{23}	- 19.8	$-0.0140\epsilon_1 \\ -25.53 \\ +0.0107\epsilon_2$	-8.12	$- 0.0271\epsilon_1 \\ - 11.3 \\ + 0.0148\epsilon_2$	-6.21	$-0.0177\epsilon_1 -26.95 +0.0177\epsilon_2$
$\frac{1}{4}\Sigma X_{ij}$	- 76.16	$- 0.0081\epsilon_1 \\ - 61.6 \\ - 0.00272\epsilon_2$	$+0.0073\epsilon_1$ -39.45 +0.0005 ϵ_2	$-0.0155\epsilon_1 \\ -21.86 \\ -0.0053\epsilon_2$	$^{+0.011\epsilon_1}_{-25.34}_{+0.0008\epsilon_2}$	$- 0.00995\epsilon_1 \\ - 42.67 \\ - 0.0027\epsilon_2$

TABLE VII. Anharmonicities (fully corrected).

TABLE VIII. Anharmonicities by product method.

	H ₂ O	HDO	D_2O	DTO	T ₂ O	нто
X11	- 43.89	- 23.86	-22.81	-16.65		-16.79
X 22	- 19.50	- 14.98	-10.44	- 8.90	- 7.37	-13.48
X 33	- 46.37	- 45.1	-24.90	-23.9	-17.75	-45.2
X_{12}	-20.02	- 13.00	-10.56	-8.32	- 7.37	-10.28
X_{13}	-155.06	-113.0	81.92	-68.6	-57.45	-94.6
X_{23}	- 19.81	- 17.12	-10.62	- 9.61	- 7.53	-16.23
$\frac{1}{4}\Sigma X_{ij}$	- 76.1	- 56.8	-40.3	34.0	-28.3	-49.15

TABLE IX. Resonance splitting parameters for symmetrical water molecules.

Molecule	(cm ⁻¹) (calc.)	(cm ⁻¹) (experimental)
H ₂ O	+71.7	+74.8
D_2O	+38.5	
T_2O	+27.4	

 TABLE X. Resonance splitting parameters for asymmetrical water molecules,

Molecule	(cm ⁻¹) calc.	
HDO	88.2	
DTO	71.8	
ΗΤŎ	77.8	

Other first-order terms exist but are negligible for the water molecules. The second-order terms are negligible also for these molecules. The calculation of \bar{P}_{z^2} is made by expressing P_z , the perpendicular component of the "internal angular momentum," as $(-aQ_2-cQ_3)P_1+(aQ_1+bQ_3)P_2$ $+(cQ_1-bQ_3)P_3$, where the P_i 's are the momenta conjugate to the Q_i 's. Integrating

$$\int \psi_{i,j,k}^* P_z^2 \psi_{i,j,k} dz$$

gives the result. Weinberg and Eckart¹² showed this to be

$$\frac{h}{2\pi}\right)^{2} \begin{cases} a^{2}(n_{1}+\frac{1}{2})(n_{2}+\frac{1}{2})\left(\frac{\nu_{1}}{\nu_{2}}+\frac{\nu_{2}}{\nu_{1}}\right) \\ +b^{2}(n_{1}+\frac{1}{2})(n_{3}+\frac{1}{2})\left(\frac{\nu_{1}}{\nu_{3}}+\frac{\nu_{3}}{\nu_{1}}\right)-\frac{1}{4} \\ +c^{2}(n_{2}+\frac{1}{2})(n_{3}+\frac{1}{2})\left(\frac{\nu_{2}}{\nu_{3}}+\frac{\nu_{3}}{\nu_{2}}\right) \end{cases}$$

where $a^2 + b^2 + c^2 = 1$.

The corrections to the anharmonicities therefore are

$$\Delta X_{12} = \frac{1}{2c} \left(\frac{h}{2\pi}\right)^2 a^2 \left(\frac{\nu_1}{\nu_2} + \frac{\nu_2}{\nu_1}\right),$$
$$\Delta X_{13} = \frac{1}{2c} \left(\frac{h}{2\pi}\right)^2 \left(\frac{\nu_1}{\nu_3} + \frac{\nu_3}{\nu_1}\right),$$
$$\Delta X_{23} = \frac{1}{2c} \left(\frac{h}{2\pi}\right) c^2 \left(\frac{\nu_2}{\nu_3} + \frac{\nu_3}{\nu_2}\right),$$

if the constant term is neglected to preserve the form of the expression for the energy as a power



FIG. 2. Theoretical values for $(HDO)(H_2)/(H_2O)(HD)$.

TABLE XI. Frequencies and anharmonicities of hydrogen molecules.

H2	HD	D_2	DT	T_2	НТ
4405.30 62.66	3817.09 47.01	3117.07 31.36	2845.64 26.14	2546.50 20.94	3598.14 41.80
	TABLE 2	XII. <i>H</i> 0º (calories pe	r mole).	

Molecule	H ₂ O	HDO	D ₂ O	DTO	T ₂ O	нто
H_0^0 Molecule H_0^0	13,241	11,480	9,682	8,951	8,148	10,771
	H ²	HD	D2	DT	T ₂	HT
	6,253	5,423	4,433	4,049	3,625	5,114

TABLE XIII. $(F - H_0^0)/T$ values (calories/degree).

Molecules	25°C	100°C	200°C	300°C	400°C	500°C
H ₂ O	-37.20	-39.00	-40.88	-42.40	-43.70	-44.90
HDO	-39.80	-41.55	-43.50	-45.10	-46.40	-47.50
D_2O	-39.42	-41.15	-43.10	-44.65	-46.00	-47.20
DTO	-41.55	-43.20	-45.20	-46.80	-48.15	-49.40
$T_{2}O$	-41.02	-42.64	-44.58	-46.20	-47.57	-48.72
HTO	-40.45	-42.30	-44.10	-45.70	-47.05	-48.30
H_2	-24.37	-25.90	-27.48	-28.78	-29.85	30,88
HD	-27.48	-29.06	-30.60	-31.88	-33.00	34.00
D_2	-27.72	-29,26	-30,80	-32.15	-33.25	-34.25
DT	-30.07	-31.64	-33.35	-34.60	-35.67	-36.65
T_2	-29.70	-31.26	-32.82	-34.18	-35.26	-36.20
HT	-28.55	-30.10	-31.66	-32.94	-34.08	-35.03

series in $(n_i + \frac{1}{2})$. This point was discussed in a preceding paragraph.

Table VI gives the corrections and Table VII the final values for the X_{ij} .

Table VIII gives the X_{ij} values calculated by the method used by Darling and Dennison¹ for D_2O . The agreement for individual X_{ii} 's is quite good for the symmetrical molecules and poor for the asymmetric ones, though the contributions to the zero-point energy, $\frac{1}{4}\sum X_{ij}$, are in fair agreement in all cases. The coefficients ϵ_1 and ϵ_2 are



FIG. 3. Theoretical values for $(HTO)(H_2)/(H_2O)(HT)$.

taken to be of the same order as the other quartic coefficients, the β 's. With this assumption their effects on $\frac{1}{4}\sum X_{ij}$ are of the order of 1 cm⁻¹ which is quite small. More accurate experimental investigation will require their evaluation, of course. Since the ϵ 's refer to bending coordinates, considerations of the type used by Redlich¹⁴ further justify the expectation that they are small.

III. INFRA-RED SPECTRA AND RESONANCE INTERACTIONS

A valuable check on the results discussed above would be afforded by an experimental determination of the infra-red and Raman spectra of HDO by subtraction of the H₂O and D₂O spectra from the composite obtained for a 50 percent solution of H_2O and D_2O .

Fuson, Randall, and Dennison¹⁵ have given values for about eighty lines of the infra-red spectrum of HDO obtained in this way. An attempt was made to check the frequencies and anharmonicities calculated above against these lines. All lines definitely known to belong to HDO were attributable to relatively probable transitions in the calculated infra-red spectrum. The fit usually was as close as 1 or 2 cm^{-1} . In the absence of intensity data, however, a completely conclusive test can hardly be obtained with so few lines.

The expression (3) for the energy levels is

¹⁴ O. Redlich, J. Chem. Phys. 9, 298 (1941). ¹⁵ N. Fuson, H. M. Randall, and D. M. Dennison, Phys. Rev. 56, 982 (1939).

directly applicable, except for the Fermi¹⁶ resonance effect arising in the cases of certain overtones. Dennison and Darling have discussed this problem for the symmetrical H₂O, and D₂O molecules. They found serious interaction between the levels (n_3, n_1, n_2) and (n_3+2, n_1-2, n_2) . The levels are split symmetrically, the new separation being $(\delta_0^2 + \delta_1^2)^{\frac{1}{2}}$ where δ_0 is the separation for no resonance interaction and δ_1 is given by

 $\delta_1 = 2b_{n_3+2, n_1-2, n_2}^{n_3, n_1, n_2}$

where

$$\gamma = \frac{1}{2}\beta_{13} - \frac{\alpha_{13}^2}{\omega_1} + \frac{\alpha_1\alpha_{31}}{2\omega_1} + \frac{\alpha_{12}\alpha_{32}}{4(2\omega_1 - \omega_2)} - \frac{\alpha_{12}\alpha_{32}}{4(2\omega_1 + \omega_2)}$$

TABLE XIV. Masses and moments of inertia.

 $=hc[n_1(n_1-1)(n_3+1)(n_3+2)]^{\frac{1}{2}}\gamma$

Molecule	Mass	IABC ·10120 (g cm2)
H ₂ O	18.01626	5.869
D_2O	20.02946	40.67
T_2O	22.03410	120.5
HDO	19.02286	16.6
DTO	21.03178	70.84
НТО	20.02518	29.40
		I 0.1040
H_2	2.01626	0.4599
$\overline{D_2}$	4.02946	0.9191
T_{2}	6.03410	1.376
HD	3.02286	0.6131
DT	5.03178	1.102
HT	4.02518	0.6894

Table IX contains γ values for the symmetrical molecules.

For the molecules HDO, HTO, and DTO the most seriously resonating levels are (n_3, n_1, n_2) and (n_3, n_1-1, n_2+2) . For these

$$\delta_1 = hc[n_1(n_2+1)(n_2+2)]^{\frac{1}{2}}\gamma$$

where $\gamma = \alpha_{21}/\sqrt{2}$.

Table X gives these γ values.

IV. ISOTOPIC EQUILIBRIA BETWEEN THE WATER AND HYDROGEN MOLECULES

The equilibrium constants for the following equilibria can now be evaluated.

(1)	$H_2O+HD=HDO+H_2$
(2)	$H_2O+HT=HTO+H_2$
(3)	$D_2O + DT = DTO + D_2$
(4)	$D_2O+HD=HDO+D_2$
(5)	$H_2O + D_2O = 2HDO$
(6)	$T_2O + DT = DTO + T_2$
(7)	$T_2O+HT=HTO+T_2$
(8)	$H_2O + T_2O = 2HTO$
(9)	$D_2O + T_2O = 2DTO.$

The fundamental frequencies and anharmonicities for the hydrogen molecules are given in Table XI.

Equilibrium	20°C	100°C	200°C	300°C	400°C	500°C
(1) $\frac{(\text{HDO})(\text{H}_2)}{(\text{H}_2\text{O})(\text{HD})}$	3.78	2.65	2.09	1.75	1.54	1.37
(2) $\frac{(\text{HTO})(\text{H}_2)}{(\text{H}_2\text{O})(\text{HT})}$	6.24	3.83	2.66	2.09	1.77	1.52
$(3) \frac{(\mathrm{DTO})(\mathrm{D}_2)}{(\mathrm{D}_2\mathrm{O})(\mathrm{DT})}$	1.58	1.37	1.17	1.15	1.12	1.08
$(4) \frac{(\text{HDO})(\text{D}_2)}{(\text{D}_2\text{O})(\text{HD})}$	1/3.00	1/2.27	1/1.78	1/1.55	1/1.40	1/1.29
(5) $\frac{(\text{HDO})^2}{(\text{H}_2\text{O})(\text{D}_2\text{O})}$	4.10	4.13	4.16	4.17	4.17	4.18
(6) $\frac{(DTO)(T_2)}{(T_2O)(DT)}$	1/1.77	1/1.45	1/1.36	1/1.24	1/1.19	1/1.18
(7) $\frac{(\text{HTO})(\text{T}_2)}{(\text{T}_2\text{O})(\text{HT})}$	1/5.00	1/3.10	1/2.27	1/1.84	1/1.62	1/1.52
(8) $\frac{(\text{HTO})^2}{(\text{H}_2\text{O})(\text{T}_2\text{O})}$	3.18	3.57	3.71	3.77	3.82	3.83
(9) $\frac{(DTO)^2}{(D_2O)(T_2O)}$	3.32	3.66	3.74	3.78	3.78	3.79

TABLE XV. Equilibrium constants.

¹⁶ E. Fermi, Zeits. f. Physik 71, 250 (1931).

Temp. (°C) Reference K_{Theor} $K_{1}Exp$ 20 3.78 2.67 (1)3.2 (2a, b)Corrected from value of 3.8 for liquid water 527 1.37 1.28 (3)

TABLE XVI.

A. Farkas and L. Farkas, Trans. Faraday Soc. 30, 1076 (1934).
 ²⁶ Bonhoeffer and Rummel, Naturwiss. 22, 45 (1934).
 ²⁶ K. F. Bonhoeffer, Zeits. f. Elektrochemie 40, 469 (1934).
 ³ See reference 4 in text.

The values for D_2 and HD are those given by Teal and MacWood.17 The other values were calculated from the H₂ values by use of the ratios of the reduced masses of the molecules.

Table XII contains the H_0^0 values for the water and hydrogen molecules calculated from the fundamental frequencies and anharmonicities contained in Tables I, VII, and XI.

Table XIII contains $(F - H_0^0)/T$ values for the water and hydrogen molecules, nuclear spin entropies being omitted.

The masses and moments of inertia used are listed in Table XIV.

The equilibrium constants are given in Table XV, K_1 and K_2 are plotted in Figs. 2 and 3. They should be accurate to about two percent.

V. DISCUSSION

The experimental values for $(HDO)(H_2)/$ $(H_2O)(HD)$ reported in the literature are given in Table XVI.

¹⁷G K. Teal and G. E. MacWood, J. Chem. Phys. 3, 760 (1935).

TABLE XVII. Experimental values for $(HTO)(H_2)/(H_2O)(HT).$

Temp. (°C)	$K_{\text{Theor.}}$	$K_{Exp.}$	Source
20	6.24	6.3 ± 0.08	Taylor and Black Private communi-
28	5.80	5.3 ± 0.5	Author
280	2.00	1.9 ± 0.1	Author

The analogous tritium constant $(HTO)(H_2)/$ $(H_2O)(HT)$ can be measured by equilibration with Pt of a H₂O, H₂ system containing tritium in both the H₂O and H₂ species as HTO or HT. The concentration of tritium will be so low $(\sim 10^{-10}M)$ that no precautions need be taken about other equilibria. After equilibration the hydrogen and water vapor are introduced into the gas of a Geiger-Müller counter or electroscope and the relative specific radioactivities determined. The author has made a few measurements of this constant and a more extensive study is being made by Mr. James F. Black and Professor H.S. Taylor of Princeton University. Table XVII gives the results to date.

In view of the agreement for the tritium case and the difficulties of the determination in the deuterium case due to other equilibria, the author believes that the fundamental assumption of the essential identity of the potential functions of isotopic molecules is correct.

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APPENDIX I.	EXPRESSIONS FOR	THE	ANHARMONICITIES	IN	TERMS	OF
	THE POTE	NTIAL	CONSTANTS			

$$X_{11} = \frac{3}{2}\beta_1 - \frac{15}{4} \frac{\alpha_1^2}{\omega_1} - \frac{\alpha_{12}^2}{2\omega_2} - \frac{\alpha_{13}^2}{2\omega_3} - \frac{\alpha_{12}^2}{8(2\omega_1 - \omega_2)} + \frac{\alpha_{12}^2}{8(2\omega_1 - \omega_2)} - \frac{\alpha_{13}^2}{8(2\omega_1 + \omega_3)} + \frac{\alpha_{13}^2}{8(2\omega_1 - \omega_3)},$$

$$X_{22} = \frac{3}{2}\beta_2 - \frac{15}{4} \frac{\alpha_2^2}{\omega_2} - \frac{\alpha_{23}^2}{2\omega_3} - \frac{\alpha_{21}^2}{2\omega_1} - \frac{\alpha_{21}^2}{8(2\omega_2 + \omega_1)} + \frac{\alpha_{21}^2}{8(2\omega_2 - \omega_1)} - \frac{\alpha_{23}^2}{8(2\omega_2 - \omega_3)} + \frac{\alpha_{23}^2}{8(2\omega_2 - \omega_3)},$$

$$X_{33} = \frac{3}{2}\beta_3 - \frac{15}{4} \frac{\alpha_3^2}{\omega_3} - \frac{\alpha_{31}^2}{2\omega_1} - \frac{\alpha_{32}^2}{2\omega_2} - \frac{\alpha_{31}^2}{8(2\omega_3 + \omega_1)} + \frac{\alpha_{31}^2}{8(2\omega_3 - \omega_1)} - \frac{\alpha_{32}^2}{8(2\omega_3 - \omega_2)} + \frac{\alpha_{32}^2}{8(2\omega_3 - \omega_2)},$$
(5)



APPENDIX II. EXPRESSIONS FOR THE POTENTIAL CONSTANTS OF ONE ISOTOPIC MOLECULE IN TERMS OF THOSE OF ANOTHER

$$\begin{aligned} \alpha_{i} &= \alpha_{1}' \gamma_{1i}^{3} + \alpha_{2}' \gamma_{2i}^{3} + \alpha_{12}' \gamma_{1i}^{2} \gamma_{2i} + \alpha_{21}' \gamma_{2i}^{2} \gamma_{1i} + \alpha_{31}' \gamma_{2i}^{2} \gamma_{1i} + \alpha_{32}' \gamma_{2i}^{2} \gamma_{2i} \gamma_{2i}, \qquad (i = 1, 2, 3) \quad (6) \\ \alpha_{ij} &= 3\alpha_{1}' \gamma_{1i}^{2} \gamma_{1j} + 3\alpha_{2}' \gamma_{2i}^{2} \gamma_{2j} + \alpha_{12}' (\gamma_{1i}^{2} \gamma_{2j} + 2\gamma_{1i} \gamma_{2i} \gamma_{1j}) + \alpha_{21}' (\gamma_{2i}^{2} \gamma_{1j} + 2\gamma_{1i} \gamma_{2i} \gamma_{2j}) \qquad (i, j = 1, 2, 3) \\ &+ \alpha_{31}' (\gamma_{3i}^{2} \gamma_{1j} + 2\gamma_{1i} \gamma_{3i} \gamma_{3j}) + \alpha_{32}' (\gamma_{3i}^{2} \gamma_{2j} + 2\gamma_{2i} \gamma_{3i} \gamma_{3j}), \qquad (7) \\ \alpha_{123} &= 6\alpha_{1}' \gamma_{11} \gamma_{12} \gamma_{13} + 6\alpha_{2}' \gamma_{21} \gamma_{22} \gamma_{23} + 2\alpha_{12}' (\gamma_{11} \gamma_{12} \gamma_{23} + \gamma_{11} \gamma_{22} \gamma_{13} + \gamma_{21} \gamma_{12} \gamma_{33}) + \alpha_{32}' (\gamma_{3i}^{2} \gamma_{2j} + 2\gamma_{2i} \gamma_{3i} \gamma_{3j}), \qquad (7) \\ \alpha_{123} &= 6\alpha_{1}' \gamma_{11} \gamma_{12} \gamma_{13} + 6\alpha_{2}' \gamma_{21} \gamma_{22} \gamma_{23} + 2\alpha_{12}' (\gamma_{11} \gamma_{12} \gamma_{23} + \gamma_{11} \gamma_{22} \gamma_{23}) + 2\alpha_{31}' (\gamma_{31} \gamma_{32} \gamma_{13} + \gamma_{31} \gamma_{12} \gamma_{33} + \gamma_{11} \gamma_{32} \gamma_{33}) \\ &+ 2\alpha_{32}' (\gamma_{21} \gamma_{22} \gamma_{13} + \gamma_{21} \gamma_{12} \gamma_{23} + \gamma_{11} \gamma_{22} \gamma_{23}) + 2\alpha_{31}' (\gamma_{31} \gamma_{32} \gamma_{13} + \gamma_{31} \gamma_{12} \gamma_{33} + \gamma_{11} \gamma_{32} \gamma_{33}) \\ &+ 2\alpha_{32}' (\gamma_{31} \gamma_{32} \gamma_{23} + \gamma_{31} \gamma_{22} \gamma_{33} + \gamma_{21} \gamma_{32} \gamma_{33}), \qquad (8) \\ \beta_{i} &= \sum_{1}^{3} \beta_{j}' (\gamma_{ji})^{4} + \beta_{12}' (\gamma_{1i}^{2} \gamma_{2i}^{2}) + \beta_{13}' (\gamma_{1i}^{2} \gamma_{2i}^{2}) + \beta_{23}' (\gamma_{2i}^{2} \gamma_{2i}^{2}) + \epsilon_{1} (\gamma_{1i} \gamma_{2i}^{2}) + \epsilon_{2} (\gamma_{2i} \gamma_{1i}^{3}), \qquad (i = 1, 2, 3) \quad (9) \\ \beta_{jk} &= 6 \sum_{1}^{3} \beta_{i}' \gamma_{ij}^{2} \gamma_{ik}^{2} + \beta_{12}' (\gamma_{1j}^{2} \gamma_{2k}^{2} + 4\gamma_{1j} \gamma_{2j} \gamma_{1k} \gamma_{2k} + \gamma_{1k}^{2} \gamma_{2j}^{2}) + \beta_{13}' (\gamma_{1j}^{2} \gamma_{2k}^{2} + \gamma_{1k} \gamma_{2k} \gamma_{2j}^{2}) + \beta_{13}' (\gamma_{1j}^{2} \gamma_{2k}^{2} + \gamma_{1k} \gamma_{2k} \gamma_{2j}^{2}) + \beta_{2}' (\gamma_{1j}^{2$$