

Millimeter- and submillimeter-wavelength spectra and molecular constants of HTO and DTO†

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The rotational spectrum of DTO and HTO in the ground vibrational state has been measured with high-resolution microwave techniques in the 50–700-GHz region. We have measured and assigned 41 transitions of DTO. Analysis of these data yielded the following rotation and distortion parameters of the Watson formulation (in MHz): $\alpha = 410\,174.145 \pm 0.078$, $\bar{\alpha} = 172\,101.952 \pm 0.045$, $\mathfrak{C} = 119\,127.850 \pm 0.045$, $\Delta_J = 5.199034 \pm 0.003$, $\Delta_{JK} = -15.50411 \pm 0.015$, $\Delta_K = 180.31052 \pm 0.010$, $\delta_J = 1.941256 \pm 0.0010$, $\delta_K = 12.8893 \pm 0.012$. We measured 22 previously undetected transitions of HTO. Analysis of these, together with 26 lines already known, gave the following rotation and distortion parameters (in MHz): $\alpha = 677\,849.040 \pm 0.170$, $\bar{\alpha} = 198\,197.489 \pm 0.128$, $\mathfrak{C} = 150\,462.412 \pm 0.128$, $\Delta_J = 5.212023 \pm 0.003$, $\Delta_{JK} = 48.52276 \pm 0.02$, $\Delta_K = 271.27533 \pm 0.06$, $\delta_J = 1.414126 \pm 0.0005$, $\delta_K = 51.32833 \pm 0.07$. The usual distortion-free rotational constants derived from these Watson constants are (in MHz): for DTO, $A' = 410\,160.3$, $B' = 172\,050.2$, $C' = 119\,183.6$; and for HTO, $A' = 677\,777.7$, $B' = 198\,089.7$, $C' = 150\,604.4$. The latter constants and corresponding ones previously obtained for other isotopic species of water were used to calculate substitutional structures of the molecule. The averages of the structural parameters thus obtained are 0.9577 Å for the bond length and 104.66° for the bond angle.

INTRODUCTION

Water and its isotopic species have been studied extensively by infrared spectroscopists for many years. A number of recent analyses based on microwave spectra have been made. With the work reported in this paper on HTO and DTO, the techniques of high-resolution microwave spectroscopy have now been used for study of all the hydrogen, deuterium, and tritium species of ^{16}O water. Except for H_2O , which requires the inclusion of infrared data, it has been possible to observe a sufficient number of rotational lines to derive solely from microwave data spectral constants which are independent of the details of the data set.^{1–6} These constants allow the prediction of the rotational spectrum over a wide range of J_τ states.

To our knowledge, no previous measurements of rotational transitions of DTO have been published although Staats, Morgan, and Goldstein⁷ have reported observation of vibrational spectra of DTO and HTO in the near-infrared region. Measurement and assignment of 41 rotational transitions of DTO in the ground vibrational state and an analysis of this spectrum are made in the present study. Recently, Bellet, Steenbeckeliens, and Stouffs⁸ have reported the measurement of 26 microwave rotational lines of HTO between 10 and 300 GHz. The present work includes measurement of 22 additional transitions of HTO, primarily in the submilli-

meter region, with an analysis which includes the 26 previously measured lines.

EXPERIMENTAL PROCEDURE

Our earlier report⁴ on T_2O includes a description of the gas-handling system for the tritiated species and of the spectroscopic techniques used in the present study. Sealed sample cells, which made use of an activated uranium getter to remove unwanted residual gases and decay products, were used. Millimeter and submillimeter energy was produced by harmonic generation⁹ and detected with a 1.6°K InSb photoconducting detector.

Since no previous rotational studies of DTO had been reported, it was necessary to make an initial approximation of its rotational constants from the known structural parameters of other isotopic species. Because of the inertial defect, it was not possible to calculate adequately the rotational constants of DTO by a simple isotopic substitution. In a later section of this paper, it is shown how these effects can be minimized and how consistent structures can be calculated for the several isotopic species. These techniques can also be used for calculation of good approximations to the rotational constants of DTO. Because of the large rotational distortion of the molecule, these rigid-rotor constants alone are inadequate, even as a starting point for the prediction of the rotational spectrum.

It is reasonably straightforward, however, to make estimates of the P^4 distortion terms to adequate accuracy to allow assignment of enough low- J lines for an initial analysis.

The 26 lines of HTO observed and assigned by Bellet, Steenbeckeliers, and Stouffs⁸ formed the basis for our initial work on this species. When the low- J submillimeter lines which we observed were added to them, the set proved adequate for the prediction of other lines with good accuracy. For both HTO and DTO, transitions were initially located and identified by use of a bootstrap procedure in which the reliability of the predicted spectra was gradually improved as additional lines were measured and added to the analysis.

THEORY

As in the previous papers of this series, the Watson formulation¹⁰ of the molecular rotational Hamiltonian was used for the analysis of the rotational spectra of DTO and HTO. For DTO the following form of this Hamiltonian was found to be adequate:

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_d^{(4)} + \mathcal{H}_d^{(6)} + \mathcal{H}_d^{(8)} + \mathcal{H}_d^{(10)}, \quad (1)$$

$$\mathcal{H} = \frac{1}{2}(\mathcal{A} + \mathcal{C})P^2 + [\mathcal{A} - \frac{1}{2}(\mathcal{A} + \mathcal{C})](P_x^2 - b_p P_y^2), \quad (2)$$

$$\mathcal{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_x^2 - \Delta_K P_x^4 - 2\delta_J P^2 P_x^2 - \delta_K (P_x^2 P_y^2 + P_y^2 P_x^2), \quad (3)$$

$$\mathcal{H}_d^{(6)} = H_J P^6 + H_{JK} P^4 P_x^2 + H_{KJ} P^2 P_x^4 + H_K P_x^6 + 2h_J P^4 P_x^2 + h_{JK} P^2 (P_x^2 P_y^2 + P_y^2 P_x^2) + h_K (P_x^4 P_y^2 + P_y^2 P_x^4), \quad (4)$$

$$\mathcal{H}_d^{(8)} = L_{JK} P^6 P_x^2 + L_{KKJ} P^2 P_x^6 + L_K P_x^8 + l_K (P_x^6 P_y^2 + P_y^2 P_x^6), \quad (5)$$

$$\mathcal{H}_d^{(10)} = P_{JK} P^8 P_x^2 + p_K (P_x^8 P_y^2 + P_y^2 P_x^8). \quad (6)$$

In the above equations \mathcal{A} , \mathcal{B} , and \mathcal{C} are the rotational constants; Δ_J , H_J , etc. are the centrifugal distortion parameters through P^{10} ; $b_p = (\mathcal{C} - \mathcal{B}) / (2\mathcal{A} - \mathcal{B} - \mathcal{C})$ is Wang's asymmetry parameter; and $P_x^2 = (P_x^2 - P_y^2)$. Although the choice of higher-order terms which are retained in this Hamiltonian is not unique, the rotational constants and lower-order distortion constants, which relate most directly to molecular parameters, are essentially unaffected by any reasonable choice of higher-order terms. Procedures for the selection of terms to be retained in the Hamiltonian as well as methods for the evaluation of the matrix elements have been discussed by Cook, *et al.*¹¹ A general discussion of asymmetric rotor theory is contained in the book by Gordy and Cook.¹²

For HTO the Hamiltonian has a similar form:

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_d^{(4)} + \mathcal{H}_d^{(6)} + \mathcal{H}_d^{(8)} + \mathcal{H}_d^{(10)}, \quad (7)$$

$$\mathcal{H}_r = \frac{1}{2}(\mathcal{A} + \mathcal{C})P^2 + [\mathcal{A} - \frac{1}{2}(\mathcal{A} + \mathcal{C})](P_x^2 - b_p P_y^2), \quad (8)$$

$$\mathcal{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_x^2 - \Delta_K P_x^4 - 2\delta_J P^2 P_x^2 - \delta_K (P_x^2 P_y^2 + P_y^2 P_x^2), \quad (9)$$

$$\mathcal{H}_d^{(6)} = H_J P^6 + H_{JK} P^4 P_x^2 + H_{KJ} P^2 P_x^4 + H_K P_x^6 + 2h_J P^4 P_x^2 + h_{JK} P^2 (P_x^2 P_y^2 + P_y^2 P_x^2) + h_K (P_x^4 P_y^2 + P_y^2 P_x^4), \quad (10)$$

$$\mathcal{H}_d^{(8)} = L_{JK} P^6 P_x^2 + L_{KKJ} P^2 P_x^6 + L_K P_x^8 + l_K P^2 [P_x^4 P_y^2 + P_y^2 P_x^4] + l_K [P_x^6 P_y^2 + P_y^2 P_x^6], \quad (11)$$

$$\mathcal{H}_d^{(10)} = P_K P_x^{10} + p_K [P_x^8 P_y^2 + P_y^2 P_x^8]. \quad (12)$$

RESULTS AND ANALYSIS

The 41 rotational transitions of DTO observed in the region between 50 and 700 GHz are listed in Table I. Also in Table I are transition frequencies, calculated from the spectral constants in Table II, which represent the ground-state rotational spectrum of DTO below 700 GHz for $J \leq 10$. The uncertainties in each of these calculated frequencies are obtained from the relation¹³

$$\sigma^2 = \sum_{i,j} \sigma_i \sigma_j \rho_{ij} C_i C_j = \sigma^2 \sum_{i,j} A_{ij}^{-1} C_i C_j, \quad (13)$$

where σ_i is the standard error in the i th spectral constant, C_i is the corresponding coefficient in the frequency expression, ρ_{ij} is the correlation coefficient between the i th and j th constants, and where

$$\rho_{ij} = A_{ij}^{-1} \sqrt{(A_{ii}^{-1})} \sqrt{(A_{jj}^{-1})} \quad (-1 \leq \rho_{ij} \leq 1). \quad (14)$$

After this analysis had been completed, a list of unassigned lines was received from Steenbeckeliers. Three of these can be assigned to DTO and are listed in Table I although they are not included in the analysis. The measured frequencies of these lines are consistent with the predicted uncertainties of the calculated frequencies and the expected experimental uncertainty (≤ 0.1 MHz). The rms deviation of this fit is 0.066 MHz, which is on the order of the expected experimental uncertainty.

The 48 rotational transitions observed for HTO in the frequency range between 10 and 700 GHz are listed in Table III. Also listed in Table III are calculated transitions of HTO below 700 GHz for $J \leq 13$. This spectrum was calculated by means of the Hamiltonian of Eq. (7) and the constants listed in Table IV. The corresponding statistical uncertainties in these frequencies were derived from Eq. (13).

Each of the 41 observed transitions of DTO and each of the 48 observed transitions of HTO can be predicted to within expected theoretical and experimental uncertainties from analyses which do not contain the transition itself. In addition, the rotational constants and lower-order distortion constants of both molecules are essentially independent

TABLE I. Microwave spectrum of DTO (MHz).

Transition		Observed frequency	Calculated frequency (Est. uncertainty) ^a	Obs.-calc.
Upper state	Lower state			
9(7, 2)	9(7, 3)		2.084(0.000)	
7(6, 1)	7(6, 2)		3.575(0.000)	
5(5, 0)	5(5, 1)		4.159(0.000)	
10(7, 3)	10(7, 4)		11.402(0.002)	
8(6, 2)	8(6, 3)		24.379(0.002)	
6(5, 1)	6(5, 2)		44.942(0.001)	
4(4, 0)	4(4, 1)		58.295(0.000)	
9(6, 3)	9(6, 4)		118.097(0.009)	
7(5, 2)	7(5, 3)		263.415(0.007)	
10(6, 4)	10(6, 5)		454.699(0.031)	
5(4, 1)	5(4, 2)		516.435(0.005)	
3(3, 0)	3(3, 1)		743.090(0.003)	
8(5, 3)	8(5, 4)		1 107.291(0.030)	
7(1, 7)	6(2, 4)		1 248.933(0.191)	
6(4, 2)	6(4, 3)		2 522.230(0.021)	
9(5, 4)	9(5, 5)		3 727.245(0.077)	
4(3, 1)	4(3, 2)		5 113.051(0.015)	
2(2, 0)	2(2, 1)		7 871.389(0.009)	
7(4, 3)	7(4, 4)		8 939.142(0.064)	
10(5, 5)	10(5, 6)		10 639.990(0.144)	
6(2, 4)	7(0, 7)		14 108.289(0.312)	
5(3, 2)	6(1, 5)		15 390.570(2.400)	
6(3, 3)	5(4, 2)	16 797.78	16 797.676(0.112) ^b	
5(3, 2)	5(3, 3)		19 823.831(0.039)	
8(4, 4)	8(4, 5)		25 553.039(0.121)	
3(2, 1)	3(2, 2)	38 186.45	38 186.367(0.033) ^b	
3(2, 1)	4(0, 4)		38 524.259(0.112)	
5(4, 1)	6(3, 4)	40 136.05	40 136.209(0.103) ^b	
3(3, 1)	4(2, 2)	51 025.424	51 025.486(0.087)	-0.062
4(1, 4)	3(2, 1)	51 905.572	51 905.472(0.065)	0.100
1(1, 0)	1(1, 1)		52 907.364(0.026)	
6(3, 3)	6(3, 4)		56 417.450(0.069)	
9(4, 5)	9(4, 6)		62 082.587(0.170)	
5(0, 5)	4(2, 2)		66 132.932(0.224)	
6(0, 6)	5(2, 3)		73 409.636(0.296)	
8(4, 5)	7(5, 2)		75 649.788(0.179)	
2(2, 0)	3(1, 3)	88 991.395	88 991.396(0.070)	-0.001
5(2, 4)	4(3, 1)	94 713.289	94 713.266(0.068)	0.023
8(4, 4)	7(5, 3)	101 466.243	101 466.242(0.127)	0.001
6(1, 6)	5(2, 3)	102 708.147	102 708.162(0.117)	-0.015
4(2, 2)	4(2, 3)	107 763.229	107 763.163(0.059)	0.066
8(6, 3)	9(5, 4)	110 556.548	110 556.542(0.101)	0.006
8(6, 2)	9(5, 5)	114 308.159	114 308.166(0.101)	-0.007
5(1, 5)	4(2, 2)	119 425.985	119 425.958(0.074)	0.027
7(3, 4)	7(3, 5)	129 854.072	129 854.054(0.095)	0.018
10(4, 6)	10(4, 7)		131 890.321(1.474)	
2(1, 1)	2(1, 2)	158 629.161	158 629.168(0.054)	-0.007
3(3, 0)	4(2, 3)	159 531.785	159 531.739(0.075)	0.046
7(2, 5)	8(1, 8)	177 050.655	177 050.656(0.131)	-0.001
7(2, 5)	8(0, 8)		184 845.961(0.392)	
9(2, 7)	8(4, 4)		186 247.016(25.00)	
10(5, 6)	9(6, 3)	194 595.352	194 595.338(0.120)	0.014
10(5, 5)	9(6, 4)	205 353.409	205 353.425(0.119)	-0.016
7(4, 3)	8(2, 6)		215 178.128(17.74)	
6(5, 2)	7(4, 3)	221 366.024	221 366.001(0.099)	0.023
5(2, 3)	5(2, 4)	228 651.098	228 651.152(0.084)	-0.054
2(2, 0)	3(0, 3)		228 669.523(0.082)	
6(5, 1)	7(4, 4)	230 350.066	230 350.085(0.097)	-0.019

TABLE I (continued)

Transition		Observed frequency	Calculated frequency (Est. uncertainty) ^a	Obs.-calc.
Upper state	Lower state			
3(1, 2)	2(2, 1)	235 116.740	235 116.893(0.073)	-0.153
7(3, 5)	6(4, 2)	248 085.412	248 085.407(0.093)	0.005
7(1, 6)	6(3, 3)		253 360.429(3.740)	
8(3, 5)	8(3, 6)	253 758.145	253 758.150(0.129)	-0.005
1(1, 0)	1(0, 1)	290 863.828	290 863.858(0.055)	-0.030
9(7, 3)	10(6, 4)		290 861.142(5.340)	
1(0, 1)	0(0, 0)	291 209.062	291 209.010(0.056)	0.052
9(7, 2)	10(6, 5)		291 317.925(5.340)	
6(2, 5)	5(3, 2)	314 556.550	314 556.606(0.087)	-0.056
3(1, 2)	3(1, 3)	316 236.877	316 236.900(0.066)	-0.023
4(4, 1)	5(3, 2)	316 612.544	316 612.535(0.089)	0.009
5(2, 3)	4(3, 2)	328 477.447	328 477.469(0.082)	-0.022
2(0, 2)	1(1, 1)	336 465.493	336 465.475(0.067)	0.018
4(4, 0)	5(3, 3)	336 494.646	336 494.660(0.097)	-0.014
4(3, 1)	5(1, 4)		344 505.001(1.166)	
2(1, 1)	2(0, 2)	351 658.116	351 658.043(0.053)	0.073
7(3, 4)	6(4, 3)	380 461.686	380 461.691(0.100)	-0.005
9(4, 6)	8(5, 3)	380 780.494	380 780.501(0.123)	-0.007
6(2, 4)	6(2, 5)		404 445.756(0.240)	
7(6, 2)	8(5, 3)		418 839.699(1.576)	
8(2, 6)	9(1, 9)		418 898.237(1.246)	
7(6, 1)	8(5, 4)		419 950.565(1.568)	
8(2, 6)	9(0, 9)		422 770.052(1.474)	
8(1, 7)	7(3, 4)		433 063.297(4.620)	
9(3, 6)	9(3, 7)		435 052.285(1.014)	
9(4, 5)	8(5, 4)	443 970.391	443 970.379(0.124)	0.012
3(1, 2)	3(0, 3)	455 915.048	455 915.027(0.060)	0.021
10(1, 9)	9(3, 6)		465 778.414(3.460)	
7(2, 6)	6(3, 3)	482 874.751	482 874.731(0.122)	0.020
9(1, 8)	8(3, 5)		504 945.702(4.440)	
10(2, 9)	9(3, 6)		517 162.227(4.440)	
8(3, 6)	7(4, 3)	518 999.582	518 999.588(0.117)	-0.006
4(1, 3)	4(1, 4)		522 569.719(0.095)	
1(1, 1)	0(0, 0)	529 165.461	529 165.504(0.097)	-0.043
2(1, 2)	1(1, 1)		529 494.350(0.087)	
5(5, 1)	6(4, 2)		531 854.338(0.574)	
10(2, 8)	9(4, 5)		532 734.475(31.40)	
5(5, 0)	6(4, 3)		534 380.727(0.572)	
2(0, 2)	1(0, 1)		574 421.969(0.087)	
8(2, 7)	7(3, 4)		581 084.543(0.588)	
8(7, 2)	9(6, 3)		593 150.680(9.420)	
8(7, 1)	9(6, 4)		593 269.045(9.420)	
9(2, 8)	8(3, 5)		594 383.272(1.932)	
9(5, 4)	10(3, 7)		594 646.438(76.80)	
4(1, 3)	3(2, 2)	612 661.581	612 661.557(0.091)	0.024
4(1, 3)	4(0, 4)	612 999.562	612 999.449(0.092)	0.113
7(2, 5)	7(2, 6)		631 854.844(0.960)	
2(1, 1)	1(1, 0)		635 216.154(0.087)	
6(4, 2)	7(2, 5)		642 429.413(11.30)	
3(0, 3)	2(1, 2)		649 784.955(0.092)	
4(2, 2)	4(1, 3)		653 082.283(0.404)	
5(2, 3)	5(1, 4)		667 869.419(1.174)	
10(3, 7)	10(3, 8)		672 397.789(4.240)	
3(2, 1)	3(1, 2)	676 566.044	676 566.125(0.114)	-0.081
10(4, 7)	9(5, 4)		679 850.870(1.048)	

^aThe calculated uncertainties represent two standard deviations in the statistical analysis.

^bFrom list of unassigned lines of G. Steenbeckelers (private communication). Added to data set after analysis.

of both the details of the data sets and of reasonable choice of higher-order constants. As a result, it may be concluded that the Watson Hamiltonian, in general, and the form of Eqs. (1) and (7), in particular, constitute an accurate model for the rotational spectrum of DTO and HTO and, furthermore, that an adequate amount of microwave data has been acquired to characterize the spectra of both DTO and HTO over a wide range of J_r states.

The rotational constants (\mathcal{A} , \mathcal{B} , \mathcal{C}) of the Watson Hamiltonian differ from the A , B , C of Kivelson and Wilson¹⁴ because distortion effects are absorbed in \mathcal{A} , \mathcal{B} , and \mathcal{C} . Values of A , B , and C for DTO and HTO derived from \mathcal{A} , \mathcal{B} , and \mathcal{C} by a procedure earlier described¹¹ are given in Table V. The A , B , C also contain some distortion effects in their definition.¹² Their removal yields the distortion-free rotational constants A' , B' , C' , which are also shown in Table V.

As previously demonstrated,⁴ it is possible to calculate with useful accuracy both the P^2 rotational constants and the P^4 distortion constants of a molecule from measured frequencies of a relatively small number of low- J transitions. The results of fitting the 11 observed transitions of DTO (6 submillimeter) for which $J \leq 3$ to the 8 rotation-distortion constants $\leq P^4$ are shown in Table II.

TABLE II. DTO spectroscopic constants (MHz).

	Regular analysis		P^4 analysis	
	Constant	2σ	Constant	2σ
\mathcal{A}	410 174.145	0.078	410 173.143	0.358
\mathcal{B}	172 101.952	0.045	172 101.970	0.877
\mathcal{C}	119 127.850	0.045	119 128.159	0.877
Δ_J	5.199 034	0.003	5.238	0.020
Δ_{JK}	-15.504 11	0.015	-15.595	0.12
Δ_K	180.310 52	0.010	179.213	0.11
δ_J	1.941 256	0.0010	1.935	0.005
δ_K	12.8893	0.012	12.732	0.42
$10^4 H_J$	5.9488	0.7		
$10^3 H_{JK}$	4.1358	0.8		
$10^2 H_{KJ}$	-6.444 26	0.10		
$10^1 H_K$	3.466 981	0.009		
$10^4 h_J$	2.9687	0.16		
$10^3 h_{JK}$	2.962	0.42		
$10^2 h_K$	8.087 15	0.16		
$10^5 L_{JK}$	1.3294	0.4		
$10^4 L_{KKJ}$	1.7846	0.2		
$10^4 L_K$	-8.214 27	0.2		
$10^4 l_K$	-6.7028	0.7		
$10^8 P_{JK}$	-6.0406	1.3		
$10^6 p_K$	6.1777	0.8		
Number of constants	21		8	
Number of lines	41		11	

Comparison of the resulting constants with the corresponding ones obtained from full analysis of all observed lines shows that the agreement is good.

The observed spectrum of HTO contains 12 transitions (7 submillimeter) for which $J \leq 3$. The results of fitting only these 12 lines to the 8 spectral parameters of $\leq P^4$ are compared in Table IV with the results of the full analysis. Inspection shows that the agreement for HTO is not as good as that obtained for T_2O or DTO. This can be ascribed to the significantly larger A rotational constant of HTO. For the calculation of structures and other molecular parameters, however, the constants obtained from this small data set are satisfactory. Fayt and Steenbeckeliers¹⁵ have previously analyzed 26 microwave lines, which fall between 10 and 300 GHz, by combining them with a large number of infrared data points. The deviations of the P^2 and P^4 constants which they obtained are similar to the deviations which result from our analysis of the 12 microwave lines for which $J \leq 3$. We have discussed previously the difficulty of analyzing accurately the spectra of light asymmetric rotors when the low- J submillimeter lines are not available for inclusion in the data set.²

STRUCTURES

It is instructive to make a comparison of the molecular structural parameters obtained in different ways from the rotational constants of the several isotopic species of water which have now been studied by means of microwave spectroscopy. Water is the lightest of the stable triatomic molecules, and isotopic substitution for hydrogen in the water molecule causes probably the greatest effect on the ground-vibrational-state structures to be found among the polyatomic molecules. The various types of structures commonly derived from microwave spectra—effective (r_o structures), substitutional (r_s structures), average ($\langle r \rangle$ structures), equilibrium (r_e structures)—and the different methods for calculating them are described in a recent monograph.¹²

For a triatomic molecule such as H_2O having C_{2v} symmetry, there are only two independent structural parameters, and, were it not for the inertial defect, the effective structure for the ground vibrational state (the r_o structure) could be accurately determined from any combination of two of the three moment-of-inertia constants derivable from ground-state rotational spectra. The three inertial constants for a planar molecule are related by the expression

$$\Delta = I_c^v - I_a^v - I_b^v, \quad (15)$$

TABLE III. Microwave spectrum of HTO (MHz).

Transition		Observed frequency	Calculated frequency (Est. uncertainty) ^a	Obs.-Calc.	Ref.
Upper state	Lower state				
12(7, 5)	12(7, 6)		1.513(0.002)		
6(5, 1)	6(5, 2)		1.811(0.000)		
9(6, 3)	9(6, 4)		2.178(0.001)		
13(7, 6)	13(7, 7)		5.007(0.008)		
4(4, 0)	4(4, 1)		5.195(0.000)		
10(6, 4)	10(6, 5)		8.657(0.003)		
7(5, 2)	7(5, 3)		10.822(0.001)		
11(6, 5)	11(6, 6)		29.211(0.011)		
5(4, 1)	5(4, 2)		46.599(0.000)		
8(5, 3)	8(5, 4)		46.629(0.003)		
12(6, 6)	12(6, 7)		86.817(0.031)		
3(3, 0)	3(3, 1)		145.492(0.001)		
9(5, 4)	9(5, 5)		161.988(0.009)		
6(4, 2)	6(4, 3)		231.859(0.002)		
13(6, 7)	13(6, 8)		232.979(0.090)		
10(5, 5)	10(5, 6)		481.288(0.026)		
7(4, 3)	7(4, 4)		844.113(0.006)		
4(3, 1)	4(3, 2)		1 014.481(0.004)		
11(5, 6)	11(5, 7)		1 267.708(0.067)		
8(4, 4)	8(4, 5)		2 507.048(0.015)		
12(5, 7)	12(5, 8)		3 031.278(0.166)		
2(2, 0)	2(2, 1)		3 337.045(0.005)		
5(3, 2)	5(3, 3)		4 029.986(0.015)		
7(1, 7)	6(2, 4)		5 418.655(0.280)		
7(2, 5)	8(1, 8)		6 405.194(0.400)		
9(4, 5)	9(4, 6)		6 429.073(0.035)		
13(5, 8)	13(5, 9)		6 689.610(0.408)		
6(3, 3)	6(3, 4)	11 953.200	11 953.106(0.036)	0.094	b
10(4, 6)	10(4, 7)		14 725.227(0.064)		
3(2, 1)	3(2, 2)	16 562.530	16 562.542(0.021)	-0.012	b
7(3, 4)	7(3, 5)	29 356.410	29 356.423(0.065)	-0.013	b
11(4, 7)	11(4, 8)	30 786.400	30 786.399(0.096)	0.001	b
1(1, 0)	1(1, 1)	47 520.710	47 520.712(0.028)	-0.002	b
10(3, 8)	9(4, 5)	48 598.400	48 598.439(0.138)	-0.039	b
4(2, 2)	4(2, 3)	48 889.950	48 889.919(0.047)	0.031	b
5(2, 3)	6(1, 6)	56 425.590	56 425.504(0.155)	0.086	b
12(4, 8)	12(4, 9)	59 615.350	59 615.514(0.108)	-0.164	b
8(3, 5)	8(3, 6)	62 890.660	62 890.738(0.088)	-0.078	b
10(1, 9)	9(3, 6)		66 007.660(6.960)		
11(5, 7)	12(4, 8)	77 009.150	77 009.284(0.147)	-0.134	b
7(2, 5)	8(0, 8)	88 680.414	88 680.409(0.164)	0.005	c
8(2, 6)	9(1, 9)		93 254.124(0.410)		
13(4, 9)	13(4, 10)	107 979.061	107 979.061(0.174)	0.000	c
5(2, 3)	5(2, 4)	110 811.643	110 811.602(0.073)	0.041	c, b
4(1, 3)	3(2, 2)	116 130.270	116 130.264(0.095)	0.006	b
6(2, 4)	7(0, 7)	116 405.330	116 405.350(0.116)	-0.020	c
9(3, 6)	9(3, 7)	121 066.840	121 066.909(0.092)	-0.069	b
8(2, 7)	7(3, 4)	121 264.400	121 264.424(0.135)	-0.024	b
11(5, 6)	12(4, 9)	137 892.640	137 892.506(0.147)	0.134	b
2(1, 1)	2(1, 2)	142 495.100	142 495.143(0.066)	-0.043	b
8(2, 6)	9(0, 9)		147 160.234(0.356)		
12(4, 8)	13(2, 11)		147 763.566(56.40)		
6(3, 3)	7(2, 6)	151 984.194	151 984.159(0.114)	0.035	c, b
8(4, 5)	9(3, 6)	172 464.740	172 464.767(0.135)	-0.027	b
4(2, 2)	5(1, 5)	185 982.720	185 982.869(0.093)	-0.149	b
6(2, 4)	6(2, 5)	211 927.550	211 927.443(0.089)	0.107	b
10(3, 7)	10(3, 8)	213 290.392	213 290.412(0.112)	-0.020	c, b
2(0, 2)	1(1, 1)	214 424.620	214 424.747(0.100)	-0.127	b

TABLE III (continued)

Transition		Observed frequency	Calculated frequency (Est. uncertainty) ^a	Obs.—Calc.	Ref.
Upper state	Lower state				
7(2, 5)	6(3, 4)	218 846.850	218 846.875(0.133)	-0.025	b
5(2, 3)	6(0, 6)	230 097.908	230 097.875(0.150)	0.033	c
13(4, 10)	12(5, 7)		231 526.921(17.32)		
5(3, 3)	6(2, 4)	237 740.320	237 740.356(0.131)	-0.036	b
9(2, 7)	10(1, 10)	252 373.246	252 373.248(0.177)	-0.002	c
8(3, 5)	9(1, 8)		252 722.531(5.860)		
10(3, 7)	9(4, 6)	268 317.973	268 317.924(0.136)	0.049	c
3(1, 2)	3(1, 3)	284 644.070	284 644.074(0.088)	-0.004	b
9(2, 7)	10(0, 10)		286 858.207(0.706)		
8(4, 4)	9(3, 7)	296 038.757	296 038.724(0.134)	0.033	c
11(1, 10)	10(3, 7)		307 378.836(6.860)		
2(2, 1)	3(1, 2)	320 262.772	320 262.681(0.131)	0.091	c
13(4, 9)	12(5, 8)		342 537.259(17.38)		
11(3, 8)	11(3, 9)	348 183.910	348 183.904(0.170)	0.006	c
1(0, 1)	0(0, 0)	348 639.061	348 639.057(0.069)	0.004	c
9(2, 8)	8(3, 5)	355 877.351	355 877.342(0.173)	0.009	c
7(2, 5)	7(2, 6)	358 877.810	358 877.928(0.124)	-0.118	c
3(2, 1)	4(1, 4)	373 621.836	373 621.829(0.105)	0.007	c
11(3, 9)	10(4, 6)	379 032.308	379 032.311(0.177)	-0.003	c
4(2, 2)	5(0, 5)		422 535.433(0.206)		
5(3, 2)	6(2, 5)	453 697.802	453 697.785(0.130)	0.017	c
12(1, 11)	11(3, 8)		457 436.269(7.200)		
4(1, 3)	4(1, 4)	473 189.609	473 189.552(0.098)	0.057	c
10(5, 6)	11(4, 7)		477 486.559(13.06)		
10(2, 8)	11(1, 11)		477 935.725(1.494)		
10(2, 8)	11(0, 11)		499 583.264(1.840)		
10(5, 5)	11(4, 8)		508 754.246(13.06)		
13(1, 12)	12(3, 9)		509 015.688(12.96)		
1(1, 0)	1(0, 1)	526 911.988	526 912.045(0.111)	-0.057	c
12(3, 9)	12(3, 10)		531 779.642(1.070)		
10(2, 9)	9(3, 6)		540 459.329(0.928)		
8(2, 6)	8(2, 7)		554 475.281(0.360)		
5(1, 4)	4(2, 3)	569 350.080	569 350.038(0.152)	0.042	c
2(1, 1)	2(0, 2)	577 543.126	577 543.213(0.107)	-0.087	c
7(4, 4)	8(3, 5)		585 302.889(0.732)		
3(0, 3)	2(1, 2)	597 144.023	597 144.022(0.119)	0.001	c
2(2, 0)	3(1, 3)		608 243.801(0.148)		
7(3, 4)	8(1, 7)		630 626.733(4.120)		
11(4, 7)	12(2, 10)		638 957.689(49.60)		
7(4, 3)	8(3, 6)		649 037.740(0.768)		
2(1, 2)	1(1, 1)	649 472.828	649 472.817(0.108)	0.011	c
3(1, 2)	3(0, 3)		659 509.057(0.147)		
11(2, 10)	10(3, 7)		663 558.411(3.120)		
4(3, 2)	5(2, 3)		663 582.991(0.404)		
3(2, 1)	4(0, 4)		679 622.079(0.218)		
12(3, 10)	11(4, 7)		687 837.379(1.214)		
13(2, 12)	12(3, 9)		690 123.368(14.52)		
2(0, 2)	1(0, 1)	693 816.158	693 816.080(0.097)	0.078	c

^aThe calculated uncertainties represent two standard deviations in the statistical analysis.

^bJ. Bellet, G. Steenbeckeliens, and P. Stouffs. See Ref. 8.

^cPresent work.

where Δ is the inertial defect, a small constant which arises mostly from interaction between vibration and rotation. Because of the inertial defect, the effective bond length and bond angle are

not uniquely determined; they depend to some extent on the choice of the two inertial constants used in their evaluation. The degree of this dependence is determined by the magnitude of Δ

TABLE IV. HTO spectroscopic constants (MHz).

	Regular analysis		P^4 analysis		Reference 15	
	Constant	2σ	Constant	2σ	Constant	2σ
\mathcal{G}	677 849.040	0.170	677 845.611	0.180	677 860.5	2.0
\mathcal{B}	198 197.489	0.128	198 191.085	0.120	198 198.8	0.2
\mathcal{C}	150 462.412	0.128	150 468.779	0.120	150 465.3	0.5
Δ_J	5.212 023	0.003	5.204	0.004	5.2393	0.0034
Δ_{JK}	48.522 76	0.02	48.298	0.03	48.469	0.060
Δ_K	271.275 33	0.06	267.361	0.02	273.29	0.39
δ_J	1.414 126	0.0005	1.393	0.0017	1.4113	0.0005
δ_K	51.328 33	0.07	47.625	0.05	50.872	0.084
$10^4 H_J$	5.190 72	0.4			5.28	0.45
$10^2 H_{JK}$	3.943 27	0.06			3.500	0.071
$10^2 H_{KJ}$	-6.347 43	0.18			-8.61	1.77
$10^4 H_K$	8.963 777	0.11			11.880	0.910
$10^4 h_J$	1.7818	0.08			1.45	0.065
$10^2 h_{JK}$	1.7126	0.02			1.520	0.047
$10^4 h_K$	5.383 48	0.13			4.671	0.121
$10^4 L_{JK}$	-5.429 21	0.3			-2.88	0.48
$10^3 L_{KKJ}$	1.985 79	0.08			3.82	1.96
$10^3 L_K$	-8.340 15	0.7			-29.3	10.1
$10^3 l_{KJ}$	-9.1126	2.0				
$10^3 l_K$	-8.1573	0.7			-4.54	0.34
$10^3 P_{KKJ}$					-0.153	0.080
$10^4 P_K$	1.104 22	0.17			0.898	0.380
$10^5 p_K$	5.956 55	1.1				
Number of constants	22		8		21	
Number of lines	48		12		26 Microwave + Infrared	

relative to the magnitude of the moments of inertia. For a light molecule such as H_2O , these effects of the inertial defect are generally large. This was demonstrated in a previous paper of this series⁴ by comparisons of the structures calculated from each of the three combinations of ground-state moments of inertia for H_2O , D_2O , and T_2O . The range of difference in H_2O was 0.0143 Å for the bond length and 3.4° for the bond angle. These deviations decreased to 0.0092 Å and 2° for the heavier T_2O . It is possible to obtain more accurate values of the parameters by correcting for effects of Coriolis interactions, as is done below for the substitutional structures.

TABLE V. Rotational constants of DTO and HTO (MHz).

	DTO	HTO
A	410 180.0	677 852.1
B	172 069.9	198 164.0
C	119 154.0	150 492.8
A'	410 160.3	677 777.7
B'	172 050.2	198 089.7
C'	119 193.6	150 604.4

One can also derive the molecular dimensions from relations which involve the inertial constants of different isotopic species. Structures derived in this way are designated as substitutional, or r_s structures. Kraitchman¹⁶ has developed convenient equations for calculation of r_s values. Generally, one isotopic substitution is required for each parameter thus determined, and only one substitution for each atomic position gives independent information. The r_s structures have an inherent uncertainty arising from the assumption necessary to the application of the method, that the isotopic substitution of a particular atom does not alter the positional coordinates of the atom, whereas slight changes in the effective interatomic distances are expected from differences in the vibrational energy of the two isotopic species. Costain¹⁷ has shown, however, that r_s structures generally approximate more closely the r_e structures than do r_0 structures. For a diatomic molecule it is easy to show¹² that $r_s \approx \frac{1}{2}(r_0 + r_e)$. The hypothetical equilibrium structures r_e are, of course, free of all vibrational effects. For this reason, r_s structures for different isotopic species are generally more consistent than are the r_0 structures. One can use the substitutional method to get approximate equilibri-

TABLE VI. Substitutional structures of water.

Species	$(I_a : I_b)$	$(I_a : I_c)$	$(I_b : I_c)$	$(I_a : I_c)_{\text{corr}}$	$(I_b : I_c)_{\text{corr}}$
H ₂ ¹⁶ O : H ₂ ¹⁸ O : HT ¹⁶ O	0.9590 Å 104.43°	0.9607 Å 106.72°	0.9641 Å 99.46°	0.9594 Å 104.61°	0.9598 Å 103.83°
H ₂ ¹⁶ O : H ₂ ¹⁸ O : HD ¹⁶ O	0.9585 Å 104.58°	0.9613 Å 106.43°	0.9640 Å 100.74°	0.9590 Å 104.73°	0.9592 Å 104.21°
D ₂ ¹⁶ O : D ₂ ¹⁸ O : HD ¹⁶ O	0.9567 Å 104.65°	0.9622 Å 104.49°	0.9620 Å 105.30°	0.9562 Å 104.48°	0.9566 Å 104.66°
D ₂ ¹⁶ O : D ₂ ¹⁸ O : DT ¹⁶ O	0.9580 Å 104.65°	0.9604 Å 105.38°	0.9630 Å 103.00°	0.9584 Å 104.70°	0.9593 Å 104.38°
D ₂ ¹⁶ O : D ₂ ¹⁷ O : HD ¹⁶ O	0.9567 Å 104.65°	0.9622 Å 104.49°	0.9619 Å 105.31°	0.9562 Å 104.48°	0.9565 Å 104.67°
D ₂ ¹⁶ O : D ₂ ¹⁷ O : DT ¹⁶ O	0.9580 Å 104.65°	0.9604 Å 105.38°	0.9630 Å 103.00°	0.9585 Å 104.70°	0.9592 Å 104.39°
H ₂ ¹⁶ O : H ₂ ¹⁸ O : D ₂ ¹⁶ O	0.9575 Å 104.72°	0.9618 Å 105.11°	0.9628 Å 103.90°	0.9574 Å 104.71°	0.9574 Å 104.74°
H ₂ ¹⁶ O : H ₂ ¹⁸ O : T ₂ ¹⁶ O	0.9576 Å 104.70°	0.9612 Å 105.03°	0.9626 Å 103.93°	0.9575 Å 104.69°	0.9575 Å 104.71°
H ₂ ¹⁸ O : H ₂ ¹⁶ O : D ₂ ¹⁸ O	0.9575 Å 104.72°	0.9619 Å 105.12°	0.9628 Å 103.90°	0.9575 Å 104.72°	0.9575 Å 104.72°
D ₂ ¹⁶ O : D ₂ ¹⁷ O : H ₂ ¹⁶ O	0.9575 Å 104.72°	0.9618 Å 105.11°	0.9629 Å 103.90°	0.9574 Å 104.71°	0.9580 Å 104.65°
D ₂ ¹⁶ O : D ₂ ¹⁸ O : T ₂ ¹⁶ O	0.9576 Å 104.67°	0.9606 Å 104.95°	0.9623 Å 103.96°	0.9576 Å 104.67°	0.9581 Å 104.60°
D ₂ ¹⁶ O : D ₂ ¹⁸ O : H ₂ ¹⁶ O	0.9575 Å 104.72°	0.9618 Å 105.11°	0.9629 Å 103.89°	0.9574 Å 104.71°	0.9580 Å 104.64°
D ₂ ¹⁶ O : D ₂ ¹⁸ O : T ₂ ¹⁶ O	0.9576 Å 104.68°	0.9606 Å 104.95°	0.9624 Å 103.95°	0.9576 Å 104.67°	0.9582 Å 104.59°
Average	0.9577 Å 104.66°	0.9613 Å 105.25°	0.9628 Å 103.40°	0.9577 Å 104.66°	0.9581 Å 104.52°
σ	0.0006 Å 0.08°	0.0007 Å 0.65°	0.0007 Å 1.64°	0.0009 Å 0.09°	0.0010 Å 0.26°

um structures but not the expected differences in the effective molecular dimensions caused by isotopic substitution.

The new spectral constants for HTO and DTO, together with those earlier measured for other species, make possible the calculation of substitutional structures of water from a number of different isotopic combinations. We have made such calculations. The results are shown in Table VI.

TABLE VII. Comparison of the structural parameters of the water molecule.

Substitutional structure			Equilibrium structure ^a
$(I_a : I_b)$	$(I_a : I_c)_{\text{corr}}$	$(I_b : I_c)_{\text{corr}}$	
0.9577 Å 104.66°	0.9577 Å 104.66°	0.9581 Å 104.52°	0.9572 ± 0.0003 Å 104.52 ± 0.05°
Effective structures ^b			
H ₂ O	D ₂ O	T ₂ O	
0.9650 Å 104.8°	0.9631 Å 104.6°	0.9623 Å 104.6°	

^a From Ref. 21.^b From Ref. 4.

The substitutional structures obtained from the two smaller moments of inertia I_a and I_b of the different combinations are remarkably consistent, as can be seen from comparison of the values in the first column of Table VI. Surprisingly, these structures are also very close to the equilibrium structure, as is shown in Table VII. In contrast, rather large inconsistencies in the r_s structures are obtained when the I_c values are employed in the calculations (see columns 2 and 3 of Table VI).

The effective moment of inertia of a bent, triatomic molecule in a vibrational state v can be expressed¹² as

$$I_\alpha^v = I_\alpha^e + \sum_s (v_s + \frac{1}{2}) \epsilon_s^\alpha, \quad (16)$$

where $\alpha = a, b, c$, I_α^e is the equilibrium moment of inertia, and ϵ_s^α is the rotation-vibration parameter. The latter can be separated into harmonic and anharmonic parts:

$$\epsilon_s^\alpha = \epsilon_s^\alpha(\text{har}) + \epsilon_s^\alpha(\text{anhar}). \quad (17)$$

The last term arises from the anharmonicity in the potential function and thus vanishes for a harmonic potential function. The $\epsilon_s(\text{har})$ depends on the Co-

riolis coupling. This Coriolis contribution can be calculated from the vibrational frequencies with the relation¹⁸

$$\epsilon_s^\alpha(\text{Coriolis}) = \frac{-\hbar}{\pi^2 c} \sum_s \frac{\omega_s^2}{\omega_s(\omega_s^2 - \omega_{s'}^2)} (\zeta_{ss'}^\alpha)^2. \quad (18)$$

Because there are no out-of-plane vibrations for bent triatomic molecules, $\zeta_{ss'}^{(a)} = 0$ and $\zeta_{ss'}^{(b)} = 0$ when, as is true here, the c axis is perpendicular to the molecular plane. Thus the effects of the Coriolis interactions on I_a and I_b vanish for molecules of this type. In contrast, the Coriolis coupling effects on I_c are rather large. They can be readily calculated from the three fundamental vibrational frequencies ω_1 (symmetric stretch), ω_2 (bend), and ω_3 (antisymmetric stretch). As shown by Darling and Dennison,¹⁹ $\zeta_{1,2}^{(c)} = 0$, $\zeta_{1,3}^{(c)} \approx 0$, and $\zeta_{2,3}^{(c)} \approx 1$ for H_2O and D_2O . For bent XYZ molecules such as the species studied here in which the central Y atom is much heavier than the X or Z atoms, this condition also holds closely.²⁰ With these approximations, the effects of the Coriolis interactions on I_c were calculated from Eq. (18)

to give a corrected I_c . These were then used with I_a and I_b , which have no Coriolis effects, for calculation of the substitutional structures in the last two columns of Table VI. Examination will show that these "corrected" structures, like those from $I_a:I_b$ are also reasonably consistent.

Table VII shows a comparison of the average substitutional structures shown in Table VI and the equilibrium structure calculated by Benedict, Gailar and Plyler.²¹ The agreement among these structures is almost within the error limits assigned to the equilibrium structure. The r_0 structures previously derived by us⁴ for H_2O , D_2O , and T_2O are also included.

From these results we conclude that the principal effects of vibration on the substitutional structures of H_2O arise from Coriolis interactions and that the other vibrational effects largely cancel and have little effect for structural calculations of this kind. Darling and Dennison¹⁹ showed that the effects of anharmonicity on the inertial defect are zero in the H_2O molecule and that the Coriolis interaction is the principal factor in determination of the inertial defect.

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